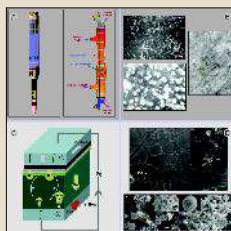


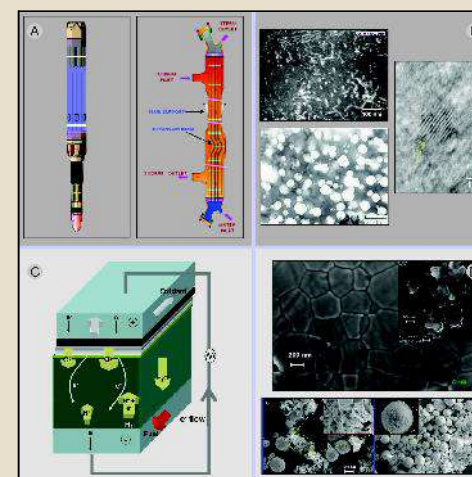
Proceedings of the Indian National Science Academy

Thematic Issue: Science Based Technologies for Sustainable and Adequate Energy for India



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Thematic Issue: Science Based Technologies for Sustainable and Adequate Energy of India

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GUEST EDITORIAL

Science Based Technologies for Sustainable and Adequate Energy for India

Energy is an indispensable prerequisite to do work. The word “energy” comes from the Greek word *energeia*, meaning operation or activity. It plays a fundamental role in human existence and life processes, since energy is the key to advancement of civilization through improvements in quality of life. India today faces a challenge to realize increasing energy demand for our growth with equity, quality of life and sustainability. Realising this challenge, the Indian National Science Academy entrusted us to bring out a thematic issue of the *Proceedings of Indian National Science Academy* on “**Science Based Technologies for Sustainable and Adequate Energy for India**”, focusing on the international and national status of energy harvesting and utilization, current status of research and technology, future trend of development of pilot plants and policy, and training of human resources needed. A primary purpose of the collection of the articles in this issue is to provide valuable information on the subject to the policy makers, researchers, students, journalists and all those who are interested in and concerned with energy.

The scope of the contributions was chosen based on the diversified aspects of energy generation, application, storage and distribution, transmission and materials. Most experienced professionals of our country with significant expertise have prepared the Chapters on the following topics: Clean Heat and Power from Solid Fuels – Modern Approaches; Low Grade (Waste) Energy Conversion: Science and Technological Challenges; Emerging Biomass Conversion Technologies for Obtaining Value Added Chemicals and Fuel from Biomass; Biofuels and Hybrid Fuel Sector; Materials Research and Opportunities in Solar (Photovoltaic) Cells; Materials Research and Development Opportunities in Fusion

Reactors; Electrochemical Energy Storage Devices; Hydro Energy Sector in India – The Past, Present and the Future Challenges; Geothermal Energy; High Temperature Fuel Cell; Proton Exchange Membrane Fuel Cell Technology; Solar Thermal Power Sector; Advances in Thermoelectric Materials and Devices for Energy Harnessing and Utilization; Materials Research and Opportunities in Thermal (Coal-based) Power Sector including Advanced Ultra Super Critical Power Plants; Solar Photovoltaic Energy Harnessing; Electrical Power Transmission and Energy Management System; Biofuels – Engineering and Biological Challenges; Science based Technologies for Sustainable and Adequate Energy for India Wind and Tidal Energy Sector; Hydrogen Energy in India: Storage to Application; Ocean Energy; Materials Science Research and Challenges in Nuclear Power Sector (fission) including Fast Breeder Technology; Methane Recovery from and CO₂ Disposal In Hydrate Reservoirs; Simulation, Modeling and Design of Hydrogen Storage Materials; Overview of Beneficiation, Utilization and Environmental Issues in Relation to Coal Processing.

These topics are covered in a lucid and readable manner with precise and requisite details. We believe that this thematic issue will be a treasure to all those who are interested in understanding and pursuing the energy aspects as profession, career and subject of study. We thank INSA for proposing to us to edit such a valuable publication. We are indebted to all the authors and reviewers for their contributions and advice.

Editors

Baldev Raj
Indranil Manna
U Kamachi Mudali

ABOUT THE GUEST EDITORS

Dr Baldev Raj is Director of National Institute of Advanced Studies, Bangalore, was distinguished scientist and former Director of the Indira Gandhi Centre for Atomic Research, Kalpakkam. He is well known for materials technology, energy, cultural heritage, medical technologies, nano science and technology and education, with more than 1000 papers in journals and 75 books. Dr Raj has received many prestigious awards and honours including the Padma Shri from Government of India, the Life Time Achievement Award of Indian Nuclear Society, National Metallurgist Award by Ministry of Steel, Homi Bhabha Gold Medal, Distinguished Materials Science Award, Distinguished Alumnus Award of Indian Institute of Science. He is a Fellow of all the Science and Engineering Academies of India, German Academy of Sciences and the World Academy of Sciences.

Dr. U Kamachi Mudali is an Outstanding Scientist and Associate Director of Corrosion Science and Technology at IGCAR, Kalpakkam. He is currently the Head, Reprocessing R&D Division, and Convener, IGCAR

Patents & Technology Transfer Cell. He is a Fellow of INAE, ECSI, NACE (USA), ASM (USA), APAM, and IIM. Dr. Mudali made excellent contributions in advanced materials and coatings, localized corrosion, corrosion testing and monitoring with 370 papers in journals and 14 books/proceedings. He is a Senior Professor at Homi Bhabha National Institute, and has received National Metallurgists Day Award, Homi Bhabha Science and Technology Award, INS Medal, VASVIK Award and GD Birla Gold Medal.

Professor Indraneel Manna is a renowned materials engineer with research interests in structure-property correlation in nano-metals/ceramics, laser/plasma-assisted surface engineering, nano-fluid and bainitic steel. Currently, he is Director of IIT-Kanpur. He was Director of CSIR-CGCRI, Kolkata (2010- 2012) and a faculty at IIT-Kharagpur for 25 years (1985-2010), besides working as a guest scientist in different institutions abroad. Professor Manna has over 250 publications and is a recipient of TWAS prize (2014). He is the current Vice President of the Indian Institute of Metals and the Indian National Academy of Engineering.

FOREWORD

Science Based Technologies for Sustainable and Adequate Energy for India

Energy is one of the key resources for sustaining quality life on the earth planet. Energy, security, affordability, equity and ethics are intertwined aspects which define policies and the choice basket of technologies for a given country. Furthermore, energy, water, food and healthcare need to be considered in a balanced manner to answer the demands of the country.

India, the second most populous country in the world with approx 270 GW(e) installed capacity of electrical power generation, is also one of the fastest growing economies. Hence, the importance of defining energy policies and technologies, with short, medium and long horizon perspectives. It is true that one-fourth of India's present population (~ 300 million) has no access to electricity. About two-third of India's installed capacity of electrical power comes from fossil fuel based thermal power plants of various generations and efficiency spectra, with less than one-fifth from hydro-electricity and all other renewable and clean sources (wind, biomass, solar and nuclear). This pattern in the power generation has not seen much change for Indian basket in last three decades. We have large variations in consumption; near zero to approx. 10000 kwh per capita per annum. It is considered prudent that India should aim at an average 2500-3000 kwh per capita per annum to be a developed country with 8-10% GDP sustained growth in next two decades to alleviate poverty, ensure security of the nation and provide deserved better quality of life to our citizens, with emphasis on sustainability. This aspiration requires the net installed capacity to be approx 800-900 GW(e) by 2035 so as to satisfy quality of life expectations and economic emergence. We need to accord high importance to energy efficient technologies and low CO₂ foot print energy generation, transmission and distribution, energy utilisation by industry, transport, housing and indeed all walks of life.

It can be argued that our continued emphasis on fossil fuels is not sustainable with reference to availability of resources and constraints imposed by deteriorating environment quality and climate change.

Various scenarios on energy have been debated though with divergent opinions. It is important that the science and engineering community in the country undertakes a thorough and comprehensive study to comprehend the status and opportunities related to science, technology innovations, education, human resources and management. It is true that despite our plans and predictions of energy targets and roadmaps, energy aspirations have largely remained unrealized. The Science and technology community, with interdisciplinary and cohesive approach must work with industries, bureaucrats and policy makers to realise adequate energy availability, enhancing, security of resources and sustainability. This needs to be done in an expeditious manner.

I congratulate Dr. Baldev Raj, Prof. Indranil Manna and Dr. Kamachi Mudali, with patronage and support of the Indian National Science Academy, for compiling and editing an excellent compendium of articles covering science, technology, materials, innovation and systems integration related to both renewable and non-renewable energy sources with special emphasis on requirements of India. It is heartening that scholars and specialists from academia, industry and R&D units have contributed with concise and clear perceptions on status of science, technology gaps and possible pathways of pursuits. It is to be appreciated that in the energy domain, from concept to commercialisation, we need a lifecycle of approximately 20-30 years to effect the changes in the energy basket. The experiences and inevitability of long lifecycle demand, posing the challenges, prioritising domains and pathways supported with appropriate human resources and funding, establishing

synergy and review mechanisms to achieve success with mission mode mindset and the directions of meeting energy aspirations of India.

I trust that this thematic issue of the *Proceedings of the Indian National Science Academy* will attract interest of students, teachers, researchers, industry and policy makers. The purpose shall be served better when the knowledge in this publication acts as a catalyst for realizing paradigm changes through good collaborations and sustainable and affordable technologies.

I wish the readers a rewarding experience.



C N R Rao

National Research Professor and Linus
Pauling Research Professor
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Review Article

Clean Heat and Power from Solid Fuels – Modern Approaches

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This article is concerned with the science and technology of the conversion of solid fuels such as coal and bio-residues (wood, agricultural and urban solid wastes) into a clean combustible gas that drives gas turbines or reciprocating engines at a variety of power levels. Large coal gasification systems employ high pressure reactors along with gas treatment to enable the gas to be used in combined cycle mode with gas turbines and heat recovery steam generators. A review of the international experience suggests that these are very expensive in the Indian context and have not found their way despite many efforts over the last three decades. Alternative strategies involving flameless combustion/gasification at medium power levels (10-50 MWe) needing development are discussed here. Biomass wastes form a large sector for utilization and by the nature of their properties and availability are most suited for small power generation (a few thousand kg/h or equivalently a few MWe). All solid biomass waste is expected to be processed to eliminate extra organic material (sand, grit, etc.) and brought to regular shape, size and high density (700 to 1000 kg/m³) to facilitate thermal conversion process in fixed bed high temperature reactor at moderate oxidant (air) fluxes to produce combustible gas having CO, H₂, CH₄ and inerts. The gas is cooled (usually) and cleaned of particulate matter and any sulphur-related compounds before being used for heat or electricity generation. Fuel-to-electricity conversion efficiencies of 27% to 30% for small power and up to 35 % at medium power levels can be achieved. The strategy allows the lowest possible emissions with unit investment costs comparable to large power systems. Recognition and encouragement for these routes will add significant value to the national effort on heat and power generation.

Keywords: Energy Conversion of Solid Fuels; Gasification of Solid Fuels; Combustion of Solid Fuels; Clean Combustion; Coal and Biowaste Conversion

1. Introduction

Clean conversion of solid fuels to useful energy which is different from the classical approach involves producing combustible gas that can generate better or multiple outputs – (a) better conversion efficiency from fuel to electricity (η_{fe}), (b) reduced gaseous emissions of CO₂, SO_x and NO_x, apart from complex heavy metals in the ash stream, (c) CO₂ capture so that as much of carbon can be sequestered into useful products for societal need or stored in the earth or under the sea and (d) electricity combined with chemicals (Maurstad, 2005; Parthasarathi, 2009; Intnet1, 2012).

Better conversion efficiency implies reduced use of the solid fuel and a reduction in the corresponding emissions. Beyond this, reduction in SO_x and NO_x calls for the introduction of specific unit operations into the flow path; SO_x is to be converted to sulphur or sulphuric acid and NO_x should be converted to N₂ to the extent possible. Further reduction in CO₂ is caused by separating it from the flue gases and using it as a chemical reactant to produce other substances of importance, such as for instance silica from sodium silicate or storing it deep underground or under the sea. In order to aid the separation process, air is replaced partially or completely by oxygen. This leads

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Table 1: Combustion or gasification process outputs for coal/biowastes

Oxidizer	Reaction products	Pollutants	Output	Pressure	Comments
Air	CO ₂ , H ₂ O, N ₂	SO _x , NO _x	Heat, electricity	Ambient	Combustion-steam generator
O ₂	CO ₂ , H ₂ O	SO _x , NO _x	Heat, electricity	Ambient	Oxy-fuel combustion
Air	CO, H ₂ , CH ₄ , CO ₂ , H ₂ O, N ₂	H ₂ S, NH ₃ , Tars	Heat, electricity, chemicals	High/ambient	Gasification to producer gas; high pressure - IGCC plant
O ₂ -steam	CO, H ₂ , CH ₄ , CO ₂ , H ₂ O	H ₂ S, NH ₃ , Tars	Heat, electricity, chemicals	High/ambient	Gasification to Syngas, IGCC and/or liquid hydrocarbons

(Adapted from Klass, 1998; Mukunda, 2011)

to the oxy-fuel process. It is possible to add steam to the process to generate combustible gases rich in CO and H₂. This gas can be used as a feedstock for conversion to liquid hydrocarbons through the familiar Fischer-Tropsch process (Maurstead, 2005; Parthasarathi, 2009).

When one moves from combustion to gasification (as it happens in two lower rows of Table 1), (i) the products change largely into combustible gases, and (ii) the pollutants change their character as well. Further, the outputs can be multiple – one can design the process to obtain chemicals as well (Table 1). For instance, if one uses coconut shell as a fuel, we can design a gasifier that produces 30% char and heat for steam generation and subsequent power or steam for activation leading to activated charcoal (Mukunda, 2011). This can replace the existing pit method to produce charcoal and therefore yield multiple benefits. Rice husk is a fuel used in fluidized bed boilers to produce high pressure steam for electricity generation. The residue is black char that has about 10% to 15% carbon and 20% ash (with respect to rice husk as reference); the ash has 95% precipitated silica. In addition to electricity generation, it is possible to obtain precipitated silica and activated carbon (about 5% to 7% of the rice husk mass). Also, CO₂ in the exhaust can be used to produce precipitated silica. This is perhaps the most integrated approach in generating renewable energy (Mukunda, 2011).

Section 2 describes the solid fuel usage in India – coal and biomass, and section 3, the properties of these fuels; these form the background for the technology description to follow. Section 4 addresses

the distinguishing features of combustion and gasification as a part of thermal conversion process, the basic processes of which are explored in section 5; the critical aspects of gasification are delineated in section 5.1. Section 6 discusses the conceptual technological features of systems from other countries for coal and also presents the status in India. Gasification technologies for small and medium scale power levels are discussed in section 7. The final section discusses the way forward.

2. Fuel usage in India

Coal is an important fuel source used for generation of electricity. As the number of steam power plants increases to meet the increasing demand, so does the use of coal in excess of 550 mmt (million metric tonnes) in 2012 (Mukunda *et al.*, 2010). Solid biofuels in the form of firewood, agricultural residues and dried cowdung are used in cooking in over 120 million households to a total of 420 mmt. While coal used in power stations leads to fuel-to-heat efficiencies, η_{fh} of 75% to 85% (with accompanying fuel-to-electricity efficiencies, η_{fe} of 35% to 36.5%), biomass used in domestic stoves occurs with utilization efficiencies, η_u of 10-20% that is composed of η_{fh} of 30% to 50% and heat transfer efficiency, η_{ht} of 35% to 40% ($\eta_u = \eta_{fh}\eta_{ht}$) (Mukunda, 2011). The use of biomass wastes occurs in small thermal power stations with η_{fh} of 60% to 70% as the combustion system has to accept fuels of varying shapes, sizes, moisture and ash content.

Coal contains impurities that affect emission performance also. While Indian coals contain a small amount of sulphur which on combustion leads to acid-rain forming sulphur dioxide, they are also laden with large amount of inorganic material leading to high ash fraction (of up to 40 %). Imported coals from Australia and Malaysia have lower ash content but larger amount of sulphur that needs to be dealt with to limit the emission of sulphur oxides.

3. Properties of Fuels

To appreciate the critical aspects of the thermal conversion process, it is important to examine the properties of the fuels considered as shown in Table 2. The density of coal is large and that of biomass varies widely. Coal is used in the form of sized pieces on a grate or in a pulverized form in special injection systems. Biomass is used either in as-received form of agro-residues or in processed form as firewood, or densified into pellets or briquettes with a mix of agro-residues. While the as-received form of biomass can consist of moisture up to 50%, sun-drying condition reduces it to about 10%. The lowest ash content in biomass occurs with wood or some agro-residues such as coconut shell. The largest ash fraction occurs with rice husk and rice straw (~20%); other agro-residues have ash content <5%. The ash content of urban solid waste should largely be <10% allowing for a small amount of pickup of sand, grit and mud due to the inclusion of sweepings. However, the pickup can be as large as 50% and it is necessary to process the urban solid waste to shed the pickup and reduce

the ash content. Coal is produced because of natural biomass processing at high pressure and temperature deep inside the earth. This is why (a) biomass whose volatile content is ~75% loses a large part to be reduced to about 30 %, (b) density increases (to 1200-1500 kg/m³) even after the loss of volatiles reducing the active mass by 50%, and (c) the amount of ash depends on the geological history of the process with some regions adding only a few percent and others adding large amounts. Owing to some of these features, the calorific value of some coals is not very different from biomass.

4. Features of Combustion and Gasification

The energetic parts of coal and biomass are made up of carbon and hydrogen elements which are to be converted to carbon dioxide and water vapour in the combustion process. The amount of air required for this purpose varies from 6 to 10 kg per kg fuel. Thus, the gaseous products are 7 to 11 times the fuel consumption rate. The presence of undesirable emissions in the products implies that a large throughput of the product gas needs to be handled if their fraction has to be brought down. An alternative process would be to convert the solid fuels into fuel gas by a process known as gasification which is essentially an aero-thermo-chemical process more intricate than combustion. The amount of air required for the conversion is about 20% to 25% of the air required for complete combustion—about 1.5 to 2 times the fuel throughput. Thus, the fuel gas flow rate will be 2.5 to 3 times the solid fuel throughput.

Table 2: Properties of typical solid fuels

Fuel	ρ , kg/m ³	f_{ash} , %	f_{moisture} , %	Shape/size	LCV, MJ/kg	f_{volt} , %
Coal, Lignite	~1200	5-30*	5-20	Pulverize or size	15-25	20-40
Sized wood pieces	300 to 600	<1	10 (sundry), 50 (green)	Can be sized	16, 9	~80
Agricultural residues, woody	As above	<1	As above	Can be sized	As above	~70
Agricultural residues, leafy	50 to 150	4-20	As above	Varying, needs densification	14-10 (sundry)	60-65
Urban solid waste	~ 250	<10	As above	Same	Similar	~70

ρ = density, f_{ash} = ash fraction, f_{moisture} = moisture fraction, LCV = Lower calorific value, f_{volt} = volatile fraction, f_{fc} = fixed carbon, * By MoEF (Govt. of India) order, coal washeries should be used to ensure coal that transported to power plants beyond 1000 km from pithead should have $f_{\text{ash}} < 34\%$. (Adapted from Klass, 1998; Mukunda, 2011)

Alternatively stated, the fuel gas flow rate is about a third to half of the final burnt products. Any treatment process of this gas to limit the presence of undesirable products is performed with less expense since the amount to be treated is much less for the same fuel throughput. What more, the gas so produced that is composed of CO, H₂, CH₄, (the three combustibles) CO₂ and H₂O (inerts) in proportions that depend on whether the fuel is biomass or coal and the actual conversion process used, typically with active combustible matter amounting to 50% is capable of being used in gas turbines or reciprocating engines for electricity generation. Further, with the thermal energy left behind in the exhaust gas, it will be possible to operate a steam cycle as well. Thus, the η_{fe} of the combined cycle works out to 40% to 42%. This operation called integrated gasification combined cycle (IGCC) constitutes the essence of “clean power”. Thus, with the use of the gasification technologies, one can obtain higher efficiency and lower emissions at justifiable extra costs. The oxidizer used in classical power plants is air.

The more interesting point is that the gasification process can be introduced even for domestic cook stoves (at thermal power levels of 3 to 4 kW) raising the η_u to upwards of 45% (up to 65 % in community kitchen size stoves with power levels of 15 kW) because it is possible to achieve η_{fh} of 90% to 92% through the gasification process and heat transfer efficiencies of more than 50%.

5. How Does Combustion of Coal and Biomass Proceed?

Much more is known about combustion of coal as it is widely practised. When large pieces of coal (5 to 50 mm size) have to be burnt, it is done on a grate. A bed of burning coal moves on a travelling grate inside a furnace. The rate of travel is so adjusted that most of the coal would have burnt off by the time the end is reached. Air is allowed to flow through the bed and also introduced over the bed. After initial heating to bring up the entire furnace to over 600°C at which condition, radiation and convection cause ignition of an incoming coal particle and allow it to be burnt through the travel over the grate. This process consists

of release of moisture initially and then volatiles which burn up in the gas phase. During the rest of the travel period, the coal char burns up largely with heterogeneous reactions between the oxidant – oxygen in the air and surface carbon. The effectiveness of this process is controlled by the amount of ash, the magnitude of which is higher due to loss of some active material in terms of volatiles. The carbon conversion fraction in this process may not be the highest since some large particles may be dropped off before all the carbon in them is fully oxidized. In large size systems, fluidized bed combustion is also practiced. The coal particles remain in suspended form surrounded by air and other hot products and burn up with efficiencies better than on grate. Achieving this calls for limiting the size of the coal particles to a narrower range.

In order to achieve better combustion efficiency (η_{fh}), coal is pulverized to 70 to 100 microns and burnt in pulverized fuel burners. Combustion is much better in such systems because the particle size is much smaller and it burns in a suspended state surrounded by hot oxidizer-rich products. Most of this is diffusion-limited combustion both in the volatile and char oxidation modes.

Combustion of solid biomass whether it is a stove or a furnace occurs largely in a diffusion mode with the flame surrounding the particle or a firewood stick. The volatile regime for biomass is much more vigorous and energy carrying than for coal since the volatile fraction is much higher. Combustion of fine particulate matter such as sawdust or leafy matter occurs with volatile release taking a very short time (less than a few seconds utmost) and the char may or may not get oxidized unless the environment is sufficiently hot and oxygen-rich.

Since the rate processes in large-scale systems handling coal or biomass become less efficient than theoretical expectations, the air flow that must be provided will need to be higher, slightly or not-so slightly depending on the design and operational features so that the emissions of undesirable gases is limited. This is described as excess air ratio that varies between 10% and 30%; it ensures better oxidation, reduction

of the emission of undesirable intermediate products of combustion and the power required for the blower. In the case of internal combustion engines such as gas turbines, the combustion process has to meet other requirements of compactness of the combustion chamber with appropriate wall cooling and causing required dilution of hot gases to provide the set turbine inlet temperature and profile.

5.1 What is Critical about Gasification?

Two questions arise: what is so different about gasification compared to combustion? How come, there are so many different approaches to gasification when such variability does not exist for combustion?

The important distinguishing feature in gasification is that the entire conversion process must be conducted with oxidant flow rates about a quarter of that for combustion. This implies that the conversion of *volatiles* itself will be at around *stoichiometry* for coal, but very *rich* for biomass, this distinction is due to the fact that volatile fraction in coal is about a third of that in biomass. In fact, a simple distinction between coal and biomass would be that the process is largely coal-char centered for coal and volatile-centered for biomass. The first process is termed oxidative pyrolysis or flaming pyrolysis to distinguish this from the classical pyrolysis process that occurs in the complete absence of oxidant. Gases emanating from the volatile conversion process will contain some unconverted products such as CO, poly-aromatic hydrocarbons (PAH) and other oxygenated compounds apart from CO₂ and H₂O. The latter two complex compounds that have a condensation temperature of 50–250°C are called tars. Those that condense at higher temperatures are called heavy tars and others, light tars. All biomass gasification technologies are seriously concerned with producing near-tar-free gas. Classical updraft systems (see later) including coal have copious amounts of tar in the gas and need extensive treatment if they have to be used in engines for power generation; most usually, they are contemplated for thermal applications and Europe has many industries supplying biomass and coal systems up to 100 t/h capacity.

Producing clean combustible gas demands

thermo-chemical reactions of the products of oxidative pyrolysis, CO₂ and H₂O and the complex chemicals (PAH and other oxygenated compounds) with char. These reactions are essentially reducing in nature and so endothermic; the rate is strongly dependent on temperature as also the reactivity of the char. Fig. 1 shows the reaction of various fuels as a function of temperature. Normally, the reaction rate varies with temperature following the Arrhenius law: $r_m \sim \exp(-E/RT)$, where E is the activation energy and E/R is called the activation temperature and this is the reason that the plot has $\ln(r_m)$ vs. $1/T$. It is clear from the plot that among chars, biomass char has the highest reactivity and pet coke the lowest. Lignite and coal lie in between the two.

Experiments have shown that char *per sé* can reduce the tars apart from converting CO₂ and H₂O to simpler compounds and CO and H₂. It is important that sufficient residence time in the high temperature range be allowed to enable the final composition reach near-equilibrium conditions. Such a condition ensures the breakdown of the complex compounds to simpler ones. The complex compounds are classified as “tar” – heavy and light (the distinction of heavy and light is made depending on the condensation temperature). The concern for the presence of the tars is that when the gases are cooled, they will deposit in the passages and other difficult-to-access locations. The magnitude of the tars will be between 0.1 and 10 g/nm³ of the gas. In large throughput systems, the magnitude of the tar generated in some designs (such as updraft and fluid bed systems to be discussed later) is so large that collection and management of the tars itself is an

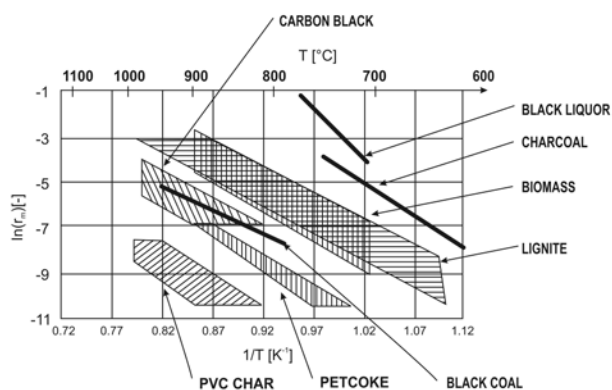


Fig. 1: Reactivity of various fuels (drawn from Parthasarathi, 2009)

issue unless the magnitude is limited by design. This issue is even more important for electricity generating systems using reciprocating engines since the valve seatings have small passages and deposition has been known to occur in these passages. Thus, the efficiency of gasifier design is measured by gasification efficiency (which is the ratio of the energy contained in the gas to that of the fuel) and the simplicity of design in reducing the magnitude of the tars. If the design is complex, the operability of the system becomes compromised due to either a heavy load on instrumentation for monitoring the operation or enhanced maintenance.

6. Gasification Technologies

Gasification technologies can be classified into those meant for large and small systems. This distinction almost completely covers the differences between coal and biomass systems. Much more has been written about large coal gasification systems and even a cursory internet browsing will reveal description of these systems and their performance; a number of international conferences on clean coal technologies seem to be taking place biannually (intnet1, 2012). The four major commercial gasification technologies in order of decreasing capacity installed are (a) Sasol-Lurgi (Dry Ash), South Africa, (b) Shell, (c) GE (originally developed by Texaco) and (d) ConocoPhillips E-gas (originally developed by DowChemicals).

The Sasol-Lurgi gasifier (developed by Lurgi) has gained extensive commercial experience at the synthetic fuel plants in South-Africa. The design is of the fixed bed and non-slugging type (ash is dry). The other three gasifiers belong to the entrained flow slugging (ash is melted and extracted) type. Shell and GE-Texaco gasifiers have considerable commercial experience with gasification, while ConocoPhillips has less experience. Still, the three companies GE, Shell and ConocoPhillips are all perceived as major players with respect to future IGCC projects which concentrate on entrained flow slugging gasifiers.

Fluidized bed gasifiers are less developed than the two other gasifier types. Operating flexibility is more limited for this class of gasifiers because of the

need to perform several functions (e.g. fluidization, gasification and sulphur removal by limestone injection) with limited design flexibility (for example, the air blown KRW fluidized bed gasifier was not able to start up successfully in projects during 1998 to 2000). Fig. 2 shows the features of three designs of high pressure gasifiers. Of these, the Pratt and Whitney design is undergoing development and hence is not discussed any further here (see Maurstad, 2005 and Fusselman *et al.*, 2006, for more details).

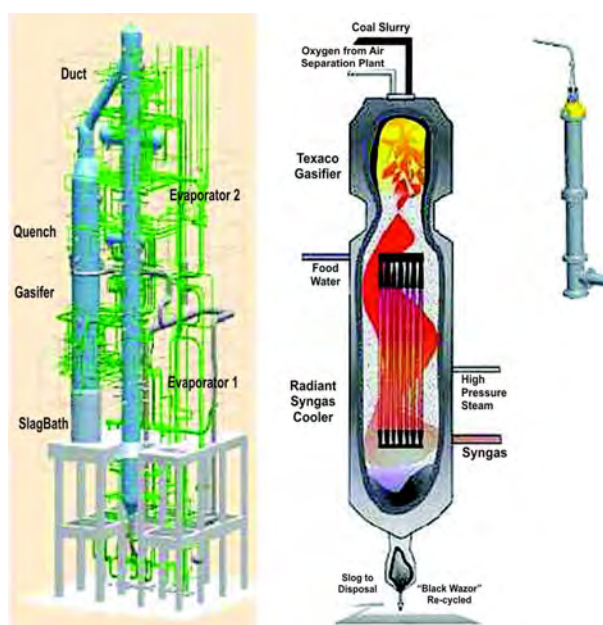


Fig. 2: Three designs of high pressure coal gasification systems. Left: Lurgi design; Middle: GE design and Right: Pratt and Whitney rocket-based design (adapted from Fusselman *et al.*, 2006)

There are several options for many elements of the current working IGCC system as shown in Table 3. The pressurized entrained-flow Shell gasifier uses a dry-coal feed and 95% pure oxygen (from an air separation unit) to produce a medium heating value fuel gas. The syngas produced in the gasifier at about 1700 K is quenched to around 1200 K by cooled recycled syngas. Then, the gas passes through a convective cooler and leaves at around 600 K. High-pressure saturated steam is generated in the syngas cooler and is joined with the main steam supply. Raw gas leaving the syngas cooler is cleaned of particulate matter and passes through a COS (carboxy-sulphide)

Table 3: Design element features for various high pressure gasification technologies (Maurstad, 2005)

Technology/ Design feature	Shell	GE –Texaco	E-Gas (Conocophillips)
Feed system	Dry coal, lock hopper + pneumatic conveying	Coal-in-slurry (65:35)	Coal-in-slurry (65:35)
Gasifier configuration	Single stage entrained up-flow	Single stage down-flow	Two stage up-flow
Gasifier wall	Membrane wall	Refractory	Refractory
Pressure (atm)	<45	<45	35-70
Composition of the gas cooled to 25°C, % v	CO ~ 58, H ₂ ~ 30, N ₂ ~ 8, CO ₂ ~2, Ar~1, H ₂ S~0.21, COS~0.02, Others* ~ 0.01	CO ~ 40, H ₂ ~ 40, N ₂ ~ 2, CO ₂ ~15, Ar ~ 2, COS + H ₂ S ~ 0.3, Others* ~ 0.2	Composition similar to GE –Texaco system
Observations	With heat recovery	Quench or with heat recovery	With heat recovery

*Others at trace levels: HCN, NH₃, HCl, NH₄Cl, Ni(CO)₄, HF, Pb, Hg, As, Fe(CO)₅, etc.

hydrolysis reactor before entering a Sulphinol-M acid gas (H₂S) removal process. Elemental sulphur is produced as a salable byproduct. The clean gas is conveyed to the combustion turbines where it serves as fuel for the combustion turbine/heat recovery steam generators (HRSG)/steam turbine power conversion system.

The features of GE-Texaco gasifier vessel are described in Table 3. Coal-water slurry is transferred from the slurry storage with a high-pressure pump. At the top of the gasifier vessel is located a combination fuel injector through which coal slurry feedstock and oxidant (oxygen) are fed. The high temperature reactor operates at around 1600 K to produce syngas. Hot syngas and molten solids from the reactor flow downward into a radiant cooler where the gas is cooled to 800 K and the ash solidifies. Raw syngas continues downward into a quench system and then into a syngas scrubber for removal of entrained solids. The gas goes through a series of gas coolers and cleanup processes including a COS hydrolysis reactor, a carbon bed mercury removal system, and a Selexol acid gas removal plant (CO₂ and H₂S). Slag captured by the syngas scrubber is recovered in a slag recovery unit. Regeneration gas from the acid-gas removal plant is fed to a Claus plant, where elemental sulphur is recovered. Humidification of the syngas and nitrogen dilution helps in minimizing formation of NO_x during combustion in the gas turbine

burner section. The gas composition lends itself also as a feedstock for chemicals such as hydrocarbons through Fischer–Tropsch process. One of the drawbacks of the composition is that the desired H₂:CO of 2:1 is not fulfilled here. Gas separation may be needed to obtain the right composition. A key feature of the high pressure-high temperature reactors is that there is very little tar-related problem largely because they run on oxygen.

Gaseous emissions from the gasification systems are presented in Table 4. Higher conversion efficiency to electricity implies the need for lesser fuel for the same output. This reduces the amount of CO₂ emitted. The significant difference in emissions between advanced technologies and classical technologies in practice for power generation in India is evident in Table 4. While the advanced technologies are more expensive (per unit capacity installed), their inherent worth in being environment friendly is clearly obvious. The gas clean-up costs are reduced through the choice of oxygen as the oxidant because this increases the concentration of CO₂ in the gas enabling its removal before use for power generation. In the choice of fuels for these systems, biomass is factored in so that the issue of reduction in carbon footprint is better addressed. The central problem is that biomass in as-received form has very high moisture and when this is reduced the densities are about a third of coal. This implies that the volumes to be handled are very

Table 4: Comparison of the performance of various gasification technologies (Parthasarathi, 2009)

Technology	η_e , %	SO _x , mg/kWh	NO _x , mg/kWh	PM, mg/kWh	CO ₂ , g/kWh	Waste/by-products, g/kWh
AFBC*, steam-turbine	36	1400	800	100	774	Gypsum = 20, Fly-ash =25
PC ⁺ - Steam-turbine	36	2500	2300	300	852	Nearly same as above
GE-Texaco, IGCC	41	130	350	20	745	Same as above
Shell-Siemens, IGCC	43	100	50	20	712	S = 4, Fly-ash = 2, Slag = 220
NGCC - reference	56	7	540	20	350	None

*Ambient pressure fluidized bed reactor, ⁺Pulverized coal combustor, NGCC = Natural gas combined cycle

large. This makes the inclusion of biomass problematic in power plants that handle over a million tonnes per year of coal even at the level of 10 % of biomass inclusion. Therefore, the inevitable valid conclusion in Western countries is that biomass plays a weak role in large-scale electricity generation. The question of relevance is: which advanced coal technology is appropriate for India?

6.1 Indian Technologies on IGCC

BHEL (Trichy) has taken an initiative in developing the know-how at 6.2 MWe and gained experience on its operations. A visit to the facilities and technical exchange on the fundamentals associated with the design features (intnet2, 2012) showed that several conversion-related aspects needed reconsideration. Beyond this, the office of the Principal Scientific Advisor to the Prime Minister tried to develop a 125 to 180 MWe IGCC project for India (intnet3, 2015). However, there has been no progress on ground eight years after the effort. IGCC is often considered an advanced area and many intricate aspects of the technology are held close to the chest by the overseas technology holders making it difficult for others to access. A true impediment is that the cost of the technologies is high-going up to Rs. 1000 crores (2 billion USD) for a meaningful project of 100 to 150 MWe) with uncertainties of high ash coals not addressed adequately. If IGCC class of technologies has to be developed, it is important to find an alternative path that does not involve large first investment cost and risk perception. The latter is possible with enough fundamental research and demonstration on a plant

at some appropriate scale. New pathways and their foundations are described below.

7. Technology and the Basis for Small Plants – Biomass and Coal

Biomass gasification technologies are usually designed for smaller power levels – typically less than a few MWe. This is because of the sustainable availability of biomass for the expected life of the plant. In both USA and Canada, there are large biomass-based power plants of medium capacity – 20 to 50 MWe. In countries such as India, land holdings are small (~1 ha per family) and sourcing waste biomass from plantations or agricultural residues is a significant issue. The price at which the biomass is available at the plant site will vary with season and on a year-to-year basis to such an extent that it is only the power plants based on captive bio-waste that can be expected to function. Rice husk based power plants in some Indian states in India (such as Chattisgarh) have functioned well. Even though a large number of steam power plants based on agricultural residues at power levels of 4 to 10 MWe have been built, many of them function at suboptimal conditions and some have been closed as well, all because the year-to-year projected biomass procurement price levels were substantially exceeded later. In fact, even at present, several power plants of over 10 MWe are being conceived and investments made without fully realizing the implications of the sustainability of biomass.

This situation can be averted if one contemplates the choice of gasification technologies that have unit

power levels of 1 to 2.5 MWe since the annual requirement of fuels will be in the range of 10 to 20 thousand tonnes per year. If biomass availability allows larger power levels, the use of multiple units can be contemplated without loss of economy of scale since the cost per MWe reaches saturation at around a MWe level. Through the use of ambient pressure gasifier and the promise of clean gas for use in high grade heat, chemical feedstock or electricity at throughput levels requiring a few kg/h to a few t/h, one can at the least create solutions towards the possibility of overcoming problems noted earlier. The power generation system will be based on reciprocating engines rather than gas turbine engines. When it comes to the use of coal, the economic power level will need to be raised to at least 10 MWe in an IGCC mode with reciprocating engines for the principal electricity generation and the exhaust heat for heat recovery steam-power generation (HRSG). This conceptual frame research is new and needs explanation. A conventional IGCC depends on gas turbines. The open cycle efficiencies (η_{fe}) are typically 30% and the HRSG adds another 10% to 12%. In the case of reciprocating engines in excess of 500 kWe, η_{fe} is nearly 28% to 35% with HRSG adding about 8% to 9% to a total of 36% to 44%. The recovery from the steam route is less than that of gas turbines because the electricity-to-heat ratio is higher for reciprocating engines than gas turbines. It is important to recognize that gasification process for biomass has been studied in India far more intensively than in the rest of the world for over three decades at the laboratory and in the field with extensive inputs from one to the other that India can rightfully claim leadership in this area. This understanding should also benefit the coal gasification at medium throughputs (1-3 t/h). Scaling to 10-50 t/h coal technologies needs new ideas and will be discussed below.

7.1 Biomass Gasification Technologies

Section 5.1 has already dealt with the steps involved in gasification. Much research has been performed in India with the financial support from the Ministry of New and Renewable sources of Energy. All the research over the last three decades on this subject by the author and colleagues can be found in Mukunda

(2011). The core of the technology lies in the aero-thermo-chemically controlled reactor-fluid flow effects, heat and chemistry determine the quality of the hot gas generated. While the effects of heat and chemistry has been well-appreciated in design over the last 50 years, the fluid flow effects have been treated so empirically over this time that progress has occurred in the recent past in elucidating these effects; these have been integrated into the modern design. The principal reactor designs are atmospheric pressure fixed bed updraft and downdraft. In an updraft reactor (Fig. 3A), air flows from the bottom upwards through a packed bed of sized biomass pieces which moves downward as biomass gets gasified (the gas is extracted at the top region) leaving behind the ash that is extracted from the bottom; this is a counter-flow feature. In a closed top downdraft design (Fig. 3B), air and sized biomass pieces move down together. Both gas and ash are drawn off and extracted from the bottom region. In the case of updraft system, complete char oxidation with air occurs first. Then, the hot gases get partly converted to producer gas in reaction with the char layers above and move through the biomass bed. This process causes the release of volatiles and hence the gas that exits from the reactor has the maximum amount of condensable tars, typically about 10 g/nm³; this magnitude is also roughly matched by fluidized bed gasifiers in which the pathway from solid particles to gas is not systematic; no intersection of the gas with char particles is assured. As such, its behavior is similar to fixed bed updraft systems. Thus, both these systems are suitable only for thermal applications. Any attempt to deploy them for electricity generation via reciprocating engines requires such an expensive, elaborate clean-up system that it will be practically impossible to maintain the operations in a satisfactory manner. Fixed bed downdraft systems of World War II origin are always closed top. This practice is maintained even these days by most designs. A different design using open top first discussed by Thomas Reed (see Mukunda, 2011 for details) was combined with the side air nozzles of other designs to obtain results that neither of them can provide. To understand this, it is necessary to study the principles of the new design developed and patented by Indian Institute of Science (Mukunda,

2011). Fig. 3C shows the schematics of the reactors of the open top (staged air ingestion) IISc downdraft design. The best way to understand the processes occurring inside this reactor would be to examine the operation in two extreme modes: Air drawn from the top with side air nozzles closed and air drawn from the side air nozzles by keeping the top closed (to simulate in part the closed top design).

It is to be first understood that all gasifiers work by converting biomass to char which further participates in the reduction reactions to generate combustible gas; as such, the reactor is loaded with char up to the height of the air nozzles (in both cases) for the first time and biomass on the top that will be topped up on usage. The system is started by introducing a high temperature torch to the side air nozzles. Since most gasifier designs adopt a suction mode of operation with a blower downstream drawing off the gas downstream, the hot gases of the torch will light up the char inside the reactor. In a few minutes, the entire char bed is lit. Now, the air nozzles are closed and air ingestion from the top is allowed. The processes that occur in the bed cause flame propagation to the top at 100 to 200 mm/h. Once the flame reaches the top, the entire reactor will be filled with char. Beyond this point, the operation will switch

to char mode and the reactor cannot accept any more biomass. Such an operation is unacceptable unless char is continuously extracted at the rate at which it is generated (typically 30%). Even if this is arranged, the gas that is generated has a significant tar, up to 1 g/nm^3 and this needs to be brought down to the lowest possible level. This is brought down by opening the side air nozzles so that air flow is shared between the top and the side nozzles, typically around 70:30 ratio. The air from the side air nozzles burns up the flaming pyrolysis products again in the rich mode, a process called re-burn. This maintains the bed temperature making the high temperature zone much broader than that of the closed top design. The broader temperature profile helps the char-gas reactions to reduce the tar level to the lowest possible level and maintain a good composition at the exit. The flame front can be restricted to a small zone above the side air nozzles, a feature that helps maintaining a steady operational behaviour. A further problem that occurs with agricultural residue based biomass is the problem of ash fusion that is caused because the ash fusion temperature gets lowered due to the presence of potassium. This problem has been faced with straw burning furnaces as well the world over. A straightforward way of overcoming this would be to

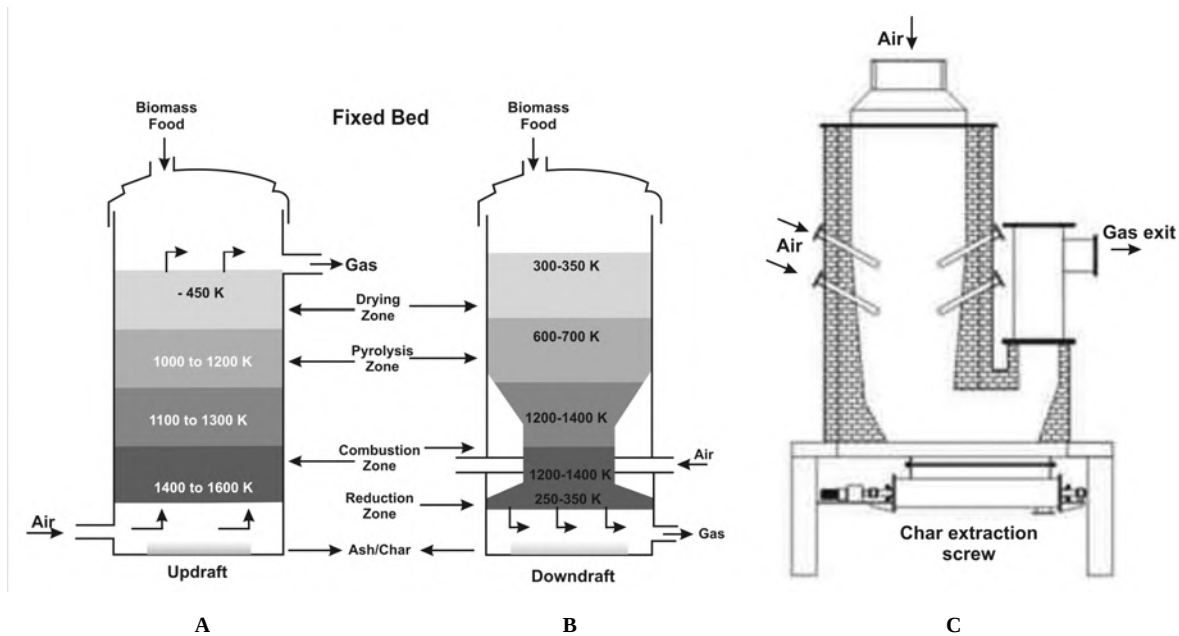


Fig. 3: Fixed bed gasifier reactor schematics – updraft (A), closed top downdraft (B) and open top downdraft (C) (drawn from Mukunda, 2011)

densify the material into briquettes of 50 to 100 mm size. This reduces the contact points between materials reducing the ash fusion possibilities and the high density will help the downward movement of the material. Thus, biomass preparation and the possibility of staged air ingestion help in allowing multi-fuel option, a feature very essential for seasonally available agro-residues. One of the key issues is related to the management of the high temperature zone that is both oxidizing and reducing in different zones. While some designers have used thick mild steel, more advanced designs have used ceramic tiles. The structure is composed of high alumina (>75% alumina) tiles on the innermost face with hot-face and cold face insulation bricks next to it to ensure that the outer temperatures are limited to acceptable industrial environment values (see extreme right in Fig. 2). The presence of high alumina tiles is crucial to avoid ash fusion with the wall material, something that can happen if the alumina content is lower.

This technology has performed with changes of fuel from coconut shell to *Prosopis juliflora* and back to coconut shell in a 1000 kg/h powering a 1 MWe (4×250 kWe + 1×250 kWe) Cummins engine system for over three years with total operating hours exceeding 18,000 hours; the changes in fuel occurred because during a period, a disease struck the coconut plantations reducing the availability of coconut shells with accompanying price rise to such levels that the fuel cost was equal to the tariff paid by the utility. More about the experiences is discussed in Mukunda (2011).

7.1.1 Domestic Cooking

A way of using gasification idea for a low thermal power (3 to 500 kWth say) has been evolved from ideas discussed above – of ensuring a flaming pyrolysis zone first and a hot char bed through which these gases pass through so that even if “tar” conversion is not complete, it does not affect the combustion that occurs almost immediately afterwards. Fig. 4 shows two designs that have been conceived and built. The first of the designs is essentially reverse of the downdraft gasifier (Fig. 4 top; Mukunda *et al.*, 2010). Air supply is from the bottom and the top of the packed

fuel bed is lit and the flame propagates downwards converting biomass to char and the hot gases pass through the char bed to produce combustible gas. This design has also been termed TLUD (Top Lit Up-Draft) in literature (Mukunda, 2011). One can construct a horizontal gasifier by creating a draft of air through the bed and ensuring that the gases from flaming pyrolysis pass through a char bed. This is enabled by providing the air supply system in interrupted struts between which gases can flow. Fig. 3C and D shows the smallest stove for 1 kg/h. Similar ideas have been used to build industrial stoves up to 150 kg/h. Typical flame temperatures are 1200 to 1600 K (larger power systems are close to the higher temperature) maintaining oxygen fraction in the hot stream of 1% to 3%. This also ensures minimal emissions of CO let alone PAH and other compounds.

7.1.2 Medium-Scale Coal Gasification

Medium-scale coal gasification is a subject on the horizon not of relevance to advanced countries. It is of importance to India where procuring capital for “risky” projects is only through government and this route has not been successful for over two decades.

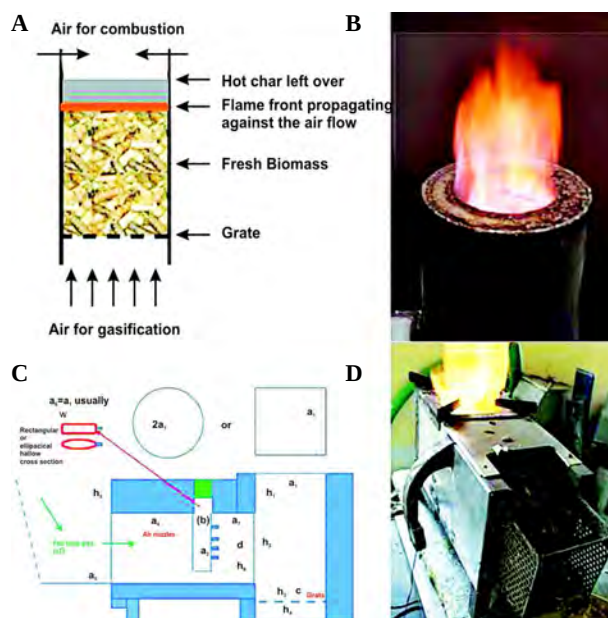


Fig. 4: Two classes of gasifier stoves. Principles of gasification-combustion (A), the combustion quality (B), Horizontal gasifier design for multiple fuel sizes and types (C) and combustion quality (D)

This requires new ideas that have been tried out for “flameless” combustion studied (for instance, Kumar *et al.*, 2002), developed and practiced for gases to obtain high efficiency with minimal emissions (particularly of NO_x) and pulverized coal (Fu *et al.*, 1986), both of which have been tested and proved at ambient pressure. The essential idea here is to separate the injection of fuel and oxidant streams and provide them at high velocity. The high velocity causes entrainment of the product gases that heats up as well as dilute both the streams till a point that the jet temperatures cross about 1300–1400 K when auto-ignition of the mixed streams is possible. This reduces the range of operating temperatures of the combustor (from 1300 to 2100 K instead of 300 to 2100 K) that is now considered similar to “stirred reactor”. This reduces the pressure fluctuations and acoustic signature of the combustor and the flame structure is very transparent due to heavy recirculation (of about 2 to 3) of hot gases inside. Fig. 5 shows the expression of these ideas in coal combustors. Use of this approach reduces the dependence on oil for flame stabilization. These ideas can be extended to gasification either with air or oxygen. The hot gases from the gasifier can be processed in cooling and cleaning system, ideas for which can be drawn from biomass gasifier system development that have already reached commercial maturity.

The gases now are ready for induction into any engine. It is possible to create design options with multiple engines of 2.5 MWe running on one or more gasifiers. Further, combined cycle operation is possible using exhaust heat based steam cycle. The benefit from such an approach is the scaling down of the

IGCC ideas into economical lower capacity systems. Simple cycle calculations show that typically 20 MWe IC engine power and 3 to 5 MWe HRSG power need an investment of less than 2500 USD/kWe (intnet3, 2015). These form the ideas for future research and development.

8. The Way Forward

Handling solid fuels is admittedly more difficult than gaseous or liquid fuels. The scientific attention paid to the conversion of solid to gaseous fuels has been inadequate. If one examines the approach that India or a few other developing countries need, it becomes clear that one needs to add to the basket of technologies, medium scale coal gasification solutions, biomass gasification technology for energy and chemicals and small-scale biomass-based heating devices. One most important feature is that there is severe scarcity of affordable solid biofuels in many areas of the country. Hence, it would be necessary to combine the research on efforts in liquid biofuels that generate significant solid wastes, other tree wastes and urban solid waste to produce substantial amounts of solid fuels in standard shapes, sizes and ash fraction, declare their properties and make them available similar to liquid or gaseous fuels. If this is combined with mature technologies for solid fuel use for heat at the domestic level as well as semi-industrial level, it will take much economic pressure off from the dependence on gaseous fuels that have become very expensive. This approach has the intrinsic advantage of being environment friendly, a feature that makes economic imperative consistent with environmental imperative.

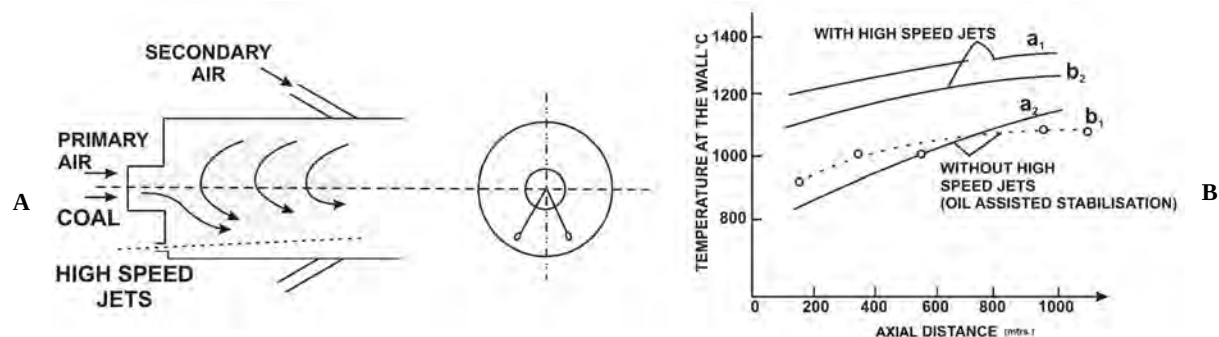


Fig. 5: Principle of flameless combustor-gasifier for gases being adopted for coal (A) and its performance in actual operation (B) (Fu *et al.*, 1986)

In the case of coal technologies, it is necessary to encourage more scientific working groups, especially from a younger generation to enable new ideas to flower into products. Encouraging this research is not entirely easy as the broad area has remained outside the active interest of most scientific groups for over three decades and hence special request for proposals has to be made outside of

traditional coal agencies to bring in freshness to the approach. Supporting such groups financially should not be a difficult task since similar class of finances is made available to researchers in other fields; a significant part of this must be supported with relatively clear end points rather than blue sky research.

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Review Article**Low-grade (waste) Energy Conversion: Science and Technological Challenges**

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Waste heat, in a classical definition, means the heat emitted by any process or utility, which cannot be economically harnessed or recycled within the process. With increasing costs of energy, the waste streams will require sliding down temperature scales for meeting the new economic viability. This means what was “good” for waste streams coming out of the process at 130°C yesterday will be imposed a penalty today and it may be demanded that the temperature has to be lowered to less than 80°C.

This paper describes how to “bridge” this new paradigm in an existing system using modern tools so that the system becomes efficient and hence sustainable. In the current discussions on energy security, energy efficiency and reduction in CO₂ to manage climate-change, waste heat energy conversion is an excellent mitigation tool. Today, modern tools such as process pinch technology, resource optimization modeling and new energy conversion devices for waste heat into useful energy, make it possible to examine every industrial process with these tools and integrate it with energy conservation measures. The paper describes all the aspects about the waste heat generated in different industrial segments, the pinch technology and resource optimization tools as well as various waste to energy options. Prominent among the energy conversion devices, Organic Rankine Cycle (ORC), which can convert even low-grade energy into electricity, is discussed in detail.

Adoption of these ‘Waste To Energy’ (WTE) technologies will have an enormous positive impact and saving of precious primary resources such as oil & gas and hence form a very critical component in the debate on energy security. Also, waste heat to energy means saving in CO₂ emissions, an important tool, which can mitigate the global warming.

Keywords: Organic Rankine Cycle (ORC); Heat Pump; Chiller; Pinch Technology; Climate Change

Background

Industrial processes use energy for conversion of raw materials into finished product(s). In this process of conversion, various transformations of energy and mass take place within the process and, at the end of the process, the products and effluents emerge from the process. Effluents contain constituents which are declared as “waste” both in their form (mass) and heat content. Efficiency (η) of any process is therefore defined as ratio of output (desired) to input and $(1-\eta)$

times the input is a measure of the waste generated from the process.

Thermodynamically, therefore, any process of conversion results in increased entropy which in turn ends up in the undesired product and energy being disposed into the “sink.” The increase in entropy of the universe is precisely due to this. While the first law of thermodynamics always conserves the energy and mass, the second law of thermodynamics correlates the quality of energy utilized and brings in

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the concepts of exergy and Carnot efficiency. Most of the waste energy from the process is closer to the sink or the ambient conditions and hence poses a challenge in harnessing the same. The singular challenge in waste energy is that it is a large quantity but with quality closer to sink levels. Thus, a 500 MWe power plant generates nearly 800 MWe of waste heat close to 48°C closer to the sink conditions.

Early in the industrial development phase (nineteenth and most part of twentieth century), the focus was clearly in terms of obtaining the desired product in large quantities with very limited attention to the efficiency aspects. This resulted in almost every synthesis and industrial process utilizing enormous quantities of energy and raw materials making waste inevitable, set off from any industrial activity. Even the electricity generating technology based on Rankine cycle is built on a 30% conversion efficiency resulting in loss of two-thirds of primary energy (coal or oil & gas) as waste energy.

Energy Efficiency as the Key

Only in the early seventies and late eighties, when the world woke up to the reality of the exhaustible nature of energy resources and the toxic impact of effluents from industrial activities on nature including the climate change challenge posed by the use of fossil fuels, the need for examining the processes from the efficiency lens began. Enhancing the efficiency of the process by process intensification, energy efficiency and use of low grade energy became the key feature of the industrial process development. The impact of such development is immediately evident from the fact that today automobiles consume one-fifth of the diesel consumed three decades ago, ammonia fertilizer plant consumes less than half the energy consumed by plants designed in the seventies, power plants produce power at 50% more efficiency than the early generation power plants and the list goes on.

The thrust therefore has been three-fold, viz., (1) at a very basic level, explore options of energy recovery within the process itself (pinch technology and resource optimization), (2) carefully evaluate the balance energy exiting as waste energy and (3) build

appropriate technologies for utilization of the waste heat within the process itself or integrate it within the utility systems. This three-tier system would be the underpinning of the waste to energy conversion strategy for the industry.

Each of these steps is discussed in subsequent paragraphs of this article. Before we do that, Table 1 and Fig. 1 provide a glimpse on the waste heat from various Indian industries and the total potential of recovery of such energy. Apportioned energy reduction in the selected main industrial sectors is to the tune of 3.53 MTOE (Million Tons of Oil Equivalent) (Kumar, 2012), which forms a substantial portion of the energy generated in India. Fig. 1 depicts the bar graph of industry-wise waste energy potential in equivalent TOE (Tons of Oil Equivalent).

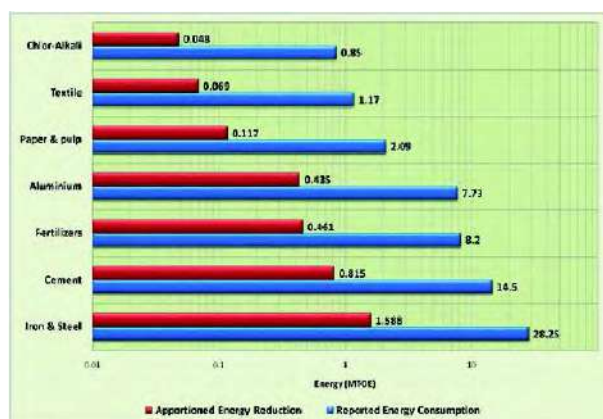


Fig. 1: Indian industry – energy scenario (Kumar, 2012)

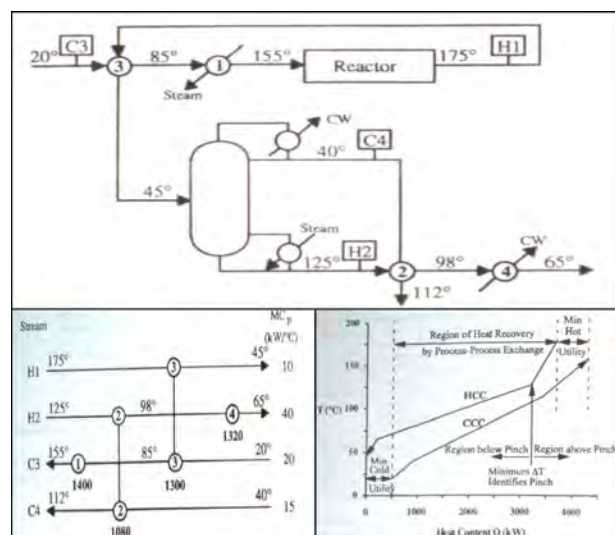
Pinch – Resource Optimization – Waste to Energy Technologies

Pinch technology (Shenoy, 1995) is a powerful tool to identify energy recovery within the process itself so that the net energy requirements can be minimized to a large extent. In this approach, any complex process is systematically decomposed into various streams where the hot fluid needs to be cooled and cold fluid needs to be heated. A coupling is established using a GCC (Grand Composition Curve), which identifies the temperature beyond which heat is to be added and the temperature below which heat is to be removed from the process.

Table 1: Indian Industry – Energy scenario (Kumar, 2012)

S.No.	Industry	No. of identified consumers	Reported energy consumption (MTOE)	Shared percentage (%)	Apportioned energy reduction (MTOE)
1.	Iron and steel	74	28.25	44.99%	1.588
2.	Cement	84	14.5	23.09%	0.815
3.	Fertilizer	29	8.2	13.06%	0.461
4.	Aluminium	10	7.73	12.31%	0.435
5.	Paper and pulp	31	2.09	3.33%	0.117
6.	Textile	90	1.17	1.86%	0.069
7.	Chlor-alkali	22	0.85	1.35%	0.048
Total		340	62.79	100%	3.533

Fig. 2 depicts these concepts of pinch technology in a typical process of distillation where multiple energy exchange takes place with some streams needing heating and some streams cooling. The first law of thermodynamics shows that net heat needed is only 80 kW and the pinch analysis shows that the pinch temperature is 115°C; and further analysis depicts the way the heat exchange must be organized which is not so obvious if carried out in a conventional manner.

**Fig. 2: Concepts of pinch technology in distillation process**

The hot utility for the illustrated process is 605 kW at temperatures above 120°C and cold utility is 525 kW at temperatures below 18°C. This analysis can save the energy needs of the process by a very large percentage to the tune of 50% to 250%. The need for larger heat transfer area and heat exchanger network is the only limiting factor in aiming for higher extraction of energy. The approach used in the heat exchanger determines the minimum approach temperature for the pinch analysis.

Once these limits are established, then the problem moves to the second stage of the resource optimization domain to organize the most optimum way for the utilities to be managed. Here, the energy needs of the process for heating, cooling and electricity generation can be met with a poly-generation facility which combines the heat and power in the most elegant manner to maximize the efficiency of the combined system.

After this phase of analysis, the process presents itself for carrying out the “waste heat” review and technologies needed for recovering this balance energy in the most effective manner. The generation of waste energy is directly proportional to the fine tuning of the first two processes, viz., if the first two processes are carried out in a coarser manner or the process constraints pose limitation to extract energy

from within the process, then, the net energy escaped from the process – which is waste energy– will need to be managed using the waste heat technologies.

Waste to Energy Options

The waste to energy (WTE) technologies can be grouped under the following two concepts. The first is the heat pumping technology, where the waste energy available can be converted into cooling energy or some intermediate level of energy or even transform the lower energy into higher grade energy. These are carried out using the concept of heat pumping – a unique methodology using a two-component mixture cycle. The two-component two-phase systems can be coupled in different ways to convert the low-grade energy into cooling energy (below ambient), or higher grade energy (higher than the waste grade) or even a lower than lower grade energy (hot water) depending on the applications.

Heat pumps offer the most energy-efficient way to provide heating and cooling in many applications, as they can use renewable heat sources in our surroundings. Even at temperatures we consider to be cold, air, ground and water contain useful heat that is continuously replenished by the sun. By applying a little more energy, a heat pump can raise the temperature of this heat energy to the needed level. Similarly, heat pumps can also use waste heat sources such as from industrial processes, cooling equipment or ventilation air extracted from buildings.

Normally, compression heat pumps have a limitation for the level of waste heat. Heat only above 70°C is considered as useful heat in electricity-driven heat pumps. Commercially, absorption heat pumps (heat transformer) giving 160°C hot water are in running-condition and it is possible to extend up to 200°C.

Absorption heat pumps are of two types (Herald *et al.*, 1996). Type 1 absorption heat basically runs on a chiller cycle. In this type, useful heat source temperature is in between energy source and waste heat temperatures, which is normally near-ambient for e.g. cooling water conditions. The useful heat

obtained in this case is about 1.7 times the source heat. The Carnot COP (Coefficient of Performance) (Herald *et al.*, 1996) of this system is given by

$$\text{COP} = 1 + \left(\frac{T_{\text{heatsource}} - T_{\text{usefulheat}}}{T_{\text{heatsource}}} \right) \times \left(\frac{T_{\text{wasteheat}}}{T_{\text{usefulheat}} - T_{\text{wasteheat}}} \right)$$

Type 2 absorption heat pump or Heat Transformer can raise the temperature of waste heat source (say 100°C) to a useful heat at a higher temperature (say 160°C) without using any external energy. The useful heat obtained in this case is a fraction of the available waste heat and balance is rejected in the sink (say 40°C). The Carnot COP of this system (Herald *et al.*, 1996) is given by

$$\text{COP} = \left(\frac{T_{\text{wasteheat}} - T_{\text{sink}}}{T_{\text{wasteheat}}} \right) \times \left(\frac{T_{\text{usefulheat}}}{T_{\text{usefulheat}} - T_{\text{sink}}} \right)$$

Figs. 3 and 4 show Carnot COP of Types 1 and 2 absorption-heat-pumps respectively at various waste-heat and useful-heat temperature.

By using a vapour absorption chiller, the available waste heat can be utilized to generate refrigeration and the refrigeration capacity will correspond to the

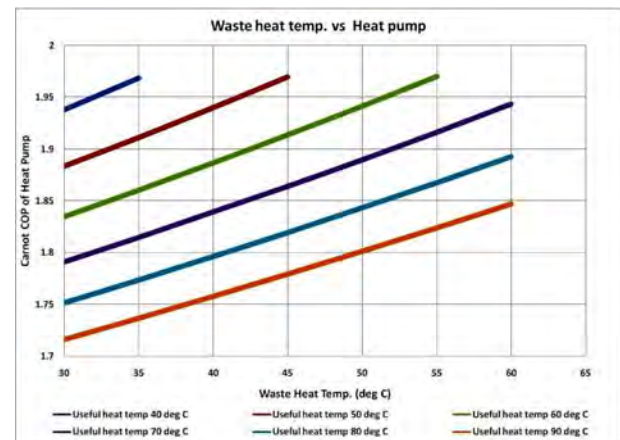


Fig. 3: Carnot COP of absorption heat pump (Type 1)

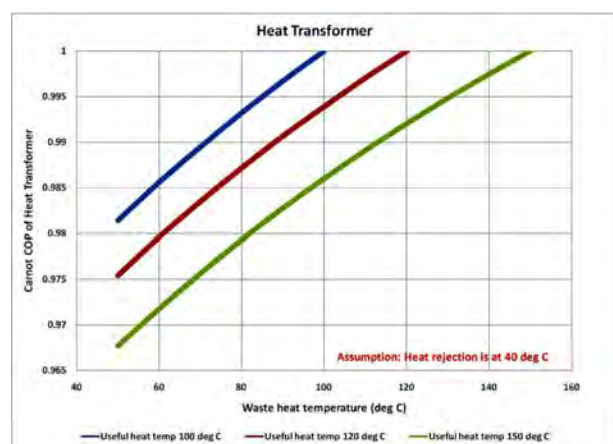


Fig. 4: Carnot COP of heat transformer (Type 2)

COP of the vapour absorption chiller. The actual COP of vapour absorption chiller for various waste heats are provided in Table 2.

Table 2: COP of vapour absorption chiller

S.No.	Temperature of waste heat Deg C	Type of waste heat	Heat recovered down to Deg C	Chiller COP	Chiller type
1	200	Sensible	100	0.7	Single effect
2	350	Sensible	140	1.4	Double effect
3	450	Sensible	190	1.8	Triple effect
4	100	Latent	100	0.7	Single effect
5	140	Latent	140	1.4	Double effect
6	190	Latent	190	1.8	Triple effect

The second concept in WTE is the new Rankine cycle using other than water as a medium. The Organic Rankine Cycle (ORC) is very attractive option used increasingly for generating electricity from low-grade energy. The choice of organic fluids is dependent on the number of parameters such as temperature of the waste heat source, ambient temperature, turbine speed and its power generation methodology (direct coupled or connected via gear box), toxicity of the fluids, availability of the organic fluids and their ODP and GWP (ozone depleting potential and global warming potential).

Organic fluids offer many advantages over steam/water to harness such low potency/low quantity waste heat. A comparison of the TS diagram (temperature entropy diagram, Fig. 5) of a typical organic fluid with water would illustrate the following advantages.

- (1) **Evaporation at low temperature:** Organic fluids evaporate at a very low temperature. The saturation pressure of R245fa is 18.25 bar at a temperature of 118°C whereas for water the saturation pressure is 1.86 bar at the same temperature. This means that for a waste heat source of about 130°C, the organic fluid vapour can be generated at sufficiently high pressure to run a Rankine cycle for power generation. However, for water with 1.86 bar saturation-pressure at 118°C, the Steam Rankine Cycle is not a technically viable option. An ORC is more viable for generating power from low temperature waste heat streams.
- (2) **Lower heat of evaporation than water:** The heat required for evaporation or the latent heat of evaporation at a temperature, is very low for organic fluid than water. For example at 118°C, the latent heat evaporation of R245fa is 115 kJ/kg; while for water, this is 2207 kJ/kg. Lower the latent heat of evaporation, higher is the heat recovery due to lower pinch problem. Hence, supercritical ORC (latent heat of evaporation is zero) offers better 'heat recovery efficiency' than even standard ORC.
- (3) **Positive slope of vapour line:** The vapour line of most of the organic fluids, has a positive slope while vapour line of water has a negative slope. While expanding in a turbine or an expander, the organic fluid becomes more and more superheated whereas the steam becomes more and more wet (higher super heat is not possible while recovering heat from a low potency waste heat). Hence, the isentropic efficiency of organic fluid turbines is higher than that of steam turbines. Also, erosion-problems caused by liquid droplets during the last stage of steam turbines do not exist in organic fluid turbines.

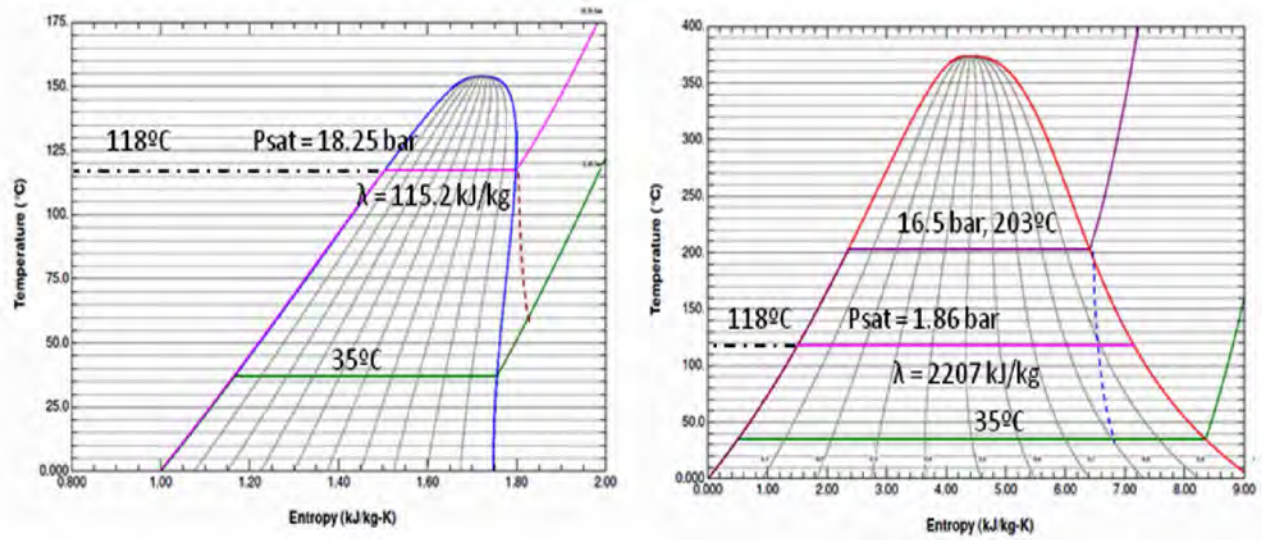


Fig. 5: TS diagram of R245fa and water (NIST 2013)

- (4) **Higher density:** The density of the most organic fluids is about 12 to 16 times higher than that of steam at the same temperature. For example, the density of R245fa is 111.6 kg/cu.m and the density of steam is 8.3 kg/m³ at 188°C. This results in a very compact system.

Hence, ORC has many advantages over conventional Steam Rankine Cycle for generating power from low potency (temperature) heat.

India needs to undertake leadership in this technology space since the large number of small and medium enterprises consuming very expensive primary energy resource exerts that extra strain on the already stretched India's energy security. Hence, the development of some of the technologies such as ORC and heat pumping systems are very important milestones. Thermax Limited, a technology company that focuses on energy and environment has initiated a pioneering effort in this field by building world class heat pumping systems using LiBr-H₂O, NH₃-H₂O, multi-salt systems, and adsorption-based cooling systems. These have been built over the years involving an enormous amount of indigenous efforts.

Innovative products such as waste heat to cooling, combined heating and cooling, heat

transformers, tri-generation systems have been built and deployed in different sectors. Also, Thermax has developed ORC-based waste heat to electricity systems with capacities ranging from 30 kW onwards. The indigenously built ORC systems provide huge opportunities for adapting these new power cycles in the waste to energy mission of the country.

Fig. 6 shows an indigenously developed 100 kW_e ORC power skid which has the capability to use waste heat at temperatures as low as 120°C.



Fig. 6: Indigenously developed 100 kW_e power skid

These technologies need a huge impetus from the policy makers to increase their presence and funding since such technologies are the immediate need of the hour.

Conclusion

Waste to energy technology, is an important field of energy science and technology and is a part of larger challenge of process optimization using pinch technology and resource optimization. The potential for saving energy is enormous as evident from the savings in TOE (tons of oil equivalent) and power generation based on the industrial waste energy emission data. WTE can generate additional energy without use of additional fossil energy, which makes it a very attractive technological option in the energy sustainability dialogue.

The heat pumping technologies (for cooling and heating) and the ORC-based power generating technologies are the two foundation stones of the WTE field. There are multiple science and engineering disciplines involved in this with heat transfer as the major focus for technology development. Enhanced heat transfer surfaces, innovative heat cycles, rotor dynamics, power electronics, material science and corrosion are a few areas which merit attention in the WTE field.

In the growing space of renewable energy, the integration of WTE with solar energy and bio energy will further aid in the development of waste energy to sustainable energy systems. Concentrated solar thermal technologies integrated with WTE cycles can result in very high conversion efficiency as well as improving the reliability of the systems.

There are many groups both in academia and industry who are working in this vital field. Thermax Limited is working on both the above concepts and taking up a leadership position in both absorption-based heat pumping and ORC systems. It has built an impressive array of technologies around these two concepts and also integrated waste heat with renewable energy resources such as solar, biomass and even geothermal energy resources.

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Review Article

Overview of Beneficiation, Utilization and Environmental Issues in Relation to Coal Processing

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In this overview, a brief description of Indian coal characteristic is presented. Based on the current production and looking at the future demands, beneficiation of Indian coal is emphasized. Two relevant case studies dealing with coal beneficiation are discussed. These studies show that low grade coal with 10% ash could be achieved by detailed characterization and beneficiation. The relevant issues dealing with various technological options such as selective mining, fine coal processing, dewatering, dry beneficiation, blending, coal to coke conversion, etc., are discussed. Finally, some of the environmental issues affecting future technology scenario are highlighted.

Keywords: Coal Maceral; Coal Utilization; Beneficiation; Dewatering; Blending

Introduction

Coal is considered as an energy mineral, and it is the most abundant source of fossil fuel energy in the world. It will continue to play a major role in economic development of India with particular reference to metallurgical and energy sectors. The bulk of the coal produced in India is thermal coal, which is primarily used for power generation. It provides 60% of the nation's electricity (Future of coal, 2013). The significant resources of coal in comparison to other fossil fuels have enabled this valuable mineral to remain at the centre stage of India's energy scene. Commercial energy consumption in India has grown from a level of about 30% to 60% of total energy requirement in the last four decades. It has grown at a rate of 7.2% during the last two decades as against the world average of only 2.2% (B.P. Statistical Review, 2013). Today, there are several conceivable problems associated with coal and the main one is that traditional technologies used for the generation of electricity from coal give rise to serious environmental concerns such as emissions of NO_x, SO_x and CO₂. The development and deployment of

technologies for zero-emission power generation from coal is thus a necessary condition in a CO₂-constrained world (Trombley and Kissonock, 2007). The sooner we understand this aspect, the sooner we will be able to mitigate the problem.

Reserves of coal are more evenly distributed across the world and therefore it can be procured from a number of countries practically from all continents. It is pertinent to mention that reserves of hard coal are equivalent to about 255 years of production at the present rate and the reserves of lignite may last for about 130 years of present production. In contrast, the estimated reserves of oil and natural gas are expected to last for 40 and 65 years, respectively, at the current rate of production (Iwaro and Mwasha, 2010).

The total geological reserve of coal in India is about 287 Bt (billion ton) as on 1st January 2013. Coking and non-coking coal resources of India are given in Table 1 (The energy policy, 2015). The total coking coal reserve is only 32.3 Bt as against 222.9 Bt of non-coking coal. This indicates that India has acute

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Table 1: Coking and non-coking coal resources of India

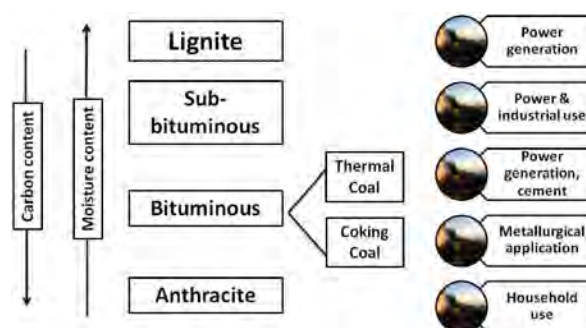
Types of coal	Estimated reserve in Bt
Coking:	
Prime coking	5.4
Medium coking	25.3
Semi-coking	1.7
Sub-total coking	32.3
Non-coking	222.9
Total (Coking and non-coking)	257.6

shortage of coking coal reserves and as a result there is an increasing trend of imports every year for metallurgical purposes. Around 90% of coal reserves come under non-coking coal category. Most of the coal reserves in India are of low quality and drift origin. These are difficult to wash because of intermixing of coal and inerts (both macerals and mineral matters) resulting from geological phenomena typical to Indian coals of Gondwana origin. The quality of coal is further deteriorated due to mechanized bulk mining and exploitation of poor quality seams. Most of the non-coking coals have high ash content varying from 40–55% with high near-gravity materials. As a result, this coal has poor washability character. Washability refers to theoretical potential of clean coal at particular ash content. The demand of coal is increasing day-by-day — it was 474 Mt (million ton) in the 2006–07 but the indigenous coal production was 434 Mt and the balance amount of 40 Mt was met via import. The demand for coal by power sector for 2011–12 has been pegged at around 730 Mt but the production target for the same period is at around 680 Mt. The Planning Commission of India has estimated that the country's coal demand to go up to 1000 Mt by the end of the 12th Plan period (2012–2017), and the import of coal may exceed over 200 Mt. Due to less production and higher demand of coking coal, India's coal imports is increasing every year and it has reached 101 Mt in 2012. Clearly, coal in the Indian context is the most secure and abundant fossil fuel and as such, its inclusion in the energy mix offers benefits in terms of energy security.

Most of the coal produced in India is high in ash with low useful heat value. Therefore, one critical issue that would control large-scale utilization of our coal is environmental pollution. In order to utilize coal in an environment-friendly way and to improve coal utilization efficiency, it is imperative that clean coal technologies such as integrated gasification and combined cycle (IGCC), the pressurized bed combustor (PBC) combined cycle, etc., are adopted. These technologies require cleaning of thermal coals, coal-water slurry preparation, underground coal gasification, carbon and CH₄ capture, etc. For this purpose, the most advanced characterization technique and beneficiation practice must be developed. It would then be possible to develop strategies and systems for coal upgrading and feed preparation for emerging clean coal technologies. Here, we discuss results of our research on characterization of coking and non-coking coal focusing on structure, macerals, petrography, etc., along with some case studies on beneficiation.

Coal Characteristics

Coal is a special type of rock — it is a sedimentary rock composed of organic carbonaceous matter — macerals and inorganic minerals. The coal has different constituents that can be measured in a laboratory which include proximate and ultimate analyses involving fixed carbon, volatile matter, moisture, and ash percentages. The different types of coal and its use in different sectors are shown in Fig. 1. The various coal types recognized principally by differences in volatile matter and H/C atomic ratio are progressively eliminated from bituminous to anthracite ranks. The grade of low rank coals is

**Fig. 1: Types of coal and its utility**

usually very low and limited to power generation. The major problem of utilization of low rank coals is linked to high moisture and high ash content. Drying, cleaning and blending prior to the use of low-grade coal are essential.

Coal Structure

Coal is a naturally occurring combustible solid. Geologists believe that coal deposits were formed about 250-300 million years ago due to degradation of plants and trees over a period of million years. Coal is predominately carbon and hydrogen with various impurities of different elements. According to rank, there are four types of coal: lignite, sub-bituminous, bituminous and anthracite. The carbon content of coal ranges from 40% for lignite to about 98% for anthracite. Coals of different varieties have different chemical compositions, and therefore different structures. Even within a certain rank of coal such as lignites or bituminous coals, the structure may vary depending on the environment in which a particular coal is formed. It has a high molecular weight, much higher than that of natural gas or petroleum. A natural gas is mostly methane with a molecular weight of 16 and that of octane with a molecular weight of 114. Coal is somewhat similar to mixture of many aliphatic and aromatic compounds and can be treated as a polymer of many such compounds. Basically, it consists of large heterocyclic monomers, held together by the three-dimensional C-C groups. A typical structure of coal is shown in Fig. 2, where the carbon atoms are arranged in an aromatic structure (Mathews and Chaffee, 2012). Simple aliphatic and alicyclic hydrocarbon groups predominate the coal structure. However, on the surface, there are many groups such as phenol, alcohol, aldehydes, etc. From a practical standpoint, it is important to

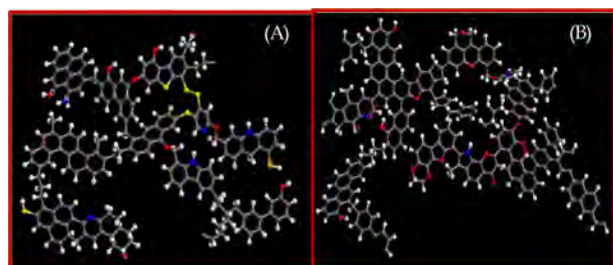


Fig. 2: Example of coal structure

recognize oxidation of coal that involves transformation of surface groups leading to poor flotation performance.

Mineral Matters

Coal consists of two classes of material: organic components or macerals, and a range of minerals and other inorganic constituents, broadly referred to as “mineral matter”. Thus, mineral matter represents the mineralogical phases as well as other inorganic elements in coal. After burning, the residue of mineral matter is termed as ash. The quality and quantity of ash depend upon type and rank of coal. Mineral matters vary widely in coal seams. The amount, mode of occurrence, and composition of the mineral matter in coal are factors of great practical importance in determining its market acceptability and economic value. The yields and qualities of products obtainable by cleaning the coal are also dependent upon the characteristics of mineral matter. According to its mode of origin, mineral matter within a coal seam may be classified into the following two categories: inherent and extraneous mineral matter. Inherent mineral matter cannot be separated from coal by simple washing while extraneous mineral matter can be removed from coal.

Macerals

Macerals are the various organic components that make up coal and control its overall behaviour. These are the descriptive equivalent of minerals which are the inorganic components of rocks. It can be considered as the organic part of coal having distinct physical and chemical properties. The macerals are of three major groups: liptinite, vitrinite and inertinite. The liptinite group is derived from the waxy and resinous parts of plants. The vitrinite group is derived from coalified woody tissue. The inertinite group is derived from woody tissue that has been altered by fire or biochemical processes. The major inertinite macerals are fusinite and semifusinite derived, respectively from coalified charcoal and semicharcoal. The order of reactivity of macerals is as follows: vitrinite>inertinite>liptinite (exinite). Most of the maceral characterization has been performed *in situ* with petrographic methods.

Petrography

Coal petrography provides detailed description and identification of different macerals present in coal (Crelling, 2008). It uses reflected light microscopy and polished sections of the material being studied. It has various applications in the field of coal characterization, carbonization, combustion, beneficiation, etc. Here, we provide an example of Hingula coal of Talcher area (Report, 2015). The macerals can be determined on volume basis or volatile and mineral material-free (vmmf) basis. It has been observed that the vitrinite macerals dominate in Hingula coal with 38% by volume (49% vmmf). It shows flat surfaces and appears as grey in colour. Oxidized vitrinite is found in significant amount up to 12% (16% vmmf) showing oxidation cracks. Inertinites are dominated by semi fusinites with small cellular cavities. The fusinites show prominent cell cavities and bright colour. Inertodetrinites appear as bright fragmental form and contribute up to 19% by volume (25% vmmf). Liptinite macerals occur with thread-like dark appearance up to 8% by volume (10% vmmf). Mineral matter (mainly the argillites and carbonate minerals) occur as dark colour either in cavity filling form or in disseminated form contributing upto 23% by volume. The macerals constituents are provided in Table 2. The gross calorific value of the coal was found to be 4535 kcal/kg. A micrograph showing oxidized vitrinite with mineral matter is shown in Fig. 3.

Beneficiation

Coking Coal

Beneficiation of coking coal in India is being practised by Coal India Ltd., SAIL and Tata Steel. The total

Table 2: Maceral constituents of Hingula coal of Talcher coal belt

Petrographic constituents	Vol. % basis	Vmmf basis
Normal vitrinite	38	49
Vitrinite oxidized	12	16
Inertinite	19	25
Liptinite	8	10

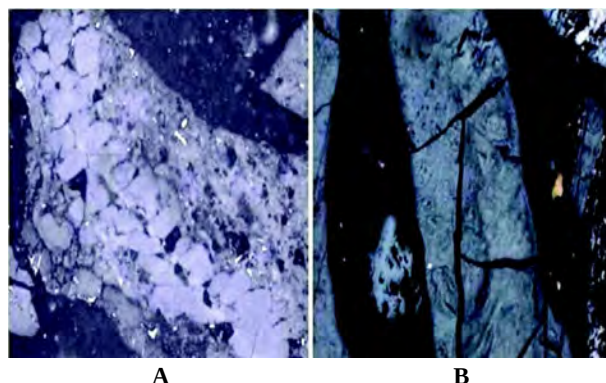


Fig. 3: A: Micrograph of oxidized vitrinite with oxidation cracks and mineral matter under reflected light and B: Micrograph of oxidized vitrinite with mineral matter and inertodetrinite under reflected light

production of coking coal in India is approximately 18-19 Mt per annum. The shortfall is more than 25 Mt per annum which is being imported. The ash content in run-of-mines coking coal is as high as 30-45%. Presently, the coal is being supplied to steel plants after beneficiation in washeries. At present, the cut-off ash level for coke making is between 13% and 18% depending on the coal characteristics and available equipment facility in the washery. In coking coal washery, heavy media cyclone, jig, and flotation processes are used for beneficiation (Das *et al.*, 2008 a; Cloke *et al.*, 1997; Atesok, *et al.*, 1993; Singh and Das 2013). In heavy media circuits, coal is crushed to below 13 mm size and classified at 0.5 mm size. The -13+0.5 mm size fraction is treated in heavy media circuit. In this circuit, concentrate, middling, and tailings are generated in two-stage heavy media cyclone processes. Good amount of middling is generated in this process because of the high percentage of near-gravity materials in the coal. Mostly, this middling is used for power generation. Depending on the feed quality of coal, tailings are also used for power generation. In heavy media circuit, special grade magnetite is used to control the density of separation. Magnetite as the media plays a vital role in reduction of misplacement materials. The Fe value of magnetite should be high (71-72% Fe) and particle size distribution be such that -45+30 mm fraction and -30 mm fraction should be 85% and 15%, respectively. This concept has been successfully tested by Tata Steel in West Bokaro washery to improve the

separation efficiency of heavy media cyclone. The heavy media circuit generates -0.5 mm size fraction which is beneficiated by flotation process. Till today, conventional flotation circuit is being practised to recover carbon values in desired quality. The overall performance of flotation cell is not up to the desired level and as a result a good amount of coal is lost in flotation tailings. It can be improved further in flotation circuit by adopting advance column flotation technology (Hacifazlioglu, 2012; Jena *et al.*, 2008).

Many washeries do not get the desired yield due to change in characteristics of coal. For this reason, R&D organizations in India are working towards reducing the ash content by suitable beneficiation strategies. Although there is successful reduction of ash content in case of foreign coals by the adoption of advanced techniques, the same may not be applicable to Indian coal due to varying nature and association of carbonaceous and ash materials in it. The technology as adopted for USA, Australia, Brazil, Germany, and other countries for coking coal beneficiation, cannot be adopted directly for Indian coal. Due to the unique character of Indian coal, it is necessary to make modification to the existing technology or develop new equipment suitable for beneficiation of Indian coal to reduce the ash content to around 10%.

Non-coking Coal

Beneficiation of non-coking coal in India was not given due importance till 2000 or so, due to its low calorific value and lower cost competitiveness. However, realizing the low useful heat value of non-coking coal coupled with stringent environmental requirements with respect to ash generation, many coal industries in India are forced to set up non-coking coal washeries. Few washeries have been set up to beneficiate non-coking coal by Coal India and private agencies at different places (having total capacity of around 100 million tons per annum). The coarser size fractions are beneficiated using jig, heavy media bath, and heavy media cyclone. In most of the cases, the fine coal (below 1 mm size) is not being processed and it is either rejected or partly utilized by blending with beneficiated coal based on the ash content. In

some of the non-coking coal washeries, below 1 mm size fraction is classified by hydrocyclone and the undersize is used in power plants after dewatering and the hydrocyclone overflow is rejected directly to the tailings pond. The underflow of hydrocyclone is further treated in specific cases by spiral concentrators to improve the quality. The ash content in these fines varies from 45-55% depending on the input ash of the washery. It contains good amount of ultra fine clay minerals, which cannot be dewatered by currently available dewatering technology. It creates many environmental problems in the surrounding areas of the washery. The generation of this fine is quite high due to banded formation of coal seam. The quantum of this ultrafine coal from the washery typically ranges from 5% to 7% of feed coal. As it is fine in nature, gravity technique cannot be utilized. The flotation technique is required to upgrade this ultra fine nature of coal. However, surface of non-coking coal always gets oxidized when it is exposed to the oxygen atmosphere. As a result, the floatability characteristic of coal decreases. To improve the floatability, pre-treatment is needed before flotation. The overflow of the hydrocyclone, i.e. the washery tailings should be beneficiated by a combination of physical/chemical/biological processes. The combination of many advanced techniques to achieve quality clean coal is the prime objective for efficient productivity of the user industries. There are several attempts being carried out to beneficiate the non-coking coal in India. It is observed that in most of cases, the ash could be reduced to 15-17% from as high as 40% ash (Dey *et al.*, 2013; Panda *et al.*, 2012; Dwari and Hanumantha Rao, 2006; Mathur *et al.*, 2003; Xia *et al.*, 2013).

Case Study I: Quality enhancement of coal for its effective utilization

Non-coking Coal

Under 10th five year plan, CSIR undertook an extensive characterization and beneficiation studies on different coal samples from India representing all types of coals to evaluate their quality and to prepare strategies for their effective utilization. These studies include detailed characterization, washability, and

beneficiation studies to reduce the ash content. Several different coal samples from Mahanadi, Eastern, Central and South-east coal fields were studied. The main characteristics of coal samples are presented in Table 3. The washability characteristics of different coals are given in Table 4 (Report, 2015). It is observed that the washed fraction of Rajmahal, Kalinga, and Religarah coals show better burnout than their unwashed fractions. However, the washed fractions of Chitra coal show a different trend. Blending studies (which is discussed later) show that a significant proportion of the low volatile matter high rank coal can be blended with the low-ranklow-ash coal for achieving good burnout.

Table 3: Characteristics of coal samples

Origin of coal	Ash %	Moisture %	Volatile matter %	Ash fusion temperature °C
MCL	35-50	5.0- 7.0	27.0-45.0	1200-1400
ECL	36-48	2.6-8.3	38.5-40.0	1280-1400
CCL	24-30	2.0-3.0	37.7-40.0	-
SECL	34-36	6.5-9.0	26.0-27.0	-

Table 4: Washability characteristics of coal samples

Details of coal samples	Washability characteristics		Utilization pattern	Techniques adopted and response to beneficiation
	Ash %	Yield %		
MCL	34.0 25.0	86.0 53.0-60.0	Good for power generation	Jig/HM cyclone. Clean coal with 25.0% ash for sponge iron can be produced
ECL	34.0 25.0	58.0-92.0 30.0-80.0	-do-	Jig/HM separation to produce clean coal for sponge iron
CCS	25.0	84.0	-do-	Heavy media separation: Clean coal with 25.0% ash for direct reduction
SECL	34.0 31.0	25.0 13.30	-do-	Heavy media separation: Clean coal with 34.0% and 26.0% for direct reduction and power generation

Coking Coal

Characteristics of the lower seam coals of the Jharia Coalfields and West Bokaro Coalfields show high ash percent, low volatile matter and poor coking property. Washability studies on the raw coal crushed to 75 mm showed poor washability characteristics and the theoretical yield for steel grade coal is considerably low. The washing scheme developed for the treatment of coals from the lower seams of Eastern part of Jharia Coalfields may not be applicable to the coal of western part. Moreover, clean coal for metallurgical industries and power plants may not be generated simultaneously. Application of computer simulation on washability data for prediction of achievable power grade coal from coarser fraction and steel grade coal from finer fractions yielded the following results (Mohanta *et al.*, 2010). Muraidih OCP coals: 12.0% yield at 17.5% ash level (steel grade) 19.5% yield at 34.2% ash level (power plant grade) and 67.6% yield at 56.1% ash (FBC); Kuju OCP coals: 13.7% yield at 17.5% ash (steel grade) 60.1% yield at 34% ash (power plant grade) and 26.2% yield at 49.9% ash (FBC). Investigations were also carried out on fine coal samples (–0.5 mm) generated at Patherdih,

Table 5: Comparison of characteristics of different coal fines

Details	Patherdih	Bhojudih	Munidih	Muraidih	Muraidih (oxidized)
(a) Ash %					
	34.3	25.8	22.1	32.0	40.4
(b) Size Analysis					
+500	27.2	8.8	10.3	0.5	1.2
+300	20.4	8.1	7.3	24.2	41.1
+150	18.8	12.5	8.2	15.9	14.6
+75	18.1	15.7	6.0	7.9	13.1
+45	9.3	5.3	16.3	10.4	7.8
-45	6.2	49.5	51.9	41.1	22.2
(c) Release Analysis					
Ash %		14.4	14.1	15.2	14.7
Yield %		75.0	61.2	76.0	38.8

Bhojudih, Munidih and Muraidih coking coal washeries. The physical and chemical characteristics are compared in Table 5 (Sastry *et al.*, 1988). These studies indicate that the ash content of the samples varies from 22.0% to 40.4%. The size analysis indicates that the fraction below 45 micron also varies widely (15.0% to as high as 68.0%). This indicates that the nature of these fines generated at different washeries varies widely. The recovery process needs to be tailor-made and each sample has to be investigated for all possible techniques to arrive at optimum technology to beneficiate these fines efficiently. In view of the above, all the samples were studied for release analysis, and flotation by cell and column. All the results are compared in Table 6. The results indicate that all the samples are amenable for beneficiation by flotation technique. These can be beneficiated by conventional cell or column to reduce the ash to below 17.0%. These results indicate that flotation column technique yields superior performance compared to cell. Flotation column can yield better grade product (2-3% less ash) for same yield or higher yield (5-10%) at same ash level. However, these results need to be compared with the performance of advanced gravity units using combination of spirals and flotation, oil agglomeration, oleo flotation, etc., before selecting the optimum technique to enhance the performance of final coal recovery from these fines.

Table 6: Comparison of results of different coal fines

	Clean coal by cell flotation		Clean coal by column flotation		Feed ash %
	Ash %	Yield %	Ash %	Yield %	
A. Patherdih	17.7	54.4	14.34	60.8	34.3
	20.8	71.6	17.40	76.5	34.3
B. Bhojudih	13.2	75.0	9.0	61.1	25.8
	14.6	79.0	12.0	68.0	
C. Muraidih	14.1	87.3	9.8	81.0	22.1
	11.0	72.00	5.0	52.0	22.1
	11.6	80.3			
D. Munidih (Oxidized)	14.0	71.4	12.3	68.5	32.0
	16.5	78.4	9.7	51.0	32.0
E. Muraidih	18.8	42.0	18.7	62.8	40.4

Case Study II: Beneficiation to Achieve 10% Ash from High Ash Indian Coal

Non-coking coal forms 90% of the total national coal reserve. The pattern of deposit of non-coking coal is in banded form. Depending on the thickness of the coaly bed, selective mining may be emphasized to achieve 25-30% ash coal. This coal can be further beneficiated using either jig or heavy media cyclone to achieve around 10% ash coal with reasonable yield. This category of mines may be preserved for utilization in metallurgical industries.

Major Recommendations

- Dry beneficiation studies of non-coking coals of India for power plants.
- Development of 3 or 2 product schemes to produce clean coal for sponge iron and cement industries by complete utilization.
- Identifying the coals suitable for sponge iron industry and increase the resource base for the above industries by suitable beneficiation.
- Technology to establish small capacity washeries for sponge iron and cement industries.
- Optimization and simulation of existing coking coal washeries to improve yield.
- Modernize the existing coking coal washeries by introducing advanced techniques.
- Development of suitable reagents for beneficiation of non-coking coal fines and oxidized coals.

The natural slimes generated during crushing of the coal for processing can be beneficiated by flotation process to produce two products with high ash rejects. In one of the products, it is possible to achieve 10% ash with 20% yield of total feed to the flotation circuit. This product can be used as coal fines for coal injection either in blast furnace or in DRI processes. Low volatile coking coal which has high ash and liberated below 100 micron size, can be utilized after flotation for coal injection in iron and steel industries after blending with low ash high volatile coal. The

Table 7: Beneficiation results of Hingula coal (Report 2015)

Size in mm	Feed		Product		Tails		Total	
	Wt. %	Ash %	Wt. %	Ash %	Wt. %	Ash %	Wt. %	Ash %
-25+6	60.0	27.5	21	10	39	37	60	27.5
-6+1	18.0	25.0	8	10	7	40	15	24
-1+0.1	15.0	24.0	9	10	9	40	18	25
-0.1	7.0	25.0	4	10	3	45	7	25
Overall	100	26.38	42	10	58	38.2	100	26.38

technology, product carrying capacity, wash water input, and retention time. Available design criteria available in literature would provide adequate information for a successful flotation circuit design.

Dewatering of Coal

Dewatering is an unit operation integral to any wet coal beneficiation plant. The natural sedimentation rate of the particles present in colloidal and finely divided suspended form is very slow. At present, screen, centrifuge, and filter of various kinds are used for dewatering of coal concentrate. Tailings/slimes generated in coal washeries are disposed to tailings pond via thickener in the form of high concentration slurry. However, till today dewatering of slimes is not practised. In coal processing plants, a large volume of waste water containing a variety of solids are being generated. The amount of waste water is increasing year after year as a result of continuous mining and cleaning of coal in the coal industries. The increase of ultrafine particles and inorganic impurities in wastewater poses technical and economic difficulties in handling, settling of suspended particles, and recirculation of water into the plant. Fine coal processing is therefore, the most difficult and costly operation. For this reason, a suitable dewatering method is essential for dewatering the tailings slurry containing high clay content. The utilization of wastewater in coal washeries can be enhanced by dewatering of slimes using high pressure filter. Flocculation technology employing polymeric flocculants in conjunction with fine magnetite may be applied to achieve faster settling rate with lowest level

of water turbidity (Das *et al.*, 2008 b). The characteristics of washery reject water and proper choice polymeric flocculants is very much important. This of course depends on the chemical and physical characteristics of the pollutants present in the waste water.

Dry Beneficiation

Undoubtedly, wet processing of coal requires huge quantity of water. This provides enough incentive for dry beneficiation of coal which has great promise as a cleaning method, particularly from an environmental standpoint. There are different types of dry coal processes such as sorting, electrostatic separation, magnetic separation, and mechanical separation for dry coal beneficiation. These processes depend on the differences in physical properties between coal and gangue minerals such as density, size, shape, luster, magnetic conductivity, electrical conductivity, radioactivity, etc. Air dense medium fluidized bed separation process, pneumatic jig, and FGX are used commercially for beneficiation of coal on dry basis. Indian coals are not amenable to dry processing as most of the coal types are liberated at extremely fine sizes. Several studies carried out in India using heavy media fluidized bed separator and tribo-electric separator indicated that coal can be cleaned only up to 30% ash (Sahu *et al.*, 2005; Dwari and Hanumantha Rao, 2008; Dwari *et al.*, 2015). However, in recent years, much research effort is directed towards dry processing of fine coal particles in electrostatic separator which hold great potential to treat Indian coal. Advantages of the dry beneficiation are as follows:

- Reduction in process water requirement
- Reduction in water pollution due to effluent slurry
- Elimination of tailings pond
- Elimination of dewatering equipments
- Reduction in specific cost for transportation

Blending

In order to achieve the consistence coal quality, coal blending technique has been recognized as a well-

accepted practice in coal washeries in India as well as abroad. Coal-blending techniques generally target one or more desired coal-blend quality such as size, ash, sulphur content, etc. However, this practice has shown that the behaviour of blends does not always comply with the expected weighted average value of parameters from the individual coals comprising the blend. Moreover, these changes in behaviour of the coal blend affect the downstream processing of the coal. Although a variety of simulation software is available, the simulated results do not agree well with the real-life plant operations due to variations in coal composition (Mohanta *et al.*, 2012). It is a potential area for further research in an Indian context to induce a change in property of the coal blend than that of the individual coals. More importantly blending in an overall sense can have an effect on the performance of different downstream equipment.

Non-Coking Coal for Coke Making

Coking coals differ in their plasticity and fluidity properties from non-coking coals. Also these coals differ with respect to hydrogen content in their molecular structure. It is assumed that lack of hydrogen content leads to non-agglomerating behaviour of coal particles. Typically, coking coals have high hydrogen content of more than 5.5%. Non-coking coals can be utilized for coke making by the following processes: (i) Hydrogenation of coal, (ii) Blending with high grade prime coking coal, (iii) Blending with carbonaceous materials and (iv) mixing inorganic/organic binder. Hydrogenation of coal requires high temperature (300 to 700°C) and pressure (3 to 20 MPa) for its reaction. By this method, non-coking coal is structurally changed to coking coal which then can be used for coke making. Non-coking coal can be blended with prime coking coal to produce coal blend which could be used for making good quality coke. Another way of utilizing non-coking coal is by blending it with carbonaceous materials such as pitch, waste plastics, molasses, sawdust, coconut shell, etc. to improve the hydrogen content and plasticity of coal.

Environmental Issues

Coal mining and thermal power plants significantly impact the local environment. Furthermore, mining

operations affect land, water, forests and habitats. Key environmental concerns in the coal-power sector in India include:

- Flue gas emissions-particulates, sulphur oxides (SO_x), nitrous oxides (NO_x), and other hazardous chemicals;
- Pollution of local streams, rivers and groundwater from effluent discharges and percolation of hazardous materials from the stored fly ash;
- Soil contamination due to storing of fly ash.

India is projected to need over 400 GW (Gigawatt), by 2030 which is nearly same as the current installed energy capacity of Japan, South Korea and Australia combined. As a result, India will become the world's third largest CO₂ emitter by 2015. A global roadmap for the new low carbon economy, investigates how global economic development can be achieved while avoiding dangerous climate change. This calls for zero emissions and coal technology. Low emissions coal technology is more costly than a traditional pulverized coal plant, and this along with other barriers prevent widespread implementation of such installations in India. Nonetheless, a two-pronged long-term strategy must be assessed: the reduction of fuel costs and emissions through efficiency gains and the removal of CO₂ from the conversion process through its capture and storage. Clean coal technologies for improved efficiency of the conversion cycle is the need of the hour. Carbon capture and sequestration (CCS) is the critical enabling technology to reduce CO₂ emissions significantly while allowing coal to meet world's pressing energy needs. Emission reductions can be achieved partly by the employment of coal technologies that improve on conventional steam-cycle power plants (Vorrias *et al.*, 2013). With the current best available technique (BAT), energy conversion efficiency of coal-fired power plants is around 46% for hard coal plants and 43% for lignite plants. Improved combustion technologies include ultra-supercritical (USC), pressurized fluidized bed (PFB) and oxygen-rich combustion which are expected to improve efficiency above 50%, possibly up to 60%. For each of these, further effort is required

to increase their scale, reduce costs and develop new materials. Crucially, CCS can only be applied post-combustion in such plants; and methods for adding this final step to the power plant without an undue efficiency penalty, still need to be demonstrated.

Coal Gasification

Coal gasification is a technology which is used to convert coal into gas for various applications such as production of synthetic natural gas, liquid fuels, gaseous fuels, hydrogen gas, etc. During coal gasification, coal reacts with high pressure steam and oxygen, to produce the gas (Vorrias *et al.*, 2013). As Indian coal is associated with high clay minerals, direct run-off-mines coal cannot be used for gasification. It leads to increase slag formation in the furnace and ultimately cause fouling of the syngas cooler. The coal needs to be beneficiated to remove the major portion of the clay minerals before its utilization. Besides, in order to improve coal gasification, better understanding of slag behaviour and the characteristics of the slagging process is needed. New power plants of the future will differ from conventional plants in significant ways. Here, the coal is converted into a fuel gas, and then thoroughly cleaned for burning in a manner similar to that used to burn natural gas. The first step is to capture the carbon dioxide created when coal is turned into a fuel gas. In the second stage, one of the components of the fuel gas, carbon monoxide, is mixed with water to produce hydrogen as fuel. In this process, emissions of conventional pollutants such as sulphur, soot and smog-forming nitrogen, will be extremely low. Coal cannot be called 'clean' until its CO₂ emissions are captured and utilized/stored safely. The CO₂ emission can be tackled by sequestration from coal-fired source such as power plants, coke ovens, blast furnace, etc. The separation of carbon dioxide mixed with methane from natural gas is well-proven. It may be mentioned here that capture of carbon dioxide from flue gas streams following combustion in air is much more difficult and expensive, as the carbon dioxide concentration is only about 14% at best. The carbon dioxide captured from a power plant can be injected into rock body at least a mile down along deep underground wells. It is routinely injected underground, but mostly into oil-bearing rocks,

to force oil to the surface. Any project that aims at carbon dioxide capture from power plants will be a milestone for no reason other than to keep CO₂ out of the atmosphere. Engineers and geologists must monitor the spread of carbon dioxide underground and find out a suitable solution to neutralize its adverse effect.

Fly Ash

Fly ash is the finest coal combustion residue (CCR) generated due to the transformation of mineral matter present in coal particles during combustion. Indian coals have very high ash content. Coal with an ash content of around 40% and more is predominantly used in India for thermal power generation. As a consequence of its usage for power generation, a huge amount of fly ash is generated in thermal power plants, causing several disposal-related problems. The generation of fly ash is projected to increase to about 170 Mt with increase in consumption of coal in power plants to a level of 500 Mt by 2012. For disposal of 170 Mt of fly ash, roughly 120,000 hectares of land will be needed. In India, the problem is further compounded by the use of wet fly ash collection systems by a large number of power plants, which results in degradation of the pozzolanic characteristics of the ash, an essential ingredient for several ash-based products. Thus in the coming years, fly ash disposal would be a major challenge unless adequate initiatives are undertaken by the thermal power plants to popularize commercial usage of fly ash. Presently, fly ash is being utilized for brick-making, land filling, construction purposes, soil amendment, etc. Major areas of fly ash utilization are (1) making of bricks/blocks, cellular concrete products and lightweight aggregates, (2) manufacture of cement, (3) road construction and (4) embankment, backfill, land development, etc. At present, processes have been developed to use fly ash in building brick production by cold setting method. In this process, fly ash is reacted in presence of alkali activator to form hydrous alumino-silicate phases which develop binding property in the product both under atmospheric and curing conditions. This process has been established in pilot scale for manufacture of building bricks having crushing strength of 80-150 kg/cm² by using 80-90%

fly ash and blocks having 150-300kg/cm² crushing strength containing 50-60% fly ash by weight. Fly ash is also used for production of sintered aggregates which requires about one ton of fly ash per ton of aggregate. The sintered fly ash aggregate pellet is produced in accordance with the specification of natural aggregate (IS: 383-1970) that ranges from 4 to 20 mm in size. The sintered lightweight aggregate is suitable for application in making low density concrete, sub base road and other building material products (Muduli *et al.*, 2014). Mineral carbonation is a thermodynamically stable process for trapping of atmospheric CO₂ where materials rich in alkaline earth metals (Ca, Mg, and Fe) combine with CO₂ to form stable carbonates. Fly ash is a potential source for mineral carbonation by proper chemical co-ordination to capture atmospheric CO₂. The carbonated material can find application as a substrate and soil conditioner for agriculture (Muduli *et al.*, 2010).

Conclusions

Coal will continue to be the principal source of energy

in India. Production of quality coal for power plants, metallurgical and cement industries, and other industrial use is a growing challenge. Therefore, the beneficiation of high ash coal will play a vital role in the days to come. The role of beneficiation is quite important, particularly in the context of non-coking coal, due to its complex nature that necessitates adoption of advanced technologies and processes to achieve the desired ash content at acceptable yield. Processes such as flotation, enhanced gravity separation, dewatering, blending, etc., must be given due importance. Furthermore, coking coal production in India must be reconsidered. India has very limited reserves of coking coal which is a key raw material for production of steel and other metallurgical goods. Hence, a concerted research effort must be directed to use non-coking coal after converting it into coke.

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Review Article

Materials Research and Opportunities in Thermal (Coal-based) Power Sector Including Advanced Ultra Super Critical Power Plants

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The Integrated Energy Policy of the Government of India envisages an ambitious programme for power capacity addition to about 800 GWe by 2031-32 towards meeting the energy demands of the country for ensuring the required economic growth and improved standards of living. For minimizing carbon dioxide emissions, through achieving the highest possible energy efficiency and reducing coal required per unit of power generated, it is planned to adopt clean-coal-based power generation technologies such as supercritical, ultra-supercritical, advanced ultra-supercritical and integrated gasification combined cycle, which are in different stages of development, demonstration and commercialization worldwide. Certain innovative options such as carbon dioxide capturing and sequestration and high-temperature bio-waste and bio-fuel based plants are also being explored. This paper discusses the materials research and opportunities of these power generation technologies.

Keywords: Advanced Ultra Super Critical Technology; Power Plants; Materials; Indigenization; Boiler Tubes, Welding, Non-Destructive Evaluation; Integrated Gasification Combined Cycle; Bio-Waste, Bio-Fuel

Introduction

Coal is India's main source of energy, with about 66% of power generation being dependent on coal. India's coal reserves are currently assessed at 286 billion tonnes, with proven reserves being about 114 billion tonnes (Coal India Limited, 2014). Among various energy sources for capacity addition in power in India, coal would continue to be the most predominant (more than 50%) source of energy at least till the middle of the 21st century. However, it is also a fact that coal is the single largest source of carbon dioxide emission through power generation, which is a cause of concern from the perspective of climate change. India therefore needs to adopt a cautious approach for using coal as the primary source of power generation. India desires

to adopt clean coal-based power generation technologies that help minimize carbon dioxide emissions, while yielding the highest possible energy efficiency and reducing the coal required per unit of power generated. Thus, adoption of such technologies would also enhance energy security for the nation by increasing the longevity of coal reserves.

Several clean coal technologies have been and are being developed worldwide. These include supercritical, USC, Advanced Ultra Super-Critical (AUSC), Integrated Gasification Combined Cycle (IGCC) etc., which are in different stages of development, demonstration and commercialization. Besides, certain innovative options are also currently explored, albeit in small measures, in Carbon dioxide

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Capturing and Sequestration/storing (CCS) (Logan *et al.*, 2007), just as any other power plant effluents are safely repositied. The CCS process involves capturing of carbon dioxide from power plants and other sources, transporting it to suitable locations and injecting it into geological reservoirs. While the technology of CCS for capture, transport and sequestration exists, the additional cost involved, environmental and safety issues are still concerns that need to be solved for a successful implementation of CCS as a successful industrial practice. The future options also include combining energy cycles such as Rankine (steam) and Brayton (gas), so as to reap an overall efficiency of about 60% (Fig. 1) (Logan *et al.*, 2007).

Several countries in the world are adopting increasing steam parameters in order to attain higher and higher efficiency and thus leading to lower and lower carbon dioxide emissions. Supercritical technology has already been adopted commercially worldwide and also in India. Supercritical power plants have higher steam cycle parameters than conventional sub-critical power plants, thus offering higher efficiency, consuming less coal per unit power produced and emitting less carbon dioxide per MWe-h. In India, of the initial 660 MWe supercritical power plants, with steam parameters of 247 kg/cm²/537°C/565°C (247 kg/cm² main line steam pressure/537°C main line steam temperature/565°C reheat line

steam temperature), a few have been commissioned. Subsequently, plants of 660 and 800 MWe units, with higher steam parameters of 247 kg/cm²/565°C/593°C are under construction.

In recent years, several pulverized coal-fired power plants with Ultra Super-Critical (USC) steam parameters (i.e., ≥ 250 kg/cm²/ $\geq 600^\circ\text{C}$ / $\geq 600^\circ\text{C}$) have been set up or are under construction in Europe, Japan, China and Korea. These have higher efficiencies than supercritical power plants. Power plants with USC steam parameters are likely to be set up in India in the next few years, once the initial supercritical plants are in regular operation. Further, research and development (R&D) is in progress in USA, Europe and Japan on the AUSC cycle with steam parameters of ≥ 300 kg/cm²/ $=700^\circ\text{C}$ / $=700^\circ\text{C}$. With such enhanced steam parameters, the efficiency of the power plant is expected to be in the range of 45-47% (gross on higher heating value basis) with Indian coal under Indian ambient conditions, with carbon dioxide mitigation potential in the order of 20-25% as compared to conventional sub-critical power plants (Table 1). It can be observed from Table 1 that the specific carbon dioxide emissions from an AUSC plant will be about 17% less than those from a typical sub-critical plant. Typically, for an 800 MWe AUSC plant, this will translate to a reduction in carbon dioxide emissions of about 1 million tons per year. Thus, the introduction of AUSC power plants can help reduce the carbon dioxide emission intensity of India, and this would enable India to address the issue of climate change even with continued reliance on coal with concomitant reduction in consumption of coal.

An ambitious programme for power capacity addition has been envisaged in India for meeting the energy demands of the country to ensure the required economic growth and improved standard of living through the introduction of supercritical and USC power plants. According to the Integrated Energy Policy of Government of India, the country needs an installed capacity of about 800 GWe by 2031-32 (Planning Commission, Government of India, 2006).

Potential for AUSC Power Plants in India

Considering the high and growing energy demand in

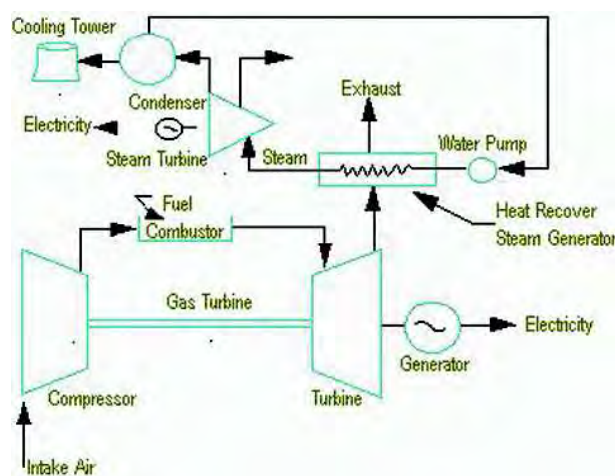


Fig. 1: Schematic of combined cycle power plant (Logan *et al.*, 2007)

Table 1: Efficiencies and carbon dioxide emissions from various types of plants

Plant type with power rating	Steam pressure (kg/cm ²)	Steam temperature (°C)	Efficiency (%)	Carbon dioxide emissions (kg/MWe-h)
Sub-critical plant (500 MWe)	170	540/540	35-38	900
Super-critical plant (660/800 MWe)	250	560/590	40-42	830
Advanced ultra super-critical plant (800 MWe)	300	700/>700	45-47	740

the country, there is an excellent scope for setting up clean coal technology based AUSC power plants in India with reduced carbon dioxide emission. Under the National Mission Programme on Clean Coal (Carbon) Technologies, development of AUSC thermal power plants has been identified as one of the projects to be taken up on priority. This project is proposed to be executed in two phases. The objective of the first phase would be to undertake R&D on all aspects of AUSC technology for thermal power plants in order to improve power plant efficiency, reduce carbon dioxide emissions and reduce coal consumption per unit of power generated. In the second phase, an 800 MWe AUSC demonstration power plant will be established based mainly on the technology developed in the first phase. Once a first demonstration 800 MWe AUSC power plant is proven to be technologically successful, a large number of such plants can be designed with AUSC technology. This could mean a potential of as high as 10-15 units of 800 MWe sets per year. As technology matures with time, the unit ratings of sets could also go up, reducing the specific cost further.

Developing AUSC Technology Indigenously – A Necessity

In addition to pursuing indigenization efforts, India has been acquiring proven technologies in power generation and other areas from abroad. While acquiring technologies is easier and expeditious to implement, it should be noted that by and large only

manufacturing and limited design information is transferred by foreign collaborators. This results in perpetual dependence on foreign suppliers and in the long run proves more expensive due to the continued dependence on import of key materials and technologies. For instance, the import content of the technology acquired in the early eighties for 500 MWe sub-critical boiler turbine generator sets still continues to be as high as 30%.

Technology acquisition in the present scenario also involves a high level of business sharing, which not only raises costs but also slows down the technology absorption process, and thus severely affecting the indigenization and potential savings of costs. For supercritical sets of 660 or 800 MWe rating, the import content is currently about 50%, which will gradually decrease with time.

With indigenous development of AUSC technology, including indigenization of materials, the long-term import content would be significantly reduced. This will also reduce India's dependence on imports even for our existing fleet of coal-fired power plants. While development of the technology involves an upfront investment in R&D, in the long run, it will prove to be much less expensive than acquiring the technology after a few years, of course with conditions attached for the imported technology. Import of equipment, once developed and commercialized abroad, has always proven to be expensive. Further, with continued dependence on imported technology, India's national priorities could be vulnerable to changes in the priorities and time schedules set by the technology developers, apart from their willingness to share such advanced technologies. Indigenous development of AUSC technology also has significant spin-off benefits in related industries, as it has happened in the case of space and nuclear sectors.

Ultra Super-Critical Technology

Any steam cycle unit with steam pressure greater than the critical point of 225 kg/cm² is said to be super-critical. There is no standard definition for USC power plants, and different parameters are being used in different parts of the world to categorize a power plant as a USC plant. However, as a common practice,

any supercritical coal-based power plant having main-steam temperature of 600°C or above has been considered as ultrasuper-critical. In addition, the steam pressure in USC plants is more than 250 kg/cm². The total number of supercritical coal-based power generation units globally is about 600, of which about 60 are USC units. These USC power plants are in the capacity ranging from 350 MWe to 1000 MWe. Brief information about some of these plants is given in Table 2.

International Efforts in AUSC Technology Development

The USC technology for steam parameters up to 280 kg/cm² and 600°C superheater/reheater temperatures can generally be considered as a mature technology in the world and is ready for adoption. In order to further improve the power plant efficiency and mitigate specific carbon dioxide emission, studies are currently being conducted in the European Union,

Table 2: Some ultra super-critical (temperature >593°C; pressure >250 kg/cm²) installations

S.No.	Name of power plant	Country	Capacity (MWe)	Pressure (kg/cm ²)	Temperatures (°C)	Year of operation
1.	Matsuura No. 2	Japan	1000	255	598 / 596	1997
2.	Haramachi No. 1	Japan	1000	245	600 / 600	1997
3.	Haramachi No. 2	Japan	1000	259	604 / 602	1998
4.	Nanaoota No. 2	Japan	700	255	597 / 595	1998
5.	Chougoku EPCo.	Japan	1000	246	600 / 600	1998
6.	Tsuruga No. 2	Japan	700	255	597 / 595	2000
7.	Tachibana-Wan No. 1-2	Japan	2 x 1050	259	605 / 613	2000
8.	Misumi No. 1	Japan	600	250	605 / 600	2001
9.	Isogo No. 1 (J-Power)	Japan	600	255	600 / 610	2002
10.	Isogo No. 2	Japan	500	245	600 / 600	2002
11.	Tomato-Atsuma No. 4	Japan	700	255	600 / 600	2002
12.	Neiderausen	Germany	1000	290	580 / 600	2002
13.	Hitachinaka No. 1	Japan	1000	245	600 / 600	2003
14.	Maizuru No. 1	Japan	900	245	595 / 595	Under construction
15.	Hirono No. 5	Japan	600	245	600 / 600	Under construction
16.	Shandong Zouxian	China	2 x 1000	250	600 / 600	2006
17.	Torrevaldaliga	Italy	6 x 660	250	600 / 610	2006
18.	Yuhuan No. 1-4	China	4 x 1000	268	600 / 600	2006-2007
19.	Zouxian No. 4,7-8	China	3 x 1000	241	600 / 600	2006-2007
20.	Wai Gao Qiao No. 3-4	China	2 x 1000	275	600 / 600	2007-2008
21.	Jiangsu Taizhou No. 1-2	China	2 x 1000	255	600 / 600	2007
22.	Neurath No. 1-2	Germany	1100	295	600 / 605	2008
23.	Westfalen	Germany	2 x 800	275	600 / 610	2011
24.	Eemshafen	Netherlands	2 x 800	275	600 / 610	2012
25.	Luenen	Germany	1 x 800	270	600 / 610	2012
26.	Mainz	Germany	1 x 800	273	600 / 610	2013

USA and Japan for use of steam parameters of 300 kg/cm² and more pressure and 700°C and more steam temperatures (Table 3). These conditions have been termed as AUSC to distinguish them from the USC plants that are being already considered worldwide. In this context, for India, AUSC plants with steam parameters of 310 kg/cm² and steam temperatures of 710°/720°C are being considered.

Table 3: Steam parameters being considered for AUSC plants in different countries

Year (start)	Country	Temperature (°C)	Pressure (kg/cm ²)
1990	USA	760	350
1998	Europe	700	350
2007	China	700	300
2008	Japan	700	350
2010	India	710/720	310

Efforts by the European Union

The European Union has supported efforts on increasing the steam parameters of power plants by co-financing research projects COST, AD700 and COMTES700 (Klenk *et al.*, 2010), targeting materials development, manufacturing, testing, evaluation and demonstration employing test loops in existing power plants. A consortium of utilities, equipment manufacturers, materials manufacturers, universities and research institutions has participated in these programmes. For example, the main tasks of AD700 programme were as follows (Klenk *et al.*, 2010).

- (i) Demonstration of nickel-base super-alloys for long-term operation in the temperature range of 700-720°C.
- (ii) Development of new fabrication methods for components made of super-alloys.
- (iii) Development of new austenitic steels for boiler tubes operating in the temperature range of 600-700°C to minimize the use of the expensive super-alloys.
- (iv) Investigation of corrosion resistance of the new alloys operating at 700-750°C

The AD700 Project was realized in different phases. The first phase focused on the development and mechanical testing of new materials, development of new furnace designs, and techno-economic study regarding the economic viability of the new plant concept. The second phase included demonstration of manufacture of new materials, design of component test facility and preparatory work for the demonstration phase. The third phase included demonstration of developed materials in two small-scale test installations under the COMTES700 project (Klenk *et al.*, 2010). The main objective of the COMTES700 project has been the demonstration of the new materials in a component test facility at a German power plant and in a small test rig in a Danish power plant. The testing period of the components has been approximately 20,000 hours, spread over a period of more than four years starting from 2005. A further component test programme ENCIO has been initiated to test the creep behaviour of thick cross-section components at a power plant in Italy. It was expected that the design of an AUSC power plant can start by 2015, with the operation of the first demonstration plant by 2020 (Klenk *et al.*, 2010).

Efforts by the USA

US DOE has launched and co-funded a National Project “Vision 21 Power Plants” for developing new materials with USC steam parameters, along with EPRI and a consortium of power equipment manufacturers (Viswanathan *et al.*, 2005). The goals of the research program are as follows.

- (i) Identification of the materials performance issues that limit the operating temperatures.
- (ii) Identification of improved alloys, fabrication processes and coating methods that will permit boiler operation at steam temperatures up to 760°C and steam pressures up to 378 kg/cm².
- (iii) Definition of issues impacting designs that can permit power generation at temperatures greater than or equal to 870°C.

The first phase has been completed. Alloy 740H was identified as the most suitable material. In the next phase, efforts are on to identify a power plant

where components can be tested in actual conditions. This phase is likely to be completed by 2020. Subsequently, a demonstration plant is expected to be set up.

Efforts by Japan

The Japanese government launched the “Cool Earth-Innovative Energy Technology Program” in 2008 to promote international cooperation and actively contribute to substantial reduction in global greenhouse gas emissions. Twenty-one technologies that can contribute to substantial reductions in carbon dioxide emissions by efficiency improvement and low carbonization were selected. A 700°C class boiler, turbine and valve technologies, including high-temperature materials technology, are being developed. The aim is to commercialize 700°C class pulverized coal power system with efficiency of 46% by 2015 and 48% by 2020. Candidate materials for boilers are being tested, and turbine rotor and casing materials are being developed and tested. Steam power plants that have been built recently usually have 250 kg/cm²/600°C steam conditions. By developing 700°C class A-USC from the latest 600°C class USC, carbon dioxide emissions can be reduced by more than 10%. In addition to efficiency improvement, biomass co-firing and carbon dioxide recovery technology will be adopted to reduce carbon dioxide emissions further. A double reheat system with the steam condition of 350 kg/cm² main steam pressure, 700°C main steam temperature and 720°C reheat temperature can achieve the thermal efficiency of 46% (high heating value basis). The National Institute of Materials Science (NIMS) and leading power equipment manufacturers are associated in the program.

Efforts by China

The first application of supercritical boilers in China was in 1992 (2×600 MW units at Shidongkou). Supercritical and USC units began to be installed in 2002 and have expanded very fast since then; with more than 150 supercritical and USC units with 600 MW or higher capacity in operation or under construction. In December 2004, China’s first domestically built 600 MW SC unit of Qinbei Power

Plant was put into operation. The 4×1000 MW Yuhuan Power Plant is China’s first commercially operated power plant using domestically built 1000 MW USC pressure boilers (240–275 kg/cm²/600°C superheater/reheater steam; 46% net efficiency) during 2006 to 2008; 2×1000 MW USC units at Zouxian Power Plant went into operation during December 2006 to July 2007; 4×1000-MW USC power units have been commissioned since end of 2007. During 2008–2009, 6 sets of imported and 50 sets of indigenous 1000-MW USC power units (250/263 kg/cm², 600°C/600°C) were ready and more than 90 sets of 600-MW USC power units were planned to be commissioned.

By 2010, supercritical and USC units accounted for over 40% of the total newly built thermal power generating units. By end of 2008, 90 GWe of supercritical and 11.2 GWe USC units were in operation and more than 100 GWe of supercritical and USC units were under construction. China’s top three power equipment producers, Dongfang Electric, Harbin Electric and Shanghai Electric, have imported the manufacturing technology for supercritical and USC plants. From 2010 to 2020, new power plants with unit capacities of 600 MW and more will be supercritical units and about half of the newly built power generating units will be USC units. Consequently, supercritical units would have accounted for over 15% of the total power capacity by 2010 and 30% by 2020. China has also initiated programmes for development of A-USC technology.

In the next 15 years, several measures will be undertaken in China’s power industry. These would include (i) constructing large-capacity power units, retrofitting old power units, shutting down small-sized power units, developing cogeneration units, optimizing unit operation, and applying new technologies for energy conservation to improve the efficiency of coal-fired power generation; (ii) applying high-efficiency dust-separation technology and new FGD/de-NO_x techniques to reduce the pollutant emission from thermal power plants; (iii) using an air-cooling technology for water conservation; (iv) actively introducing and developing large-capacity supercritical power units; and promoting clean coal power generation (Yongping *et al.*, 2010).

Development of AUSC Technology in India

Supercritical power plants currently under construction and being planned in the country are either being supplied by foreign companies or are being manufactured by Indian companies through various collaborations under which technology is being provided by the foreign collaborator. Various strategies have been considered for transfer of know-how of supercritical technology to India. Foreign manufacturers are also setting up their manufacturing base in India, thus ensuring that the technology remains in their hands.

The above approach would ensure large-scale penetration and utilization of supercritical technology in India. However, in order to further improve the power plant efficiency, to mitigate carbon dioxide emissions, for reduced use of coal per MWe, and considering huge capacity addition through coal power generation, it is essential that indigenous AUSC power plants are adopted if the country has to reap the benefits of indigenous technology. It can be concluded from the international efforts that AUSC plants having $300 \text{ kg/cm}^2/700^\circ\text{C}$ or above steam cycle parameters are being designed by a few countries. However, it should be borne in mind that no mature, off-the-shelf technology is available for such plants. Materials for use at temperatures up to and above 700°C are being used in many Indian industries except in the thermal power sector. Considering India's ambitious capacity addition programme, which will be largely based on coal as the source of energy up to about 2050, it is most opportune that India develops its own AUSC technology, which will not only go a long way in serving its own needs but also could be a major source for meeting global requirements.

Recognizing that the country has planned installation of a large number of supercritical plants of 800 MWe capacity plants, it is prudent to select 800 MWe rating for an indigenous AUSC demonstration plant. Development efforts needed for smaller unit of 660 MWe would be no different than that for 800 MWe plant and unit energy cost would also be higher for smaller units.

The materials choice for steam temperature of about 700°C is well-documented. From the objectives of higher plant efficiency of at least 46%, resulting carbon dioxide mitigation and reduced amount of coal per MWe, steam parameters of 310 kg/cm^2 and 710°C and 720°C as the main steam and reheat steam temperatures, respectively, have been selected for detailed design (Fig. 2).

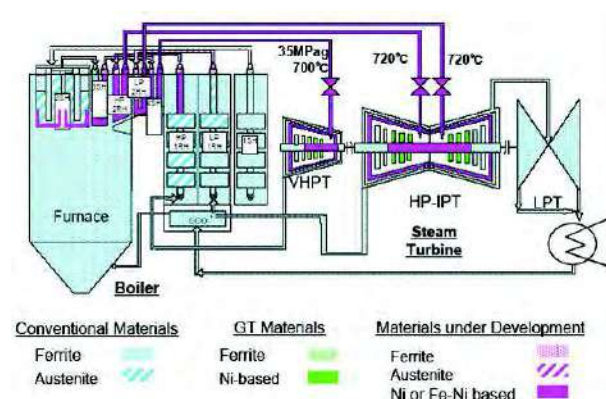


Fig. 2: Schematic layout of the proposed Indian AUSC plant (Jayakumar *et al.*, 2014)

Overview of Development Approach for AUSC Technology –Indian Perspective

Selection of Materials and R&D for AUSC Power Plants

Selection of superheater and reheater materials, manufacturing technology and equipment development constitute important areas to be addressed while considering the $710^\circ/720^\circ\text{C}$ steam cycle. It is important to note that a large $710^\circ/720^\circ\text{C}$ AUSC plant will have materials in some of the components similar to the mature sub-critical units in the country. These components include condenser, feed-water heaters, water pumps and feed-water piping. The boiler will have different materials for waterwall and superheater zone, with each material optimized according to steam temperature and pressure conditions. The materials for the waterwall and the first-stage of superheater and reheater boiler tubing can be adopted from the current USC power plants of 600°C steam temperature. Advanced materials need to be developed only for the top-end of superheater and

reheater boiler tubing, main steam and hot reheat piping, high-pressure and intermediate-pressure stop and control valves, high-pressure and intermediate-pressure turbine, and turbine integral piping for the AUSC plants of 710°/720°C steam temperature. The turbine design can be modular in nature, with the turbine being designed with changes in the high-pressure and intermediate-pressure portions to suit the higher steam parameters.

One of the most critical aspects in the development of AUSC technology is the choice of materials for high temperature zones. The criteria for selection of materials for different components of the AUSC plant should be based, apart from their physical properties, on their inclusion in ASME Code or Code Case or equivalent international code. This would ensure that there is a strong basis for design of components and wide commercial availability of materials. Additionally, the materials for the AUSC plants of 710°/720°C steam temperature would have to be selected for different components based on: (a) adequate high temperature mechanical strength, viz. average stress to rupture of 100 MPa for 100,000 hours at design temperature of component; (b) high thermal conductivity and low thermal expansion coefficient to minimize thermal stresses; (c) good formability and weldability; (d) satisfactory corrosion resistance in steam and flue gas environment; (e) moderate creep-fatigue interaction; (f) industrial availability/confidence in indigenous development; and, (g) economy. The relatively new materials that are proposed to be used in the AUSC plants include the following.

- (1) Grade-23 steel (2.25Cr-1.6W-V-Nb-B, as per ASME code case 2199) for water walls;
- (2) Grade-91 steel (9Cr-1Mo-V-Nb-N, as per ASME SA-213) for superheater and reheater tubing.
- (3) 304HCu austenitic stainless steel (18Cr-9Ni-3Cu-Nb-N, as per ASME code case 2328) for the final stage of superheater tubing, in which the finely dispersed spherical copper precipitates (of 32 nm size) are highly stable in the austenite matrix even after long-term ageing upto 10,000h at 650°C (Bai *et al.*, 2013).

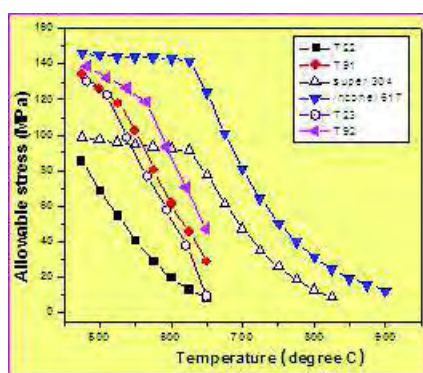
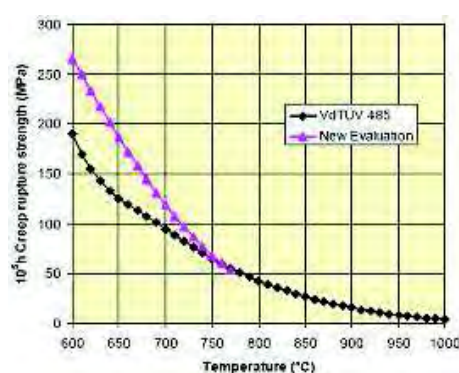
- (4) Nickel-base Alloy 617 (52Ni-22Cr-13Co-9Mo, as per ASME SB-167 specification), with controlled composition (Alloy 617M) for the final stage of superheater and reheater tubing at the hottest zone, with the higher requirements of A617M including notably stringent limitations on elements such as C, B, Cr, Ti, Fe, Si and Mn, and a solution annealing temperature higher than 1160°C.

Any other material, such as Alloy 740H (Ni-25Cr-20Co as per ASME code case 2702) and Sanicro-25 (X7NiCrWCuCoNbB25-23-3-3-2 as per VdTüV 555), with promising mechanical properties, should also be examined for suitable applications. The extent of use of these materials will depend on the optimisation studies of cost-benefit in the hot regime of the boiler. The preferred materials for the high-pressure and intermediate-pressure turbine parts, viz. rotor, blades, valves, casings etc., would be Alloy 617M for the wrought products and Alloy 625 for the cast products. However, extensive equipment manufacturing technology development would have to be adopted. For development of materials and manufacturing technology, a pragmatic approach would have to be adopted considering the existing industrial base and pace at which industrial capabilities can be enhanced. Industrial base exists in the country for boiler tubing, and can be extended for piping, pipe fittings and valves. Wherever possible, efforts have to be made to indigenously produce advanced materials and manufacture components based on these materials developed indigenously. The chemical compositions of the candidate materials for the AUSC plants are provided in Table 4. The allowable stresses (as per ASME) as a function of temperature for the different candidate AUSC boiler materials is given in Fig. 3A, while that for Alloy 617M is given in Fig. 3B (Dietz *et al.*, 2009). In this regard, it is important to mention that the design temperature of the tube mid-wall will be 40°C higher than the steam temperature.

With the initiative and funding from the Office of the Principal Scientific Adviser (PSA) to the Government of India, a beginning has already been

Table 4: Chemical compositions (in wt. %) of candidate materials for AUSC plants

Element	T23 (ASME)	T91 (ASME)	304HCu SS (ASME)	Alloy 617 (ASME)	Alloy 617 (VdTüV 485)	Alloy 617M
Carbon	0.04-0.10	0.07-0.14	0.07-0.13	0.05-0.15	0.05-0.10	0.05-0.08
Manganese	0.10-0.60	0.30-0.60	1.00 max	1.0 max	0.7 max	0.3 max
Phosphorous	0.03 max	0.02 max	0.040 max	0.015 max	0.012 max	0.012 max
Sulphur	0.01 max	0.01 max	0.010 max	0.015 max	0.008 max	0.008 max
Silicon	0.50 max	0.20-0.50	0.30 max	1.0 max	0.7 max	0.3 max
Nickel	–	0.40 max	7.50-10.50	44.5 min.	Balance	Balance
Chromium	1.90-2.60	8.50-9.50	17.00-19.00	20.0-24.0	20.0-23.0	21.0-23.0
Molybdenum	0.05-0.30	0.85-1.05	–	8.0-10.0	8.0-10.0	8.0-10.0
Cobalt	–	–	–	10.0-15.0	10.0-13.0	11.0-13.0
Copper	–	–	2.50-3.50	0.5 max	–	0.5 max
Niobium	0.02-0.08	0.06-0.10	0.30-0.60	–	–	–
Titanium	–	0.01 max	–	0.6 max	0.2-0.5	0.3-0.5
Tungsten	1.45-1.75	0.02 max	–	–	–	–
Vanadium	0.20-0.30	0.18-0.25	–	–	–	–
Nitrogen	0.03 max	0.03 max	0.05-0.12	–	–	0.05 max
Aluminum	0.03 max	0.07 max	0.003-0.030	0.8-1.5	0.6-1.5	0.8-1.3
Boron	0.0005-0.006	–	0.001-0.010	0.006 max	–	0.002-0.005
Iron	Balance	Balance	Balance	3.0 max	–	1.5 max

**A****B****Fig. 3: Allowable stresses as a function of temperature of (A) different AUSC boiler materials, and (B) Alloy 617M (“New Evaluation”) (Jayakumar *et al.*, 2014)**

made through the launching of the pre-project R&D for the Development of Boilers with Advanced High Temperature Materials by a three-organization

consortium of Indira Gandhi Centre for Atomic Research, Bharat Heavy Electricals Limited and NTPC Limited. This pre-project R&D activity has,

within a time frame of 2 years, led to the indigenous development and production of 52 mm diameter boiler tubes of 304HCu stainless steel of 9.5 mm wall thickness (Fig. 4) and Alloy 617M of 11.9 mm wall thickness, and their matching composition welding consumables, in collaboration with Mishra Dhatu Nigam Limited and Nuclear Fuel Complex. Appropriate welding procedures have also been developed for similar and dissimilar weld joints for the 304HCu stainless steel (Fig. 5) and Alloy 617M tubes. Evaluation of the mechanical properties (tensile, short-term creep, low-cycle fatigue, impact, quasi-static fracture and fatigue crack growth) of these two high-temperature tube materials and their weld joints indicates that their mechanical properties are comparable to the internationally reported values as also the codified values in the VdTÜV (German) standard.



Fig. 4: Indigenously manufactured 304HCu SS boiler tubes of 6-7 m length (Jayakumar *et al.*, 2014)



Fig. 5: Welded boiler tubes of indigenous 304HCu SS (Jayakumar *et al.*, 2014)

Development of Major Equipment

The development approach for each of the major sub-systems and equipment for the AUSC power plant would have to be based on analysis at the generic level, and the knowledge, skills and facilities available. Current capabilities in the country, together with additional skills that would be developed within the next few years during the execution of ongoing 660/800 MWe sub-critical boilers, would enable the full range of capabilities required to develop the boiler for an 800 MWe AUSC power plant.

Augmentation is needed for turbines, in particular, towards indigenous design capability, production of forgings in nickel-base Alloy 617M, castings in nickel-base Alloy 625 and welding technology for welded-rotor for HP and IP turbine, for an economic design. The turbine poses the biggest challenge for economic realization of AUSC plants both in India and abroad.

Design Criteria, Codes and Standards

The current Indian Boiler Regulations do not address comprehensively the design, materials, inspection, etc. relevant to AUSC components. Hence, there is a need to develop specific design criteria, codes and standards for the AUSC power plant components. Accordingly, design rules following the philosophy of “design by formula” as given in ASME codes would have to be used for the preliminary assessment of thickness of pressure boundary components. Further, the design would be confirmed by “design by analysis” accounting for the effects of thermal stresses, discontinuity stresses, namely thermal fatigue, ratcheting, etc., adopting the practices followed in the design of the nuclear components (liquid metal and gas cooled reactors). Due consideration would have to be given to evolving design rules recommended in German (VdTÜV), French (RCC-MR) and British (CEGB-R5 and R6) codes or any other relevant international codes. A few aspects, introduced as special rules specific to structural materials, would be validated by experimental benchmark tests on specimens having component features. It would definitely be a challenge to evolve robust state-of-the-art design with advanced materials to ensure high

confidence in design, manufacture and operation.

Advanced Non-destructive Evaluation Techniques and Online Damage Assessment

Technology for the non-destructive evaluation (NDE) during manufacture is available and the rules have been defined in codes of practice such as ASME. Nevertheless, pre-service inspection records are required to be generated to assess the performance during operation and life extension. From the in-service inspection point of view, reliability centred maintenance, quantitative risk-based inspection programs and condition-based maintenance to manage the systems will assume greater significance. Ultimately, the results of non-destructive testing need to be combined with issues of critical flaw size, fracture mechanics, probability of failure and acceptable level of risk for optimizing inspection schedules and extending plant life. Many of the components of AUSC power plants will be subjected to service conditions that lead to high levels of stresses, creep, fatigue and creep-fatigue interaction, and varied extent of fire-side corrosion and steam oxidation. Therefore, special attention would have to be given for development of on-line monitoring and inspection methodologies to assess life-limiting aspects (e.g. material degradation, creep-fatigue damage, etc.) and thereby improve plant availability. For this purpose, capability exists in the country but significant developmental efforts are needed. Some of the areas which need attention include design and development of high-temperature sensors, techniques and procedures for early-damage detection, online monitoring and continuous life-prediction methods, non-contact and global area monitoring, NDE modelling, signal analyses and image-processing techniques for enhanced sensitivity and quantitative NDE.

Testing and Validation

Testing of indigenously developed components in appropriate locations of operating power plants and in newly created dedicated test facilities/loops to assess the performance and validate the design and technology would have to be also taken up. It may be noted here that such challenges are being faced

internationally in the development of materials and manufacturing of components for AUSC plants.

Challenges and Current Capabilities in India for AUSC Technology

The indigenous development of AUSC power plant technology is very challenging on account of the following reasons:

- (i) AUSC technology has yet not been fully developed anywhere in the world.
- (ii) New nickel-base alloys are required for which manufacturing technologies such as welding, manufacture of tubes and pipes, castings and forgings, are yet to be fully established. Commercial scale manufacturing facilities in the sizes and volumes required are not available anywhere in the world. In India, facilities for manufacture of such items even for supercritical plants are not available.
- (iii) Equipment such as boilers and steam turbines has not been developed *ab initio* in India so far.

Although the task is challenging, there is confidence that India has well-established capabilities for development of the AUSC power plant technology. With the objective of enhancing plant efficiency and/or reducing the cost, further innovations in plant design would have to be considered and adopted, if found to be feasible, in terms of cost vis-à-vis benefit, reliability, and complexity in design, manufacture, layout and operations.

Issues involved with Materials Development of AUSC Technology

Development of AUSC technology in the country would essentially require the following.

- (i) Forgings for turbines in nickel-base Alloy 617M
- (ii) Thick piping header in Alloy 617M/Cr-Mo steels
- (iii) Economic route for production of boiler tubes in different grades
- (iv) Development of forming, welding, and other manufacturing processes/capabilities.

- (v) Welded rotor technology of Alloy 617M/10Cr-Mo steel for HP and IP turbines

Gaps in the Development of AUSC Technology

The Indian AUSC power plant development project would have to aim at development of *ab initio* equipment and component design. Such an approach has not been followed so far even for sub-critical plants, where designs had been developed through technology transfer/collaborative route. Also, the materials are largely imported for these plants. The indigenous design, materials, manufacturing and erection of 800 MWe AUSC plant would be a challenging and rewarding mega-initiative for India. The expertise available in the Indian industries, R&D organizations and academic institutions would need to be pooled and synergized, as detailed below, to realize the indigenous USC plant.

- (i) Selection of materials and development of materials to incorporate in the indigenous plant, based on detailed materials testing and evaluation in existing plants under simulated conditions and/or in specific testing facilities will be another mega-challenge. In particular, testing under simulated conditions will be crucial to qualify the advanced materials. For this purpose, existing power plants would have to innovatively incorporate while new power plants should have provisions for testing of the new materials. Adequate testing, evaluation and characterization facilities would have to be established after due consideration of availability of existing facilities and expertise.
- (ii) Development of material technology for wrought and cast products, forming and machining processes, welding consumables, and welding processes, along with necessary facilities and capacity additions, will be an important manufacturing challenge.
- (iii) While a few facilities are available for material testing (for creep and fatigue), testing of a variety of AUSC materials at elevated temperatures of 750°-800°C to provide short-term material creep data simulating 710°/720°C

steam plant design conditions requires enhancement of testing facilities dedicated to development of AUSC technology.

Integrated Gasification Combined Cycle

The integrated gasification combined cycle (IGCC) is a technology that uses a gasifier to turn coal and other carbon-based fuels into synthesis gas (syngas) from which pollutants such as sulphur are removed before the syngas is combusted, thereby lowering emissions of sulphur dioxide, particulates, etc. With additional process equipment, the carbon in the syngas can be shifted to hydrogen via the water-gas shift reaction resulting in nearly carbon-free fuel, with the carbon dioxide from reaction being amenable to compression and storage. Excess heat from the primary combustion and syngas-fired generation is passed to a steam cycle resulting in improved efficiency compared to that from conventional pulverized coal. The lower emissions that IGCC technology allows, in comparison to conventional power plants, would be important as emission regulations are tightened due to growing concern for impact of pollutants on the environment. The gasification process can produce syngas from a wide variety of carbon-containing feed-stocks such as high-sulphur coal, heavy petroleum residues and biomass. The type of plant is called “integrated” because the syngas produced in the gasification section is used as fuel for the gas turbine in the combined cycle, and the steam produced by the syngas coolers in the gasification section is used by the steam turbine in the combined cycle. In a normal combined cycle, so-called “waste heat” from the gas turbine exhaust is used in a heat recovery steam generator to produce steam for the steam turbine cycle. An IGCC plant (Fig. 6) improves the overall process efficiency by using the higher-temperature steam produced by the gasification process in a steam turbine cycle to generate additional electrical power (Maurstad, 2005).

IGCC is now considered as “capture ready” and could potentially capture and store carbon dioxide. Around 30 IGCC plants are in operation around the world with electrical output of up to 300 MW with a cumulative operating experience of over one million

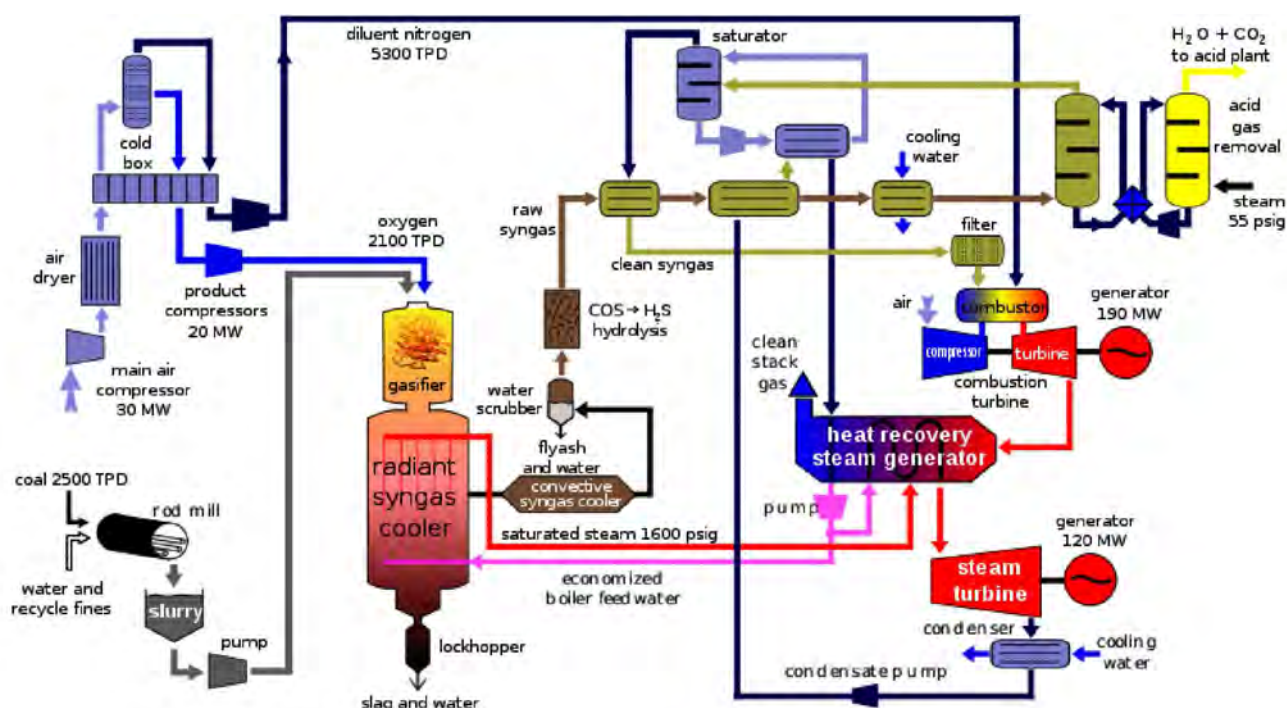


Fig. 6: Schematic of an IGCC power plant (Maurstad, 2005)

hours. In Tiruchchirappalli, India, a 6.2 MWe experimental coal gasification plant has been in operation for over 15 years. Efforts to set up a larger demonstration plant have not materialized due to unfavourable cost economics and lack of full-funded government support. There are several refinery-based IGCC plants in Europe that have demonstrated good availability (90-95%) after initial shakedown periods. The following factors are responsible for their poor / limited performance.

- (i) None of these facilities use advanced technology gas turbines.
- (ii) All refinery-based plants use refinery residues, rather than coal, as the feedstock. This eliminates coal handling and coal preparation equipment and associated problems. Also, there is a much lower level of ash produced in the gasifier, which reduces cleanup and downtime in its gas cooling and cleaning stages.
- (iii) These non-utility plants have recognized the need to treat the gasification system as an upfront chemical processing plant, and have

reorganized their operating staff accordingly.

The high cost of IGCC is the biggest obstacle to its integration in the power market; however, most energy executives recognize that carbon regulation is coming soon. With carbon capture, the cost of electricity from an IGCC plant would increase approximately by 30%. For a natural gas combine cycle, the increase is approximately 33%. For a pulverized coal plant, the increase is approximately 68%. Thus, the potential for less expensive carbon capture makes IGCC an attractive choice for keeping low cost coal as an available fuel source in a carbon constrained world.

Next generation IGCC plants with carbon dioxide capture technology will be expected to have higher thermal efficiency and to hold the cost down because of simplified systems compared to conventional IGCC. The main feature of these next generation plants is that, instead of using oxygen and nitrogen to gasify coal, they use oxygen and carbon dioxide. The main advantage is that it is possible to improve the performance of cold gas efficiency and

to reduce the unburned carbon (char). The carbon dioxide extracted from the gas turbine exhaust gas can also be utilized. Use of a closed gas turbine system capable of capturing the carbon dioxide by direct compression and liquefaction obviates the need for having a separation and capture system.

High-Temperature Bio-Waste and Bio-Fuel-based Plants

Bio-fuel is most commonly defined as a renewable source of energy, which is produced from biological material or biomass, such as sugarcane, corn, cellulose or vegetable oils. The strategic goal of bio-fuel is to supplement or even replace fossil fuel which is constantly and rapidly diminishing in quantity. The most common types of bio-fuel these days are ethanol and bio-diesel. It is interesting to note that certain traditional fossil fuels, for example coal, may also be treated as a kind of bio-fuel since coal also originates from biological material.

Used-oil recycling is one of the ways to generate bio-fuel energy. Another method of obtaining bio-fuel is based on fermentation, from which is obtained ethanol that can be produced from any biomass, containing carbohydrates (mostly plants that are rich in starch or sugar). The resources for producing ethanol can vary from crops, grown specifically for that purpose, to manure, available in large amounts at cattle farms. Ethanol as a type of bio-fuel can be used as a direct source of energy, or it can also be mixed with conventional gasoline to increase the octane value and lower harmful emissions into the atmosphere.

There are several major types of bio-fuel: solid, liquid and gaseous. Bio-diesel is the example of liquid bio-fuel, while ethanol represents gaseous type of this alternative energy source. Solid bio-fuels such as fuel pellets made from wood chips, sawdust or agricultural wastes are also produced around the world; however, they are not as popular as other types of bio-fuel in view of their higher environment pollution potential. Nowadays, the second and even the third generation of bio-fuels being developed aim at generating energy from non-food crops, cellulose and even certain living algae that produce ethanol during the life activity (Scott

et al., 2010). India is also considering algae-based bio-diesel as an option for generation of bio-fuel as it has the potential to produce oil more efficiently than crop plants.

Substitution of conventional gasoline with bio-diesel or ethanol in transportation can significantly reduce (up to 100%) emission of greenhouse gases into the atmosphere. Though carbon dioxide and some other harmful chemicals are also produced while burning bio-fuel, their amount is much lower than the emissions during burning fossil fuels. In addition to being clean for the environment, bio-diesel is also considered to be a better option for diesel engine than conventional diesel fuel. Bio-diesel provides better lubrication and leaves fewer residues in the engine after its burning. Besides, bio-diesel is completely biodegradable and safe.

On the other hand, thoughtless development and wide implementation of any alternative energy source may pose new serious challenges in the economy and environment. In case of bio-fuel, it is necessary to keep in mind that growing popularity of bio-diesel requires more and more land to be used for growing plants as the resource for bio-fuel. However, many of these crops exhaust the soil and can even make it unsuitable for growing foodcrops. Hence, it is of vital importance to evaluate all the pros and cons of every type of alternative energy source before its wide popularization.

Several institutes and companies, including ICT Mumbai, NCL Pune and NIIST Trivandrum are actively pursuing R&D on ethanol production from ligno-cellulosic waste. The energy output to input ratio is a useful parameter to take stock of the attractiveness of the various processes. Simultaneously, one could ascertain relative attractiveness vis-à-vis the other options such as direct combustion and power generation through gasification. However, it is necessary to quantify the ecological suitability, economic attractiveness and the overall appropriateness factors of different bio-fuel options obtained from different energy feedstock, e.g., bio-diesel and briquette from *Jatropha* or ethanol and bagasse from sugarcane (Bharadwaj *et al.*, 2007). Similarly, more than one type of chargeable energy

input can be used in producing the bio-fuels, e.g., a different biomass or other renewable energies, fossil fuel or human energy.

Over the last decade, substantial progress has been made towards *Jatropha* bio-diesel, especially at the downstream end. *Jatropha* B100 bio-diesel has proved itself adequately as a fuel which can be utilized in mobile and stationary engines without any engine modification and with exceedingly low emissions. This was the successful outcome of the collaboration with Daimler Corporation and others. General Motors (USA) and U.S. Department of Energy seek to ascertain productivity of *Jatropha* fruiting under realistic conditions prevailing in wasteland and at the same time to carry out a comprehensive life cycle analysis (LCA) under the overall philosophy of “Local use of local produce”. This is being done in Gujarat covering both very rocky wastelands (Neswad and Chorvadla in Bhavnagar district) and Gochar land (Halol in Panchmahal district). Further, this study has been carried out with the best germplasm available in India and propagated through cuttings and micro-propagation. Use of *Jatropha* cake is also taken up as a part-substitute of synthetic fertilizers in the spirit of integrated nutrient management. Since the bio-diesel process, now covered through grant of a U.S. patent, is well-established and conforms to stringent emission norms at this point of time, the requirement is assured availability of sufficient biomass. On the other hand, there is a critical need to make a reliable assessment of the true potential of seed biomass from marginal lands.

It has been conclusively established that seed-raised plantations lead to greater heterogeneity of performance compared to plantations raised from cuttings of elite mother plants. Hence, there is need to emphasize cultivation through true-to-type plants. This may not, however, be practical, as adequate numbers of cuttings would not be available. Micro-propagation is the best answer and a protocol has been developed for micro-propagation.

The *Jatropha* empty shell briquette has had a profound bearing on *Jatropha* bio-diesel carbon

balance. The energy output to input ratio, now standing at ca. 6 is more than a factor of 2 higher than for soya and rape bio-diesel. The briquettes have been demonstrated to burn satisfactorily in domestic “chuhlas” and boilers. However, no study has been conducted on the characteristics of the smoke. Nothing is also known about the utilization of the ash in the *Jatropha* field. Hence, these areas need further studies to address the concerns.

Concluding Remarks

Adoption of AUSC power plants in India, with enhanced steam cycle parameters, i.e. 310 kg/cm² and 710°/720°C, provides an excellent scope for improving gross plant efficiency to better than 46%, and reducing coal consumption per MWe as well as carbon dioxide mitigation potential compared to conventional sub-critical power plants. Although, USC technology for 280 kg/cm² and 600°C superheater/reheater steam parameters is considered as mature technology internationally that is ready for adoption, no mature off-the-shelf technology is available for 310 kg/cm² and 710°/720°C steam parameters. The EU, USA, Japan and China have been putting considerable efforts in developing AUSC technology by co-financing various research projects, targeting materials development, manufacturing, testing and evaluation and demonstration in existing power plants. In view of the above, setting up of an indigenous 800 MWe AUSC demonstration plant, with 310 kg/cm² and 710°/720°C steam parameters, on a national mission mode, is most opportune, to meet growing energy demands of the country, in an efficient manner.

The integrated gasification combined cycle (IGCC) plants also have the potential of becoming a less expensive carbon capture technology for utilizing low-cost coal as an available fuel source in a carbon constrained world. Similarly, high-temperature bio-waste and bio-fuel based plants can conform to stringent emission norms but require quantification of ecological suitability, economic attractiveness and evaluation of overall appropriateness factors of different bio-fuel and bio-waste options obtained from different energy feedstock.

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Review Article

Emerging Biomass Conversion Technologies for Obtaining Value-Added Chemicals and Fuels from Biomass

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Biomass is a renewable fuel. Several technologies have been developed for biomass conversion to obtain value-added chemicals and fuels such as gasification, anaerobic digestion, hydrolysis, fermentation, and hydrogenation. Biomass may also be directly used for power generation. Interest in the production of bioethanol, biodiesel and biogas from the biomass has increased the world over. Efforts are also underway to make the production of hydrogen from the biomass cost effective. Availability of biomass is to be increased manifold. Improved scientific planning and management may help in growing plenty of biomass, which may be compressed and collected. Development of cost-competitive biomass conversion technologies such as chemical, thermochemical and biochemical conversion processes may afford the utilization of biomass to obtain hydrogen, biogas, alcohols, biodiesel and other cleaner fuels for power generation and transport. Biomass may also afford the production of feedstock for chemical, petrochemical and other industries. This may help in establishing bioeconomy of the future.

Keywords: Biomass Conversion Technologies; Bioethanol; Biogas; Biodiesel; Biogasoline

Introduction

Manifold increase in oil prices, i.e. beyond US \$140/barrel had compelled the world to think seriously about national energy securities. Oil reserves of the world may not last for more than 40-50 years at the present rate of consumption (Shafiee and Topal, 2009). Rate of consumption of oil is increasing with increase in world population and with increase in the standard of living of the masses. Coal reserves of the world are also limited and may not last for more than 100-150 years (Shafiee and Topal, 2009).

By 2050, world population may have doubled and thus fossil fuel consumption may also double. There is need to follow the trend which may afford an economic growth rate of 8-9% with perfect human resource management.

The world is undergoing a transition of moving to renewable energy sources which are cleaner and

can be easily adopted in rural areas as well. Renewable energy sources such as solar photovoltaic, solar thermal, wind, geothermal, wave, mini-hydel energy, etc. generate power. However, these do not produce oil and natural gas which are required for transport, shipping, mining, etc. and also provide feedstock for fertilizer, dyes, and pharmaceuticals, chemical and petrochemical industries. In fact, bioenergy is the only renewable source of energy which can afford liquid as well as gaseous fuels, besides power. Fig. 1 shows a schematic representation of the current biomass conversion technologies for obtaining value-added fuels and chemicals.

Need for Transition to Biofuels and Bio-sequestration

The combustion of fossil fuels generates much CO₂ – a greenhouse gas, responsible for global warming. There is an increasing thrust on biosequestration of

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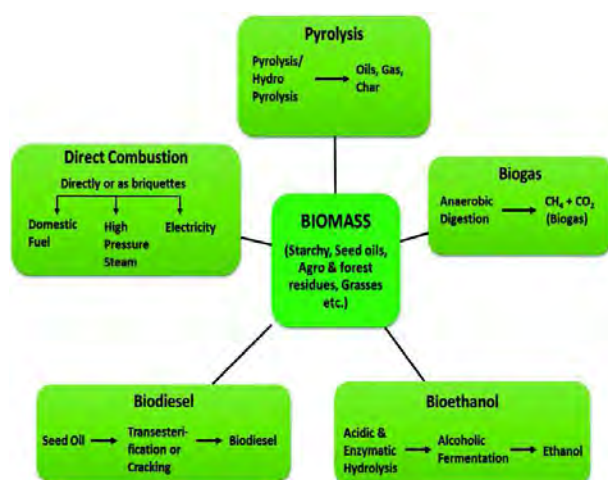


Fig. 1: Common methods of biomass utilization

CO₂ by growing more trees to arrest the ill effects of global warming. Gupta and Demirbas (2010) reported that out of 6.49 billion tons of biomass available globally, only a small amount of approximately 2.48 million tons is in use. Almost all countries in the world are giving due importance to bioenergy and thus moving towards bioeconomy. However, one major challenge to the establishment of bioeconomy is that oil and coal are being utilized the world over at a scale of millions of tons per annum (<http://www.bp.com/content/dam/bp/pdf/Energy-economics/statistical-review-2014/BP-statistical-review-of-world-energy-2014-full-report.pdf>) and therefore there may be a requirement for the production of biomass on a large scale to replace these. Thus, more biomass should be generated and made available for biomass conversion units. Sustainable energy production from agricultural waste and wastewater will help in decreasing our dependency on fossil fuels for our energy requirements (Angenent *et al.*, 2004).

First generation biofuels include biogas production from cellulosic wastes (animal dung), ethanol from wheat or corn starch, sugarcane, beetroot, grapes, carbohydrates, etc., pyrolysis of biomass, direct combustion of biomass through fluidized bed combustion or improved stoves or through gasification, etc. Second generation biofuels such as biodiesel from lipids derived from oil seeds – palm, soybean, sunflower, castor, *Jatropha curcas*, *Pongamia pinnata* (non-edible seeds), etc. are

already under the consideration of energy managers. The use of edible seed oils has led to the food versus fuel controversy. Therefore, in India there is a thrust to use non-edible seed oils as feedstock for biodiesel production. Research and development on third generation biofuels, i.e. production of biodiesel or biogasoline from microalgae has also started. Production of hydrogen and ethanol from microalgae and alcohol and biogas from macroalgae is also receiving attention.

Bioenergy and Biosequestration of CO₂

Arresting unprecedented climate change, maintenance of global economic growth and substituting the role played by depleting oil are the major driving forces behind bioenergy development. There is need to reduce 25-40% of the CO₂ emissions by 2020 and 80-90% of the CO₂ emissions by 2050 to restrict global temperature rise by 2°C (as agreed by the 2009 Copenhagen Climate Change Summit, Stephens *et al.*, 2010). Biomass production leads to utilization of CO₂ through photosynthesis.

Technological Options for Biomass Conversion

There are three main routes which are available for biomass conversion to value-added chemicals, fuels, and other products (Goldstein, 1981; Wise, 1983).

- 1) Chemical Conversion Technologies
- 2) Thermochemical Conversion Technologies
- 3) Biochemical Conversion Technologies

Sharma and his researchers have extended research to the area of conventional and renewable energy sources and other areas in the last several years (Sharma, 2005a; Sharma, 2005b; Singh *et al.*, 1984a; Biswas and Sharma, 2012; Biswas *et al.*, 2013; Biswas and Sharma, 2013) Research has been conducted on the development of biomass conversion technologies in the past by several researchers (Gupta and Demirbas, 2010).

Production of Biodiesel

The world total biodiesel production was around 1.8 billion litres in 2003. In the EU, biodiesel is by far the

biggest biofuel and represents 82% of the biofuel production (Demirbas and Balat, 2006). The EU production of biodiesel was 2.3 billion litres in 2006 (Demirbas, 2009a), Ma and Hanna (1999) concluded that biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. They also stated that challenges in biodiesel production lie in its cost and limited availability of fat and oil resources. *Jatropha curcas* (non-edible) seed oil is the main crop being proposed to be used for producing biodiesel in India. In order to improve the yield of oil from *Jatropha curcas*, research may be required in the area of genetic engineering to prepare suitable germ plasm, etc. (Discussion Meet DBT, 2007). However, *Pongamia pinnata* is also being considered as a potential oil seed species for the production of biodiesel (Fig. 2). For efficient production of biodiesel via transesterification, the following parameters will be important: the nature of feedstock, amount and type of alcohol and catalyst, operating temperature, and reaction time (Shahid & Jamal, 2011). Glycerol may be utilized in cosmetic and other chemical industries. Cracking of *Jatropha* oil or any other seed oil seems to be another option other than trans-esterification (Biswas and Sharma, 2012, 2013; Biswas *et al.*, 2013). Co-processing of biomass with other fuels has also been studied by the author and his research group (Biswas and Sharma, 2012, 2013; Biswas *et al.*, 2013; Ahmaruzzaman and Sharma, 2005, 2007, 2008). The residual biomass may be used to obtain biogas and manure (Deeba *et al.*, 2012) Algal species such as *Chlorella vulgaris*, *Scenedesmus obliquus*, *Euglena gracilis*, *Spirulina platensis*, etc. can also be used for the production of biodiesel (Gautam *et al.*, 2013). *Botryococcus braunii* contains hydrocarbons and lipids. It produces hydrocarbons ranging from 5-60% on dry weight basis. Culture conditions can be optimized for enhanced hydrocarbon production and research in this direction is underway (Sheehan *et al.*, 1998). Algal lipids may also be subjected to cracking to obtain biogasoline and biodiesel.

Biodiesel is advantageous because it not only reduces greenhouse gas emissions but also helps to reduce a nation's reliance on crude oil imports.

Biodiesel industry provides support to agriculture industry by providing new labour and market opportunities for domestic crops. Even vehicle manufacturers have accepted that it enhances lubrication. Blends of biodiesel (up to 20%) can be used in IC engines without many modifications (Demirbas, 2009b).



Fig. 2: *Pongamia pinnata* trees – oil producing plant used for biodiesel production

Pyrolysis of Biomass – Thermochemical Conversion

Agroresidues such as bagasse, wheat straw, jute sticks, rice straw, coconut shells, etc. can be subjected to pyrolysis either in retort reactors/fluidized bed pyrolyzers/fixed bed pyrolyzers or in drums. On pyrolysis, biomass may be converted into solid char, pyrolygineous acid and tar and pyrolysis gas (Sharma *et al.*, 1994a; Sharma and Prasad, 1986). Pyrolygineous acid and tar may be used to produce value-added chemicals. Pyrolysis gas may be used as fuel (Ahmaruzzaman and Sharma, 2005, 2007b). However, further research and development in these areas may be required. These may also be co-cracked to obtain biogasoline and biodiesel as described earlier.

Hydrolysis of Cellulose (Production of Ethanol)

The world ethanol production has increased from

around 16 billion litres a year in 1991 to 18.5 billion litres in 2001 (Demirbas, 2009a). In 2008, the global ethanol production was at 20.37 billion gallons per year. The United States become the world's leading ethanol producer and alone accounts for 43.8% of the global ethanol production, followed by Brazil (33.9%), China (5%) and India (3%) (Demirbas, 2011). Novel alternative methods to produce biodiesel and other second generation fuels, from varied feed stocks, are hot topics of research, especially the ones involving synthetic biology. Along with this, focus is now being laid on improving cost effectiveness from encouraging large-scale use of alternative biofuels. Sharma and his research group have carried out research in the area of both acidic as well as enzymatic hydrolysis of lignocellulosic biomass (LCB) such as agroresidues to obtain bioethanol (Behera *et al.*, 1996; Sharma *et al.*, 1995a; Sharma and Das, 1992; Sharma *et al.*, 1991; Singh *et al.*, 1984a; Singh *et al.*, 1984b; Singh *et al.*, 1984c; Sharma and Sahgal, 1982; Sharma and Das, 1984; Sharma and Goldstein, 1990; Liu *et al.*, 2012). Integrated processes to obtain value-added chemicals and fuels from hydrolysis of biomass were developed. Hemicellulose and cellulose can be hydrolysed by using acids to obtain fermentable sugars such as xylose, glucose, etc. These reducing sugars can be further fermented to obtain ethanol, butanol, etc. Recently, other substrates are also being considered for the production of bioethanol and valuable products, such as food wastes, weeds and grasses, etc. (Ganguly *et al.*, 2012; Maitan-Alfenas *et al.*, 2015; Ruan *et al.*, 2013).

Cellulase enzyme may be used in the biochemical hydrolysis of cellulose. However, lignin inhibits the enzymatic hydrolysis of LCB. The delignification of LCB using alkali, steam, fungi or enzymes, helps in its enzymatic hydrolysis. Lignin obtained may be hydrocracked to yield aromatic chemicals and fuels. Of late, enzymatic hydrolysis of biomass is being preferred over acidic hydrolysis process (Lee *et al.*, 1999; Aden *et al.*, 2002; Zhang *et al.*, 2007; Sun and Cheng, 2011; Maitan-Alfenas *et al.*, 2015). However, further research and development is required to make the hydrolysis process cost effective and interest in this area has been revived.

Liquefaction of Biomass

Biomass can also be hydrogenated to obtain oil. Biomass can be hydrocracked at high temperature and pressure in the presence of catalyst to obtain liquid fuels which can be fractionated to yield a petroleum-like product. Fischer-Tropsch (FT) synthesis may also produce liquid fuels from CO, CO₂ and hydrogen by using iron oxide as a catalyst. Here, synthesis gas may be produced by the gasification of biomass. The author and his research group have reported the use of several effective catalysts for the same (Mohanty *et al.*, 2011). Shift reaction may convert CO to CO₂ and H₂ after reaction with steam.

Anaerobic Digestion of Biomass

Lignocellulosic biomass, animal dung, night soil and lignocellulosic biomass containing proteinaceous lipids, fats or fatty acids can be subjected to anaerobic digestion to obtain biogas (CO₂ + CH₄). In India, MNRE, Government of India has also conducted extensive research along with several other organizations in this area. The author has also extended some research in this area (Sharma *et al.*, 1995b; Sharma *et al.*, 1994b; Sharma and Mbise, 1988).

There are two established digester designs.

1. Floating Gas Holder Type
2. Fixed Dome Type

The Biogas Programme of MNRE, Govt. of India is receiving due consideration in rural areas in India which not only leads to improved sanitation but could also provide digested slurry as good manure. Bottling of purified biogas i.e., after making it free from most of the CO₂ (by scrubbing with water or alkali), has also been started for being supplied as a gaseous fuel similar to LPG or CNG. Biogas programme is also being extended in European countries such as Germany, UK, etc. and in several other nations in Asia such as China and Philippines.

Biotransformations

Enzymes can be obtained by using cheaper agro residues or forest residues by employing solid state

fermentation (surface culture technique) or by liquid state fermentation (submerged culture technique). The enzymes thus produced may be used for hydrolysis, oxidation, reduction, esterification, elimination and substitution reactions, etc. (Sharma *et al.*, 1995a). Ligninase enzyme may be used for biodegradation of lignins. White rot fungi may be used to produce ligninase or peroxidase enzymes (Behera *et al.*, 1996; Sharma *et al.*, 1997; Goldstein, 1981; Wise, 1983).

Gasification of Biomass or Solid Wastes

There is a good potential to utilize organic wastes to produce energy either through sanitary landfills or through direct incineration. Gasification refers to the conversion of biomass by partial oxidation to generate producer gas containing CO, H₂, CH₄, N₂, C₂H₆, NH₃, CO₂, etc. If the gasification is carried out under pressure, then methane may also be obtained along with other gases. The use of catalyst such as Na₂CO₃/K₂CO₃ helps in catalysing the gasification. Synthesis gas may be used in the Fischer-Tropsch synthesis for production of petroleum hydrocarbons (Mohanty *et al.*, 2011). Alternatively, this may be subjected to oxo-synthesis for the production of alcohols.

Gas obtained can be used to generate power. Producer gas may also be used to produce hydrogen by shift reaction or alcohols by oxo-synthesis. This may also be used in the synthesis of methanol.

Two designs are used in the gasification of biomass.

1. Downdraft gasifier
2. Updraft gasifier

Since biomass contains more than 20% moisture, there is no need to supply steam from outside. Even gasification reactors used in the gasification of coal may be used for the gasification of biomass. Gasifiers may be used in the production of power using fuel cells also (Gaurav *et al.*, 2010). Biomass particularly algae may also be used in the production of microbial fuel cells or by using hydrogen obtained from algae in the fuel cells (Balasundaram *et al.*, 2007).

Production of Hydrogen

Hydrogen may be produced by the following routes:

1. Biophotolysis of water using green and blue green algae i.e., *cyanobacteria*.
2. Photobiological decomposition of organic compounds including organic wastes by photosynthetic bacteria.
3. Fermentation for hydrogen production from organic wastes.

Photosynthetic bacteria such as *Rhodobacter sphaerioides*, *R. capsulatus*, *R. rubrum*, etc. can be utilized in the production of hydrogen. These bacteria can even catalyse microbial shift reactions to convert CO and water to hydrogen and CO₂. The author has extended some research on the production of hydrogen from *Spirulina* sp. by biological processing (Balasundaram *et al.*, 2007).

Hydrolysate from the acidic or enzymatic hydrolysis of lignocellulosic biomass may be either fermented to obtain hydrogen or this may be subjected to steam reforming to generate hydrogen. Glycerol may also be subjected to steam reforming to produce H₂. Hydrogen may also be obtained by steam reforming of glucose or glycerol at higher temperatures (800°C) under atmospheric pressure in the presence of Ni as a catalyst. The use of Pt catalyst affords lower temperatures (225-265°C) but requires higher pressures (27-54 bar) (Gupta and Demirbas, 2010). Electricity generated by solar energy, OTEC, wind or geothermal energy can also be used for the electrolysis of water to produce H₂. Methane of biogas may be cracked by using solar heat at 2000K. Methane breaks down to H₂ and nanocarbon materials. Steam reforming of ethanol can also generate H₂. The H₂ thus generated may be utilized in fuel cells to generate power.

Energy from Organic Wastes

There are different types of organic solid wastes e.g., rural, urban or municipal solid waste (MSW), industrial wastes and night soil and cellulosic wastes. Wastes can be subjected to incineration to generate power. However, organic wastes can also be utilized to obtain biogas and other products through digesters or landfills. Solid waste may also be disposed off in sanitary landfills and biogas can be generated, which can be

used for power generation. Both incinerator and sanitary landfill practices are prevalent in India and elsewhere in the world.

Other Methods of Efficient Utilization of Biomass

Co-processing of biomass with plastics, petroleum coke, vacuum residue, lignite, coal, coke breeze, and rubber tyres can be practised to utilize biomass for easy transportation and storage, etc. Co-processing may involve co-firing, co-gasification/catalytic gasification or co-pyrolysis/co-cracking, etc.

1. Biomass along with plastics is used for densification of briquettes for enhancement of calorific value. However, special incinerators may be required depending upon the type of plastic being used/processed.
2. Briquetting of biomass can be done to produce compact fuel.
3. Value addition in the form of drugs (Sharma and Hall, 1991; Sharma *et al.*, 1979; Parthasarathy *et al.*, 1979), nanocomposites, speciality chemicals, smart materials, biomaterials, etc. is possible using land biomass.

The author has carried out some research where the production of drugs as natural products may be linked with the production of biofuels in the industries (Sharma and Hall, 1991; Sharma *et al.*, 1979; Sharma, 2005a; Sharma, 2005b; Joseph *et al.*, 2007; Joseph and Sharma, 2010; Ahmaruzzaman and Sharma, 2007b). Coprocessing/co-cracking of biomass-derived materials with waste plastics and other waste materials has also been carried out (Biswas and Sharma, 2012; Biswas *et al.*, 2013; Ahmaruzzaman and Sharma, 2005, 2007b, 2008) to obtain biofuels i.e., biogasoline and biodiesel.

Potential of Petrocrops

There are certain plants which are laticiferous, contain essential oils or resinous such as *Calotropis procera*, *Euphorbia lathyrus*, *Euphorbia tirucalli*, *Euphorbia nerifolia*, *Simmondsia chinensis* (Jojoba), pine, *Lantana camara*, *Eucalyptus*, etc. (Kalita, 2008) (Fig. 3). These plants yield terpenes



(A) *Plumeria alba*



(B) *Euphorbia tirucalli*



(C) *Calotropis procera*

Fig. 3: Some important petrocrops

(biocrude) as extractives. Terpenes (biocrude) may be hydrocracked to yield hydrocarbons such as petroleum. Biodegradation of latex can also be studied (Sharma *et al.*, 1996; Behera *et al.*, 1995; Sharma and Sahgal, 1982). In fact, *Pittosporum resiniferum*, *Copeifera multijuga*, *Copeifera landsdorfii*, *Plumeria rubra*, *Plumeria alba*, etc. have been identified as potential candidates for petrofarming. The author has also recommended some candidates for petrofarming. Here, photosynthesis proceeds to the production of triterpenes, hydrocarbons, etc. Further research in this area is required to establish the economics of petrocrops and petrofarming. Fig. 3 shows some of the potential petrocrop species.

Bioenergy from Algae

The world has moved to the third generation of biofuels i.e. fuels from microalgae and macroalgae. Algae appeared on this earth millions of years ago and it moved from water to earth to get transformed to plants and trees later. Algae are responsible for almost 50% of the oxygen generation on earth. Algae have the potential to yield lipids (and thus biodiesel or biogasoline), biohydrogen, bioethanol and biogas. These have been commercially exploited to obtain food, feed, vitamins, proteins, cosmetics, aminoacids, dyes, fatty acids, medicines, etc. through mostly open pond reactors. USDOE had earlier conducted extensive research on screening more than 3000 algal cultures for their potential to yield biodiesel i.e., lipids



Fig. 4: Cultivation of algae in shake-flasks

(Sheehan *et al.*, 1998). Research is being extended the world over on the production of value-added fuels and chemicals from algae. Algal bioreactors are being developed to yield enhanced amounts of lipids. There is a need to extend research and development on the production of biofuels from microalgae and macroalgae. This may also involve oceanographic management as it may require the managing of the macroalgae farms or forests which may also help in the biosequestration of CO₂.

Production of Biomass at Huge Scales

A major challenge would be to enhance the production of biomass on nonagricultural land at scales matching that of fossil fuels. This would be required to establish bioeconomy. A major problem in the biomass-based industries is the cost of collection, transport, storage, moisture contents, lower calorific value and crushing of biomass (a fibrous material). The cost of collection and transportation can be considerably reduced by preconditioning, i.e. solar drying and compacting and appropriately locating the intermediate centres where the loose biomass can be compacted, stored and used in the conversion facility. However, further research may be required to grow more aquatic as well as land biomass through improved horticulture or other botanical and agricultural practices by utilizing the land which is not being exploited for food crops.

The use of tractors, trolley trailers and tractor wagons up to a short distance and of tractors and trawlers for long distances may be recommended. Transport of briquettes by trucks may be economical at all distances. However a better management of transportation of biomass may be planned depending upon the availability of biomass in a particular region.

The availability of biomass may be increased by the upgradation of degraded soil/land, by using arid or semi-arid land. Even algal ponds may be set up in abandoned mines or on rooftops for growing more biomass.

After the depletion of fossil fuels, biomass may be the only dependable source of fuels and chemical feedstock. Therefore, there is a need to grow more

biomass as land and aquatic crops. This would help in biosequestration of CO₂ and may also halt the unprecedented climate changes. Improved agricultural, horticultural, botanical, physiological and other photosynthetic techniques (using C4 crops) etc. may help in growing more biomass. Further research and development may be required to enhance manifold the availability of biomass so as to match the scales at which fossil fuels are being used in order to establish bioeconomy.

Conclusions

Extensive research was carried out during 1970-80 (as a consequence of earlier oil crisis) on the development of different biomass conversion technologies. This also included pilot plant development research on acid or enzymatic hydrolysis of biomass. Research and development may be extended further from there to make these processes cost effective.

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Current emphasis is on the production of bioethanol or biobutanol from the lignocellulosic wastes. However, considerable commercial activity has started on biodiesel production from nonedible oil seeds and this may be followed up to obtain the same from algae. There is a trend to exploit the use of grasses, agroresidues, microalgae, macroalgae, aquatic biomass, oilseeds or petrocrops, etc. for the production of value-added chemicals and pharmaceuticals. This would also help in the biosequestration of CO₂. Productivity and availability of biomass may have to be increased manifold if biomass has to replace the role played by the fossil fuels today. This may also be required to establish bioeconomy in the future.

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Review Article

Biofuels: Engineering and Biological Challenges

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The second generation biofuel technologies are evolving rapidly to provide solutions for the partial replacement of fossil fuels. Both bioethanol and biodiesel have great potential in India. Both the technologies, however, have to overcome various bottlenecks before they become commercial technologies. In this regard, several critical questions, besides science and technology, need to be resolved. This will require new ways of thinking about agriculture, energy infrastructure and rural economic development.

Keywords: Biofuels Technology; Bioethanol; Biomass; Algal Biofuel; Bioenergy

Introduction

In recent times, a great concern about fossil fuels supplies, their non-renewable nature and environmental consequences of their use has driven interest in biofuel programmes all over the world. There is no doubt that the “best substitute for petroleum is petroleum” and, as one analyst puts it, replacement of fossil fuel by biofuel is not possible, but augmentation of fuel supply probably is. As Church and Regis (2012) write in their book *Regenesi*s, “We’re now in a transitional period, caught between the age of fossil fuels and the age of biofuels.”

It is believed that a partial transition from oil to biofuels can stabilize the energy market significantly. To be a viable alternative, a biofuel should provide a net energy gain, have environmental benefits, be economically competitive and be producible in large quantities without affecting food security of the country.

The National Policy on Biofuels of India (2009) proposes a target of 20% blending of bioethanol by 2017. A target of 10% petrol blending seems more realistic for 2017. Even this seems a difficult

proposition keeping in view the present supply and demand situation. The intermediate target of 5% and 10% blending by 2007-2008 has not been achieved. The government is unable to implement compulsory blending of 5% ethanol in petrol.

First and Second Generation Biofuels

The basic routes for converting biomass to biofuel are biochemical and thermochemical. The two classic thermochemical options, namely, gasification and pyrolysis produce different intermediates. Gasification involves rapid heating and partial oxidation to produce syngas, which is largely carbon monoxide and hydrogen. The high oxygen content of biomass results in the production of significant quantities of carbon dioxide, which reduces carbon efficiency. Also the sulphur, nitrogen, phosphorous, potassium, and mineral content of biomass complicates matters further. In pyrolysis, lower temperatures are used to break down biomass into smaller molecules such as oxygenated aromatics, ketones, organic acids, and other oxygenates, as well as light hydrocarbon gases. In addition to the lower energy input to achieve biomass deconstruction, pyrolysis has a high theoretical yield for liquid products.

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In biochemical processing, biomass is typically processed to yield monosaccharides, which are then converted by microbes to produce fuels. Though bioethanol is an established biofuel, there is an alternate view that it would be a good idea to look at the conversion of lignocellulose into organic acids rather than sugars.

Another biochemical route uses anaerobic digestion to produce biogas, a mix of methane and carbon dioxide. Here, natural consortia of bacteria decompose organic matter into methane in the absence of oxygen. Although much of the biomass resource might be dedicated to biofuel production (thus diminishing its role in electricity generation), biogas technologies could provide a small but nontrivial part of a renewable electricity portfolio, particularly given their flexibility and potential for distributed generation.

The feedstock for first generation biofuels produced through biochemical routes are primarily food crops, such as sugar cane, grain (corn), oil seeds and vegetable oils. Their limited contribution to meet the energy demands of the future has raised questions about their role in the transport fuel mix of the future. This makes the need for second generation biofuel technologies inevitable and desirable.

The feedstock for second generation biofuels is non-food biomass, such as lignocellulosic materials (bagasse, cereal straw, forest residues, and short-rotation energy crops). The second-generation biofuel production has the potential to provide benefits such as consuming waste residues and making use of abandoned land. Job creation and regional growth are probably the most important drivers for the implementation of second-generation biofuel projects in major economies and developing countries.

According to the estimates of International Energy Agency (2010) biofuels are expected to provide 9% (11.7 EJ) of the total transport fuel demand (126 EJ) in 2030, 26% (29 EJ) of total transportation fuel (112 EJ) in 2050, with second-generation biofuels accounting for roughly 90% of all biofuels.

Biofuels derived from lignocellulosic biomass and algae are promising additional sources to meet energy

demands of the country. Both can play a significant part to solve energy supply picture in the future provided key obstacles are overcome. Both, however, are future technologies as there are no commercial plants, but a considerable number of pilot and demonstration plants have been planned or set up in recent years, mainly in North America, Europe, Brazil, China, India and Thailand.

In India, the commercial viability of both the options is highly dependent on the future price of oil and the government policy. There is thus a promise as well as an uncertainty. The promise is to significantly reduce our dependence on imported oil, create new jobs, improve rural economies, reduce greenhouse gas emissions, and enhance national fuel security. The major uncertainties are feedstock availability and cost, conversion technologies and cost, and the impact of technologies on the environment. The milestones (USDOE, 2006) that are suggested for the development of biofuels are provided in Fig. 1.

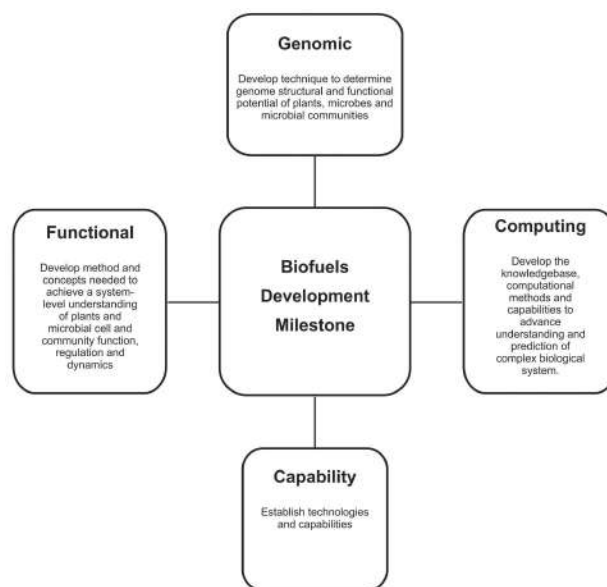


Fig. 1: Biofuels development milestones (USNAS, 2012)

A brief overview on the future of cellulose and algae-based biofuels is given here.

Cellulose-Based Biofuel

Production of ethanol from biomass follows various conversion routes (Fig. 2). Ethanol is produced in India

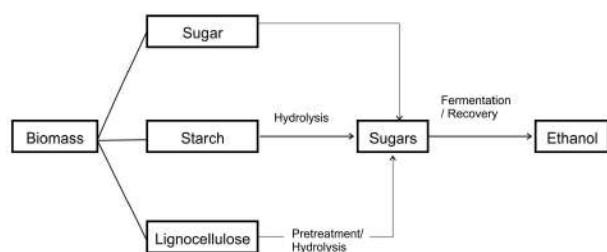


Fig. 2: Biomass-based bioethanol conversion routes

from cane molasses. Efforts to produce ethanol from other sugar-based feedstock such as sweet sorghum, sugar beets, and sweet potatoes are at present in the experimental stage. Lower molasses availability and consequent higher prices impact ethanol's cost of production, thereby causing a disruption in the supply of ethanol at pre-negotiated fixed ethanol prices.

All the countries in the world are looking for solutions for their growing energy needs using sustainable and renewable resources. The first-generation technologies for bioethanol production based on sugars and starches cannot provide long-term solution. They compete for land with food crops, resulting in misleading cost-benefit analysis. What we need is a cheap, abundant and renewable raw material that does not interfere with food production. Lignocellulosic biomass (LCB) is such a feedstock for the production of second-generation bioethanol.

Supply of Biomass

The global supply of cellulosic biomass is estimated to contain energy that is equivalent to much more than the world's current annual consumption of transportation fuel. The sources of cellulosic biomass include crop wastes, forest residues, and dedicated energy crops. Lignocellulosic biomass (LCB) is less expensive than sugar or starch-based feedstock, but its conversion to ethanol at present is more costly. The commercialization of this technology thus has to overcome various bottlenecks. These include feedstock availability, scale of operation, cheaper and effective pretreatment technologies, efficient hydrolytic agents, availability of recombinant organisms capable of co-fermenting the whole range of sugars at a temperature compatible to optimum

hydrolysis, and better co-product value (Ghosh and Ghose, 2003).

Supply of biomass is one of the most critical factors for the development of a viable bioethanol technology. Three distinct goals need to be met for the development of biomass-based biofuels, namely, maximizing the total amount of biomass produced per hectare per year, maintaining sustainability while minimizing inputs, and maximizing the amount of fuel that can be produced per unit of biomass. Exact values for each of these parameters would vary, depending upon the type of energy crop and the growing zone. Logistics of raw material supply (availability, collection, storage and handling) to meet large demands of biofuels is a major issue of concern. In addition, the availability of the feedstock on a sustainable basis would need either large storage facilities or availability of plants to operate on multiple feedstock for their continued operation throughout the year.

Ideal Pretreatment Technology

Pretreatment of LCB continues to be a major barrier for the development of a viable technology. In the LCB-based bioethanol technology, cellulose and hemicellulose present in the lignocellulose are hydrolysed to sugars (hexoses and pentoses) using acids or enzymes. Lignin is the major interference in the hydrolysis of native lignocellulose. In the enzymatic process, the LCB is pretreated in order to increase the accessibility of cellulolytic enzymes (cellulases) to the substrate. Typically, hydrolysis yields in the absence of pretreatment are less than 20% of theoretical yields, whereas yields after pretreatment often exceed 90%. The rationale for pretreatment has thus been to separate individual components of LCB with minimum component losses, concomitant with an increase in surface area and a decrease in crystallinity.

An ideal technology is expected to produce a reactive fibre that will require little or no size reduction, and can be operated at a high solid/liquid ratio. One needs to ascertain what is more important for enzymatic hydrolysis – the extent of delignification that requires harsher conditions for complete lignin

separation or loosening of cellulose – hemicellulose-lignin bonds under milder conditions. The benefits of lignin solubilization need to be weighed against the potential for fermentation inhibition by soluble lignin derivatives.

Various mechanical, physical, chemical, and biological approaches, either singly or in combination have been attempted to meet these objectives, but none has shown the promise expected from an ideal pretreatment technology. Development of LCB-based energy plants with traits such as increased cellulose and hemicellulose and less lignin not only has the potential to improve ethanol yields, but also the possibility of application of much simpler pretreatment technologies. Metabolic engineering of the lignin biosynthetic pathway has been suggested as a method for modifying lignin content in the feedstock.

Enzyme and Enzymatic Hydrolysis

The important parameters of enzymatic hydrolysis are sugar yield, duration of hydrolysis, enzyme loading, characteristics of substrate cellulose, and enzyme cellulases.

The most desirable attributes of the enzyme cellulases include the ability to produce a complete cellulase system with high catalytic activity against crystalline cellulose, thermal stability, decreased susceptibility to enzyme inhibition by the products of hydrolysis (glucose, and cellobiose), selective adsorption of the enzyme on cellulose, and the ability to withstand shear forces. Strategies to improve cellulases include discovering new enzymes through bioprospecting, creating new/better mixtures of enzymes, and developing improved expression systems through protein engineering. *De-novo* and *in-silico* designing of improved cellulases are also being attempted. Creating a more effective cellulose binding domain in the enzyme molecule is another approach to increase enzyme efficiency.

A critical element for the success of bioethanol technology is the availability of cheap cellulases. Industrial enzyme producers are trying to achieve reduction in enzyme cost in order to support an economical and robust cellulose biorefinery. Cellulase

enzymes are too expensive for bioethanol. For example, costs of amylase enzymes for converting grain starch to ethanol are about ten times cheaper than the most optimistic cost estimates for cellulase preparations. There is, however, a good possibility of producing effective cellulases at a much reduced cost. For the hydrolysis of pretreated biomass, extremely complex cellulases may not be required; simpler cellulase systems may serve the purpose. The major market for cellulase enzymes is the textile industry, and the enzymes produced are tailored to meet the requirement of this industry. It is important to recognize that biofuels application needs are significantly different from textile applications.

An Ideal Ethanol Producing Organism

The bioethanol process needs an efficient organism with capability to convert sugars (both hexoses and pentoses) to ethanol. An ideal ethanol producing organism should have characteristics such as high ethanol tolerance, capacity to withstand high osmotic pressure, high temperature, and low pH, high cell viability, appropriate flocculation and sedimentation characteristics, capability to ferment broad range of sugars mainly to ethanol and possibly negligible levels of by-products (such as acids and glycerol), and resistance to inhibitory compounds present in the pretreatment/hydrolysis stream. A strategy for increasing ethanol tolerance or other traits uses evolutionary engineering concepts and methods. This strategy allows the microbial process to evolve under proper selective pressure (in this case, higher ethanol concentrations) to increasingly higher ethanol tolerances.

Conversion of cellulose and hemicellulose to ethanol comprises hydrolysis followed by fermentation of hexoses and pentoses by ethanol producing organisms. Simultaneous saccharification and fermentation (SSF) integrates the processes of hydrolysis with fermentation. The development of thermophilic ethanol-producing organisms for use in SSF could allow the consolidated process to run at higher temperatures, thus realizing significant savings by reducing cellulase enzyme requirements. Combining cellulase production, cellulose hydrolysis,

and co-fermentation of hexose and pentose sugars in a single step, called “consolidated bioprocessing”, is considered the ultimate low-cost configuration for cellulose hydrolysis and fermentation.

Companies are engaged in creating synthetic microbes to accelerate the conversion of agricultural waste to ethanol. Diverse microbial strains collected from the seawater is being used to create new synthetic microbes. The hunt is on for a better microbe that will cheaply and efficiently break down cellulose to sugars and then ferment those sugars into ethanol. Such designer organisms are yet not available.

Commercialization of Technology

The projected cost of ethanol from LCB has declined significantly in the last ten years. Further cost reduction is needed. This is possible by employing a cellulose and hemicellulose rich, but lignin lean feedstock.

Relatively large investments are required to install LCB-based bioethanol plants. In India ethanol plants are comparatively small in capacity. This brings to the fore another related issue, namely, scale of operation vis-à-vis feedstock availability. Keeping in view the logistics of feedstock procurement, it is needed to decide if it is advisable to build very large plants as increased feedstock cost (due to collection and transport of large amounts of feedstock) may offset savings due to economies of scale.

Commercialization of ethanol needs the attention of researchers, entrepreneurs, and more importantly, the policy makers. India has the capacity to produce 4000 million litres of ethanol from molasses, but it produces around 2800 million litres. A sizable utilizable capacity needs to be utilized. It will depend upon how pricing issues are addressed.

A Global Market Survey (Ethanol 2020), reports that it is possible to replace 20% of gasoline consumption in the US, China, and India by 2020, if the promises of competitive, large-scale cellulosic ethanol production are realized, and if national import/export policies for biofuels are further liberalized.

These are big ‘ifs’. There are many questions that need to be resolved, both at the researchers and

planners stage. Large-scale lignocellulose-based bioethanol technology will require major changes in supply chain infrastructure. It will require new ways of thinking about agriculture, energy infrastructure, and rural economic development.

Algal Biofuel

The National Bio-diesel Mission (NBM) has identified *Jatropha curcas* as the most suitable tree-borne oilseed for bio-diesel production on wastelands. Biodiesel production in India is very small due to inadequate supplies of *Jatropha*. NBM had set an ambitious target of covering 11.2 to 13.4 million hectares of land under *Jatropha* cultivation by the end of 2011-12.

The Government of India’s ambitious plan of producing sufficient bio-diesel to meet the mandate of 20% blending with diesel by 2011-12 has proceeded slowly. According to trade and industry estimates, *Jatropha* has been planted across 500,000 hectares of wasteland, of which 65-70% is estimated to be new plantation, and would take three to four years to mature. As a result, there are insufficient *Jatropha* seeds available for biodiesel production.

Lack of high-yielding, drought-tolerant *Jatropha* seeds, smaller land holdings, ownership issues with government or community owned wastelands, little progress made by state governments to meet large scale *Jatropha* plantations, and negligible commercial production of biodiesel have hindered the efforts and investments made by both private and public sector companies in this sector.

According to the report on Biofuels for Transportation Programme for 12th Five Year Plan prepared by the sub-group constituted by the Ministry of New and Renewable Energy, the absence of guaranteed national market due to the absence of minimum support price is bound to deter the investment especially in long duration crops with little history of cultivation such as *Jatropha curcas* or *Pongamia pinnata*.

There are about 20 large capacity biodiesel plants (10,000 to 100,000 tons per year) in India that produce biodiesel from edible oil waste (unusable oil fractions),

animal fat and non-edible oils. Commercial production of biodiesel from *Jatropha* and non-edible oilseeds is small, with estimates varying from 140 to 300 million litres per year. The biodiesel produced is sold to the unorganized sector (irrigation pumps, agricultural usage, diesel generators, etc.), and to experimental projects carried out by automobile and transport companies. Biodiesel production cost is higher than the government notified purchase price. This is mainly due to the lack of supply of *Jatropha* seeds.

An Ideal Algae

Algae are an attractive way to harvest solar energy, and turn carbon dioxide into biofuel. Much money is thus being poured into the idea of turning algae into mini oil wells.

The algae-derived biofuel is projected to reduce fossil fuel consumption equivalent to 6% of road transport diesel by 2030. An efficient algae-based biofuel process promises around 40000 litres of oil per hectare of land. The worldwide microalgal manufacturing infrastructure is devoted to extraction of high value products such as carotenoids and omega 3 fatty acids used for food and feed ingredients. Although microalgae are not yet produced at large scale for bulk applications, recent advances, particularly in the methods of systems biology, genetic engineering, and biorefining present opportunities to develop this process in a sustainable and economical way, within the next twenty years. But the challenges are many.

Algae use carbon dioxide to produce oil molecules via photosynthesis. In non-stressed growing algae, lipids are mostly present in the form of phospholipids in the cell membranes. Some microalgae, when exposed to stress conditions (e.g., nutrient deprivation or high light intensities), accumulate lipids in the form of triacylglycerols in so-called oil bodies. This accumulation occurs at the expense of energy used for growth, leading to a decrease in growth rate and a consequent decrease in productivity. The carbon dioxide discharged from power plants and oil refineries can be captured by algae and used to produce biofuel, and thereby reducing carbon dioxide build up in the atmosphere. A schematic of algae-based biodiesel

processing is provided in Fig. 3.

An ideal algae that can produce biofuel should have high yield on high light intensity, large cells with

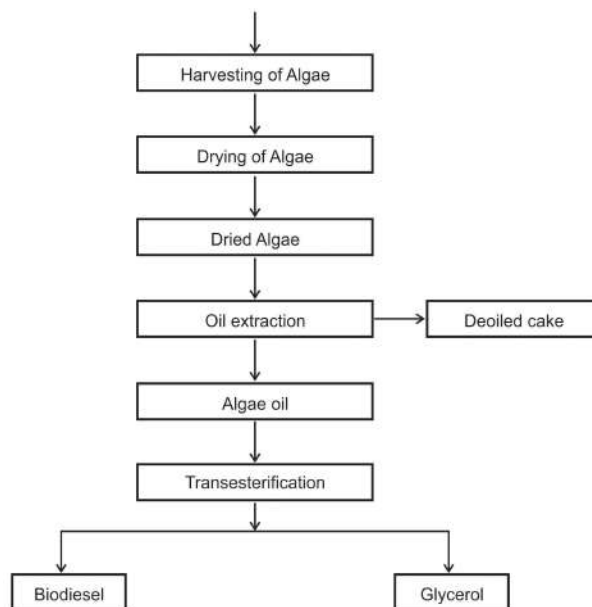


Fig. 3: Algae-based biodiesel processing

thin membranes, stable and resistant to infections, and insensitive to high oxygen concentration. Algae should be able to grow and produce lipids at the same time, should form flocs, and preferably should excrete oils outside the cells. Such a magic bug has not been discovered yet. Efforts, nevertheless, are being made to design such magic bugs.

Knowledge of the biosynthesis mechanism of triacylglycerols and their accumulation in oil bodies is limited and often based on analogies with higher plants. If the mechanisms are known, it could open the possibility of inducing lipid accumulation in oil bodies without having to apply a stress factor. A detailed insight into metabolic pathways may lead to strategies to induce lipid accumulation based on process conditions, defined nutrient regimens, and/or the use of metabolic engineering techniques.

Mass Cultivation of Algae

Both open and closed mass cultivation systems can be used for growing algae. Table 1 summarizes the pros and cons of open and closed system. The obvious problems with open systems are low biomass growth

Table 1: Algal Biofuel. Open and closed systems (USDOE, 2006)

Parameter	Open system	Closed system
Cost	Lower	Higher
Pumping energy	Lower	Higher
Ease and scale up	Greater	Lower
Evaporative water loss	Higher	Negligible
Land area required	Higher	Lower
Contamination risks	Higher	Lower
Productivity	Lower	Higher
Productivity stability	More variable	Less variable
Sparged CO ₂ loss	Higher	Lower

and biomass loss due to lesser control on growth parameters, including disrupted availability of sunlight. Prevention of algae from the predators and contamination by natural strains are other obvious difficulties (USNAS, 2012).

Closed and controlled photobioreactors are more efficient. The design and fabrication of efficient photobioreactors equipped with optimal lighting techniques and configurations with emphasis on light efficiency, less shear damage and low cell adherence at the surface of the bioreactor is quite expensive. Advantages and disadvantages of typical closed bioreactors for algal biofuel production are mentioned in Table 2 (Kunjapur and Eldridge, 2010).

In recent years, much effort is put into increasing photosynthetic efficiency of microalgae under oversaturating light (the normal condition on a sunny day). Certain strains of microalgae can harness 3% of the incoming sunlight to make plant matter, as opposed to roughly 1% for corn or sugar.

The photosynthetic efficiency can be increased by developing new microalgae strains with smaller antenna sizes, and by decreasing the light path of photobioreactors, while increasing mixing in high cell density cultures. Researchers obtained high photosynthetic efficiencies under bright sunlight in

Table 2: Closed Bioreactors: Advantages and disadvantages (Kunjapur and Eldridge, 2010)

Reactor type	Advantages	Disadvantages
Flat plate	Shortest oxygen path Low power consumption	Low photosynthetic efficiency
Tubular	High volumetric biomass density	Oxygen accumulation Photoinhibition Most land use
Vertical	Greatest gas exchange Best exposer to light/ dark cycles Least land use High photosynthetic efficiency	Support costs Scalability

systems with lower energy requirements by reducing the light intensity at the reactor surface. To reduce the cost of manufacturing these systems, vertical panels made from thin plastic films such as polyethylene have been used.

Arranging for carbon dioxide that could be utilized for commercial algae production is challenging; a total of 1.8 kg of carbon dioxide is needed to produce 1 kg of algal biomass. While carbon dioxide could be sourced from power plants for sequestration, arranging large quantities of fresh or saline water is extremely difficult. In addition, algae like any plant would require nutrients such as NPK and other micronutrients for optimal growth.

For sustainable production of biofuel from microalgae, it will be important to make use of residual nutrient sources, and to recycle nutrients as much as possible. Utilization of wastewater will also achieve twin objectives of algal biomass production and wastewater treatment. Waste-water may offer a useful point source, which can be either municipal, organic industrial (e.g., food processing), organic agricultural (e.g., confined animal facilities), or eutrophic waters with low organic content but high nutrient content (e.g., agricultural drainage, lakes and rivers). Microalgae can also grow in seawater. Even deserts would be suitable if there is access to salt aquifers.

Algae Harvesting and Processing

After the growth, the algal biomass needs to be harvested, the lipids extracted, and the remaining cell components recovered. Harvesting of microalgae is expensive because of the high energy requirements and capital costs involved.

Since most microalgae are small individual cells, centrifugation is often used as a preferred harvesting method. However, as the biomass concentration is generally low (<3 g/L), centrifugation of diluted streams requires a large capacity of the centrifuge, which makes the process energy-demanding and expensive. Flocculation, followed by sedimentation and flotation, before centrifugation or filtration will substantially reduce harvesting costs and energy requirements. Ideally, algae should flocculate spontaneously at a certain stage of the process.

The process involves extraction of stored oil from the algae (by breaking oil-rich algae). This adds to downstream processing cost. The algal oil is extracted from the algal cells and then converted into biodiesel by transesterification with short-chain alcohols or by hydrogenation of fatty acids into linear hydrocarbons.

After harvesting, the cells are disrupted and the oil extracted with solvents. Most microalgae strains are, in general, relatively small and have a thick cell wall. For this reason, very harsh conditions (e.g., mechanical, chemical, and physical stress) are needed to break the cells for extraction of the products. Excretion of the oils, in a manner similar to what naturally occurs in the microalgae *Botryococcus braunii*, will lead to a simplified biorefinery and improve downstream economics. However, it will not provide a complete solution because the remaining cell components still need to be recovered from the cells.

Thin cell membranes, such as those present in *Dunaliella*, strong enough to prevent shear damage during production, would facilitate cell disruption. Research is needed to explore mild cell disruption, extraction, and separation technologies that retain the functionality of the different cell components.

A genetically engineered bacteria (*E. coli*) has shown promise to convert sunlight, carbon dioxide and water into different hydrocarbons, including biodiesel. The bacterium grows happily (three times faster than the yeast) at tropical temperature. The designed organism secretes oil, instead of storing it inside the organism, so as to reduce downstream costs.

Concluding Remarks

It is now a well-established fact that fossil fuels are in short supply and have limited reserves. They need to be replaced. It must, however, be recognized that their full replacement is neither desirable, nor possible. Its partial replacement seems to be a reality. Among the alternatives available, biofuels have great potential in India, because of the availability of feedstock, environmental benefits, and the possibility of improved rural economies.

The potential of a technology is one thing and its availability at the desirable 'cost' is another. India has to overcome various bottlenecks before it becomes a commercial technology. The country has to answer several critical questions. The answer to these questions will decide the future of biofuels technology in India. The questions, related to technology and its dissemination, include: What kind of support, other than science, will be needed for its viability? Who will be the major promoter of policy – agricultural sector, sugar industry or petroleum industry? What kind of government support is needed to make this technology viable? Who will be the major promoter of large scale biofuel technology? Other than science, what kind of support is needed to make this a viable technology? Under what circumstances or conditions can refiners consider participation in the ethanol industry? These questions continue to bother researchers and planners. Large-scale lignocellulose based bioethanol technology will require major changes in supply chain infrastructure. It will require new ways of thinking about agriculture, energy infrastructure, and rural economic development.

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Review Article

Biofuels and the Hybrid Fuel Sector

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To enable India to cope with the predictable and challenging situation of a scarcity of petroleum fuels for surface transport in the future, we examine and evaluate in this study potential alternatives that can ensure adequate energy for the transport sector with acceptable environment implications. These alternatives can be broadly categorized into three groups from the perspective of planning a smooth transition from a conventional petroleum fuel-based transport system to sustainable energy alternatives. The first group includes non-conventional fossil-based resources such as compressed natural gas (CNG), liquefied petroleum gas (LPG), methane from coal beds and gas hydrates, shale oil, shale gas, etc. Use of these resources could provide energy security but cannot guarantee environmental benefits. The second group includes first generation biofuels (alcohol and biodiesel), and biomass-to-liquid (BTL) fuels. These fuels are renewable but their current production methods and base feedstock do not appear promising enough to provide for a large-scale supply of fuel in a sustainable manner. The third group includes second generation biofuels and hydrogen. The feasibility of large-scale hydrogen production from renewable resources holds promise for scalable implementation and sustainability in the future but this would require huge technological challenges to be overcome. This study describes the potential of this proposed fuel resource scenario for transport fuels and discusses the technological challenges that would have to be addressed for its large-scale implementation.

Keywords: Biofuels; Hybrid Fuels; Biodiesel; Alcohols; Fischer-Tropsch Liquids; CNG; DME; GTL; BTL; CTL

Introduction

We are confronted today with the twin crises of uncertainty of energy supply resulting from fossil fuel depletion and environmental degradation due to emission of harmful pollutants from the combustion of fossil fuels. In such a scenario, renewable alternative fuels hold promise for assured sustainable development with the security of energy supply along with acceptable environmental implications. Fuels for transport sector are required to meet additional challenges such as adequate energy density and lower pollutant emissions in the exhaust which are harmful for human health. Energy requirement of the Indian transport sector stood at 47.12 MTOE (million tonnes

of oil equivalent) in 2008, and is expected to cross 103 MTOE by 2020 and 200 MTOE by 2035 with an average annual growth rate of 5.5% (US EIA, 2011). This poses a huge challenge for energy security and its planning. In the present situation, almost all transport fuels originate from petroleum resources. Generally, fuels used in internal combustion (IC) engines, other than mineral diesel and gasoline, are recognized as alternative fuels. These alternative fuels include natural gas (NG: CNG/LNG), liquefied petroleum gas (LPG), hydrogen, unconventional fossil oils, electricity, Fischer-Tropsch liquids, ethers, alcohols, biodiesel, etc. Some of these alternative fuels are renewable while others are produced from non-renewable resources.

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For ensuring adequate and sustainable energy supply to the transportation sector, the requirement of uninterrupted fuel supply can be fulfilled by an appropriate mix of these alternative transport fuels and conventional fuels. Chapter 2 describes the availability, utilization technology, environmental impact and the role of various alternative fuels in constituting a transport fuel mix for the future.

Natural Gas

Natural gas is a mixture of ethane, propane, butane, carbon dioxide, nitrogen, etc., with methane (80-98% v/v), being the main constituent, depending on the production source (Korakianitis *et al.*, 2011; Ramadhas, 2011). Natural gas is found either with other fossil fuels (such as crude petroleum in oil fields, or coal in coal beds) or on its own in dry gas wells. It is used as a fuel in SI engines as well as in CI engines in dual-fuel mode. In SI engines, it offers several advantages, such as (i) possibility of increasing engine efficiency (associated reduction in CO₂ emissions) by increasing engine compression ratio due to higher octane rating of natural gas in comparison to gasoline, (ii) reduction in quantity and toxicity of HC emissions, (iii) reduction in CO emissions, etc. It can be also utilized by retrofitting CI engines, which include (i) modifications such as installing an ignition source, (ii) reduction of compression ratio and (iii) fitting of fuel storage and delivery system, which would result in reducing local pollution levels. Utilization of natural gas in SI engine results in 10-15% reduction in power output compared to identical gasoline-fuelled engine, which may be compensated by direct injection of fuel with the expected availability of special injectors in the near future (Korakianitis *et al.*, 2011). Currently for vehicular use, natural gas is stored in cylinders at 200 bar pressure, however the operating range of natural gas-fuelled vehicles still remains lower than gasoline and diesel-fuelled vehicles due to its lower storage energy density (Korakianitis *et al.*, 2011; Ramadhas, 2011a; Speight, 2007). Though natural gas originates from a non-renewable resource, its main constituent methane can also be produced from biomass, which is a renewable resource available in abundance (Porpatham *et al.*, 2008). Waste biomass from agriculture can be converted to transport fuel

by producing natural gas, biomass-to-liquid (BTL) or ether from it. The process of collecting, purifying and using methane obtained from biomass decomposition is relatively simpler compared to the Fischer-Tropsch (FT) process used in gas-to-liquid (GTL) conversion (Korakianitis *et al.*, 2011). However, at the current stage of technological development, well-to-wheel energy consumption (3.5 MJ/km) of methane obtained from biomass (D'Agosto and Ribeiro, 2009) is higher than fossil natural gas, gasoline and diesel (2 MJ/km) (Dimopoulos *et al.*, 2008). Future developments in natural gas-fuelled engine technology and gas purification technology might ensure more efficient utilization of renewable methane from biomass. In recent years, technological advancements for utilization of shale gas, coal bed methane (CBM) and the possibility of utilization of methane obtained from gas hydrates renders natural gas an extremely important fuel for future use in the transportation sector. According to an assessment by the US Energy Information (EIA; April 2011), technically recoverable shale resources in India are 63 trillion cubic feet (TCF) compared to 1,275 TCF for China, and 1,250 TCF for US and Canada combined (US EIA, 2011; Nakao *et al.*, 2008; US EIA, 2011b). Technically recoverable resources of shale gas in India are sufficient to fulfill our natural gas demand for at least the next 33 years (US EIA, 2011b).

Liquefied Petroleum Gas

Liquefied petroleum gas (LPG) is another gaseous, fossil origin, alternative fuel, which is primarily a mixture of butane and propane. It is derived from lighter hydrocarbon fractions produced during refining of crude petroleum in a fractional distillation column, it is also recovered from the heavier components present in natural gas, which are removed before natural gas is distributed and utilized (MacLean and Lave, 2003). LPG is also produced during petroleum refining processes, such as fractional distillation, reforming and cracking. Separating propane and butane from crude oil is necessary for its stabilization before it is distributed through pipelines or tankers (Selim, 2011). LPG's engine utilization is similar to natural gas with the additional advantage of higher storage energy density because it can be easily

liquefied and stored as liquid at reasonable pressures (10–14 bars). However, its cold-starting characteristics and cold-start emissions are relatively inferior compared to natural gas (MacLean and Lave, 2003; Selim, 2011). LPG is expected to last as a viable fuel option as long as fossil crude oil and natural gas are available, therefore its supply potential is rather limited and is directly linked to availability of petroleum. Technology should be developed to efficiently utilize LPG as an alternate fuel in engines, which are designed to run on other fuels. In India, it is already a very popular fuel in the transport sector for dual fuel cars.

Unconventional Fossil Sils

When petroleum which is found in an underground reservoir, is a free flowing liquid, which can be recovered by pumping, it is referred to as conventional petroleum. Other fossil fuel resources, whose extraction and conversion into liquid fuels is relatively difficult and expensive, are referred to as unconventional oil. Extra-heavy oil, natural bitumen (oil sands, tar sands) and oil shale are three important resources of unconventional oil (Mohr and Evans, 2010). Natural bitumen and extra-heavy oils are remnants of very large volumes of conventional oils that have been generated and degraded, principally by bacterial action. Chemically and texturally, bitumen and extra-heavy oils resemble the residuum generated by refinery distillation of light oil (WEA, 2010). Extra-heavy oils are much more difficult to recover in comparison to conventional petroleum. Constituents of heavy oil have significantly higher viscosity than conventional petroleum, and primary recovery of heavy oils usually requires thermal stimulation of reservoir. Natural bitumen also known as “tar sand” and “oil sand” is impregnated with dense, viscous organic material called bitumen (WEA, 2010; Speight, 2007b). Oil shales are fine-grained sedimentary rocks containing relatively larger amount of organic matter (known as “kerogen”), from which, significant amount of shale oil and combustible gases can be extracted by using destructive distillation (Mohr and Evans, 2010; WEA, 2010). According to estimates of the World Energy Council (2010), the resource base of natural bitumen and extra-heavy oil is immense and there

can be no constraint on the expansion of production. These resources can make an important contribution to future oil supply, if they can be extracted and transformed into usable refinery feedstock at sufficiently high rates, and at costs which are competitive in comparison to other alternative resources (WEA, 2010). According to EIA, the largest fractions of future unconventional liquid fuel production includes 239 MTOE/year of Canadian oil sands, 69.7 MTOE/year of Venezuelan extra-heavy oil and 194.2 MTOE/year of biofuels (109.6 and 84.7 MTOE/year of U.S. and Brazilian biofuels, respectively) (US EIA, 2011). Unconventional fossil oils are predicted to account for roughly 7% of the global liquid fuel supply by 2035 (US EIA, 2011).

Currently, shale oil is more expensive to produce when compared with petroleum-based crude oil because of the additional cost of mining and extraction of energy from oil shale. Owing to its higher costs, only a few deposits of oil shale are currently being exploited in China, Brazil, and Estonia. However, with the continuing decline in petroleum supplies, accompanied by increasing cost of petroleum, oil shales present an opportunity of adequate supply of fossil energy to the world in the years ahead (DGA, Government of India). The Directorate General of Hydrocarbons (DGH), under the Ministry of Petroleum and Natural Gas, Government of India has embarked upon projects for the evaluation of oil shale resource potential in India and its extraction by involving international collaborations with many experienced companies working in the area of extraction of shale oil (DGA, Government of India). Currently, extraction of shale oil deteriorates the land and produces large quantities of polluted water and toxic gases, which are environmentally hazardous. Further research is therefore required for developing technological methods that are cost-effective and environment-friendly for the extraction of shale oil.

Hydrogen

Hydrogen is an energy carrier and not an energy resource because free hydrogen is not available in nature and one or the other form of primary energy is required to be invested for its production (MacLean

and Lave, 2003; Verhelst and Wallner, 2009). Its usefulness as an excellent energy carrier is also limited because of its low energy content on a volume basis, limiting the possibility of its on board storage in vehicles (MacLean and Lave, 2003). The primary advantage of hydrogen over other fuels is its clean exhaust because its oxidation does not produce carbon dioxide or other carbonaceous species. Hydrogen can be used as a transport fuel via two routes: hydrogen fuel cell (H_2 FC) vehicles and hydrogen IC engine (H_2 ICE) vehicles. Addition of hybrid electric vehicle (HEV) technology improves the fuel economy of both these powertrains. Currently, efficiency and cost of H_2 FC powertrain is higher than H_2 ICE power-train (Verhelst and Wallner, 2009). Generally, hydrogen can be produced by electrolysis or thermal decomposition of water, steam reforming of natural gas and other hydrocarbons, pyrolysis of hydrocarbons, plasma refining process, etc. (Ramadhas, 2011b). Steam reforming of natural gas converts it into synthesis gas, from which CO_2 and CO are required to be removed (Ramadhas, 2011b) to generate hydrogen. The method of producing hydrogen which requires the production of interim energy carrier-like electricity prior to production of hydrogen has significant efficiency disadvantage (MacLean and Lave, 2003). Abbott proposed the possibility of using solar hydrogen produced by solar thermal collectors through the H_2 ICE route as a viable and promising solution for future transport fuel requirement for large-scale applications (Abbott, 2009). Challenges related to production and storage of hydrogen are covered in greater detail elsewhere in this volume.

Electricity

Electric vehicles use charge stored in batteries. They do not emit any combustion-generated pollutants on the roads and their operation is quieter. However, the source of electricity generation used to charge the batteries determines the life cycle emissions of this means of transportation. Electricity can be generated without creating air pollution such as by using nuclear, hydro, solar, wind energy, etc. Electricity generation by natural gas or coal however results in significant upstream emissions (MacLean and Lave, 2003). Therefore, if non-renewable sources are used for

electricity production, life-cycle emissions of electricity as a transportation fuel could be significantly higher. Therefore, there is a need to develop carbon-neutral decentralized electricity generation capability. At the current level of technological advancement, batteries have low energy density; therefore, electric vehicles have a rather limited operating range (MacLean and Lave, 2003). Electrical powertrains do not bring additional primary energy source into the application but provide a way to utilize coal and nuclear energy resources for transportation and are also helpful in controlling localized on-road pollution, thereby improving urban air-quality, which is of prime importance to congested Indian cities such as Delhi, Bombay, Calcutta, Bangalore, etc. Challenges related to further developments in efficiency and ability of energy storage of fuel cells, which are currently more efficient than battery-based electricity storage systems, are covered in greater detail elsewhere in this volume.

Biofuels

Biofuel refers to solid, liquid and gaseous fuels produced from biomass (Nigam and Singh, 2011; IEA, 2011). However, from the perspective of using these as alternative mass transport fuels, the relevant biofuels are gaseous and liquid fuels such as ethanol, methanol, biodiesel, Fischer-Tropsch liquids, hydrogen, di-methyl ether, methane, etc. primarily generated from biomass (Nigam and Singh, 2011). Depending on the pressure on natural resources for unit energy production and current status of technological developments, biofuels are categorized primarily as first, second and third generation biofuels with increasing order of technological complexity, advancement and lowering the burden on natural resources.

Bioethanol and biodiesel produced from fermentation of starch and transesterification of vegetable oils are the most widely used first generation biofuels today. Fig. 1 summarizes various biofuel options and their current technology status. Generally, biodiesel and bioethanol produced from different technologies have similar properties; hence, partial mitigation towards biofuels is undertaken depending

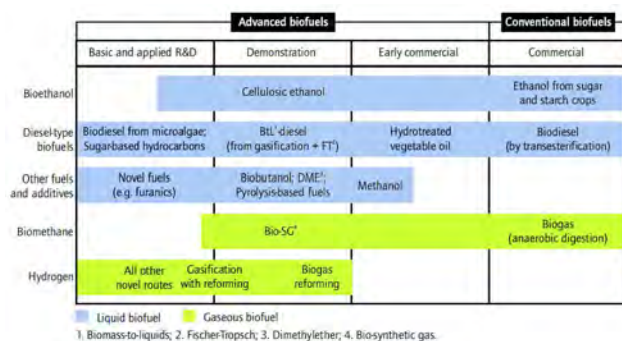


Fig. 1: Current technology status of biofuel options (IEA, 2011; Bauen *et al.*, 2009)

on the availability of feedstock for producing these fuels. The utilization of such biofuels would increase with increasing production due to advancements in fuel production technologies (Fig. 1). The current biofuel policy of the Government of India has an ambitious goal of achieving 20% blending of biofuels, both biodiesel and bioethanol by 2017, in all commercially available diesel and gasoline in the country (MNRE, Government of India). In 2010, India launched a National Ethanol Blending Programme, making it mandatory to blend 5% ethanol in gasoline across 20 states in the country. However, the supply chain and availability of bioethanol in such large quantities posed a key challenge for this programme and it could not be implemented across the board. The following sub-section describes production and engine utilization technologies of various liquid biofuels.

Dimethyl Ether

Di-methyl ether (DME: $\text{CH}_3\text{-O-CH}_3$) exists in the form of a colourless gas at room temperature with slight odour. It is necessary to keep it in closed containers for normal use and distribution (Spencer, 2011). Vapour pressure of DME lies in between that of propane and butane (Spencer, 2011). DME is considered as an extremely clean burning alternative fuel for CI engines, and is potentially very helpful in reducing localized urban air pollution. It can easily auto-ignite due to its very high cetane number and results in practically soot-free combustion due to easy vaporization and complete absence of carbon-to-carbon bonds (Park and Lee, 2013; Semelsberger *et*

al., 2006). Similar to hydrogen, it is also not found in nature. For DME production, organic feedstocks such as biomass, coal or natural gas are converted into synthesis gas, which is a mixture of carbon monoxide, hydrogen and other trace gases. Synthesis gas is then converted into methanol and finally into DME by dehydrogenation of methanol (Spencer, 2011; Park and Lee, 2013). Power output of DME-fuelled engines is generally lower than diesel-fuelled engines, primarily due to significantly different vital properties of diesel and DME such as higher compressibility, and lower calorific value of DME compared to mineral diesel. Lower lubricity and viscosity of DME causes durability issues in the fuel injection system (Park and Lee, 2013). These issues therefore need to be addressed before a large-scale implementation strategy should be formulated.

Fischer-Tropsch Liquids

Fischer-Tropsch (FT) is a process which produces a variety of hydrocarbon fuels, primarily from coal or biomass. The primary product is a diesel-like fuel synthesized from syn-gas (H_2/CO), which can be produced by auto-thermal reforming of natural gas, biomass or coal (MacLean and Lave, 2003; Nigam and Singh, 2011; Gill, *et al.*, 2011). Depending on the starting material, the process could be termed coal-to-liquid (CTL), gas-to-liquid (GTL) or biomass-to-liquid (BTL) conversion process. The FT liquid fuel has no sulfur, almost no aromatics and a high cetane number, therefore it is an ideal diesel engine fuel. These properties make this an extremely attractive alternative fuel for CI engines (MacLean and Lave, 2003). The feedstock for BTL is biomass, which is renewable, therefore BTL can be produced from biomass residues of food crops with minimal interference with the food economy and much less strain on land, air and water resources, in comparison to alcohols or oil-seed-based fuels such as biodiesel. However, the conversion technologies such as hydrolysis and gasification are still under development (Gill *et al.*, 2011) and a significant amount of research is required before these technologies mature enough to become ready for implementation.

Alcohols

Methanol, ethanol and butanol and their blends with gasoline are used as alternative transport fuels in SI engines (Nigam and Singh, 2011; Agarwal, 2007; Balki *et al.*, 2014). Methanol is the shortest carbon chain primary alcohol, which burns cleanly due to its simple chemical structure and very high oxygen content (50% w/w). Methanol however poses an environmental hazard in case of accidental spill, because it is highly toxic and is completely miscible with water. Ethanol is similar to methanol, but it is considerably cleaner, less toxic and less corrosive (Agarwal, 2007). On the other hand, butanol is far less corrosive than ethanol and can be shipped and distributed through existing pipelines and filling stations (Nigam and Singh, 2011), however it has a very strong stench. Use of lower gasoline-alcohol blends in SI engine results in reduction in CO, HC and NO_x emissions compared to baseline gasoline, while producing almost similar torque output (Agarwal, 2007; Balki *et al.*, 2014), however, aldehyde emissions increase (Agarwal, 2007). For using higher blends of alcohol in SI engines, few engine modifications are essential in order to cater to alcohol's relatively higher octane number, lower volatility, lower calorific value and different chemical reactivity *vis-a-vis* baseline gasoline (Agarwal, 2007; Kremer *et al.*, 1996). Alcohol blends can also be used in CI engines as supplementary fuel (Agarwal, 2007). For use of higher concentration ethanol blends (>20% v/v), fuel additives are essential for stabilizing the mixture and for attaining the desired cetane number (Ramadhas, 2011c). Higher percentage of ethanol in diesel requires a double injection or fumigation system, which are helpful in emissions and noise reduction but increased control complexities (Ramadhas, 2011c). Alcohols can also be blended with straight vegetable oils, biodiesel and mineral diesel (Yilmaz and Sanchez, 2012; Kumar *et al.*, 2003). Alcohol-biodiesel-diesel blends result in lower NO_x and particulate emissions from CI engines (Shi *et al.*, 2006; Zhu *et al.*, 2010). Transesterification process for biodiesel production utilizes methanol/ethanol and straight vegetable oils as process inputs. This procedure of utilizing alcohol as an engine fuel is definitely preferred because aldehyde emissions and corrosion of engine parts by alcohols are not encountered in

this method (Nigam and Singh, 2011).

Economic viability of bioethanol can be improved by developing more efficient enzymes, value improvement of co-products such as fructose and dried distiller's grains with soluble (DDGS), and better energy efficiency can raise the conversion efficiency; thus, reducing production cost (IEA, 2011; Kumar and Maithel, 2006). For large-scale successful implementation of bioethanol/ethanol blends, assessment of feedstock options for bioethanol production is essential and technologies for economic conversion of ligno-cellulosic feedstock to bioethanol need to be developed (Kumar and Maithel, 2006).

Straight Vegetable Oils

Plant-derived oils, waste cooking oils or waste/residue triglycerides can be converted into diesel-like fuels through several routes. Vegetable oil-based fuels are biodegradable, non-toxic and have the potential to significantly reduce air pollution. Straight vegetable oils can be used in unmodified diesel engines. However, this approach leads to several operational issues in the engines upon long-term usage. Vegetable oils have high viscosity, poor volatility and a polyunsaturated character, which adversely affects their performance as alternate diesel fuels (Agarwal, 2007; Galle *et al.*, 2012). High viscosity of vegetable oil leads to inefficient pumping and poor spray formation with larger droplet size distribution. Therefore air and fuel are not optimally mixed and combustion remains incomplete in the engine combustion chamber, leading to pollution formation. Low volatility of vegetable oils and their ability to polymerize (due to unsaturation) leads to formation of undesirable carbon deposits in the combustion chamber, injector coking and piston ring sticking (Agarwal, 2007; Galle *et al.*, 2012), which have very serious consequences in the engine. To eliminate these issues, different processes have been developed so as to make these oils adapt to modern engines. These processes (such as direct use by blending, micro-emulsion, pyrolysis, transesterification, etc.) allow the vegetable oils to attain properties closer to mineral diesel (Staat and Gateau, 1995; Desantes, 1999; Altön, 2001). Among these, conversion of straight vegetable

oils into biodiesels, which have very similar properties to that of mineral diesel, is the most accepted route (Agarwal, 2007; Gerhard, 2010) worldwide.

Hydro-Treated Vegetable Oils

Fuel with properties and composition similar to mineral diesel can also be produced by hydro-deoxygenation of triglycerides (vegetable oils). It is termed as “hydro-treated vegetable oil” (HVO) or renewable diesel (IEA, 2011; Gerhard, 2010) or “green diesel”. Hydro-deoxygenation is a process, in which a feedstock containing double bonds and oxygen moieties, is converted to hydrocarbons by saturation of double bonds and removal of oxygen (Gerhard, 2010). Cold flow properties of renewable diesel are superior to biodiesel but the technology for its commercial production is still in developmental stage (IEA, 2011; Gerhard, 2010).

Biodiesel

Biodiesel is a fuel, which can be produced from edible and non-edible straight vegetable oils, recycled waste vegetable oils and animal fat through transesterification process, which converts triglycerides present in vegetable oils into fatty acid alkyl esters (Li, 2004; Hamelinck *et al.*, 2004; Demirbas, 2000; Kinney and Clemente, 2005). Transesterification is the reaction of triglycerides with primary alcohols in presence of a catalyst, and this reaction produces primary esters (biodiesel) and glycerol (Agarwal, 2007). Biodiesel is the name of a clean burning mono-alkyl ester-based oxygenated fuel made from natural, renewable resources such as raw/used vegetable oils and animal fats. Both edible and non-edible straight vegetable oils can be converted to biodiesel by transesterification. Fuel related properties of biodiesel are very similar to mineral diesel and this is amply illustrated by comparing properties of mineral diesel and Karanja biodiesel (Table 1). Carefully planned biodiesel implementation programmes in India can result in the following benefits:

- Biodiesel is a CI engine compatible fuel, which indicates the possibility of it being used as a diesel substitute with no or minor system hardware modifications. It will not lead to any significant

additional cost to the existing OEMs.

- Blending biodiesel with mineral diesel can compensate for the loss of fuel lubricity in low sulfur diesel since sulphur content in diesel is being reduced continuously worldwide, in order to make them comply with EURO-IV or higher emission standards (Bozbas, 2008) and meet the requirements of new engine technologies, which are being adopted to meet these stringent emission norms.
- Utilization of biodiesel is helpful in reducing GHG emissions because vegetable oil production consumes a large part of carbon dioxide, which is consequently emitted during combustion of these fuels in the engine. Blends of diesel and biodiesel may also be helpful in reducing harmful gaseous and particulate matter emissions from the engines, which helps in meeting these stringent automotive emission norms being adopted worldwide.
- Biodiesel is a safer fuel compared to mineral diesel in its storage and handling aspects because its flash point is approximately 100°C higher than mineral diesel (Bozbas, 2008).
- It is compatible with existing infrastructure for fuel delivery, transportation and distribution of mineral diesel in blended form.
- Biodiesel can be produced from locally available biomass resources. Hence developing a biodiesel industry would strengthen local industry, particularly rural agricultural economy in agrarian countries like India.
- Biodiesel can be produced from feedstocks grown in under-utilized, high salinity lands/waste lands and will be helpful in checking soil erosion and land degradation. In the process, it also has the potential to provide livelihood for the rural poor living in areas with highly degraded lands.

For large-scale implementation of the biodiesel programme, key areas for research and development include: more efficient catalyst recovery, improved purification of the by-product glycerol for cost

reduction, exploring large-scale usage of glycerol because production volume of glycerol will increase with increasing production of biodiesel, increasing shelf life of biodiesel and enhanced feedstock flexibility (IEA, 2011). With further development of technology, production of biodiesel from micro-algae based oils may reduce stress on land and water and would make large-scale implementation of biodiesel feasible (Nigam and Singh, 2011; IEA, 2011; Timilsina and Shrestha, 2011). Micro-algae can be grown in shallow water bodies, ponds as well as in shallow coastal areas, which will open up a new dimension in biodiesel production.

Though the fuel-related properties of biodiesel are largely similar to mineral diesel, there are considerable differences such as higher viscosity and density, 10-15% lower calorific value, higher/comparable cetane number, higher bulk modulus,

higher oxygen content, and lower stoichiometric air-fuel ratio (Agarwal, 2007). Currently, engine control parameters are finely tuned according to fuel properties so that stringent emission norms can be complied with. Any change in fuel properties affects the optimized domain of these parameters. Optimization of an engine with respect to these fuel properties would be essential for ensuring satisfactory engine performance and emissions characteristics of biodiesel blends. Due to differences in chemical reactivity of biodiesel, suitable changes in lubricating oil composition are also essential and a new family of specialty lubricants needs to be developed for biodiesel-fuelled engines. Material compatibility of biodiesels produced from various feedstock with fuel injection equipment and rubber components of the engine also needs to be ascertained. Therefore necessary modifications in the composition of these engine components should be done before country-wide implementation of biodiesel programme (Schumacher *et al.*, 1996).

Table 1: Properties of Karanja biodiesel vis-a-vis mineral diesel

Property	ASTM 6571 limits for Biodiesel	Biodiesel	Diesel
Density (g/cm ³) @ 30°C	0.8-0.9	0.881	0.831
Viscosity (cSt) @ 40°C	1.9-6.0	4.41	2.78
Flash point (°C) (min.)	130	168	49.5
Cetane number (min.)	47	50.8	51.2
Conradson carbon residue (%) (max.)	0.05	0.02	0.01
Ash content (%) (max.)	0.02	0.008	0.005
Moisture content (ppm) (max.)	500	<200	<200
Calorific value (MJ/kg)	-	37.98	43.78
Copper corrosiveness	3a	1a	1a
C (%)	-	74.2	87
H (%)	-	12.9	13
N (ppm)	-	3.9	9
O (%)	-	12.8	-
S (ppm) (max.)	15	2	50

Source: Dhar, 2013

Summary and Recommendations

For ensuring adequate supply of energy for the transportation sector, a mix of several primary fuels, both alternative and conventional, is required. Utilization of non-conventional fossil resources such as natural gas, shale oil may ease the pressure on petroleum supply in the short-term, but environmental issues are also likely to get aggravated with the use of these fuel options. Biodiesel and bioethanol are currently relatively mature options; however, further improvements in their economics, environmental impact and social impact are essential. India can start moving towards these options based on the current availability of these feedstock and try to develop new production technologies for expanding feedstock base with sustainable pressure on natural biomass resources. It is expected that large-scale production of biofuels in bio-refineries would promote more efficient use of biomass and bring down associated costs in addition to enhancing environmental benefits in future. For long-term energy supply, the possibility of producing large volumes of hydrogen through distributed renewable resources like solar energy or through the bacterial route seems feasible and they

should be developed as a sustainable option. Based on these discussions, the following technological and policy challenges are identified to ensure adequate supply of fuel for the surface transport sector in a sustainable manner:

- § Estimation and economic extraction of shale gas and shale oil.
- § Improvement in engine technology for more efficient utilization of gaseous fuels.
- § Modifications in engine technology to enable adopting blends of alcohol/gasoline, diesel/biodiesel/alcohol.
- § Increasing the feedstock base for production of bioethanol and biodiesel by developing technologies for ligno-cellulosic biomass

utilization and algae oil production from shallow water bodies.

- § Production of methane and biomass-to-liquid (BTL) fuels, etc. from other biomass resources, which are unsuitable for ethanol production.
- § Improvement in hydrogen-fuelled internal combustion engine technology and improvement in its safety features for large-scale implementation of hydrogen as a transport fuel in future.
- § Development of technologies for hydrogen production and storage in order to ensure sustainable and adequate supply of hydrogen from carbon-neutral primary energy sources in the future.

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Review Article**Hydrate Reservoirs – Methane Recovery and CO₂ Disposal**

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The world over, energy generation technologies such as gas turbines and fuel cells have initiated a migration towards gaseous fuels. A driving force for this trend is the C:H ratio, with the hydrogen component progressively increasing with time. In the ultimate analysis, it suggests a migration towards hydrogen. Meanwhile, the search for viable hydrocarbons continues since their combustion and utilization characteristics are understood. Gas reservoirs of limited significance have been found within the country, for example, coal bed methane and shale gas. Additionally, the prospect of obtaining gas in the long run, from gas hydrate reservoirs may become a reality. Such reservoirs have an added potential of storing large quantities of CO₂ in hydrate form. Consequently, technologies from extraction of gas hydrates, energy conversion to an appropriate form all the way to exhaust gas disposal need to be re-visited and developed in the local context. As a start, this study describes a mathematical model of multi-species multi-phase transport in a porous reservoir, based on principles of conservation of mass, momentum and energy. The model equations are discretized and numerically solved to simulate flow and heat transfer in the hydrate reservoir, bounded by a depressurization and an injection well. As seen in the simulation, depressurization extracts methane from the reservoir while CO₂ injection enhances the recovery rate largely due to the displacement of CH₄ by CO₂. At the same time, hydrate formation of CO₂ traps it in the reservoir providing additional structural integrity to the marine geological formation. The model, validated on a laboratory scale, needs to be tested under field-scale conditions.

Keywords: Gas Hydrates; Methane Recovery; CO₂ Disposal; Mathematical Modelling; Depressurization Technique

What Are Gas Hydrates?

Gas hydrates refer to a class of solid crystalline compounds where guest gas molecules are caged in a solid H₂O lattice (Sloan and Koh, 2007). Among commonly occurring gas hydrates, methane hydrate, present in the marine sediments, is now identified as a potential source of hydrocarbon fuel (Fig. 1). The global storage of methane in the hydrate form exceeds all other known hydrocarbon reserves. Extraction of methane from marine sediments however, poses multiple challenges and opportunities to the practising engineer. Safe extraction processes that keep the fragile marine-ecosystem unaltered require significant infrastructural investment. On the other hand, methane extraction from the gas hydrate provides an option for CO₂ sequestration. Furthermore, controlled

extraction impedes the possibility of accidental release of methane due to global warming. It may be mentioned that uncontrolled release of methane, a potent greenhouse gas, may seriously endanger the global ecosystem. It is, therefore, imperative to examine and identify the possible technologies for methane extraction from marine sediments. Among the possible techniques, depressurization, and injection have been identified as the two most promising ways for extracting methane from the gas hydrate stored in the marine sediments; a model arrangement for depressurization is shown in Fig. 2.

Depressurization requires destabilizing the chemical structure of the gas hydrate by lowering the pressure below the thermodynamic limit. Since the gas hydrate is stable only at high-pressure (~10 MPa)

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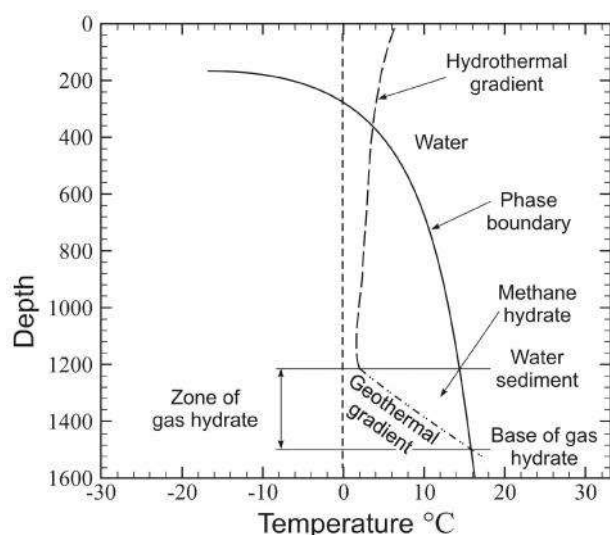


Fig. 1: Representative diagram indicating the occurrence of gas hydrates at the ocean floor; depth in metres

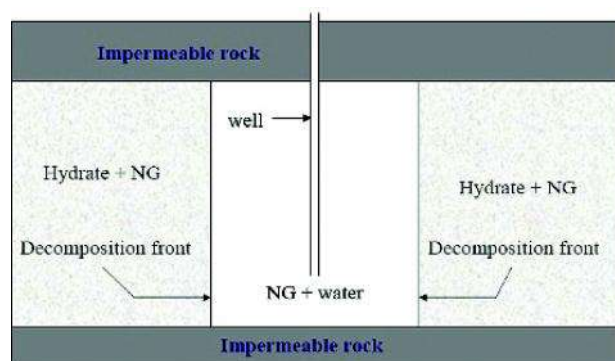


Fig. 2: A possible configuration for depressurization a gas hydrate reservoir. NG stands for natural (free) gas. In the schematic, the decomposition front moves outwards from the central well while gas released from the formation moves inwards towards the well

and below ambient temperature environment, depressurization seems to be a suitable approach for methane extraction. Such a process also guarantees controlled release of methane by precisely adjusting the extraction pressure. In contrast to depressurization, the injection processes attempt to replace the methane encaged in the hydrate-lattice with another suitable gas. Both processes have their advantages and disadvantages. While depressurization facilitates rapid release of CH_4 , the process may weaken the hydrate-bearing structure. Injection, on the other hand, ensures structural stability at the expense of being slow and energy-intensive. Additionally, the injecting gas needs

to be non-corrosive in nature and should have lower free energy than methane at the hydrate-formation environment. Recent research suggests that CO_2 may serve as a suitable injection species for hydrate extraction (White *et al.*, 2011). In undersea environment, CO_2 may form stable hydrates replacing and thus releasing CH_4 . While such a process ensures structural stability of the hydrate-bearing sediments, the effect of the acidic nature of CO_2 has to be carefully investigated. Also important is to understand the role of water salinity on the overall process dynamics. It is now agreed that no single process may be suitable for all types of hydrate reservoirs. Emerging trends include the development of hybrid processes to combine the flexibilities of both depressurization and injection for the safe extraction of CH_4 at a reasonable rate.

Apart from recovering methane, the importance of gas hydrates is immense. Among other possibilities, gas hydrate reservoirs can additionally act as a sink for natural gas apart from being a cold thermal energy storage unit. The storage capacity in the form of hydrates is considerable. For natural gas, it yields a benefit of approximately 150 times the storage capacity of compressed gas. The large storage potential of gas hydrates makes it attractive for storing and transportation of natural gas, being an alternative to liquefaction and compression.

Background

Exploration of gas hydrates was initiated in 1996 by the Gas Authority of India Limited of the Ministry of Petroleum & Natural Gas. The National Gas Hydrate Programme (NGHP) created under the Directorate General of Hydrocarbons (DGH) has attracted participation from public sector organizations such as ONGC, OIL and GAIL, and CSIR laboratories such as NGRI and NIO. Their studies have established the presence of gas hydrates under the ocean bed of the Indian peninsula (Sain and Gupta, 2012). Significant amount of free gas has been detected below the hydrate-rich formation. The estimated quantity is large enough to support the energy security of the country for the next 100 years. Gas hydrates reserves have been located at the Krishna-Godavari,

Mahanadi, Andaman, Kerala-Konkan, and Saurashtra regions at water depths of 500 to 2500 m. In general terms, gas hydrates, essentially a methane source, have been located around the world in significantly large quantities. Thus, the availability of a new energy source can be taken to be practically proven. The next step is to work out technologies of mining the energy-bearing material in a stable and cost-effective manner, and create devices to convert the available chemical energy into useful work. Related questions of environmental impact and management are significant points of concern.

Technology development for the utilization of gas hydrates calls for an intensive, yet coordinated and multi-disciplinary research. It requires an understanding of natural phenomena on one hand, and development and design of engineering systems on the other. Issues to be addressed include physico-chemical hydrodynamics of flow of methane in natural formations, energy exchanges with the host rock, chemical reactions and changes in the structural integrity of the host formation. The gas thus recovered from a site can be liquefied and transported to gas turbine installations for power generation. Alternatively, power can be generated locally using newer technologies such as fuel cells. Many of these decisions will depend on economic factors, but the need to anticipate all possible scenarios cannot be over-emphasized. In the last few years, government agencies in USA, Canada, Russia, Japan and South Korea have begun to develop hydrate research programmes to recover gas from oceanic hydrates.

The volume of CO₂ emissions from methane utilization has been estimated to be quite large. From an environmental viewpoint (specifically, global warming), it would violate international agreements, such as the Kyoto protocol and a remedial action would be called for. A suggestion being vigorously pursued internationally is the process of carbon sequestration, wherein the products of combustion (essentially CO₂) are pumped back into the gas hydrates formation (Ota *et al.*, 2005). In recent proposals, CO₂ is liquefied before being disposed into hydrate reservoirs. The presence of CO₂ in place of CH₄ has the added advantage of providing structural

support to the reservoir. The technological feasibility of such an idea is yet to be fully ascertained.

Forward modelling of chemical instability and gas recovery from hydrates, generation of phase equilibrium diagrams, and performance evaluation of engineering configurations have just commenced. The connection between laboratory-scale measurements and field scale performance, called *scale-up*, is established against the background of a mathematical model. Related tasks are parameter estimation and data retrieval from field measurements. It calls for wide ranging experiments on gas recovery, power generation, and management of the environment.

Methane Recovery

Methane can be recovered from gas hydrates by modifying the chemical equilibrium conditions in the reservoir (Fig. 3). Three methods proposed are depressurization, inhibitor injection and thermal stimulation. Cost considerations as well as environmental protection dictate the choice of the recovery method. In the depressurization technique, the reservoir pressure is reduced below the three-phase equilibrium curve. The composite hydrate molecule containing H₂O and CH₄ dissociates by

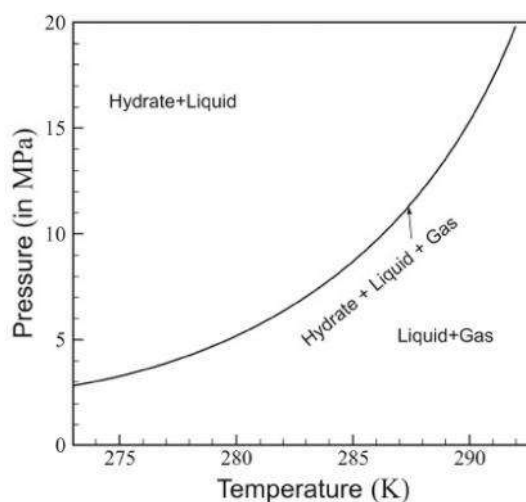


Fig. 3: Phase equilibrium line that shows the stability boundary on the pressure-temperature plane. The region below the solid line indicates gas separated from the water cage. In the region above the line, gas hydrates are stable and methane is trapped in a cage of water molecule

absorbing thermal energy from its surroundings. This step leads to a reduction in the reservoir temperature. Locally, a new equilibrium condition is achieved at a lower pressure and lower temperature but a certain amount of gas is released.

In the inhibitor injection technique, chemicals that shift the stability curve upwards are made use of. Accordingly, on injection of the chemical into the gas hydrate bed, dissociation of methane from hydrate will occur (Fig. 4). In the natural gas industry, alcohols

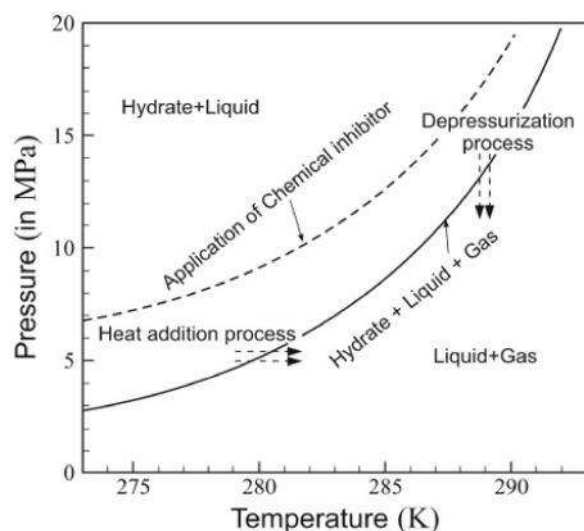


Fig. 4: Schematic drawing of the effect of chemical inhibitor on the stability curve. The movement of the stability boundary upwards shows that gas release is possible under a broader set of pressures and temperatures

(methanol) and glycols have been proposed to inhibit hydrate formation and are thus suitable for forcing dissociation of gas hydrates.

A thermal stimulator uses thermal energy to raise the reservoir temperature taking the composite hydrate molecule into a zone of instability. Thermal stimuli proposed in the literature are: (1) injection of hot fluids such as water, steam or brine, (2) combustion, and (3) electro-magnetic heating. *In situ* combustion relates to burning a portion of methane locally so that a flame front moves slowly from an injection well towards the production well. The gases released are at an elevated temperature and can be used directly for power generation. In option 3, microwaves or AC current heats up portions of the reservoir. Among the

three methods of thermal stimulation for hydrate dissociation, fluid injection is well-developed and characterized in the laboratory. Further, it has been traditionally used as an enhancement technique for oil and gas recovery from conventional reservoirs.

Mathematical Modelling

Since experiments require a high-pressure environment in excess of 100 bar, numerical simulation continues to be the preferred method for research on gas recovery from hydrate reservoirs. The complexities of modelling and simulation are however quite overwhelming. The mathematical modelling of methane extraction involves multiphase transport, comprising phase-change and chemical reactions, in a moving-boundary system. Additional complexities include multiple length and timescales, media heterogeneity, and possible flow instabilities. Scarcity of experimental results also calls for molecular-scale modelling to derive the thermophysical properties, state equations, as well as the kinetics of the process. Numerical implementation of such models requires careful simplifications as well as suitably tailored algorithms. Extraction models available in the open literature ignore many such elements of complexity. On the other hand, highly accurate models are not available in the open literature. For an introduction, refer to the recent study of Khetan *et al.* (2013).

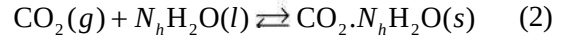
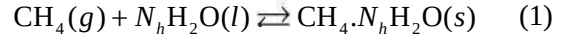
The success of modelling via a system of differential equations depends largely on the process parameters prescribed. Some of them include the permeability and dispersion tensors, interfacial transport coefficients, constitutive relations for capillary effects, and rates of reaction. Research on gas hydrates is new; references such as Moridis *et al.* (2009), White *et al.* (2011), Zatsepina *et al.* (2011), Fitzgerald *et al.* (2012) and Yuan *et al.* (2013) form a useful starting point. Accordingly, knowledge of parameters (and parametric functions) that will appear in the mathematical formulation is as yet incomplete. The expected values of these parameters must be determined from laboratory experiments. One strategy that can be used is to prepare gas hydrates on a laboratory scale and perform with it a recovery experiment. Laboratory-scale experiments can also be used to validate mathematical models of gas recovery.

Multi-phase Multi-component Model

A transient, non-isothermal, multiphase, multispecies model is presented here for the simulation of CH₄ gas production via depressurization and simultaneous CO₂ injection (Ahmadi *et al.*, 2004; Sun *et al.*, 2005; Uddin *et al.*, 2008; Anderson *et al.*, 2011; Khetan *et al.*, 2013). The governing equations are written for simplicity in a one-dimensional Cartesian geometry bounded by the depressurization well at one end, and the injection well at the other. The present model accounts for transport phenomena in five phases, namely aqueous, gas, CH₄-hydrate, CO₂-hydrate, and the geological media. While the first two phases are mobile, the other three are treated as immobile. Such a distinction helps in accounting for the thermophysical properties of CH₄- and CO₂-hydrates. At a time instant and given location, all five phases present in the system are assumed to be in thermal equilibrium with each other. Temperature itself varies considerably over the spatial extent of the reservoir and is obtained as a part of the overall solution. The gas phase comprises a mixture of CH₄ and CO₂, while the aqueous phase contains only H₂O. The solubility of CH₄ and CO₂ gases in the aqueous phase and that of H₂O in the gas-phase can be shown to have negligible impact on gas recovery.

Experimental studies have shown that CO₂ hydrates are more stable than CH₄ hydrates only for temperatures below ~283.5 K. For pressures greater than the equilibrium pressure of CO₂ hydrate at 283.5 K, CO₂ gas starts to liquefy (Ota *et al.*, 2005). Further, there is dearth of data for the kinetics of hydrate formation from liquid CO₂ and water. Hence, the present analysis is applicable to only that range of physical conditions where CO₂ remains either in gas- or in the hydrate-phase. The present model also neglects the effects of water salinity and turbidity as well as wettability and the pore size variation of the geological structure. Apart from methane recovery as a function of time, the model derives data for the distribution of pressure, temperature, and species concentration in the reservoir.

The following single step reactions describe the formation and decomposition of CH₄- and CO₂-hydrates:



Here, N_h , known as the hydration number, indicates the number of H₂O molecules required to encage each guest molecule. Mass conservation equations of CH₄, CO₂, and H₂O can be written by considering the mass of an individual species as the sum of species masses over all the phases. Hence

$$\begin{aligned} \phi \frac{\partial}{\partial t} (\rho_g s_g \omega_g^m + \rho_{mh} s_{mh} \omega_{mh}^m) \\ = - \frac{\partial}{\partial x} (\rho_g \omega_g^m v_g + J_g^m) + \dot{m}_g^m + m_{mh}^m \end{aligned} \quad (3)$$

$$\begin{aligned} \phi \frac{\partial}{\partial t} (\rho_g s_g \omega_g^c + \rho_{ch} s_{ch} \omega_{ch}^c) \\ = - \frac{\partial}{\partial x} (\rho_g \omega_g^c v_g + J_g^c) + \dot{m}_g^c + m_{ch}^c \end{aligned} \quad (4)$$

$$\begin{aligned} \phi \frac{\partial}{\partial t} (\rho_l s_l \omega_l^w + \rho_{mh} s_{mh} \omega_{mh}^w + \rho_{ch} s_{ch} \omega_{ch}^w) \\ = - \frac{\partial}{\partial x} (\rho_l \omega_l^w v_l) + \dot{m}_l^w + m_{mh}^w + m_{ch}^w \end{aligned} \quad (5)$$

Symbols appearing in the equations are described in the nomenclature. The velocity field is assumed to be Darcian and, therefore, the momentum conservation equation of each phase, in one-dimensional form, is expressed by:

$$v_\gamma = - \frac{K_{abs} k_{r\gamma}}{\mu_\gamma} \frac{\partial P_\gamma}{\partial x} \quad (6)$$

Using a volume averaged temperature over all the phases, thermal energy equation is written as:

$$\begin{aligned} \frac{\partial}{\partial t} \left[\sum_{\gamma=l,g,mh,ch} (\phi \rho_\gamma s_\gamma U_\gamma) + (1-\phi) \rho_s U_s \right] \\ + \sum_{\gamma=l,g} \left[\sum_{i=m,c,w} \frac{\partial}{\partial x} (v_\gamma \rho_\gamma s_\gamma \omega_\gamma^i H_\gamma^i) \right] + \sum_{i=m,c} \frac{\partial}{\partial x} (J_g^i H_g^i) \\ = \frac{\partial}{\partial x} \left(K_{eq} \frac{\partial T}{\partial x} \right) + \sum_{\gamma=l,g,mh,ch} \left[\sum_{i=m,c,w} \frac{\partial}{\partial x} (\dot{m}_\gamma^i H_\gamma^i) \right] + \dot{E} \end{aligned} \quad (7)$$

The closure of the set of governing equations requires appropriate constitutive relations and reaction kinetics. The binary diffusive mass fluxes appearing in the gas-phase mass transport equations are expressed by Fick's law, namely:

$$J_g^i = -\phi \rho_g s_g D_g^i \frac{M^i}{M_g} \nabla(\chi_g^i) \quad (8)$$

The present study treats the liquid as incompressible and assumes ideal gas behaviour for the gas phase constituents (Eqs. 9-12). Mass fractions of various species in the hydrate phases are functions of the hydration number N_h and are determined using stoichiometric relations, Eqs. 13 and 14.

$$P_g = \rho_g \frac{R_u}{M_g} T \quad (9)$$

$$P_g = P_g^m + P_g^c \quad (10)$$

$$\chi_g^i = \frac{P_g^i}{P_g} \quad (11)$$

$$\omega_g^i = \frac{\rho_g^i}{\rho_g} \quad (12)$$

$$\omega_{ih}^i = \frac{M^i}{M^i + N_h M^w} \quad (13)$$

$$\omega_{ih}^w = \frac{N_h M^w}{M^i + N_h M^w} \quad (14)$$

Mass generation terms for the species considered in the model arise as a result of phase changes related to hydrate dissociation or formation. Consequently, when CH_4 hydrates dissociate, CH_4 mass generation in gas phase is positive, but in CH_4 hydrate phase it is equal and negative. Therefore, for any species i :

$$\sum_{\gamma=l,g,ch,mh} \dot{m}_\gamma^i = 0 \quad (15)$$

The kinetics of hydrate formation and dissociation are driven by independent interaction of CH_4 and CO_2 with liquid H_2O as well as the exchange of CO_2 and CH_4 within the H_2O -lattice. Recent experiments show that the exchange of CO_2 and CH_4

is usually negligible in class 3 reservoirs (Yuan *et al.* 2011). The rate of change of hydrate saturation (Eq. 16) can, therefore, be described by the Kim–Bishnoi kinetic model (Kim *et al.* 1987):

$$\phi \rho_{ih} \frac{\partial(s_{ih})}{\partial t} = \dot{m}_{ih} \quad (16)$$

$$[\dot{m}_{ih}]_f = \dot{m}_{ih} = M_{ih} (\phi A_{SH} s_l + \phi^2 A_{SH} s_l s_h)$$

$$K_f^i \exp\left(-\frac{E^i}{RT}\right) (P_g^i - P_{eq}^i) \quad (17)$$

$$s_h = s_{mh} + s_{ch} \quad (18)$$

$$[\dot{m}_{ih}]_d = -\dot{m}_{ih} = M_{ih} (\phi^2 A_{SH} s_l s_h)$$

$$K_d^i \exp\left(-\frac{E^i}{RT}\right) (P_{eq}^i - P_g^i) \quad (19)$$

The following three-phase equilibrium pressure data (MPa) of water-rich pure CH_4 and CO_2 hydrates, fitted to polynomial curves as a function of temperature (K) are adapted from Adisasmito *et al.*, (1992):

$$P_{eq}^m = \left[0.1588 \left(\frac{T - 280.6}{4.447} \right)^3 \right] + \left[0.6901 \left(\frac{T - 280.6}{4.447} \right)^2 \right] + \left[2.473 \left(\frac{T - 280.6}{4.447} \right) \right] + 5.513 \quad (20)$$

$$P_{eq}^c = \left[0.06539 \left(\frac{T - 278.9}{3.057} \right)^3 \right] + \left[0.2738 \left(\frac{T - 278.9}{3.057} \right)^2 \right] + \left[0.9697 \left(\frac{T - 278.9}{3.057} \right) \right] + 2.479 \quad (21)$$

The above P - T relations may be modified by considering the effects of simultaneous presence of CH_4 and CO_2 . Further experiments are, however, necessary to identify kinetic relations compatible with the improved thermodynamics.

The absolute permeability of the medium is a function of the effective fluid porosity ϕ_{lg} . An empirical relation between the two for Berea sandstone is given as:

$$K_{abs} = 5.51721(\phi_{lg})^{0.86} \times 10^{-15} \text{ m}^2, \phi_{lg} < 0.11$$

$$K_{abs} = 4.84653(\phi_{lg})^{0.86} \times 10^{-15} \text{ m}^2, \phi_{lg} \geq 0.11 \quad (22)$$

$$\phi_{lg} = (1 - s_h)\phi \quad (23)$$

Relative phase permeability functions (k_r) use the Corey model as:

$$k_{rl} = \left[\left(\frac{s_l}{s_l + s_g} - s_{lr} \right) / (1 - s_{lr} - s_{gr}) \right]^{n_l} \quad (24)$$

$$k_{rg} = \left[\left(\frac{s_g}{s_l + s_g} - s_{gr} \right) / (1 - s_{lr} - s_{gr}) \right]^{n_g} \quad (25)$$

The pressure difference between gas and the aqueous phase, known as the capillary pressure, is adapted from Sun *et al.* (2005) and written as:

$$P_c = P_g - P_w \quad (26)$$

$$P_c = P_{ec} \left[\left(\frac{s_l}{s_l + s_g} - s_{lr} \right) / (1 - s_{lr} - s_{gr}) \right]^{-n_c} \quad (27)$$

Here, P_{ec} is the entry capillary pressure and n_p , n_g and n_c are known constants. Water phase viscosity is assumed to be independent of pressure and temperature. Equations (28-34) for the gas phase viscosities and the mass diffusivities are adapted from the available correlations and are given as (Reid *et al.*, 1987):

$$\mu_g = \frac{\chi_g^m \mu_g^m}{\chi_g^m + \chi_g^c \phi_g^{cm}} + \frac{\chi_g^c \mu_g^c}{\chi_g^c + \chi_g^m \phi_g^{mc}} \quad (28)$$

$$\phi_g^{ij} = \left[1 + \left(\frac{\mu_g^i}{\mu_g^j} \right)^{1/2} \left(\frac{M^j}{M^i} \right)^{1/4} \right]^2 \left[8 \left(1 + \frac{M^i}{M^j} \right) \right]^{-1/2} \quad (29)$$

$$D_g^{ij} = \frac{\left[3.03 - \left(\frac{0.98}{(M^j)^{1/2}} \right) \right]^2 T^{3/2}}{P_g (M^j)^{1/2} (\sigma^{ij})^2 \Omega_D} \times 10^{-2} \text{ m}^2/\text{s} \quad (30)$$

$$M^{ij} = 2 \left[\left(\frac{10^{-3}}{M^i} \right) + \left(\frac{10^{-3}}{M^j} \right) \right] \quad (31)$$

$$\sigma^{ij} = \frac{1.18(V_b^i)^{1/3} + 1.18(V_b^j)^{1/3}}{2} \quad (32)$$

$$T_r = \frac{T}{1.15 \sqrt{T_b^i T_b^j}} \quad (33)$$

$$\Omega_D = \frac{1.06036}{(T_r)^{0.1561}} + \frac{0.193}{\exp(0.47635T_r)} + \frac{1.03587}{\exp(1.52996T_r)} + \frac{1.76474}{\exp(3.89411T_r)} \quad (34)$$

Here V_b^i is the molar volume (cm³/mol) at normal boiling point and T_b^i is the normal boiling point (K) for specie i . The specific heat capacities for the hydrate phases and solid rock medium are assumed to be invariant with respect to pressure and temperature. The specific heat capacities at constant pressure for CH₄ gas, CO₂ gas and water have been taken as functions of absolute temperature and are given as (Selim and Sloan, 1989):

$$C_{pg}^m = 1238.79 + (3.1303T) + (7.905 \times 10^{-4} T^2) - (6.858 \times 10^{-7} T^3) \text{ J/kg-K} \quad (35)$$

$$C_{pg}^c = 505.11 + (1.1411T) - (89.139 \times 10^{-5} T^2) + (210.566 \times 10^{-9} T^3) \text{ J/kg-K} \quad (36)$$

$$C_{pl}^w = 4023.976 + (0.57736T) - (8.314 \times 10^{-5} T^2) \text{ J/kg-K} \quad (37)$$

The heat source term occurring in the energy equation due to mass generation of species in different phases is modelled using the heat of hydrate formation. An energy balance provides the following thermodynamic relation for the energy source:

$$\sum_{\gamma=l,g,mh,ch} \sum_{i=m,c,w} \dot{m}_\gamma^i H_\gamma^i = \sum_{\gamma=g,mh} \dot{m}_\gamma^m C_{pl}^m T + \sum_{\gamma=g,ch} \dot{m}_\gamma^c C_{pl}^c T + \sum_{\gamma=l,mh,ch} \dot{m}_\gamma^w C_{pl}^w T + \Delta H_{mh}^f(T) + \dot{m}_{mh} + \Delta H_{ch}^f(T) m_{ch} \quad (38)$$

The enthalpies of reactions in which the gas hydrate dissociates into gas and water/ice can be determined by the direct use of the Clapeyron equation. The tabulated values for enthalpy were fitted to a polynomial curve as a function of temperature. The equations obtained are summarized below (Anderson *et al.*, 2011):

The enthalpies of reactions in which the gas hydrate dissociates into gas and water/ice can be determined by the direct use of the Clapeyron equation. The tabulated values for enthalpy were fitted

to a polynomial curve as a function of temperature. The equations obtained are summarized below (Anderson *et al.*, 2011):

$$\begin{aligned} \Delta H_{mh}^f(T) = & \left[30100.0 \left(\frac{T-296.0}{14.42} \right)^9 \right] \\ & - \left[12940.0 \left(\frac{T-296.0}{14.42} \right)^8 \right] - \left[160100.0 \left(\frac{T-296.0}{14.42} \right)^7 \right] \\ & + \left[69120.0 \left(\frac{T-296.0}{14.42} \right)^6 \right] + \left[285800.0 \left(\frac{T-296.0}{14.42} \right)^5 \right] \\ & - \left[119200.0 \left(\frac{T-296.0}{14.42} \right)^4 \right] - \left[193900.0 \left(\frac{T-296.0}{14.42} \right)^3 \right] \\ & + \left[68220.0 \left(\frac{T-296.0}{14.42} \right)^2 \right] + \left[37070.0 \left(\frac{T-296.0}{14.42} \right) \right] \\ & + 420100.0 \frac{J}{kg} \quad (39) \end{aligned}$$

$$\begin{aligned} \Delta H_{ch}^f(T) = & \left[2528.0 \left(\frac{T-278.15}{2.739} \right)^8 \right] \\ & + \left[75.36 \left(\frac{T-278.15}{2.739} \right)^7 \right] - \left[9727.0 \left(\frac{T-278.15}{2.739} \right)^6 \right] \\ & + \left[1125.0 \left(\frac{T-278.15}{2.739} \right)^5 \right] + \left[4000.0 \left(\frac{T-278.15}{2.739} \right)^4 \right] \end{aligned}$$

$$\begin{aligned} & - \left[4154.0 \left(\frac{T-278.15}{2.739} \right)^3 \right] + \left[14430.0 \left(\frac{T-278.15}{2.739} \right)^2 \right] \\ & - \left[6668.0 \left(\frac{T-278.15}{2.739} \right) \right] + 389900.0 \frac{J}{kg} \quad (40) \end{aligned}$$

Symbol $\dot{E}$, in the Eqn. (7) represents the external heat transfer rate due to longitudinal heat transfer from the over-burden and under-burden and is expressed as:

$$\dot{E} = \frac{P_{cs}}{A_{cs}} \Lambda (T_{init} - T) \quad (41)$$

The equivalent thermal conductivity in this analysis is calculated using a parallel mode of conduction and is given as:

$$\begin{aligned} K_{eq} = & (1-\phi)K_s + \phi s_l K_l + \phi s_g K_g^m \\ & + \phi s_g K_g^c + \phi s_{mh} K_h^m + \phi s_{ch} K_h^c \quad (42) \end{aligned}$$

Series mode of heat conduction is also possible in the reservoir and the equivalent thermal conductivity for such a case can be written as:

$$\frac{1}{K_{eq}^s} = \frac{\phi s_l}{K_l} + \frac{\phi s_g}{K_g^m} + \frac{\phi s_g}{K_g^c} + \frac{\phi s_{mh}}{K_{mh}} + \frac{\phi s_{ch}}{K_{ch}} + \frac{(1-\phi)}{K_s} \quad (43)$$

The present study, however, shows that the difference in the evolution of temperature is largely independent of the series or parallel models of thermal conductivity. Important parameters and constants that are used to close the above system of equations are adapted from Uddin *et al.* (2008) and summarized in Table 1.

Numerical Simulation

The model equations described above are numerically simulated for a class-3 reservoir bound above and below by impermeable rock layers as shown schematically in Fig. 2. The goal of the study is to understand the dynamics of simultaneous depressurization and CO₂ injection as well as to quantify the CO₂-hydrate and secondary CH₄-hydrate formation rates. There are two boundaries to the system: (1) production well (west boundary) and (2)

Table 1: Numerical values of the parameters used in the present simulation (Uddin *et al.*, 2008)

Parameter, symbol	Value
Porosity, ϕ	0.28
CH ₄ hydrate specific heat capacity, C_{pmh} (J/kg-K)	2220.0
CO ₂ hydrate specific heat capacity, C_{pch} (J/kg-K)	2220.0
Solid rock specific heat capacity, C_{ps} (J/kg-K)	835.0
Aqueous thermal conductivity, K_l (W/m-K)	0.59
CH ₄ gas thermal conductivity, K_g^m (W/m-K)	0.030
CO ₂ gas thermal conductivity, K_g^c (W/m-K)	0.015
CH ₄ hydrate thermal conductivity, K_{mh} (W/m-K)	0.62
CO ₂ hydrate thermal conductivity, K_{ch} (W/m-K)	0.62
Rock thermal conductivity, K_s (W/m-K)	3.5
Irreducible aqueous phase saturation, s_{lr}	0.2
Irreducible gas phase saturation, s_{gr}	0.0
Hydration number, N_h	6.0
Aqueous phase density, ρ_l (kg/m ³)	1000.0
CH ₄ hydrate phase density, ρ_{mh} (kg/m ³)	919.7
CO ₂ hydrate phase density, ρ_{ch} (kg/m ³)	1100.0
Solid rock phase density, ρ_s (kg/m ³)	2675.08
CH ₄ hydrate formation rate constant, K_f^m (mol/Pa-s-m ²)	0.00290
CH ₄ hydrate dissociation rate constant, K_d^m (mol/Pa-s-m ²)	123960.0
CO ₂ hydrate formation rate constant, K_f^c (mol/Pa-s-m ²)	0.00035
CO ₂ hydrate dissociation rate constant, K_d^c (mol/Pa-s-m ²)	123960.0
CH ₄ hydrate activation energy, E^m (J/mol)	81084.2
CO ₂ hydrate activation energy, E^c (J/mol)	81084.2
Specific area of hydrates, A_{SH} (m ² /m ³)	375000.0
Aqueous phase viscosity, μ_l (Pa-s)	0.001
Pure CH ₄ gas viscosity, μ_l^m (10 ⁻⁵ Pa-s)	1.35
Pure CO ₂ gas viscosity, μ_l^c (10 ⁻⁵ Pa-s)	1.48
Entry capillary pressure, P_{ec} (Pa)	5000.0
Constant for aqueous relative permeability, n_l	4.0
Constant for gas relative permeability, n_g	2.0
Constant for capillary pressure, n_c	0.65
Longitudinal heat transfer constant, Λ (W/m ² -K)	1.0

injection well (east boundary). Initially, the reservoir core is partially saturated with CH₄ hydrate that is in equilibrium with water and free CH₄ gas. During operation, the production well is depressurized at a constant pressure, while CO₂ is injected simultaneously at a constant partial pressure at the injection well. At 283 K, CO₂ liquefies above ~4.5 MPa and the related kinetics of hydrate formation with liquid CO₂ is not well-understood. Hence, CO₂ injection pressure above 4.5 MPa and temperature above 283 K are not used in simulation. It is also assumed that the temperature always stays above the hydrate-gas-water-ice quadruple point so that no ice formation takes place. CH₄ gas production rate is defined as the rate (in kg/s) of CH₄ gas that flows out from the production well. Mathematically, the CH₄ gas production rate at the production well is calculated as:

$$\dot{M}_p^m = A_{CS} \omega_g^m \rho_g v_g \Big|_{west} \text{ kg/s} \quad (44)$$

Mass evolution rate of gaseous CH₄ in the reservoir is obtained by integrating the volumetric mass generation rate of CH₄ gas due to dissociation of CH₄ hydrates over the length of the entire reservoir as:

$$\dot{M}_e^m = - \left[\int_{x=0}^{x=L} \phi \omega_{mh}^m \rho_{mh} A_{CS} \frac{\partial(s_{mh})}{\partial t} dx \right] \text{ kg/s} \quad (45)$$

Mass evolution rate signifies the extent to which hydrates dissociate to release gas. The gas production rate is directly proportional to the mass evolution rate. However, it must be noted that the reservoir considered in this study is not a closed system and the influx of CH₄ gas from the injection well, I^m into the reservoir adds to the production rate. Hence,

$$\dot{M}_p^m = \dot{M}_e^m + \bar{I}^m \quad (46)$$

Initial and Boundary Conditions

To specify boundary conditions at each of the wells, we consider a realistic setting where several injection and production wells are laid out as a network of wells in a reservoir field. The pressure boundary condition at the production well is implemented on the total pressure rather than individual partial pressures of

the gas phase components. A Neumann boundary condition is enforced on the mass fractions of the gas components at the production well. Temperature is assumed to be distributed symmetrically around the production well and has a Neumann boundary condition. It is also possible to maintain a constant temperature at the production well by means of thermal stimulation, in which case a Dirichlet boundary condition is enforced.

The boundary condition for the total gas pressure at the injection well is difficult to specify as CO₂ gas is injected externally. For the present analysis, we assume that CO₂ is injected at such a flow rate such that its partial pressure at the injection well is always at a constant value of P_{inj}^c . Additionally, CH₄ gas partial pressure is assumed to be distributed symmetrically around the injection well and has a Neumann boundary condition. Consequently, the total gas pressure at the injection well is the sum of the CH₄ and CO₂ gas partial pressures. To take advantage of the sensible heat of injected CO₂ gas, a prescribed temperature is assigned at the injection well.

The initial and boundary conditions for the present simulations are given below.

Initial condition

$$\begin{aligned} P_g(x, 0) = P_g^m(x, 0) = P_{init}; \quad T(x, 0) = T_{init}; \quad \omega_g^m(x, 0) = 1.0 \\ s_l(x, 0) = s_{ol}; \quad s_g(x, 0) = s_{og}; \quad s_h(x, 0) = s_{mh}(x, 0) = s_{omh} \end{aligned} \quad (47)$$

Boundary conditions

$$\frac{\partial [T(0, t)]}{\partial x} = 0; \quad \frac{\partial [\omega_g^m(0, t)]}{\partial x} = \frac{\partial [\omega_g^c(0, t)]}{\partial x} = 0$$

At $x = 0$

$$\frac{\partial [s_g(0, t)]}{\partial x} = \frac{\partial [s_l(0, t)]}{\partial x} = 0; \quad P_g(0, t) = P_{dep}; \quad P_c(0, t) = P_{ec} \quad (48)$$

At $x = L$

$$\begin{aligned} P_g^c(L, t) = P_{inj}^c; \quad P_c(L, t) = P_{ec}; \quad T(L, t) = T_{init} \\ \frac{\partial [P_g^m(L, t)]}{\partial x} = 0; \quad \frac{\partial [s_g(L, t)]}{\partial x} = \frac{\partial [s_l(L, t)]}{\partial x} = 0 \end{aligned} \quad (49)$$

Solution Procedure

The numerical solution of the governing equations uses a coupled, semi-implicit, iterative technique. The semi-implicit algorithm combines explicit kinetics with implicit transport in the following manner. The solution starts from the kinetic equation using the temperature and pressure from the previous time-step (Khetan *et al.*, 2013). All other conservation equations are then solved implicitly. The temporal and spatial derivatives are discretized using forward- and central-differences, respectively while the Von Neumann and the Courant-Friedrichs-Lewy stability criteria are enforced in the determination of the time step. Within each time-step, the convergence criterion, imposed by the iterative solver, ensures the evaluation of source-terms and transport parameters using the most recent values of the variables. Such a scheme resolves the nonlinear coupling among the equations.

Grid Independence and Validation

The numerical procedure developed for the present study was extensively scrutinized for grid size (Δx) and time-step size (Δt) independence. The effect of these numerical parameters was analysed on four primary system variables – total gas pressure, temperature, CH₄ hydrate saturation and CO₂ hydrate saturation. For the grid independence studies, the grid size was varied from $\Delta x = 0.5$ m to $\Delta x = 4$ m. The pressure values at the end of 30 days of simulation were within 1% of each other, being a maximum at the farthest point from the production well. Differences between grids with $\Delta x = 0.5$ and 1 m were negligible. Hence, a constant grid size of $\Delta x = 1$ m has been chosen for the final simulation.

The time step for the simulations was varied from $\Delta t = 1.0$ s to $\Delta t = 12.0$ s. The gas pressure profiles at the end of 30 days of production were practically invariant to the time-step. Hence, a time-step size of $\Delta t = 10.0$ s was chosen for the present simulations. In addition, incremental and cumulative balance checks for mass and energy contained in the reservoir were enforced at each time-step for ensuring accuracy of the solution. All simulation results, shown here, have been carried out with uniform Δx and constant Δt .

The simulation data were validated against the research of Sun *et al.* (2005) in terms of pressure and temperature distribution as a function of time. Results obtained from the present simulation show an excellent agreement. The maximum deviations between the two results are always less than 1%.

CO₂ Sequestration

Fig. 5 shows conditions under which CO₂ can form solid hydrates in the reservoir. Since methane release lowers temperature and CO₂ injection raises pressure, the conditions become increasingly favourable for trapping CO₂ in the geological environment. Additional benefits of this approach include displacement of free methane gas and improvement in the structural strength of the reservoir, preventing it from collapse. This discussion is relevant in the context of a body of water, 1-2 km in depth, overlying the gas hydrate deposits.

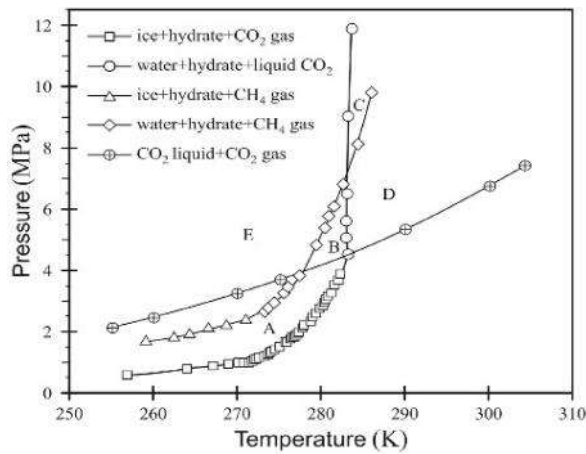
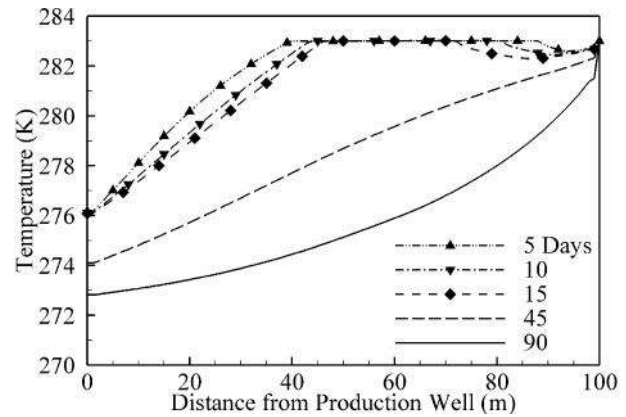


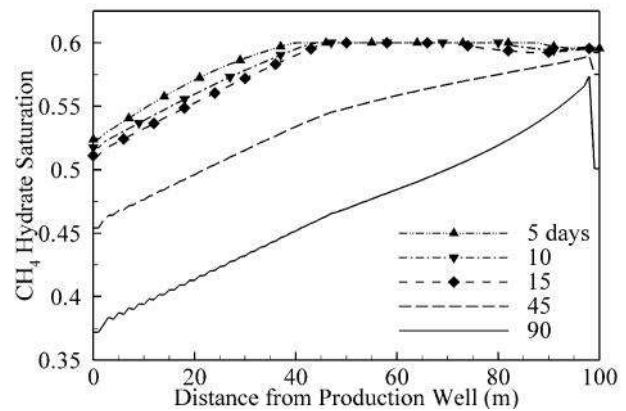
Fig. 5: Stability curves of methane and CO₂ hydrates shown jointly in the phase diagram. Since the stability boundary of CO₂ is below that of CH₄, it can act as a mobilizer of CH₄ while getting trapped in the reservoir as CO₂-hydrate. Hence, in regions marked A and B, methane is released as gas and CO₂ is trapped chemically as hydrate. Phase diagram of pure CO₂ is shown for comparison (adapted from Yuan *et al.*, 2013)

Simulation Results

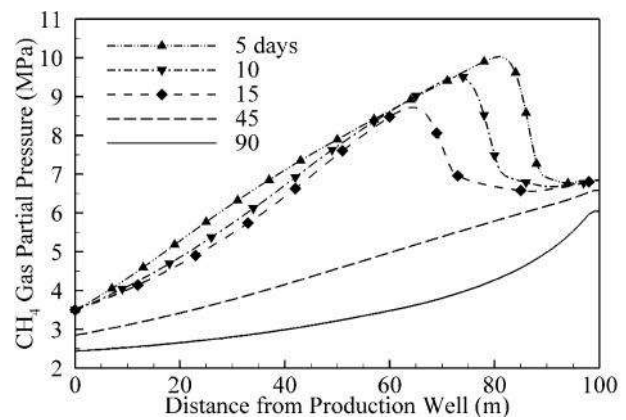
Simulation of the equations governing transport phenomena in a methane-hydrate reservoir contained between impermeable boundaries subjected to simultaneous depressurization and CO₂ injection has



A



B



C

Fig. 6: A: Transient variation in the temperature of the hydrate reservoir subjected to simultaneous depressurization and CO₂ injection. Both depressurization and injection start at time $t = 0$. B: Transient variation in the CH₄ hydrate saturation within the 100 m hydrate reservoir subjected to simultaneous depressurization and injection and C: Transient variation of partial pressure of CH₄ within the reservoir subjected to depressurization and injection

been carried out. The model includes the unsteady, multi-phase, multispecies, non-isothermal transport and kinetics in a reservoir bounded between a depressurization and an injection well. Preliminary results of the study are summarized in Figs. 6 and 7. Since methane extraction from hydrate is an endothermic process, Fig. 6 shows the reservoir temperature progressively decreasing with time. Methane content of the reservoir diminishes with time while the gas partial pressure also decreases with time. The effect of process parameters on the overall gas recovered is presented in Fig. 7. As the depressurization pressure is lowered, the hydrates are further destabilized and additional methane is generated. Increasing the injection pressure of CO_2 displaces methane and gas recovery improves again. Fig. 7 also shows that the reservoir is emptied of methane while it gets filled with CO_2 in due course of time. Fig. 7 shows a rise in methane recovery several days into the operation of the wells of the reservoir. It corresponds to the time taken by the injected CO_2 at one end to mobilize methane towards the depressurization well.

Important conclusions relevant to the overall process are the following:

- i. While CO_2 injection enhances CH_4 production, the enhancement is largely due to the displacement of CH_4 . The CO_2 -hydrate formation is a slow process and provides limited support for enhancement in CH_4 -recovery. Slower kinetics and lower mole fractions restricts the CO_2 -hydrate formation rate. While the production well pressure has minimal effect on the CO_2 -hydrate formation, its saturation increases with increase in CO_2 injection pressure.
- ii. CO_2 injection facilitates increases methane recovery, lowers reservoir temperature and can result in the formation of secondary CH_4 -hydrates. The secondary hydrate formation is, however, quite small for the range of parameters studied. Secondary hydrate formation may also be lowered by lowering the production well pressure.

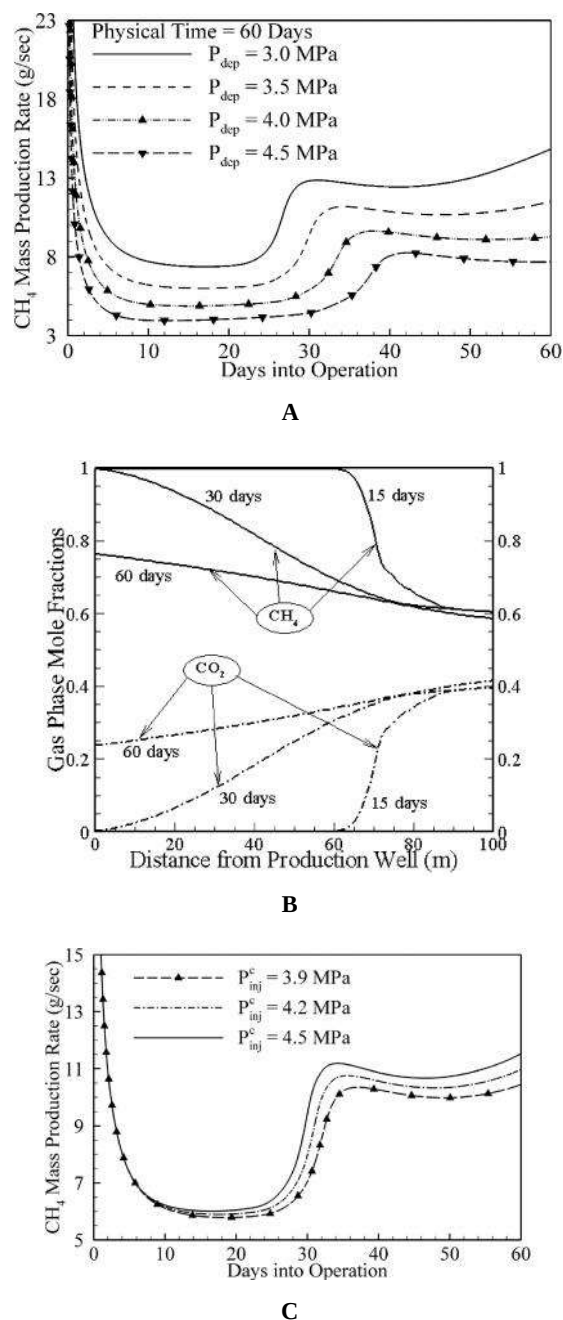


Fig. 7: A: Production rate of methane from a gas hydrate reservoir in which the left side is depressurized and the right side at a distance of 100 m has CO_2 injection. Reducing the depressurizing pressure from 4.5 to 3 MPa shows an increase in methane recovery rate, B: Amount of methane and CO_2 left in the reservoir after selected instants of time. The mobilities of the two gases are inter-related through chemical kinetics and because of the energy released and absorbed during hydrate formation and C: Influence of the CO_2 partial pressure at the injection well pressure on the mass production rate of CH_4 gas from the reservoir; CO_2 -driven CH_4 increase in the mass evolution rate

- iii. High rate of production may reduce the reservoir temperature leading to the solidification of H₂O. Such a phenomenon will reduce the reservoir permeability gradually slowing down gas production. In this respect, the gas recovery process is self-limiting. The formation of CO₂ hydrates involves an exothermic reaction and has a beneficial effect on CH₄ recovery.

Further investigations, involving a three-dimensional geometry, phase-change effects and improved multiphase kinetics, are currently in progress.

Research Directions

Selection of an exploitation technique for gas recovery from hydrates calls for a fairly sophisticated analysis. Modelling the dissociation process itself for methane and formation process for CO₂ can proceed along two directions. The simpler direction is the *thermodynamic* approach utilizing Figures 3 and 4 in simulation. A realistic description would require a *kinetic* model involving rates of gas release or capture; such information can be derived only from laboratory experiments. Alternatively, a molecular-scale model for mixture thermodynamics and kinetics needs to be developed.

Flow distribution of methane along with the injected fluid, locally released gases, and moisture in a porous formation is a topic of research. Gas release depends on the distribution of pressure and temperature. The resulting model will involve multi-component, multiphase fluid flow, heat transfer, chemical reactions, and combustion in the subsurface. The fact that the pore structure of the reservoir is nowhere close to homogeneous is a point of concern. In this context, studies on imaging, reconstruction and characterization of the porous region are important. Data shows that pores display length scales over several orders of magnitude, calling for *multi-scale* modelling of the transport process in a stochastic framework. In addition, a reservoir experiencing fracture will alter the flow path, apart from the severe predicament of process safety.

Closure

Simultaneous exploitation of gas hydrates from its natural environ and disposal of CO₂ in its place is

attractive but has considerable challenges, compelling a diversity of expertise. It calls for a need to examine and develop basic understanding of a complex interconnected system. Realizing the technology on a field scale will require across-the-board collaboration.

Nomenclature

A_{cs}	Area of lateral heat transfer (m ²)
A_{SH}	Specific area of hydrates (m ²)
C_p	Specific heat capacity (J/kg-K)
D	Mass diffusivity (m ² /s)
E	Activation Energy (J)
H	Enthalpy (J/kg)
$\bar{I}^m$	Methane influx (g/s)
J	Mass flux (g/m ² -s)
K	Thermal conductivity (W/m-K)
K_{eq}	Equivalent thermal conductivity (W/m-K)
K_{abs}	Absolute permeability
K_f	Hydrate formation rate constant (mol/Pa-s-m ²)
K_d	Hydrate dissociation rate constant (mol/Pa-s-m ²)
L	Reservoir length (m)
M	Molar mass (kg/kmol)
M^{ij}	Function of molar masses of species i and j
$\dot{M}^m$	CH ₄ production/evolution rate from the reservoir (kg/s)
$\dot{m}$	Mass generation rate at any x, t (kg/m ³ -s)
N	Hydration number
P	Pressure (MPa)
R_u	Universal gas constant (kg/kmol-K)
s	Saturation
T	Temperature (K)

t	Time (s)
v	Velocity (m/s)
x	Horizontal co-ordinate axis

Greek Symbols

ϕ	Porosity
ω	Mass fraction
χ	Mole fraction
μ	Viscosity
ρ	Density

Subscripts, Superscripts

c, ch	CO ₂ , CO ₂ hydrate
g, h, l	Gas, hydrate, liquid
m, mh	CH ₄ , CH ₄ hydrate
p	Production
w	H ₂ O
γ	Phases

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Review Article

Materials Science and Technology: Research and Challenges in Nuclear Fission Power

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The performance and integrity of structural and functional materials are key issues in the safety and competitiveness of current and future nuclear fission reactors being developed for sustainable nuclear energy applications. The challenges towards development of nuclear structural materials arise due to the demanding hostile environments with respect to radiation, temperature, stress, etc., and requirements of total reliability and high performance over the long service life (say 60 years). A successful materials science research programme in nuclear industry has to take into account these challenges to improve the performance of materials and components in the emerging scenario of extending life of existing plants and realizing advanced reactors. In this study, material challenges associated with water reactors and fast breeder reactors (FBR) with focus on short-term and long-term strategies for materials development are considered. The materials in the existing and proposed future nuclear fission reactors are summarized along with a description of major material degradation mechanisms in different environments. The priority in the nuclear industry is to extend the life of reactors with robust safety features and sufficient cost-effectiveness, beyond forty to sixty years and from sixty to even one hundred years. The importance of modelling and developing predictive tools to estimate materials behaviour for effective computing of lifetime of nuclear reactor components is fast developing to cut down cost and time and also to enhance safety and confidence in existing and new systems. The future FBR technology relies heavily on advanced waste management and effective proliferation resistance. We review advanced reactor concepts of Generation IV forum and the new materials and technologies. Nuclear energy is not the right option for every country. Careful examination of the energy basket and commitment over a long period with effective mechanisms of safety governance is the key to make a decision to harness large amounts of nuclear energy. China, France, India, Russia, USA, UK, etc. are extremely committed to use large amounts of nuclear energy. Japan after the Fukushima accident, faces a challenge of public acceptance though the country has deep and rich expertise in nuclear technology and it is advantageous to produce low carbon power, on a sustained competitive basis from nuclear energy.

Keywords: Advanced Materials; Nuclear Reactors; Fission and Fusion; Challenges

Introduction

Nuclear power is a robust facilitator of energy security in countries with inadequate domestic fossil and renewable energy resources. Nuclear power is also a way to deliver low carbon energy integrated over the life cycle of an atom, to human civilization. There is incredible power in an atom. Disintegration of a

single uranium atom produces several orders of magnitude more energy than burning of coal, oil or natural gas. However, nuclear power remains an under-appreciated marvel of modern technology. When we amplify the natural process of fission (by breeding), we can meet the entire energy need of the civilization for thousands of years with known resources of uranium and thorium. The comparison

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shows that for a 1000 MWe power plant, we may need ~160 t of natural uranium per year which can be brought in a single tractor trailer; but we may need ~2.6 million t of coal per year (i.e. 5 trains of 1400 t/day). For establishing solar or wind power, we need multifold more land compared to uranium and even coal-fired power plants. In the 1950s, the first commercial nuclear power station started operating; and today in the world, there are more than 400 commercial reactors based on nuclear fission and operating with 370,000 MWe total capacity (Raj *et al.*, 2008). These plants are supplying 15% of the world's electricity. It is expected that the nuclear energy generation capacity will increase approximately to 1500 GWe in another 40 years (Raj *et al.*, 2008). India has planned for a rapid increase in nuclear power capacity from the current installed capacity of 4120 MWe to 20,000 MWe by 2020 and 63,000 MWe by 2032 (WNA, 2014). Since awareness on the environmental issues resulting from coal-based power plants has increased, the clean nuclear energy will assume more importance in the coming decades (IAEA, 2004). Fully comprehending the setbacks from incidents such as Three Mile Island, Chernobyl and Fukushima, the nuclear industry is persistently striving to achieve higher standards of safety and reliability (WANO, 2006), especially for severe and black swan accidents (high risk, but extremely low probability). With additional conventional uranium fuel resources of 10.1 million t (Raj *et al.*, 2008) that can last for 270 years with the current capacity of nuclear power, nuclear energy can be the synonym for sustainable energy in the future (WNA, 2005). The sustainability of nuclear energy, for thousand years and beyond, depends on advancement in two key technologies; closed fuel cycle technology for fast reactor and thorium fuel cycle technologies (UIC, 2007).

Future reactors are also being designed to work in a high temperature regime providing better thermal efficiency and multiple industrial uses. This enhancement can be achieved by advanced technologies such as high temperature gas-cooled reactors and accelerator-driven systems (ADS). ADS provides excellent resistance to proliferation by *in situ* incineration, closed fuel cycle, reducing nuclear waste, and next generation fuels and coolants with improved

efficiency. Thus, nuclear industry no longer remains a mere producer of electricity; instead, it has resurged to symbolize the energy policy of the world (Raj *et al.*, 2008). The new generation nuclear systems needs to be successfully implemented by developing advanced materials and their manufacturing technology in all the stages of nuclear energy systems such as ore refining, fuel fabrication, reactor technology, reprocessing and waste management. In synchrony with this, the materials research domain is undergoing a revolution responding with advanced materials which give priority to reduce nuclear power cost, that is, achieving higher burn-ups, longer life of reactors and less operational and maintenance costs. Fusion reactors, in the future, shall face many new challenges in materials and related technologies; however, these systems shall also build on large experience of fission, in particular, fast spectrum reactors (Stork *et al.*, 2014 a, b).

Reactor Materials

Materials can be broadly classified into two main groups: For example (i) fuel assemblies, coolant channels and calandria tubes of pressurized heavy water reactor and (ii) clad and wrapper in fast reactor cores. A wide variety of materials are used as components of structures outside the core and inside the containment structures such as nuclear steam generation systems in water reactor. Conventional systems such as turbines and condensers constitute the rest of the plant components. (Fig. 1) (Dettmering, 2009). Inside the reactor core, the materials are subjected to demanding environments such as high

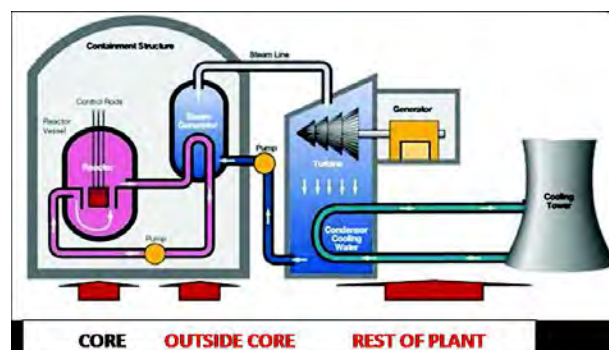


Fig. 1: Schematic of a nuclear power plant.
Source: Dettmering (2009)

temperature, temperature gradients, neutron irradiation, stress, etc. compared to out-of-core components, where temperature, stresses and corrosion are the key damage influencing parameters.

Thus, core materials need resistance to irradiation induced damages, excellent structural stability, excellent mechanical properties at high temperatures, compatibility with fuel/coolant/moderator and good fabricability and weldability. Table 1 shows the important criteria for selecting materials for components in thermal and fast reactors.

Based on the neutron energy regime of nuclear fuel fission, reactors are broadly classified into two types, thermal and fast reactors. The main criterion for choosing material for thermal reactor is low neutron absorption coefficient since fission is caused by neutrons with an average energy of ~ 0.025 eV. Zirconium-based alloys with a neutron absorption

cross-section of $2 \times 10^{-24} \text{ cm}^2$ are used for cladding. The candidate materials for pressure vessels and piping are carbon steels and low alloy steels or 12% Cr steels that are used for turbines and steam generators. Satisfactory performance of thermal reactors necessitates the extension of life from 40 to 60 to 100 years. In this context, small-sized specimen testing and advanced non-destructive evaluation coupled with modelling and simulation will enable us to obtain an in-depth knowledge of fracture mechanisms, micro-structural and structural degradations. In fast reactors where fission is caused by fast neutrons with an average energy of 0.2 to 0.5 MeV, materials experience severe hostile environment with neutron flux of $\sim 8 \times 10^{15}$ neutrons/cm²/s which is more than an order of magnitude higher than thermal reactors and high temperatures of 823 K compared to 573 K in thermal reactors. Fast reactors have a high target burn-up of 200 GWd/t compared to 80 GWd/t in

Table 1: Selection criteria of materials for components in thermal and fast reactors

Type of reactor	Component	Selection criteria
Thermal	Clad	Low neutron absorption coefficient Minimum interaction with the fuel pellet Compatible with the moderator/coolant Ability to withstand cladding stress due to fission gas release and thermal expansion Resistance to irradiation creep
	Structural	Low neutron absorption coefficient Minimum irradiation induced damage Minimum environment-induced changes such as chemical interaction with coolant and fission products, hydrogen damage, enhanced corrosion resistance under stress, irradiation and environment
	Pressure tubes	Minimum hydrogen damage such as hydrogen embrittlement, blistering and hydride cracking
Fast	Clad	Minimum dimensional changes due to void swelling and irradiation creep Reduced irradiation growth hardening and embrittlement Good compatibility with liquid sodium and fuel Stability of structure and mechanical properties
	Wrapper	Acceptable radiation damage and high temperature properties Good compatibility with sodium Good weldability and fabricability
	Structural	Good compatibility with liquid sodium Excellent structural stability high temperature mechanical properties Availability of design data Good weldability and fabricability Affordable cost

Source: Raj and Vijayalakshmi (2011)

pressurized water thermal reactors. The selected materials should possess resistance to void swelling, irradiation creep and helium embrittlement and good compatibility with sodium, fuel and fission products. Thus, for a fast spectrum reactor, candidate materials for clad and wrapper are cold worked AISI 316 SS, 15% Cr-15%Ni-Ti stabilized stainless steel (Alloy D9) and ferritic steels. For structural components, 316 L and 316 LN stainless steels and for steam generator, modified 9 Cr-1Mo ferritic steels are currently chosen (Raj *et al.*, 2008).

Light Water Reactor Materials – Present Scenario

Zircaloy, an alloy based on zirconium, is the workhorse material employed for core components of thermal reactors. The light water-cooled reactors, especially boiling water reactors (BWR), use ceramic fuel pellets of UO_2 stacked in clad tubes made of Zr alloy tubes (3-4m long) that are grouped into fuel assemblies containing typically about 100 clad tubes arranged in a square array. Each assembly is encased in a square zirconium alloy tube, typically 12 cm on a side. They transfer heat to flowing water coolant and serve as the primary barrier to contain radioactive fission products. The control rod made of stainless steel tubes filled with boron carbide for neutron absorption are clustered into cruciform-shaped control blades and pass between assemblies (BARC, 2009). There are 700-800 fuel assemblies in BWRs and 300 fuel assemblies of larger diameter in pressurized water reactors (PWR) (Zinkle and Was, 2013). PWR and BWR cores operate 18-24 months between refueling with a core residence period of 304 fuel cycles and achieve cumulative burn-up levels of $\sim 40\text{-}60 \text{ GWd/Mt}$ of uranium. Non-fuel core components are core shroud (BWR), baffle-former assembly (PWR) and smaller components such as bolts, springs, support pins and clips. Out of core components are control rod drive mechanisms and housing, vessel head penetrations made of welded austenitic stainless steel and reactor pressure vessel. A typical BWR of 1960s genre designed and developed by GE (USA) and operated with success, meeting high levels of operational and safety standards by Nuclear Power Corporation of India is shown in Fig. 2.

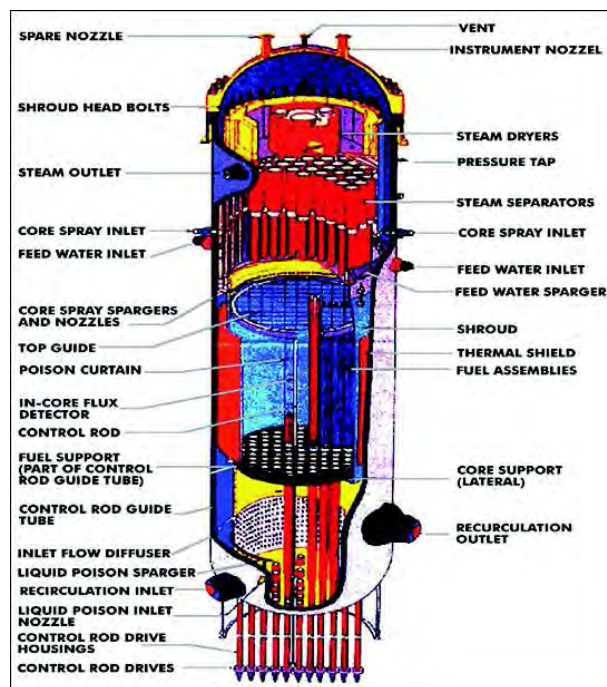


Fig. 2: Fuel assemblies and control rods of BWR (210 Mwe) at Tarapur, India. Source: BARC (2009)

Major pressure boundary components such as reactor pressure vessel (RPV), pressurizer, steam generator, steam lines, turbine and condenser are made of either low carbon or low alloyed steels. The RPV serves as a pressure barrier and containment for radioactive fission products and plays a key role in nuclear safety. RPV material is a ferritic steel with 1-2% Mn, 0.5-1% Ni, $\sim 0.5\%$ Mo and 0.15-0.4% Si (IAEA, 2009) with a wall thickness of ~ 20 cm. Austenitic stainless steels such as Types 304, 304L, 316, 316L, 321 and 347 dominate the core structural materials. Nickel based alloys are used for high strength components such as springs and fasteners. Though Alloy 600 was used for vessel penetrations and steam generator tubes, it is now replaced by Alloy 690 to overcome stress corrosion cracking susceptibility challenges.

The selection of Nickel based alloys and austenitic stainless steels for core internals and the steam generator tubes is driven by the need for good aqueous corrosion resistance at high temperature (Zinkle and Was, 2013). Condenser tubes are generally made of titanium and stainless steel.

Table 2: Reactor core environments for LWRs

System	Coolant	Pressure (MPa)	T_{in}/T_{out} (°C)	Neutron spectrum maximum dose (dpa)	Fuel	Electrochemical potential ECP
PWRs	Water-single phase	16	290/320	Thermal~80	UO ₂ (or MOX)	<~500mV _{SHE}
BWRs	Water-two phase	7	280/288	Thermal~7	UO ₂ (or MOX)	150mV _{SHE}

Source: Zinkle and Was (2013)

Table 2 shows that BWR environment has nobler electrochemical potential (ECP) (Zinkle and Was, 2013). This is due to the combination of boiling water in the core and radiolysis. However, PWRs operate at a lower potential because of the addition of hydrogen (~3 ppm) for scavenging radiolysis products. This lower ECP is better for stress corrosion cracking (SCC) and corrosion control. PWR primary water contains 1000 ppm boron as boric acid (H₃BO₃) for reactivity control along with 2-4 ppm Li as LiOH for pH control. Fuel and core components experience stress due to thermal expansion, high velocity water flow, residual stress due to welding, and stress due to radiation-induced volume expansion. All these challenges are overcome based on experience and continuing research (experiments and modelling). Typical zirconium alloy cladding materials used in BWR and PWR reactors are summarized in Table 3 (Zinkle and Was, 2013).

Pressurized Heavy Water Reactor (PHWR) Materials – Present Scenario

Pressurized Heavy Water Reactor (PHWR) of CANDU version uses deuterium, an isotope of hydrogen as moderator due to its low neutron absorption and natural uranium oxide as fuel. The

major difference in materials used in this system as compared to LWRs is the use of Zr-Nb pressure tubes that house the Zircaloy-clad fuel and high pressure D₂O. These tubes fit into Zircaloy-4 calandria tubes that pass through thin-walled 304 stainless steel calandria vessel which also contains low temperature D₂O moderator. Thus, zirconium alloys play larger role as pressure boundary materials in PHWRs than LWRs.

A large number of zirconium alloys have been developed as the core structural materials. Efforts to increase the residence time of Zr-based components inside the reactor have resulted in development of Zircaloy-2, Zircaloy-4, Zr-Nb alloys and their variants. In the 1980s, advanced radiation-resistant materials were developed such as ZIRLO (ternary and quaternary alloys of Zr-Nb), M5, E110 and DX-D4(7). M5 alloy had excellent radiation and corrosion resistance, also hydriding, irradiation creep with negligible growth (0.7%) and achieved high burn-up values of 70 GWd/MtU. The duplex cladding DX-D4 has better mechanical and corrosion properties and radiation resistance up to a burn-up of 60 GWd/MtU. Attempts are made to enhance the burn-up to about ~80 GWd/MtU by improved fuel and structural materials. India has successfully developed and

Table 3: Typical commercial zirconium alloys used as cladding in PWRs and BWRs

Reactor type	Zr alloy composition	Thermo mechanical treatment
BWR	Zircaloy-2 (1.5% Sn-0.15% Fe-0.1% Cr-0.05% Ni)	Recrystallized
PWR	Zircaloy-4 (1.5%Sn-0.2%Fe-0.1%Cr)	Cold worked and stress relief anneal
PWR	ZIRLO (1-2% Nb-1% Sn-0.1% Fe)	Quench and temper/stress relief anneal
PWR	M5(1% Nb)	Recrystallized

Source: Zinkle and Was (2013)

matured PHWR technology in the commercial domain. India has capability to design, construct and operate upto 700 MWe PHWR indigenously.

1. Materials Degradation in Water Reactor Systems

Structural materials employed in nuclear reactors degrade in their properties under radiation and corrosive environment of operation. During service, more often, the degradation of materials initiates from the surface and the conditions at the surface will be entirely different from that of the bulk of the material. Hence, materials for use in nuclear environments are specified in terms of not only the chemical composition but with respect to microstructure, distribution and structure of grain boundaries, anisotropy, effects of cold work, heat treatment, residual stresses, etc. The surface condition including roughness, chemical state and cleanliness are also specified.

Nuclear fission reactions result in the release of different types of radiations, fission products, actinides and other products. There are five important bulk radiation effects on materials by neutrons such as radiation hardening and embrittlement; radiation-induced and radiation-modified solute aggregation and phase stability; irradiation creep; void swelling and helium embrittlement. Neutron irradiation at LWR-relevant conditions (523 to 623 K) also reduces fracture toughness of austenitic SS. This will be a serious concern in ferritic/martensitic steels as it can lead to radiation embrittlement of reactor pressure vessel (Zinkle and Was, 2013). At intermediate temperatures between 573 K and 673 K, radiation-induced solute segregation and modified precipitation, void swelling, irradiation creep and anisotropic growth can occur. Materials for nuclear energy systems that exhibit irradiation growth include graphite, zirconium, beryllium and other metals or alloys (Zinkle and Was, 2013). At high temperature ($>0.5 T_M$), helium produced from (n, α) reactions within materials diffuses into grain boundaries, where it can form large bubbles that weaken grain boundary strength. Dramatic reduction in the total elongation will cause helium embrittlement. Corrosion occurs in all the major systems exposed to a water environment, including

the reactor core, steam generator, turbine, condenser and piping, valves and fittings. It occurs in a wide variety of alloys such as carbon and low alloy steels used in piping and turbine components, stainless steel used in core internals and primary flow circuits and the condenser, nickel based alloys in the steam generator and in reactor vessel penetrations and welds, and zirconium alloy fuel cladding (Zinkle and Was, 2013). As the plants age, the most important corrosion issues will be SCC and irradiation-assisted stress corrosion cracking (IASCC) and uniform corrosion.

Gamma rays can radiolyse water and create free radicals that raise corrosion potential and change water chemistry. This change in potential leads to a multitude of corrosion and SCC including irradiation-assisted phenomenon that affect the performance of structural materials. For core components of LWR that suffer from IASCC ferritic-martensitic materials with inherent radiation resistance is considered; and for radiation embrittlement problem of reactor pressure vessel in PWR, ferritic steels show better performance (Zinkle and Was, 2013).

In the last decade, light water fission reactors in the US contributed 90% average capacity factor, demonstrating very high reliability. However for extending the operating life time of these reactors, extensive R&D to investigate corrosion and neutron-induced material degradation phenomena is in progress. Fracture toughness data collected for Types 304 and 316 austenitic stainless steels in LWR conditions of 523-623 K clearly showed fracture toughness while approaching value near 50 MPa $m^{1/2}$ after 5-10 dpa (Pawel *et al.*, 1996; Rowcliffe *et al.*, 1998). Intensive investigations are completed on the possibility of neutron radiation-induced embrittlement of reactor pressure vessels (Odette and Nanstad, 2009). Long-term experiments confirmed that radiation-induced precipitation due to neutron irradiation is not limited to temperatures above 673 K, instead it can occur even at 573 K (Kenikand Busby, 2012). Research is also focused on delaying the onset of steady-state swelling regime by identifying the mechanism that extends low-swelling transient regime (Wolfer, 1984; Mansur and Lee, 1991). Though at high temperatures, recovery of radiation damage

occurs due to annealing of lattice defects, high temperature helium embrittlement reduces upper operating temperature of materials in nuclear energy systems (Zinkle and Was, 2013).

2. Material Degradation in Indian PHWR Systems Calandria

Type 304L austenitic stainless steel irradiated by fast neutrons at the calandria normal operating temperature of 60°C will experience an increase in both the yield and the ultimate strengths. This increase in strength initially is very rapid up to a fluence of approximately $5 \times 10^{24} \text{ n.m}^{-2}$, $E > 1 \text{ MeV}$. While the material becomes stronger, the ratio of the ultimate to yield strength decreases indicating that the irradiated material is less ductile. This leads to neutron irradiation embrittlement. The end shields are fabricated from Type 304L stainless steel and filled with carbon steel shielding balls. The fuelling tube sheet, end shield shell and lattice tubes are exposed to lower fluences than the calandria tube sheet and the neutron embrittlement in these components, therefore, is not a concern. The calandria tubes are manufactured from Zircaloy 2 and installed within the reactor in a near-fully annealed condition. In service, they are subjected to a high neutron flux and they consequently undergo irradiation strengthening and some loss of ductility.

The austenitic stainless steel type 304L of which the calandria and the end shields are made is susceptible to SCC in a chloride environment. An elevated temperature and the presence of oxygen tend to aggravate SCC of this material. During fabrication of the stainless steel (304L) calandria and the end shields, care is taken to limit chloride contamination of the material. By strict fabrication specification limit for chloride content in solvents and cleaners used during the course of manufacturing to 100 ppm and maintaining excellent purity of moderator and demineralized water, very low chloride condition is maintained and SCC prevented even in the presence of oxygen (Jain, 2009).

3. PHWR Coolant Channels

The coolant channel assembly of PHWRs mainly consists of pressure tubes, calandria tubes and garter

spring spacers made of zirconium alloys and end fittings made of stainless steel grade-403. Heavy water of 573 K and pressure of 10 MPa circulates through pressure tubes to transport the heat generated by fission of UO_2 fuel kept in zircaloy-4 sheathed fuel bundles to the steam generator through carbon steel feeders, headers and associated interconnected piping. The pressure tubes are the most important components in PHWRs and undergo degradation due to continuous exposure to intense radiation, high temperature, pressure and corrosive environment. Intense radiation causes atomic defects and consequent point defects resulting in microstructural, physical and mechanical changes.

Material hardening, reduction in ductility, and dimensional changes such as axial elongation, diametrical expansion and wall thinning occurs. Advanced techniques such as BARC Reactor Coolant Inspection System (BARCIS) and non-intrusive vibration diagnostic technique (NDVT) have been developed for regular in-service inspections. Pressure tubes made of Zircaloy-2 used in earlier PHWRs contain ~0.05% nickel which promotes hydrogen absorption. Hydrogen in atomic and molecular form is generated by radiolysis of heavy water coolant. Free radicals generated in radiolysis comprises H^* (D^*) and OH^* (OD^*), which on recombination produce molecules of H_2O_2 , O_2 and H_2 . Hydrogen absorbed by Zr^{-2} forms zirconium hydride. At lower temperatures such as 423 K, the solubility of hydrogen in zirconium is low and hence hydride formation above threshold level reduces stress-bearing capacity of pressure vessels and makes it brittle. In Canadian PHWR, sudden failure of pressure tubes is reported due to building up of hydrides.

The hydrogen picked up during service by the Zr alloys forms hydrides along a specific habit plane close to basal plane (Suri, 2013). The crystallographic texture formation of Zr alloys depends on degree of deformation, thermo-mechanical history and alloy composition. Deleterious effects of hydrides can be reduced by controlling the texture so that hydrides are precipitated parallel to hoop stress (Singh *et al.*, 2007). The other two important life limiting factors are excessive irradiation creep and growth controlled

by optimum level of cold work and suitable annealing temperature. Zr-2.5% Nb has high strength, corrosion resistance and reduction in hydrogen pick-up rate (Suri, 2013). The presence of Nb promotes recombination of nascent hydrogen isotopes to molecular form. Thus, hydrogen escapes in the coolant.

A computer code HYCON-95 was developed to predict hydrogen pick up by Zr-2 tubes and used for life management of all Indian PHWRs. Based on HYCON results, coolant channel replacement was made with Zr-2.5 Nb, which has better mechanical properties, higher resistance to radiation induced deformations and very low pick up of hydrogen which eliminated hydriding-induced degradation in pressure tubes of PHWRs.

4. Primary Side Flow-Assisted Corrosion (FAC)

Primary heat transport (PHT) system operates at average temperatures of 566 K (220 MWe)/577 K (540 MWe) at the outlet ends of channels in PHWRs. The PHT pipelines made of carbon steel carry hot heavy water from the channel outlets to a common header and from there to steam generators (SGs). Similar pipes also carry heavy water from the cold leg of SGs to the channel inlets after heat transfer at an average temperature of 522 K (220 MWe)/533 K (540 MWe). A protective magnetite (Fe_3O_4) film is formed on the inside surfaces of the carbon steel pipelines by a process called hot-conditioning during pre-commissioning operation. This film continues to grow during reactor operation under alkaline water chemistry (pH 10-10.5) and dissolved oxygen less than 10 ppb. Solubility of magnetite in water at pH more than 9.8 increases with increase in temperature from 423 K to 573 K. The PHT feeder pipelines have a contoured geometry, and at locations where high velocities and high temperature ~ 573 K exists at the outlet PHT feeders, higher thickness loss of magnetite results from flow-assisted corrosion (FAC). Using improved carbon steel (0.2% w/w chromium addition) and strict maintenance of pH in a range of 10.1 to 10.5 of hot coolant heavy water effectively prevented FAC (Jain, 2009).

5. Steam Generator

Steam generators with Monel 400 tube material was used in earlier generations of PHWRs. These alloys underwent SCC under high dissolved oxygen concentrations in the coolant and also exhibited higher rate of general corrosion. This resulted in the release of cobalt-59 (impurity with nickel in alloy), which generated highly radioactive cobalt-60 on irradiation with the thermal neutrons. This created radiation hazard for personnel and thus Monel 400 was replaced with Inconel-600. However, inter-granular stress corrosion cracking (IGSCC) of Inconel-600 led to the selection of Inconel-800. The Inconel-800 has demonstrated good general corrosion resistance especially under high dissolved oxygen concentration in the coolant (>100 ppb) and IGSCC. Nickel content is 30% w/w in Incoloy-800 compared to 70% in Monel-400 and hence the cobalt-59 associated with this material is nearly absent.

Tube failures in several SGs of nuclear power reactors have occurred due to material degradation mechanisms such as wastage and denting. During SG operation, sludge deposition occurs on lower tube sheet leading to circulation only in upper parts. This leads to accumulation of sodium phosphate in the intermediate region of tube sheet promoting high general corrosion of Ni-based alloys resulting in thinning of tubes and this is called wastage. Replacement of sodium triphosphate dosing by all volatile treatment (AVT) comprising hydrazine hydrate and morpholine additions to feed water, to reduce oxygen concentration less than <10 ppb and increase pH to 9.5, prevented these corrosion problems.

Due to accelerated corrosion of the tube support plates of SG made of carbon steel, voluminous corrosion products accumulate in the area between SG tube and tube hole on the drilled support plate. The flow decrease causes rise in temperature, increased evaporation and concentration of acidic chlorides caused crevice corrosion and this autocatalytic corrosion process resulted in the concentration of chlorides in the range of thousands of ppm. The bulky corrosion products thus formed exerted stress on SG tubes causing denting of tubes, and also produced tensile stresses on the ID side of

SG tubes causing primary water stress corrosion cracking (PWSCC). The change of tube support material to stainless steel solved this problem (Jain, 2009).

Use of erosion resistant stainless steel in river water cooled condensers and titanium in seawater cooled condensers avoided condenser tube leakages and contamination of SG water and thus SG tube failures by under-deposit corrosion. Continuous or intermittent blow-down of SG water keeps the water chemistry parameters within permissible limits to avoid SG tube and turbine blade corrosion.

Primary water stress corrosion cracking has been one of the major mechanisms in steam generators or control rod drive mechanism nozzles in nuclear power plants (Kim and Hwang, 2008). Environmental barrier coatings are chosen to mitigate the problem or electrochemical corrosion potential control is adopted. Alternatively, mechanically enhancing surface with induced compressive stress through a technique such as shot peening is also considered as a possible method. While electroplating with Ni is useful, electroless nickel plating is considered better due to its economical nature and robustness to coat complex geometry with ease.

Pulled tube examinations are a very convenient way of gathering essential information to gain more knowledge about the corrosion process. Laboratory examination of few hundred tubes drawn out from a plant provides extensive data on secondary side cracking, corrosion location, orientation, surface extension, length, depth, density, morphology, etc.; deposits and oxides composition; leak rate of the cracks; burst pressure of the degraded segment; mechanical properties of segments with or without cracking. Systematic evaluation of the database would help in understanding the characterization of degradation. This requires extensive validation of the non-destructive examination techniques. Therefore, non-destructive testing (NDT) gadgets should be incorporated in those tubes experiencing corrosion in PWRs (Cattant, 1997).

Life extension of SGs and plant life management require extensive survey of the ageing undergone by

several tubes. It is reported that in Alloy 800 tubes, boron precipitation at grain boundaries is attributed to ageing through operation. In addition, the effect of boron segregation on the integrity of Alloy 800 SG tubing needs further investigation (Lu *et al.*, 2012)

Fast Breeder Reactors

Fast reactors operating at high temperatures require an effective coolant such as sodium with high melting point (~ 1123 K) at atmospheric pressure. There is no need for moderator or any pressurizing of the coolant. The Pu 239-based mixed oxide fuel core is submerged in liquid sodium pool and heat is removed by primary liquid sodium cooling loop which transfers energy to the intermediate liquid sodium cooling loop. This heat energy is used to produce steam in steam generator for producing steam to drive the turbine (Suri, 2013).

During 400 years of SFR operation, important material's issues emerged in terms of liquid–solid material interactions, irradiation enhance/assisted materials evolution and life extension issues from economic point of power generation.

Due to non-uniform temperature in sodium loops of fast breeder reactors (FBRs), alloy elements dissolve in the higher-temperature region, and dissolved elements are deposited in the lower-temperature region, particularly carbon whose super saturation level varies with temperature. The carbon present in steels plays an important role in maintaining the material's strength properties. Thus, considerable emphasis should be placed on the decarburization and carburization phenomena in sodium. In a bimetallic sodium circulation loop consisting of austenitic stainless and ferritic steels, because of the difference in carbon activity between the two materials, decarburization occurs in ferritic steel, which has higher carbon activity, whereas carburization occurs in austenitic stainless steel (Bharasi *et al.*, 2012).

In addition, considering FBRs being under service at higher temperatures than light water reactors, it is necessary to understand the high temperature mechanical properties; specifically, creep and low cycle fatigue with strong interactions in terms of ratcheting or cyclic creep (Yoshida *et al.*, 2012).

Fast Reactors – Materials Aspects

The core of the fast reactor consists of fuel subassemblies containing typically (U,Pu) mixed carbide or oxide fuel which are kept in a pool of liquid sodium. The heat transport system consists of primary sodium circuit, secondary sodium circuit and steam-water system. Structural materials chosen for sodium circuit components must possess adequate high temperature low cycle fatigue strength and creep strength, and should be compatible with liquid sodium coolant. Fuel clad and wrapper materials should be resistant to irradiation-induced swelling and embrittlement, sodium corrosion and possess adequate end-of-life creep strength ductility. Steam generator materials must have sufficient high-temperature low cycle fatigue and creep strength and freedom from stress corrosion cracking (both chloride and caustic environments) and resistance to sodium decarburization. Through-thickness ductility is an important consideration in the choice of material for the top shield consisting of roof slab, large rotatable plug, small rotatable plug and control plug (Mannan *et al.*, 2003).

The subassembly of a fast reactor consists of a hexagonal wrapper tube which contains fuel pins filled with nuclear fuel pellets. A typical Indian 500 MWe FBR has 181 fuel subassemblies arranged in a triangular array and a fuel subassembly contains 217 helium bonded pins each of 6.6 mm outside diameter (Raj *et al.*, 2006). The neutron flux levels in FBRs are about two orders of magnitude higher ($\sim 10^{15}$ n/cm²s⁻¹) than thermal reactors. For economic viability, the target burn-ups required are more than 20 atom% of heavy metal (200,000 MWd/t). Fuel clad tubes experience temperatures in the range of 673-973 K under steady state operating conditions and during transient conditions the temperature can rise to 1273 K. For target burn-up of 100,000 MWd/t, the maximum neutron dose is 85 dpa. Major loads experienced by fuel clad are the internal pressure due to accumulated fission gases (~ 5 MPa) and minor loads such as temperature gradients and irradiation-induced swelling gradients. The hexagonal sheath (hexcan) of the core subassembly experiences lower temperature range of 673-873 K and transient

temperature of 1073 K. The peak neutron dose is similar (85 dpa) and the load is the internal pressure of sodium coolant (~ 0.6 MPa).

In 1970s, stainless steels (SS) and nickel-based alloys with excellent properties at high temperature were evaluated for applications in the core of fast reactors (Mannan *et al.*, 2003). Since, nickel-based alloys under irradiation exhibited helium embrittlement, three variants of steels such as 316SS and D9 (Ti-modified 15Ni-15Cr austenitic steels), 9-12 Cr-based ferritic steels and the oxide dispersant-strengthened (ODS) advanced ferritic steels were developed.

In fast reactors, void swelling and irradiation creep are the two major issues regarding materials. Void swelling refers to dimensional increase (Fig. 3A) (Garner, 1967) of the components due to condensation of vacancies into voids (Fig. 3B) (Cawthorne and Fulton, 1967). The swelling and irradiation creep susceptibility is measured as the increase in dimensions with increasing dose or stress (Fig. 3C&D) (Serenet *et al.*, 1992; Tolozko and Garner, 2004; Raj and Vijayalakshmi, 2011; Raj *et al.*, 2008).

For different types of cold-worked stainless steels, the percentage change in diameter of the material with irradiation dose (dpa) of neutrons is

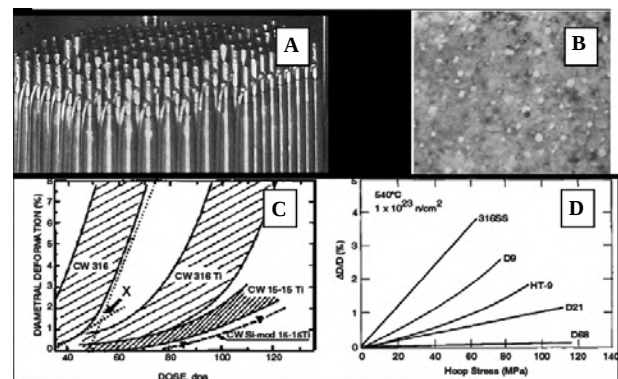


Fig. 3: Fast reactor clad material behaviour, A: dimensional change in the fuel assembly due to swelling and irradiation creep; B: Electron micrograph (60,000X) of voids (~ 0.5 μ m) in irradiated 316 SS material; C: percentage change in the diameter of the material with irradiation dose for different cold-worked stainless steels and D: creep behaviour of candidate materials. Source: a (Garner, 1994); b (Cawthorne and Fulton 1967); c & d (Serenet 1992; Tolozko and Garner, 2004)

depicted in Fig. 3c. The threshold dose is represented as the point of intersection X between the two linear portions of the curve. Irradiation creep refers to the permanent deformation of the material, leading eventually to fracture under combined effects of high temperature, stress and irradiation. Fig. 3d shows the creep behaviour of candidate materials such as D9, 316 SS, ferritic steel (HT-9) and nickel-based alloys (D21 and D68). With increasing hoop stress, the percentage diametrical strain was found to increase. These studies confirmed that the high-temperature creep properties of D9 were superior and the threshold dose was double compared to 316 SS (Latha *et al.*, 2003).

The main objective was to increase the capability of materials to withstand high fuel burn-up. The trend in the development of radiation resistant 300 series austenitic stainless steel was to increase nickel content, decrease chromium content and identify roles of solute elements such as Ti, Si, P, Nb, B and carbon for excellent void swelling resistance. Thus, the advanced core materials, 20% cold-worked D9 alloy was developed. Further improvements of D9 like D9I were achieved by modifying minor alloying elements such as Ti, P, Si and B. These alloying elements altered behaviour of the fcc matrix and the interface of the newly formed precipitates that annihilated the radiation-induced defects. Oversized elements such as Ti, P, Si and B bind with vacancies and reduce swelling. Phosphide precipitation at high temperatures occurs, and at the interface between phosphides and matrix, annihilation of point defects occurred which reduced swelling. Boron reduces mobility of carbon and nitrogen and binds to them, which enables fcc matrix to retain beneficial elements such as Ni, Mo, Si and Nb, and suppress the deleterious mechanism called solid solution decay. Oversized precipitates such as TiC-trapped vacancies and lattice strains around the precipitates are responsible for the superior properties of D9 (Fig. 4) (Divakar *et al.*, 2003). Hence, D9 alloy has been selected as clad material in FBRs.

The fundamental difference in the behaviour of solutes and point defects in bcc lattice makes the ferritic steel superior to radiation damage. They can withstand fluences up to 180 dpa compared to ~ 100

dpa for D9 alloy and 45 dpa for 316 SS. Hence 9Cr-1Mo or 12Cr-1Mo ferritic steel are the candidate materials for wrapper in future sodium-cooled fast reactors. The maximum achievable burn-up has increased from 30 to 200 dpa which has shifted the focus of core component applications from austenitic stainless steel to ferritic steel. The advantages of ferritic steels are lower thermal expansion, higher thermal conductivity, better compatibility with liquid sodium than austenitic SS. Thus, creep-resistant 9-12 Cr ferritic/martensitic steels are candidate materials for core (clad, wrapper and ducts) and out-of-core applications such as sodium storage tank, piping and steam generators in fast spectrum reactor systems. The major disadvantage of these steels is deterioration of creep properties above 823 K and this has been overcome by developing oxide dispersion-strengthened ferritic-martensitic steels (ODS) (Ukai *et al.*, 1993). During development of new variant ferritic steels, irradiation embrittlement, inferior high-temperature mechanical properties and Type IV cracking in their welds are observed. Under reactor exposure conditions, ferritic steels undergo microstructural changes (formation of secondary phases such as G-phase, M_6C and χ -phase) that lead to irradiation hardening, creep and embrittlement. By optimizing Cr content, 9Cr and 12Cr, strict control of tramp elements P, Pb, Sb, S and Sn (below 50 ppm), and by grain boundary engineering, ferritic steels exhibited

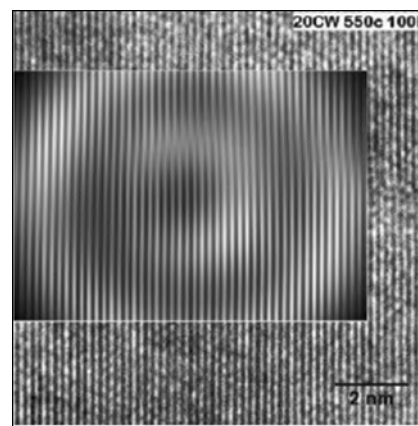


Fig. 4: High resolution transmission electron micrograph of 20% cold-worked D9, aged at 823 K for 100 h; the inset showing fringes that provide information on lattice strains around TiC precipitates. Source: Divakar *et al.*, 2003

resistance to embrittlement. Grain boundary engineering involves enhancing low energy-coincident site lattice (CSL) boundaries in the steel and reducing the connectivity of the crack-resistant high angle boundaries. The operating temperatures have to be limited around 773K due to irradiation creep. Hence, ferritic steels are preferred in wrapper applications over clad tubes in oxide fueled fast reactors. The limitations of ferritic steel can be overcome for increased burn-up of FBRs with 100 years as lifetime at an operating temperature of 973K by development of oxide dispersion-strengthened ferritic-martensitic steels (Raj and Vijayalakshmi, 2010).

Reactor Assembly

The reactor assembly consists of core, grid plate, core support structure, main vessel, safety vessel, top shields and absorber rod drive mechanism. The inlet sodium temperature in the primary pool is 670 K and the mean core outlet temperature is about 820 K during normal operation and 923 K during transient conditions. The environment of operation is liquid sodium or aerosol of argon with sodium vapour or nitrogen gas. Except for grid plate near core which experiences an irradiation dose of 1 dpa in 40 years of design life, for all other components, irradiation is not a consideration. Austenitic stainless steels are chosen as the major structural material in view of their adequate high temperature mechanical properties, compatibility with liquid sodium coolant, good weldability, availability of design data, good irradiation resistance and vast satisfactory experience from sodium cooled reactors. Designers of FBRs prefer monometallic construction for liquid sodium systems to avoid interstitial element transfer (carbon in particular) through liquid sodium due to difference in thermodynamic activity in a bimetallic system. Localized corrosion of SS is absent since surface is clean in sodium (no passive film) and electrochemical reaction is not possible. However, mass transfer of metallic elements in SS can take place under the influence of non-metallic impurities in liquid sodium such as oxygen and carbon leading to formation of sodium chromite, carburization and decarburization which can influence mechanical properties. Type 316LN SS has been chosen for structural components of reactor assembly, other than

the core components, operating at temperatures above 700 K; while 304LN SS is the choice for components operating at lower temperatures (Garner, 1994).

Welding is extensively employed in the fabrication of FBR components; and weld metal cracking and heat-affected zone cracking are major concerns in stainless steel welding. Weld metal cracking was controlled by optimizing composition of welding consumables (carbon 0.045 to 0.055 wt%, Nitrogen 0.06 to 0.1 wt%; ferrite number (3 to 7 FN)). Heat-affected zone cracking was controlled by specifying lower limits of P (0.025), S (0.02), Si (0.4–0.7), B (20 ppm), Ti and Nb (Ti+Nb+Ta= 0.1) for base metal (Garner, 1994).

In PFBR, the SG is a vertical, countercurrent shell-and-tube-type heat exchanger with sodium on shell side, flowing from top to bottom and water/steam on tube side. The high reactivity of sodium with water makes the SG a key component in determining the efficient running of the plant and demand high integrity of SG. The SG material should meet requirements of high temperature mechanical properties such as creep and low cycle fatigue, resistance to loss of carbon to liquid sodium (reduction in strength), resistance to wastage (small leaks lead to sodium–water reaction) and resistance to SCC in sodium and water media. The sodium inlet and steam outlet temperatures for PFBR are 798 K and 766 K, respectively. Susceptibility to aqueous SCC in chloride and caustic environments ruled out austenitic SS and Alloy 800. Modified 9Cr-1Mo steel with strictly controlled composition with respect to lower limits of residual elements (S (0.01 max), P (0.02 max) and Si (0.2–0.5)) was selected as the SG material with improved weldability, reduced inclusion content and high degree of cleanliness. Studies showed that Mod 9Cr-1Mo steel does not exhibit drastic reduction in creep strength at longer duration due to microstructural instability and this is the most important factor that favoured the selection (Mannan *et al.*, 2003). This material also exhibited higher continuous cycling low cycle fatigue resistance than plain 9Cr-1Mo (Choudhary *et al.*, 1991).

In out-of-core applications, the major thrust is to enhance the lifetime of materials up to 100 years.

A number of techniques such as computational methods based on plant history, visual observation and dimensional measurements, non-destructive methods, microscopy of replicas, *in situ* microscopy, biopsy-mechanical property evaluation of service exposed samples, etc. have been developed for life prediction of materials (Raj and Vijayalakshmi, 2010). Different NDT techniques such as fluorescent DP test for coarse surface flaws, X-ray radiography and ultrasonic testing for cavities/blow holes cast defects in bulk, ultrasound acoustic microscopy and laser scan microscopy for surface imaging, eddy current microscopy for visualization of electric and magnetic properties, Barkhausen noise and X-ray diffraction for residual stresses, IR imaging for thickness changes and cavitation damage has been developed for inspection of components in estimating the residual life (Raj and Vijayalakshmi, 2010). Operating temperature data is needed to assess damage and a phase evolution diagram (PED) has been developed to estimate the mean metal temperature. The change in the concentration of carbon excess of saturation limit in ferrite called supersaturation of ferrite with ageing time at chosen temperature, in addition to phase-fields of different metastable phases is depicted in PED of 9Cr-1Mo steel (Fig. 5) (Raj and Vijayalakshmi, 2010).

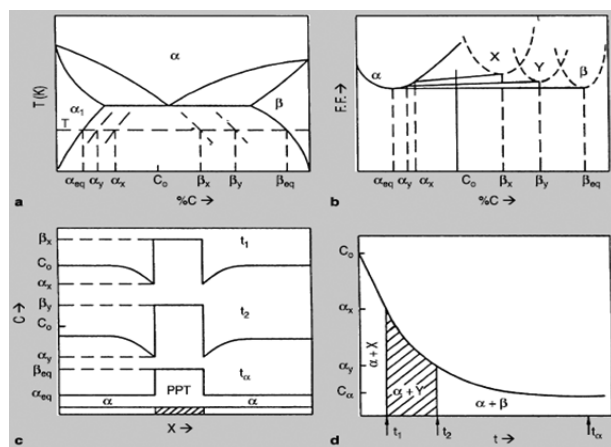


Fig. 5: Phase evolution diagram of 9Cr-1Mo steel at 1023 K: (a) schematic binary phase diagram, (b) free energy vs composition for co-existing phases, (c) profile of solute concentration near a secondary phase and (d) PED. Source: Raj and Vijayalakshmi (2010)

The welding consumable for modified 9Cr-1Mo steel has matching composition with minor modifications for Ni, Mn, Nb, V and N. There are two major limitations in the high-temperature performance of weldments in ferritic steels such as Type IV cracking in creep-loaded weldments and formation of hard zone in dissimilar joints. The fine-grained intercritical zone of ferrite and formation of Z-phase (brittle nitrides of chromium) concomitant with the dissolution of MC carbonitrides cause Type IV failure of creep-loaded weldments of ferritic steels. At the dissimilar joints of austenitic SS structural materials and ferritic steel, diffusion of carbon leads to hard zone formation. Type IV cracking is reduced by adding boron 0.01% and reducing nitrogen to 0.002%. Boron strengthens grain boundary and combines with $M_{23}C_6$ for reducing creep rate, lowering nitrogen content reduces formation of Z-phase.

Trimetallic Transition Joint

The main structural and piping material austenitic 316LN SS cannot be directly welded to steam generator material made of modified 9Cr-1Mo material as large difference exists in thermal expansion coefficients, creep strength and carbon migration between them leading to failure. Hence, a trimetallic joint configuration consists of an Alloy 800 intermittent piece welded to 316LN SS on one side and to modified 9Cr-1Mo on the other side. For welding Alloy 800 to modified 9Cr-1Mo, Inconel 82/182 welding consumable was recommended and for welding to 316LN SS, 16-8-2 filler wire was selected (Mannan *et al.*, 2003).

Top Shield (Roof Slab)

Roof slab along with rotating plugs and control plugs forms the top cover of the main vessel, which provides biological and thermal shielding and acts as support for main vessel, pumps, intermediate heat exchanger (IHX), decay heat exchanger (DHX), etc. The mechanical load on roof slab is very high and temperature range experienced will be 373-393 K during normal operation and in the event of loss of cooling, temperature can go up to 473 K. The neutron flux experienced is also low ($10^5 \text{ n/m}^2\text{s}^{-1}$). Carbon steel material A48P2 with good mechanical strength

in the temperature range of 298–493 K and good weldability was selected for this application (Mannan *et al.*, 2003).

Safety Grade Decay Heat Removal System

The safety grade decay heat removal (SGDHR) system consists of DHX, sodium to air heat exchanger (AHX) and piping connecting DHX and AHX. Since the material is susceptible to corrosion due to the humid chloride environment in the air, corrosion resistant modified 9Cr-1 Mo was selected for tubes and AISI 409SS as fin material (Mannan *et al.*, 2003).

Fast Reactors – Short-Term Strategies

In fast reactors, improvement in thermal efficiency is an aspiration. The outlet temperature of the coolant should be increased from the present 823 K to about 1123 K (Raj *et al.*, 2008). New variants in coolants such as helium gas and lead-based systems including Pb-Bi need to be evaluated and ferritic steels with better high temperature (>823 K), creep behaviour and better radiation resistance need to be developed. R&D efforts in strengthening the steel using 5 nm particles of yttria oxide dispersion strengthened (ODS) ferritic steels. Fig. 6 (Raj *et al.*, 2013) shows the distribution of nano-sized yttria particles dispersed in ferritic steel and they are capable of withstanding 923 K up to a burn-up of 200 dpa with improved creep properties. Fuel clad tubes are fabricated from ODS alloys through powder metallurgy route (Raj *et al.*, 2013; Murthy and Charit, 2008). Then, it is also essential to demonstrate dimensional accuracy during

fabrication of clad and joining with end plug for wider commercial use. It is also important to generate an engineering database and validate performance and codification as part of materials system engineering technology. Dissolution resistant clad tubes in reprocessing and evolution of microstructures during reactor core residence, validation of high burn-up performance, etc. remain key challenges to be studied and mastered.

Materials for Fuel Cycle: Present Status and Short-Term Strategies

The nuclear power programme includes two options of fuel cycling. The fuel cycle is referred to as open fuel cycle (once through fuel cycle) if the spent fuel is not reprocessed. In the open fuel cycle option, the spent fuel is considered as waste and safely deposited in deep geological repositories. If the spent fuel is reprocessed and reused, it is referred to as closed fuel cycle. In the closed fuel cycle (Fig. 7) option, reprocessing of spent fuel is adopted for recovering the fissile and fertile elements and reusing them in the reactor. Closing the fuel cycle has an added advantage of minimizing the high level waste by separating and isolating the long-lived isotopes along with recovering extra energy from the original fuel. The storage time of nuclear waste can be reduced from millions of years to thousands of years and the volume of the waste can also be decreased by a factor of 4 if we adopt closed fuel cycle. From the spent fuel, the fertile materials are isolated and reused by converting to fissile material in fast reactors and this improves nuclear fuel efficiency.

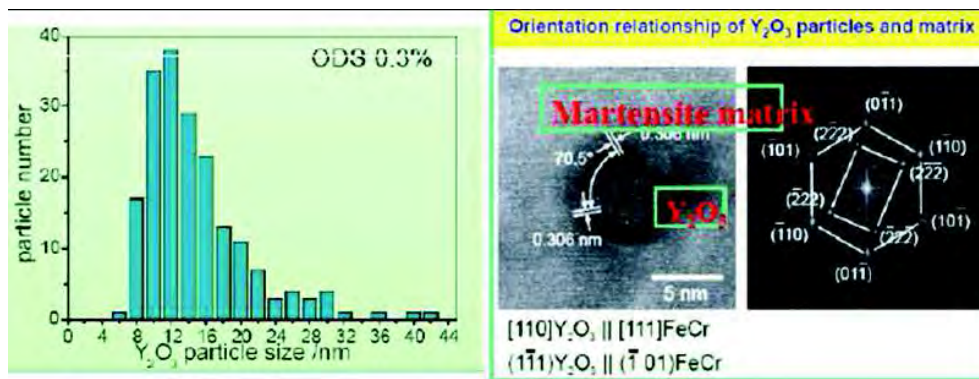


Fig. 6: Y_2O_3 particle size distribution in oxide dispersion strengthened steels and transmission electron micrograph showing orientation relationship. Source: Raj *et al.* (2013)



Fig. 7: Two fuel cycle options in nuclear programme. Source: IAEA (2009)

Table 4 shows the materials used for back-end technologies of reprocessing and waste management and the selection criteria which are entirely different from that of the reactors.

Aqueous reprocessing involves recovery of plutonium and uranium by extraction-PUREX process. Various components in the reprocessing plant are exposed to nitric acid and hence the materials need good corrosion resistance. AISI Type 304LSS was selected for the pipe and container materials due to good corrosion resistance. However, the presence of oxidizing species such as Fe(III), Pu(IV) and possibly Cr(VI) in nitric acid increases the oxidizing power causing severe intergranular corrosion even when SS is not sensitized. To combat corrosion, nitric acid grade (NAG) steel was developed (Mudali *et al.*, 1993).

Highly boiling and concentrated nitric acid led to the replacement of NAG SS with Grade 2 Ti material. The presence of Ti^{4+} ions inhibited Ti corrosion and presence of other oxidizing species did not affect Ti. An alternative material Ti-5Ta-1.8Nb has been developed with five times higher corrosion resistance than Ti and Ti-5Ta alloys. These alloys are also complemented with zirconium for dissolver vessels. The superior corrosion resistance of Zr-4 in both wrought and welded conditions in comparison to CP-Ti, Ti-5% Ta and Ti-5%Ta-1.8%Nb in 11.5 M HNO_3 has been established and considerable progress has been made in the dissimilar joining of Zr-4 to 304L SS (Mudali *et al.*, 2013). Enhancement of the lifetime of reactors to 100 years has been planned and life of reprocessing plants also needs to be extended for which development of better reprocessing materials is a must.

Highly radioactive waste solution is finally immobilized in matrixes and hence matrix material should be stable in geological repositories for approximately 1,000,000 years by which time the radioactivity will diminish to natural level (Raj and Mudali, 2006). Borosilicate glass is used to vitrify high level waste (HLW) with higher radioactivity, packed into Cr-Ni steel canisters and disposed in rock salt formations. Research is in progress to develop several other ceramic matrixes that have higher chemical durability, mechanical integrity, thermal stability and can hold higher proportion of fission products or actinides. The matrix should remain stable for several thousands of years (Joseph *et al.*, 2011). Borosilicates

Table 4: Selection criteria of materials for back-end technologies

Back-end Technology	Conventional materials	Selection criteria
Fuel reprocessing	Type 304L SS, nitric acid grade 304L SS, Ti and alloys, zirconium alloys, boron-coated SS	Stability against radiation damage. Corrosion resistance in boiling nitric acid. Necessity to remain sub-critical throughout the reprocessing
Waste management	Immobilization in borosilicate glass	Ability for high waste loadings, chemical durability, mechanical integrity, thermal stability. Incorporate many waste elements
	Vitrification in melter pots: Ni-base alloys	Ability to withstand high temperature. Radiation resistant for long time
	High-level waste canisters and over packs: copper, iron, SS, Ti alloys, Ni-base alloys	Excellent resistance to radiation, high temperature, and gradients and chemical compatibility interim storage and permanent disposal, free from failure for long time

have compatibility problems with chemically heterogeneous waste for which glass ceramics are being developed. Synroc is an advanced ceramic with multiphases, and is developed to immobilize various forms of intermediate- and high-level waste. This titanate-based ceramic is made from several natural minerals such as zirconalite (calcium zirconium titanate), hollandite (barium aluminum titanate), and calcium titanate and titanium oxides. The advantages of synroc include enhanced durability over wider geological time frames; ability to incorporate into their crystal structures nearly all the elements present in HLW; no undesirable phase-separation reactions and robust chemical, physical and thermal properties (Raj *et al.*, 2006).

The vitrified waste products will be cast and after interim storage, will be permanently disposed in a geological repository. Hence, the container material for vitrification should have a failure-free lifetime during all these stages. For additional protection against radionuclide mobilization, corrosion resistant packaging materials such as Ti 99.8-Pd, Hastelloy C-4, etc. were investigated and Ti-Pd alloy exhibited excellent corrosion resistance under salt brine conditions, temperature upto 473 K and gamma radiation of 10^3 Gy/h. The canister material also needs high corrosion resistance to geological environments containing chloride environments. Thus, the nitrogen-added stainless steels with higher corrosion resistance to chloride environments is developed which showed superior IGC resistance for 0.132% N and 0.193% nitrogen containing Type 304LN SS. Results suggest the suitability of this alloy in nitric acid and chloride containing environments of reprocessing and waste management plants (Parvathavarthini *et al.*, 2012).

The proposed use of metallic fuel as fast reactor fuel introduces complications in the reprocessing routes and compatible materials. Requirements may vary for thorium fuel cycle also. Metallic fuels are best reprocessed by pyro-chemical processes with the high-temperature electrochemical route (Nagarajan *et al.*, 2010). In the pyrochemical process, the spent fuel is electrolytically separated into reusable product and waste stream using high temperature molten salt electrolytes. This technique involves highly

corrosive environment of molten LiCl-KCl salts. Thus, a new range of corrosion resistant coatings, graphite crucibles with ceramic oxide coatings of zirconia or alumina and refractory container materials are being developed (Mudali *et al.*, 2011). Newer materials are also required for disposal of salt and solid waste generated by pyrochemical reprocessing. By melting solid metallic clad waste along with zirconium, metallic waste form is developed for geological disposal (Bairi *et al.*, 2012). Thorium fuel reprocessing is being done in 13 M nitric acid using fluorides at relatively high concentrations as catalyst and aluminum nitrate to mitigate fluoride-related corrosion of Type 304L SS dissolver vessel. Studies on improvement of thorium dissolution process for reprocessing applications (Srinivas *et al.*, 2012) could achieve high temperature sintered thoria pellets dissolution reactions in the absence of aluminum nitrate and with reduced fluoride content of 0.005-0.01 M instead of 0.3 M by changing the method of addition of the fluoride catalyst.

Surface Engineering of Materials for FBR Programme

Type 316LN SS used as structural material in PFBR operating at temperatures above 673 K is exposed to flowing sodium which removes the protective oxide film leading to self-welding at areas undergoing high contact stress. The relative movements of mating surface can also cause galling, a form of high temperature wear. Several surface coating technologies have been developed to meet the stringent requirements of high performance, long life and service. Hard facing of stainless steels with nickel-base Colmonoy was adopted for various PFBR components to minimize induced radioactivity during maintenance, component handling and decommissioning. Colmonoy deposits would retain adequate hardness and to avoid dilution from austenitic SS substrate that may reduce deposit hardness, deposition was done by plasma transferred arc welding (PTAW) instead of conventional gas tungsten arc welding (GTAW) (Raj *et al.*, 2008).

This procedure is successfully implemented for hard facing of roller bearings of the transfer arm, and the grid plate sleeves of PFBR. Wear-resistant bushes

for transfer arm gripper assembly were fabricated by a novel procedure involving weld deposition of hard facing alloy on austenitic SS alloy by TIG welding procedure followed by precision machining of hard face deposits. Chromium nitride coatings with excellent thermal stability, wear and corrosion resistance has been developed for hard facing of grid plate sleeve components for enhanced resistance against galling of contacting surfaces, fretting and corrosion. The chromium is electroplated and the surface was modified by plasma nitriding to overcome disadvantages such as micro-cracks developed during electroplating. The Cr_2N formed was found to have a superior abrasive wear property. Alumina (Al_2O_3) coatings of 300 nm thick were obtained on oxygen-free high conductivity (OFHC) copper, stainless steel and mild steel substrates for sodium pump component applications using air plasma spray equipment. To overcome the disadvantage of the porosity of the coatings, a laser surface modification procedure (Raj *et al.*, 2008) was adopted using multibeam CO_2 laser (Fig. 8).

Thus, by combining two powerful surface engineering techniques, plasma spraying and laser surface engineering, thick ($>100\mu\text{m}$) stable $\alpha\text{-Al}_2\text{O}_3$ coatings over metallic substrates were obtained.

The reprocessing plants are designed with the objective of zero incident failures as leakages of pipes, vessels and equipment can considerably delay re-starting of operation and closure of plant. Fast reactor fuels are normally reprocessed by conventional PUREX process and coatings and surface modification have been attempted for enhancing the performance and service life of components made of

Type 304L SS and titanium (Raj *et al.*, 2006).

In nuclear fuel reprocessing, through aqueous route, Type 304 SS undergoes inter-granular corrosion due to inter-granular precipitation of chromium rich carbides in the temperature range of 773-1073 K. A new laser surface melting technique was developed (Kaul *et al.*, 2009) to reduce sensitization of heat-affected zone of GTAW-welded 304 SS. The reason for enhanced IGC resistance is the significant increase in the fraction of $\Sigma 1$ boundaries, mostly subgrain boundaries. This is introduced by melting and resolidification. There are many disruptions in the grain boundary network by the intersecting subgrain boundaries that provide the IGC resistance.

Anodization was adopted to increase the corrosion resistance of titanium in both welded and wrought conditions. By the process termed as ‘double oxide coating on titanium for reconditioning’ (DOCTOR) three-fold reduction in corrosion rate of Ti was achieved. Mixed oxide coated titanium anodes MOCTAG developed for application as electrodes in reprocessing plants showed longer life compared to conventional MOCTA electrodes (Mudali *et al.*, 2003). Nanostructured Ti, TiO_2 , and ZrN coatings deposited on type 304L stainless steel (SS) by magnetron sputtering technique and Zr-based bulk metallic $\text{Zr}_{59}\text{Ti}_3\text{Cu}_{20}\text{Al}_{10}\text{Ni}_8$ alloy deposited on type 304L SS by pulsed laser deposition (PLD) technique showed improved corrosion resistance in nitric acid (Mudali *et al.*, 2011).

In sodium-cooled fast reactor with metallic fuel, preference is for pyrochemical reprocessing route involving electro refining process, where the

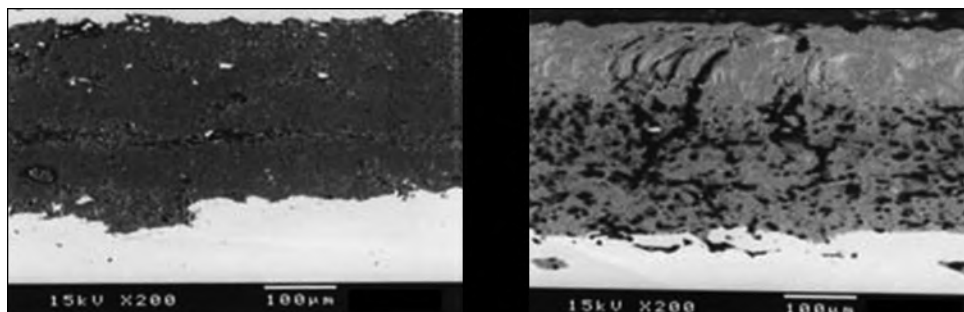


Fig. 8: Cross-sectional SEM micrograph of (a) as sprayed and (b) laser-treated alumina coating. Source: Raj *et al.* (2008)

electrolyte is molten chloride salt (LiCl-KCl) operating at 773 K. The electrorefiner is exposed to highly corrosive environments such as impure salts and high temperature. Efforts are on to select corrosion-resistant materials and protective coating technology for various operations such as salt preparation, electro refining and cathode processing. Various materials such as 410 SS, 430 SS, 316L SS and Inconel 600, 625 are being tested. Pyrolytic graphite and thermal barrier zirconia coatings were proposed to protect the equipment from aggressive chloride environment (Mudali *et al.*, 2011). Yttria-stabilized zirconia coatings of 300 μm applied on type 316L SS with a metallic bond coating of 50 μm by an optimized plasma spray process rendered good corrosion resistance and laser melting of this coated surface provided additional benefits of defect-free surface (Shankar *et al.*, 2007).

Graphite is also used for fabrication of electrodes, salt purification vessel liners and cathode processor crucible in pyrochemical processing. However, graphite degrades in molten salt and reacts with molten uranium. Cathode processor conditions were simulated by induction heat melting of uranium in yttria-stabilized zirconia and yttria-coated crucible and post-exposure characterization revealed that the coating offered better stability, ease of ingot release and coating adhesion (Shankar *et al.*, 2010). Pyrolytic graphite deposited on graphite substrates by chemical vapour deposition using methane gas and tested in molten salt at 873 K for 2000 h in controlled argon atmosphere showed excellent corrosion resistance (Jagadeesh *et al.*, 2013).

Role of Modelling in Development of Nuclear Materials

Presently, lifetimes are computed on basis of lab-based experimental data, constitutive laws, design rules and finally the available standards or codes. The empirical approaches and extrapolations are reaching their limits, and it becomes necessary to develop predictive tools to estimate materials behaviour for new materials and environments.

For radiation damage prediction, *multi-scale modeling* (Samaras *et al.*, 2009) is pursued to examine if “seamless” joining of various concepts at various

length and time scale can finally achieve an accurate prediction of lifetime of materials. This strategy combines *ab initio* calculations, molecular dynamics, Monte Carlo Method, the rate theory, dislocation dynamics, finite element methods and the continuum models. Combining the computation procedures with appropriate experimental validation would result in robust materials research.

As an example, for improving embrittlement in ferritics, grain boundary engineering was adopted. A number of modelling methods such as the Monte Carlo method, percolation model and fractal analysis have been carried out with the support of results from electron back-scattered diffraction (Karthikeyan *et al.*, 2009). Size reduction of grains by 50% and DBTT reduction by 20°C could be achieved. High fractal dimension and fracture energy confirmed that the advantage was gained due to larger number of crack deflections or a tortuous path for the crack along its propagation route.

The finite difference method, Thermo-Calc, and DICTRA have been used (Anand *et al.*, 2009) to study the mass transfer across dissimilar materials. The basic understanding of the process was based on molecular dynamics calculations which showed that sluggish diffusion of carbon in nickel compared to iron is responsible for prevention of formation of hard zone.

For predicting microstructures including the presence of delta ferrite, application of artificial neural network method successfully provided information to choose composition (Vasudevan *et al.*, 2009) of filler metal required for joining stainless steel materials. Modelling for neutron-induced damage functions, corrosion predictions, microstructure stability, fracture mitigation, etc. are ongoing pursuits with unsolved challenges. Demands for new materials and performance conditions have inspired researchers and funding organizations to pursue new fascinating pursuits.

Ageing Assessment of Power Plants

Periodic health assessment and ageing management is an integral part of nuclear power technology to ensure safety and reliability in all phases of nuclear

power, encompassing design, construction, commissioning, operation and waste management. Periodic monitoring will provide an early warning of any degradation in the components, equipment and systems of plants. Accurate technique for assessing the condition of components is the need of the hour. Special remote tools to inspect inaccessible core areas with high radiation fields and carrying out repairs are the biggest challenge to be met. NPCIL, BARC and other DAE institutes have developed many tools such as BARC Reactor Coolant inspection systems (BARCIS), Non-Intrusive vibration diagnostic technique (NIDVT), and specialized cameras, manipulators, welding tools, etc. which helped in pinpointing the exact locations, in determining the nature of repairs needed and in carrying out necessary repairs (Jain *et al.*, 2010). In Indian PHWRs, health assessment during operation using techniques developed in-house revealed life limitation of Zr-2 coolant channels due to degradation of properties on exposure to intense radiation, high temperature and pressure in a corrosive environment. Experiences in India and worldwide have led to the coolant tubes of Zircaloy-2 being replaced by Zirconium – 2.5% Niobium, a better material by carrying out success enmasse coolant channel replacement (EMCCR) using indigenous technology. The time, cost and manrem (radiation dose) levels in EMCCR have been progressively reduced through innovations in tooling and job execution. Flow-assisted corrosion (FAC) of carbon steel feeder tubes in Indian PHWRs was lower by maintaining the pH of primary coolant in a narrow band of 10.2 to 10.4. However, life was extended by replacing the same with a better carbon steel material with 0.2% chromium content which has more resistance to FAC by en-masse feeder replacement (EMFR). The detection and correction of leaky steam generator tubes helped in preventing leakage of expensive and radioactive heavy water coolant and the contamination of secondary system. Also, the Monel-400 SG tubes were replaced later by Incoloy-800.

Various NDT techniques are employed for monitoring and avoiding failures, life assessment and extension of components of nuclear power plants (Raj *et al.*, 1997). Periodic monitoring of heat exchanger

tubes is done by eddy current testing technique and to eliminate signals from unwanted parameters such as baffle plate multi frequency technique was adopted. For pre-service and in-service inspection of ferromagnetic tubes, remote Field Eddy Current Testing with higher sensitivity was adopted. Eddy current imaging technique can detect defects such as fatigue cracks, corrosion pits and electrical discharge machining (EDM) notches. Ultrasonic thickness gauges can detect exfoliation, stress corrosion cracking and material thinning by scattering of ultrasound and is detected by shear waves in an angular incidence. Ultrasonic phased array probe systems have capabilities to detect flaws even in complex geometries of pipes, elbows and nozzles. To inspect tube conditions inside the tube sheet, a technique called quantitative ultrasonic analysis system and recorder (QUASAR) or internal rotary inspection system (IRIS) has been utilized with success. FLEXIMAT is an innovative method, which uses 12 or more ultrasonic array elements on a flexible, printed strip connected to a flaw detector for continuous monitoring of corrosion/erosion in vessels, pipelines, pipe bends, etc. Radiography testing techniques have proven to be more effective for a range of components including pipes of 0.2 m OD and a wall thickness of 0.018 m using field gamma ray source of Ir-192 and Co-60 of 1000 Ci strength. Acoustic emission technique (AET) has been successfully applied for detection and location of leak paths present on an inaccessible side of an end shield of Rajasthan Atomic Power Station 1. Frequency spectral analysis approach was used and the difference in the characteristic frequency of the signal for two leak paths detected was attributed to the size, shape and morphology of the leak path. In a condition assessment campaign, two possible leaking pressure tubes among 306 pressure tubes in MAPS 1 were detected (Raj *et al.*, 1997) using AET technique where ratio of the spectral energy between two different frequency bands, namely 700 to 1000 kHz and 40 to 175 kHz and its variation with an increase in pressure helped to narrow down the suspect channels to two numbers.

For assessment of internals of pipes and tubes, a technique called laser optic tubing inspection system (LOTIS) has possibilities of reducing time for in-

service inspection. In the system, a 40 micron diameter laser beam is projected at near-normal incidence onto the tube inner surface using accurate rotational drive system and receiving optics image this spot of light into a single axis lateral effect photo detector. Intelligent pigs based on magnetic flux leakage (MFL), ultrasonics and high frequency eddy current are used for inspecting pipelines for corrosion defects. Ultrasonic pigs provide a good quantification of defect size. High frequency eddy current pigs due to its accuracy and reproducibility is used in successive inspections to determine corrosion rates of small diameter heavy-walled pipelines.

A three-level approach for life assessment has been evolved (Viswanathan *et al.*, 1997) for life extension of nuclear plant components which undergo cracking failure. Simple calculation techniques in the first level are followed by non-destructive and destructive techniques, respectively in the next two levels. Development was achieved in five select areas of technology; the life fraction rule, creep cavitations, evaluation of weldments, high temperature crack growth and estimation of toughness. Life fraction rule for creep states that while calculating cumulative damage under changing operating conditions, the ductility of the material needs to be considered. For brittle materials that are prone to Type IV cavitations, fusion line cavitations, etc., temperature accelerated tests may cause premature failure and isostress extrapolation of the accelerated test results may lead to conservative prediction of remaining life at the operating temperature. The actual remaining life under operating conditions may well exceed the estimation from accelerated tests. Attempts for quantitative correlations of cavitation with remaining life are being made on basis of interrupted-creep tests (Ellis *et al.*, 1989) on simulated heat-affected zones of materials. However, results showed that scatter was too much to verify the life-prediction model of Cane (Cainsand Shammass, 1984); and hence damage classification has been correlated with life fraction; and for each-class of material, a life-fraction range established. This data is utilized for setting inspection intervals.

The determination of critical crack-size based on knowledge of the current toughness of the material

at the critical location is a crucial last step in remaining-life analysis of cracked components. By non-destructive estimation of 50% ductile to brittle fracture appearance, transition temperature and correlating with K_{IC} , the critical crack size for failure is determined. By conducting tests at different temperatures using a small punch specimen, a curve of adsorbed energy versus temperature can be developed and midpoint was used to define ductile to brittle transition temperatures (Cainsand Shammass, 1984).

Material Challenges in Future Fission Reactors: Generation IV Perspectives

The ever increasing demand on nuclear materials is graphically represented in Fig. 9 (Zinkle and Busby, 2009). The ability to withstand increasing operating temperature, stress levels, irradiation dosages and corrosive environments, fabrication capabilities, compatibility with envisaged reprocessing schedules at the backend of fuel cycle, availability at reasonable costs and industrial friendly materials technologies are the aspirations.

Newer structural materials have to be developed that can operate at higher temperatures than the present limit set by Gen III reactor concepts that include both thermal (LWR and PHWR), fast reactor (MOX and metal-fuelled) and advanced high temperature hybrid reactor. Fig. 10 shows a schematic

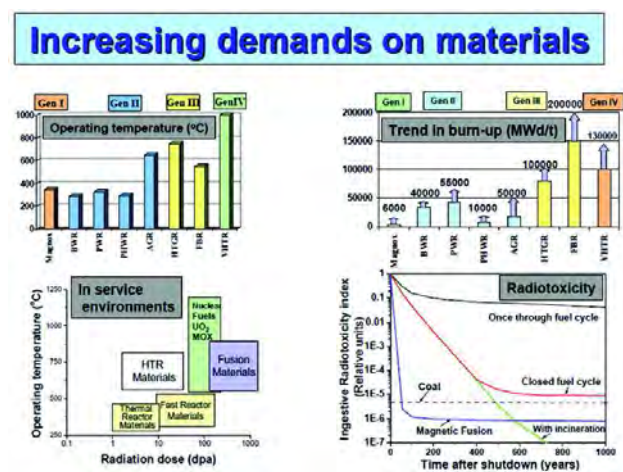


Fig. 9: Graphical summary of the increasing demand placed on nuclear materials. Source: Zinkle and Busby (2009)

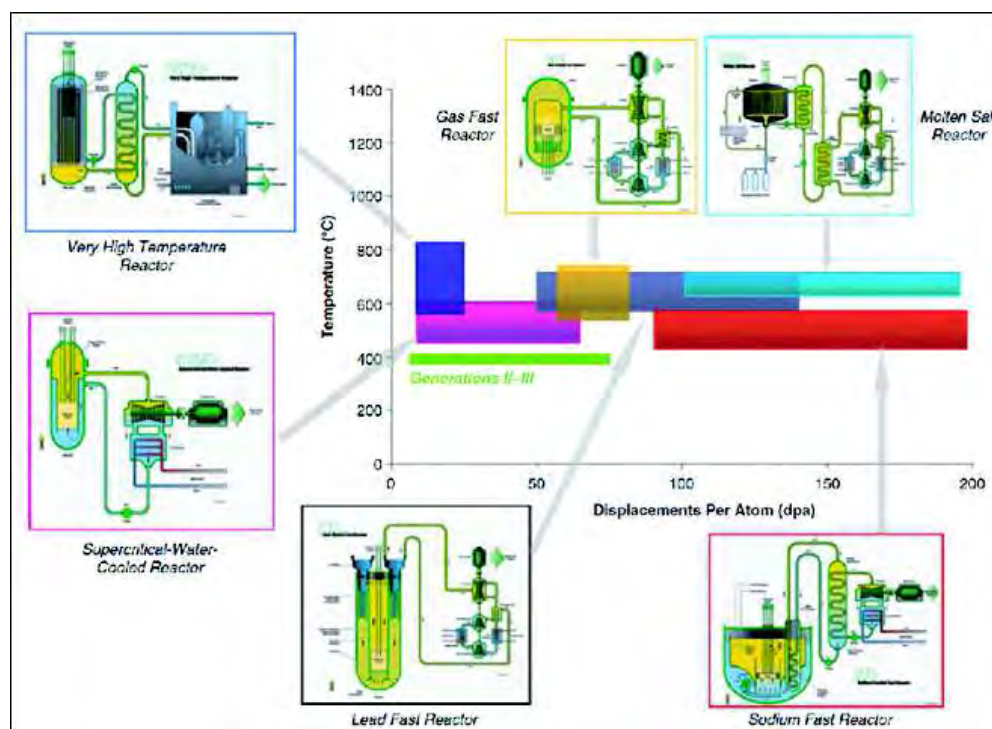


Fig. 10: Schematic collage of advanced reactor concepts. Source: Zinkle and Busby (2009)

of certain advanced reactor concepts known as “Generation IV” (Zinkle and Busby, 2009). These reactor designs for producing clean and economical nuclear energy aim at maximizing the fuel burn-up and operating thermal efficiency. Thus, the design operating temperatures are high calling for development of innovative materials. These materials also need to face extended burn-up, and should possess double the resistance for neutron and high energy gamma radiation. For better heat removal, the coolants adopted in the high temperature designs are Pb-Bi alloy. The structural materials including liquid metal pumping motors should be compatible with this more corrosive environment.

The Gen IV reactor systems aim at sustainability criteria with enhanced safety, proliferation resistance and cost competitiveness. Emphasis is laid on closed fuel cycle philosophy. Design and development of low swelling, creep resistant, acceptable corrosion mitigation, reduced activation variants of established structural materials is central to realizing advanced Gen IV reactors. Tables 5 and 6 summarize the basic characteristics of different advanced reactor types (Gen IV) and materials (Zinkle and Was, 2013).

Structural materials used in the cores of advanced reactors face high operating temperature and simultaneous presence of intense knock-on displacement damage by the fission neutrons. As per Table 5, SFR, LFR and MSR have high temperature, high-dose operating environment that place increasing emphasis on strength, creep, creep-fatigue and fracture toughness at low temperatures for the materials used. Though TiC precipitates in Ti-modified austenitic steels, it has swelling-resistant microstructure that helps to extend low-swelling transient regime. These alloys are not sufficient to avoid significant void swelling in the operating conditions of Gen IV. More radiation-resistant alloys such as 2.5-12% Cr bainitic-ferritic-martensitic steels are considered for high dose core internal and reactor pressure vessel applications (Zinkle and Was, 2013). Controlled additions of Ti and P to austenitic Fe-Cr-Ni alloys are shown to produce fine dispersions of TiC or M_2P ($M=Fe$ etc.) precipitates that provide dramatic void swelling resistance after ~ 100 dpa irradiation compared to standard Fe-Cr-Ni alloys (Lee *et al.*, 1990). Nanometer-sized Y, Ti, O-rich particles in oxide-dispersion-strengthened alloys, in current

Table 5 & 6: Advanced fission reactor core environments

System	Coolant	Pressure (MPa)	T_{in}/T_{out} (°C)	Neutron spectrum maximum dose (dpa)
Supercritical water cooled reactor SCWR	Supercritical water	25	290/600	Thermal ~30, Fast ~70
Very high temperature reactor VHTR	Helium	7	600/1000	Thermal <20
Gas Fast Reactor GFR	Helium supercritical CO ₂	7	450/850	Fast, 80
Sodium Fast Reactor SFR	Sodium	0.1	370/550	Fast, 200
Lead fast reactor LFR	Lead or Lead-Bismuth	0.1	600/800	Fast, 150
Molten salt reactor MSR	Molten salt FLiNaK	0.1	700/1000	Thermal, 200

System	Fuel	Cladding	In-core structural materials	Out-of-core structural materials
Supercritical water cooled reactor SCWR	UO ₂	F-M (12Cr, 9Cr) (Fe-35Ni-25Cr-0.3Ti), Incoloy, ODS, Inconel 690, 625, 718	Same as cladding plus low swelling stainless steel	Ferritic martensitic low alloy steel
Very high temperature reactor VHTR	UO ₂ , UCO	SiC or ZrC coating and surrounding graphite	Graphites, PyC, SiC, ZrC Vessel: F-M	Ni-based superalloys, 32Ni-25Cr-20Fe-12.5W-0.05C, Ni-23Cr-18W-0.2C, F-M w/thermal barriers, low-alloy steels
Gas Fast Reactor GFR	Mixed carbide (U,Pu) C	Ceramic	Refractory metals and alloys, ceramics, ODS, Vessel: F-M	Ni-based superalloys, 32Ni-25Cr-20Fe-12.5W-0.05C, Ni-23Cr-18W-0.2C, F-M w/thermal barriers, low-alloy steels
Sodium Fast Reactor SFR	MOX or U-Pu-Zr or MC or MN	F-M or F-M ODS	F-M ducts, 316SS grid plate	Ferritics, Austenitics
Lead fast reactor LFR	Mixed nitride (U,Pu)N	High Si F-M, ODS, ceramics, refractory alloys	High-Si, F-M, ODS	High-Si austenitic Ceramics or refractory alloys
Molten salt reactor MSR	Salt	Not applicable	Ceramics, refractory metals, high-Mo Ni-based alloy (INOR-8) graphite Hastelloy-N	High-Mo Ni-based alloys (INOR-8)

Source: Zinkle and Was (2013)

studies, assure good stability under irradiation and significant strength advantages over ferritic-martensitic alloys for high temperatures upto 923K.

In very high temperature gas-cooled reactors such as gas-cooled GFR or VHTR, where materials must withstand temperatures approaching 1000°C,

due to rapid kinetics of corrosion and oxidation, specially manufactured “nuclear” grade graphite and ceramic composites are proposed as candidates for structural materials. For the intermediate heat exchanger where high-temperature helium gas is present, nickel based alloys such as Inconel 617 and Haynes 230 are used. Oxidation, decarburization and carburization can occur at the surface of heat exchangers and development of protective coatings without compromising thermal conductivity is the most important challenge to structural materials in VHTR.

For SCWR, the only water-cooled reactor among the Gen IV design, very high pressure to maintain water in the supercritical state is needed. The major challenge for materials in the SCW environment is the resistance to SCC and irradiation-assisted SCC. Austenitic stainless steels and nickel based alloys suffered IGSCC in deaerated SCW at 400°C (Allen *et al.*, 2012) and ferritic-martensitic steels showed SCC resistance in the same temperature range (Ampornrat *et al.*, 2009). Austenitic stainless steels exhibited extreme embrittlement under neutron irradiation of 40 dpa in SCW; however, ferritic-martensitic steels showed good resistance (Teyseyre *et al.*, 2007).

Conclusions

Nuclear energy shall remain a firm option for large-scale energy production by many countries in the world. The nuclear industry is forging ahead with advanced technologies to achieve safe, economic, proliferation-resistant nuclear reactors with minimum nuclear waste. Ever since the genesis of nuclear

energy, development of materials and relevant technologies was considered as a challenging task. From Zircaloy to Zr-Nb alloys, from aluminum alloys to austenitic stainless steels and ferritic steels to oxide dispersion strengthened steels, nuclear reactor environments demand a wide spectrum of materials with high performance. State-of-the-art development in the field of materials science and technology can meet targets such as increased burn-up of fuel and enhanced lifetime of reactors. However, substantial R&D on high-temperature irradiation and creep resistant alloys, composites and ceramics for fuel rod cladding, ODS alloys with robust manufacturing process, low-activation steels, high performance coatings and the related processing technologies is essential to meet the demands of advanced nuclear technologies. With greater understanding of irradiation-assisted degradation mechanisms, a bottom-up design approach has to be evolved where controlling composition, morphology and interface-defect interaction enable us to perform atomic-scale design of extremely radiation-tolerant materials. The key direction is to replace past empiricism appropriately with accurate knowledge-based design. Exciting challenges and opportunities await materials technologists and successful response will pave the way for the society to enjoy sustainable pollution-free energy in future.

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Review Article**Materials Research and Development Opportunities in Fusion Reactors**

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Next generation fusion reactors would demand new materials and technologies that can sustain extreme nuclear environment. Materials development activities related to structural materials, shields, superconducting magnets, breeder materials, plasma facing materials, function materials and coatings have been accelerated in the last two decades. Out of these, recent research activities are focused mainly on structural materials, plasma facing materials and breeder materials. Generation of appropriate nuclear testing and materials characterization facilities is also required to complement such materials research & development activities. In this context, an overview of the scenario of materials R&D activities in India and abroad has been discussed in this chapter.

Keywords: Fusion reactor; materials; ceramics; irradiation; blanket; divertor.

1. Introduction

Thermonuclear fusion of two hydrogen isotopes results in release of energy and energetic neutrons which can be utilized for electricity generation. Out of various hydrogen isotope reactions viz. D-D, D-T & T-T (D: Deuterium, T: Tritium), the D-T reaction has the largest cross-section at the lowest energy. D-T Fusion reaction can be conducted by different confinement methods viz., gravitational confinement, inertial confinement, and magnetic confinement. While different fusion confinement techniques are being explored, the most widely pursued technique is magnetic confinement fusion. A tokamak is a device which uses magnetic field to confine plasma to the shape of a torus. Such magnetic confinement is required since no solid material could withstand extremely high temperatures of plasma. Tokamak is one of the several types of magnetic confinement devices, and is one of the most researched devices for producing controlled thermonuclear fusion power. Tokamaks such as DIII-D in San Diego, USA; Joint European Torus (JET), Culham UK; Tore Supra at CEA, Cadarache, France, etc. are being used for

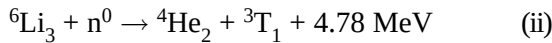
thermonuclear fusion. In November, 2006, seven partner countries viz. European Union, Japan, USA, Russia, South Korea, China and India joined hands to set up a nuclear fusion reactor named International Thermonuclear Experimental Reactor (ITER) at Cadarache, France and the first plasma shot is scheduled in 2020. “Aditya” is India’s first tokamak developed by the Institute for Plasma Research, Gandhinagar. Subsequently, as the next step, a steady state tokamak (SST-1) reactor has been commissioned and India has been working on its domestic fusion programme as well.

The fusion of deuterium (D) and tritium (T) under magnetic confinement would lead to generation of energetic 14.1 MeV neutrons by the following reaction (Naujoks, 2010):



The D-T reaction (eq. i) yields highly energetic 14.1 MeV neutrons which can be utilized to generate fuel (T) from Li as well as extract energy from the kinetic energy of neutrons. This is expressed by the following equation:

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Thus, Li utilizes the fast moving neutrons to generate T fuel and heat, which is later on converted to electricity. This conversion of energy of neutrons to heat and electricity is done by the blanket module of the reactor as discussed in section 2.2. A cutaway view of the ITER model is indicated in Fig. 1 (Suri *et al.*, 2010). This high energy of neutrons also leads to severe damage of structural and functional materials in the reactor, i.e. radiation damage, generation of transmutation products and consequences in the mechanical and metallurgical properties thereof. It is therefore necessary to understand the type of environments prevailing in different sub-systems of the fusion reactor and their operational requirements. Fig. 2 indicates a schematic of various subsystems (Suri *et al.*, 2010).

As shown in Fig. 2, the magnetically confined plasma core has a temperature of ~ 5 million $^\circ\text{C}$. The energy from 14.1 MeV neutrons has to be utilized for T production and electricity generation. The sub-

assemblies and their functional requirements are spelt out in Table 1 (Baluc *et al.*, 2007).

2. Materials-related Challenges in Fusion Environment

As discussed in the previous section, many materials research and development needs have been generated for building a suitable fusion reactor plant. Most of the R&D activities on materials for fusion reactors is mainly focused on plasma facing (first wall and divertor), breeder materials and structural materials. This includes materials development, fabrication technologies, characterization and functional validation of the developed materials. A brief overview of the materials R&D needs have been summarized in the following sections.

2.1 Plasma-facing Components and Divertor

The hot plasma confinement by magnetic confinement in a tokamak reactor involves plasma-materials interaction. The first solid surface of the reactor facing

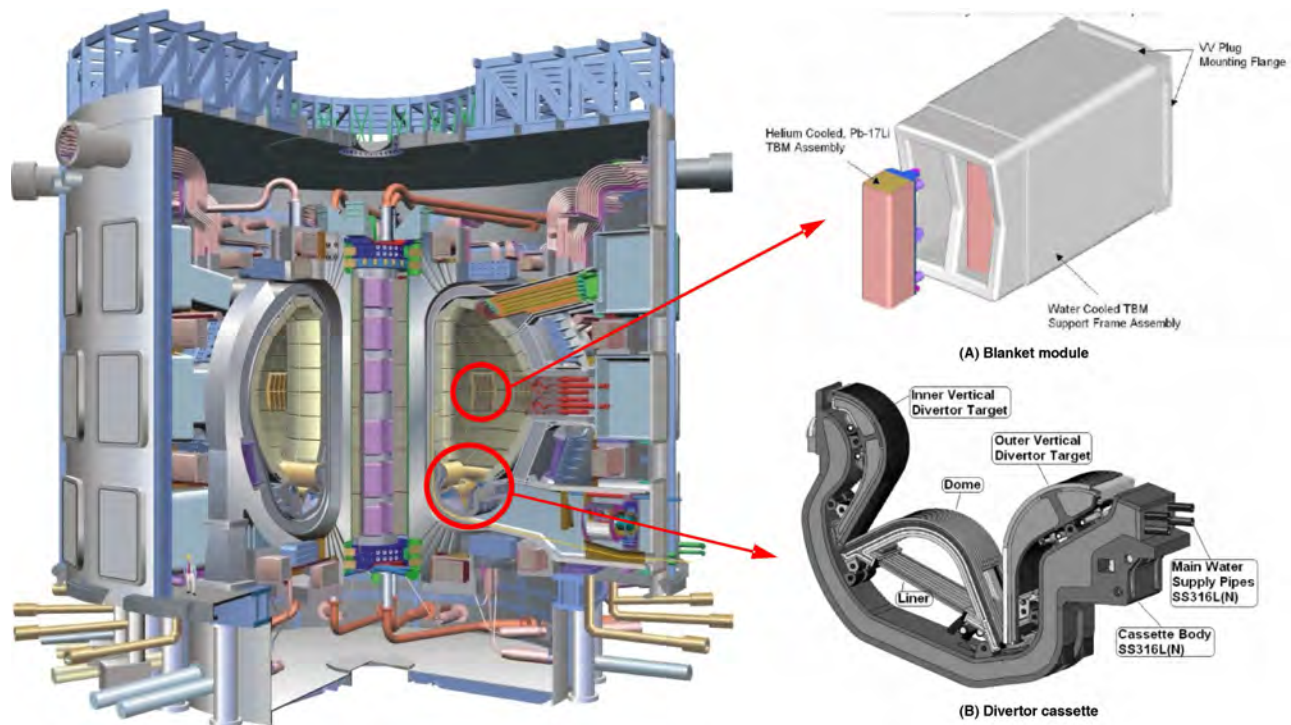
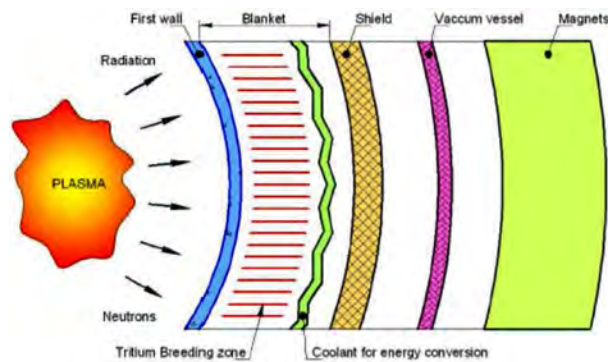


Fig. 1: (A) Cutaway view of ITER model showing the glimpse of various sub-systems such as first wall, divertor, breeder blanket module, superconducting magnetic coils, vacuum vessel etc. (B) gives a magnified view of the test blanket module (C) magnified view of the divertor cassette assembly [Ref: Suri *et al.* (2010)]

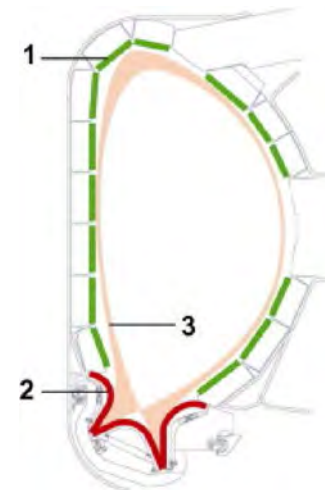
Table 1: Generic information about subassemblies and their functional objectives [Ref: Baluc *et al.* (2007)]

	First wall	Divertor	Breeder Blanket
Functional objectives	To shield subassemblies from thermal loading and plasma exposure	To extract particles / He dust, survive high heat flux	To breed T fuel, utilize 14.1 MeV neutrons, shield sub-assemblies from neutrons, extract heat for electricity generation
Plasma facing materials	W, W-based alloy, W coated SiC, Be, W coated ODS/ RAFM steels, flowing liquid Li	W-based alloy (ODS-W etc.), W-coated SiC _f /SiC; flowing liquid metal: Li, Ga, Sn, Sn-Li	As in the first wall
Neutron multiplier	—	—	Be, Be ₁₂ Ti, Be ₁₂ V, Pb
Tritium breeding material	—	—	Liq. Li, Eutectic Pb-Li, Li based ceramic pebbles (Li ₂ O, Li ₄ SiO ₄ + 2.5%SiO ₂ , Li ₂ TiO ₃ , Li ₂ ZrO ₃ , LiAlO ₂)
Structural material	RAFM steel, ODS steel, V-based alloy, SiCf/SiC	ODS steel, W-based alloy	RAFM steel, ODS steel, V-based alloy, SiCf/SiC
Coolant	—	Water, He	Water, He, Eutectic Pb-Li, Li

**Fig. 2: A schematic diagram of arrangement of sub-systems in a tokamak reactor. [Ref: Suri, Krishnamurthy *et al.* (2010)]**

the hot plasma is known as the “First wall” and the assembly is often referred to as plasma-facing components (PFC), whereas divertor is a device (or assembly) that allows the online removal of material and He ash from plasma. The first wall surface faces impact of energetic particles leading to erosion of the surface and irradiation damage, and leads to trapping of D or T in re-deposited layers of eroded species leading to a radioactive inventory buildup in the reactor. The impinging energetic particle spectrum varies across the poloidal circumference of the tokamak reactor, and hence different materials can

be used depending on the particle energy and flux at a given location in the reactor. Fig. 3 as reported by Reith and co-workers (Reith *et al.* 2013) provides an idea about the first wall and blanket assembly. As indicated in Fig. 3, area (1) indicates the first wall typically associated with the plasma facing side of the blanket assembly, area (2) indicates the plasma

**Fig. 3: The illustration shows the cross-section of a tokamak. (1) The plasma facing part of the blanket boxes – so called first wall. (2) The high heat flux cooling layout of the divertor. (3) The magnetic field lines which direct exhaust particles (mainly He) to divertor target plates [Ref: Reith *et al.* (2013)]**

facing side of the divertor and area (3) indicates the magnetic field lines which exhaust the exhaust particles to divertor target plates. The PFCs have to face high heat flux ($<1 \text{ MW/m}^2$ for blanket first wall and up to 20 MW/m^2 for divertor target plates), suffer from erosion of PFCs due to particle impingement. Reaction of D or T with eroded particles also poses a threat of radioactive dust.

The selection of material for the first wall is critical. On erosion, low Z materials are fully ionized in the central plasma and only radiate bremsstrahlung, the high Z elements still have bound electrons that emit line radiation which leads to strong plasma cooling (Schmid and Roth, 2010). On the other hand, low Z materials (viz., C, Be, etc.) have higher erosion rates than high Z elements (viz. W, Mo, etc.). The ITER first wall with a heat flux $<1 \text{ MW/m}^2$ considers Be or W as plasma-facing material. One of the reasons attributed to replacing carbon-based PFCs to W-based PFCs is the reduction of hydrogen or tritium retention (Philipps 2011). However, under high hydrogen fluence and low temperatures ($<600 \text{ K}$), blistering of W has been observed (Neu, 2010). Be poses health hazards and hence is still under evaluation stage. This W can either be coated on the structural material of first wall (RAFM steel) by thermal spray technique (e.g. vacuum plasma spray) or can be fixed as a solid tile. The fabrication process (thermal spray coating or fabrication of solid tile block) for affixing on the structural component of the first wall is being investigated globally.

The divertor assembly (Fig. 4) (Griffith, 2008) on the other hand considers both low Z and high Z materials. The main function of divertor assembly is to remove the scrape off layer (SOL) (mainly He dust), shield subsequent sub-assemblies from very high heat fluxes ($10\text{--}20 \text{ MW/m}^2$) and extract heat out of the divertor. W and Carbon Fibre Composites (CFCs) have been the preferred choice of materials for such divertor target plates in ITER. In order to improve the erosion resistance, oxide dispersion strengthening concept is being explored in target plates or first wall components and powder metallurgical processing routes are reported to be promising. (Rieth *et al.* 2013) has reported development of ODS-tungsten alloys

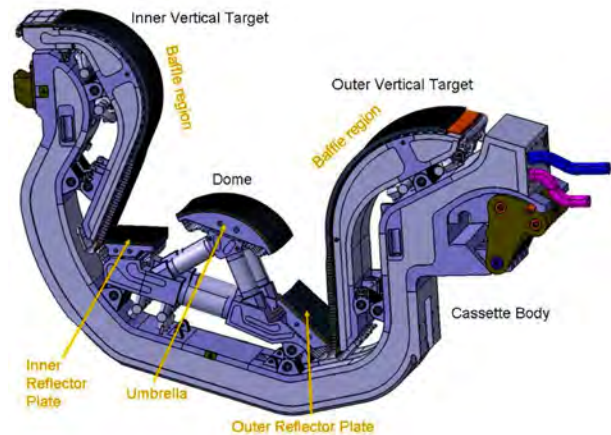


Fig. 4: Illustrative diagram of ITER divertor cassette assembly. Image emphasizes the arrangement of plasma facing components and the cooling arrangement provided to extract the heat. Multiple cassettes together will be assembled in the torus to form a divertor of reactor [Ref: Griffith (2008)]

such as $\text{W-2Y}_2\text{O}_3$, $\text{W-2La}_2\text{O}_3$ etc. in Europe, while $\text{W-La}_2\text{O}_3$, W-TiC , W-TaC and $\text{W-Y}_2\text{O}_3$ are being reported to be developed in China (Yan *et al.*, 2013). Fabrication processes such as wet chemical method, mechanical alloying, sintering of pure and doped W by spark plasma sintering, resistance sintering under ultra-high pressure are being pursued. Properties of such W-based PFCs are also being studied through embrittlement studies, blistering, hydrogen retention, radiation damage and high heat flux testing. Another challenge to divertor design is the fabrication of an appropriate heat sink along with W armour.

The heat from the armour tile has to be extracted, for which a heat sink made of CuCrZr – a precipitation hardened copper alloy has been reported as candidate material (You *et al.*, 2013; Rotti *et al.*, 2014). An SS 316 (LN) grade pipe brazed through CuCrZr alloy shall circulate water for cooling and heat extraction purpose. The joining of this CuCrZr alloy with refractory armour material such as W is a challenge owing to the large coefficient of thermal expansion (CTE) difference. Vacuum brazing of W/CuCrZr and C/CuCrZr has been found successful as a joining technique. W/Cu tile fabrication using oxide free high conductivity (OFHC) Cu casting in vacuum followed by brazing of W/Cu with CuCrZr has been found promising. Studies on functionally graded coatings of

W-Cu on CuCrZr alloys are being pursued as a promising solution. One of the limitations of W/Cu functionally graded materials (FGMs) is loss of strength at elevated temperatures due to presence of Cu. As a solution to this, recent studies (You *et al.*, 2013) have been reported on W/CuCrZr FGMs. Porous W skeletons infiltrated with CuCrZr alloy melt was prepared in the form of functionally graded composite as promising materials for divertor applications. Graded composite samples of W/CuCrZr in 1:1 ratio were reported promising for further development. Apart from this, novel concepts such as liquid metal (Li) plasma-facing components are being evaluated at Princeton Plasma Physics Laboratory. Other concepts involve vaporization of Li such as tungsten alloy with Li, wherein lithium would get evaporated and would thus be able to sustain the heat fluxes (Wong *et al.* 2001). Areas such as tritiated water corrosion of SS316 (LN) tubes are also important as the radiolytic and decomposition products enhance the corrosion rates (Bellanger, 2008). Further, presence of tritium would add to possible stress corrosion cracking issues, which need to be studied and mitigated.

2.2 Test Blanket Module

The fusion reactor programme is driven by the ultimate goal of developing large-scale power plants for production of electricity. The success of a fusion power plant is dependent on the high-grade heat extraction capability and efficiency of the tritium breeding blankets (Kumar *et al.*, 2008). A blanket module as the name suggests is an assembly which blankets the core of the fusion reactor and utilizes the energy of neutrons to generate T fuel and heat for electricity production. Thus, the main function of a breeder blanket module is to generate T fuel from Li by utilizing the 14.1 MeV neutrons generated from reactor core; to extract the heat for electricity generation purpose generated from the n-Li reaction and shield the other sub-systems from the radiation damage by the energetic neutrons. This can be achieved by appropriate design concepts, selection and or development of appropriate breeder materials and their processing techniques and the choice of appropriate structural material with relevant compatibility with

breeder material. Since the T can be generated from reacting the neutrons with ${}^6\text{Li}$ (see eq. ii), all the breeder materials are Li or Li-based compounds or alloys. Based on the form of Li, the blanket design can either be categorized as liquid breeder blanket, solid breeder blanket or mixed type. Different blanket module designs with solid or liquid or dual breeder breeder concepts have been proposed by different countries which are summarized in Table 2. The ITER reactor will be useful for testing and validating different blanket concepts as proposed by partner countries and the performance information will be helpful for development of a DEMO relevant blanket module design.

Both the solid and liquid breeder concepts have their pros & cons. The main advantage of the solid breeder is that it offers good compatibility between breeder, structural material and the coolant. However, one of the major drawbacks of solid breeder concept is the costly fabrication and re-processing of the ceramic breeder material. Against this, the liquid breeder concept offers efficient heat & fuel extraction, and easy maintenance. A general comparison between the two breeder blanket concepts is provided in Table 3 (Bornschein *et al.*, 2013). The Indian Lead Lithium Ceramic Breeder (LLCB) blanket involves use of both solid and liquid breeder concepts. The conceptual sketch of the Indian TBM (LLCB) as indicated in Fig. 5 (Rajendra Kumar *et al.*, 2012), illustrates the arrangements of the ceramic breeder columns and liquid breeder (Pb-17Li) flow channels. The flow of Pb-17Li in the RAFM steel channels results in severe corrosion of RAFM steel. (Krauss *et al.*, 2012) reported a dissolution rate of RAFMS at the rate of $\sim 400 \mu\text{m}/\text{year}$ which is approximately equivalent to $4 \text{ kg}/\text{m}^2$ per year of TBM-dissolved corrosion products. Such dissolution of structural material would not only lead to possibility of section thinning and leak out, but also poses a threat of choking of the flow channels due to re-deposition of dissolved corrosion products at colder zones. Apart from corrosion, another major concern is the T permeation into steel. The T generated from Li during the Pb-17Li flow path or from the ceramic pebble bed channels would permeate into the steel and thereby increase the radioactive T

Table 2: Overview of different breeding blanket concepts

TBM design concepts	Country	Brief outline of the blanket design
Helium Cooled Lead Lithium (HCLL)	EU	He & PbLi as coolant and breeder; RAFMS (Eurofer '97) as structural material
Dual Function Lithium Lead (DFLL) – He cooled quasi-static lithium lead (SLL)	China	He as coolant; self-cooled PbLi in quasi-static condition as breeder; RAFMS (CLAM steel) as structural material.
Dual Function Lithium Lead (DFLL) – Dual cooled Lithium Lead (DLL)	China	He/LiPb as coolant & breeder; RAFMS (CLAM steel) as structural material;
Lead Lithium Ceramic Breeder (LLCB)	India	He as coolant; self-cooled PbLi as breeder; Li_2TiO_3 as solid breeder; RAFMS as structural material
Helium Cooled Liquid Lithium	USA	He as coolant; self-cooled liquid Li as breeder; RAFMS with $\text{SiC}_f\text{-SiC}$ inserts as structural material
Lithium Vanadium (Li-V)	Russia	Self-cooled lithium as coolant cum breeder; Vanadium alloys as structural material
Helium Cooled Molten Lithium (HCML)	Korea	He as coolant; molten Li as breeder; RAFMS (Eurofer) as structural material
Water Cooled Solid Breeder (WCSB)	Japan	Li_2TiO_3 as solid T breeder; Be pebbles as neutron multiplier; He and water as coolants; SiC_f/SiC inserts; F82H (RAFMS) as structural material

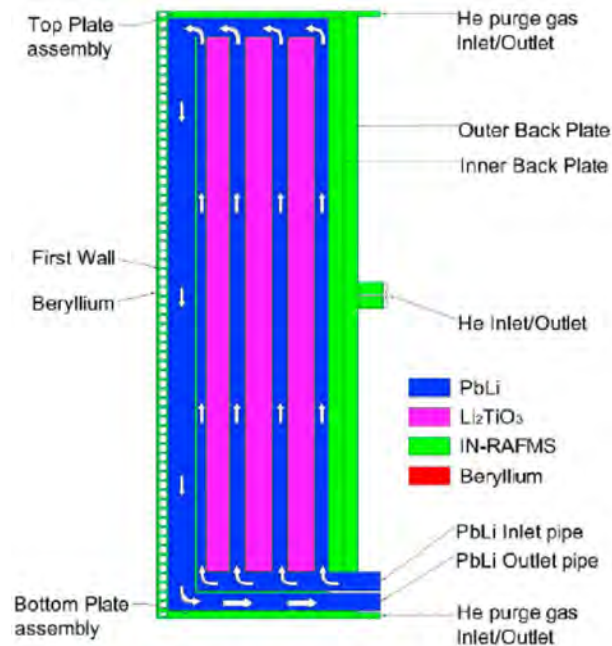


Fig. 5: Schematic diagram of Indian TBM (Lead Lithium Ceramic Breeder) concept. The arrows eutectic breeder while the columns in between (pink colour) represent solid Li_2TiO_3 breeder columns. [Ref: Rajendra Kumar *et al.* (2012)]

inventory buildup in the reactor, which is undesirable. The interaction of magnetic field B with the flowing

liquid metal also induces a magneto hydrodynamic drag (MHD), which increases the corrosion rates of steel as well as increases the required Pb-17Li pumping pressures. Coatings have been reported to be an inherent solution to all the three major issues of blanket modules. Such coatings will need to be compatible with Pb-17Li; resist permeation of T into steel with permeation reduction factor >100 ; provide electrical insulation for mitigating MHD issues and can also be coated on complex geometries (Smith *et al.*, 2002). The coatings should have low radiation induced conductivity after neutron irradiation. A variety of coatings such as AlN , Al_2O_3 , Er_2O_3 , Y_2O_3 , CaO , AlN , $(\text{Cr}_2\text{O}_3 + \text{SiO}_2) + \text{CrPO}_4$, ZrO_2 , $\text{Al}_2\text{O}_3 + \text{FeAl}$, etc. have been explored for different blanket concepts as reported in literature survey (Jamnapara 2013). Alumina and erbia coatings have been widely reported as candidates for the ITER reactor, wherein RAFM steel is considered as structural material. The structural materials are an integral part of the blanket module and its development and testing are inevitable. Studies on structural materials in blankets have been briefly spelt out in section 2.3.

Table 3: Comparison of solid and liquid breeder design concepts [Ref: Bornschein *et al.* (2013)]

	Solid breeder	Liquid breeder
Breeder material	Ceramics: LiO_2 , LiAlO_2 , Li_2SiO_3 , Li_4SiO_4 , Li_8ZrO_6 , Li_2TiO_3	$\text{Li}_{17}\text{Pb}_{83}$, Flibe (LiF , BeF_2)
Neutron multiplier	Be, Be_{12}Ti	Pb, Be
Coolant	He cooled, Water cooled	He cooled, water cooled, self cooled, dual cooled
Structural material	RAFM steel	RAFM steel
Advantages	Tritium extraction less challenging	No breeder damage or swelling; adjustable breeder composition
Difficulties	Blanket replacement, tritium permeation into coolant	MHD drag, corrosion, tritium permeation into coolant

2.3 Structural Materials

Structural materials for power plants are derived from existing high strength materials used for extreme environments. Materials and alloys having reduced activation elements (to reduce radioactive inventory), high resistance to creep, fatigue, low ductile to brittle transition temperatures, and capable of being used at higher temperatures under neutron irradiation are desired for fusion reactors (Baluc, 2006). After more than two decades of research, only three candidate material systems appear to have the potential to meet the low activation, high performance goals: 8-9 Cr ferritic/martensitic steels (including reduced activation variants), SiC_f/SiC composites and V-Cr-Ti alloys (Bloom *et al.*, 2007).

2.3.1 Effect of Neutron Irradiation

Irradiation damage occurs due to impingement of high energy particles viz. electrons, ions, neutrons, protons on the atoms of structural or functional materials, wherein the atoms are displaced from their regular lattice positions yielding Frenkel defects viz. vacancies and interstitials (Ronald and Klueh, 2001). While a few tens of eV are required to displace an atom, the neutrons in fusion reactors with 14.1 MeV energy will create significant radiation damage in the irradiated material. The extent of displacement damage is expressed in terms of how often an atom is displaced from its normal lattice position during irradiation as displacement per atom or dpa. In addition to the displacement damage, neutrons also cause

transmutation reactions with atoms of the irradiated material. Such transmutation products may either be another metal atom or gas atoms viz. helium and hydrogen by (n, α) and (n, p) reactions, respectively. It is well-known that the production of small amounts of He within lattice may have pronounced effects on material properties. Vacancies become more mobile for irradiation above $0.3T_m$, and result in formation of dislocation and cavity. Swelling of irradiated components occurs due to cavities formed by dissolved gases. As a result, the combination of gaseous transmutant products and radiation damage has to be monitored closely in the form of He/dpa ratio. An overview of the defect production in steels for different irradiation facilities has been reported by Baluc *et al.* (2007) and listed in Table 4.

Overall, it can be said that radiation damage leads to issues such as radiation-induced segregation, radiation hardening and embrittlement, phase instabilities due to radiation-induced precipitation, irradiation creep, volumetric swelling due to void formation, and high temperature He embrittlement (Tavassoli, 2002; Baluc *et al.*, 2011).

2.3.2 Reduced Activation Steels

The safety and environmental concerns in fusion reactors involve radioactivity in blanket and first wall structures. The radioactivity of the exposed fusion reactor components should be short-lived and hence, the structural material selection should involve low activation or reduced activation elements, specifically

Table 4: Defect production in steels for various irradiation facilities [Ref: Baluc *et al.* (2007)]

Defect production (in steels)	Fusion neutrons (3-4 GW reactor, 1 st wall conditions)	Fission neutrons (BOR 60 reactor)	High energy protons (590 MeV proton accelerator)	IFMIF (high flux test module)
Damage rate (dpa year ⁻¹)	20-30	~20	~10	20-55
Helium (appm dpa ⁻¹)	10-15	=1	~130	10-12
Hydrogen (appm dpa ⁻¹)	40-50	=10	~800	40-50

considering the high energy of fusion neutrons. The term “low activation material” is often used for those which allow hands-on maintenance and minimize waste disposal. In general, fusion relevant alloy development involves resistance to irradiation effects and higher temperature performance ability including structural and functional requirements.

Many studies were conducted in 1980 on type 316 austenitic stainless steels, including effects of fusion relevant He production and displacement damage on properties and microstructural stability (Zinkle, 2005). Austenitic stainless steels are reported to have higher swelling due to He bubbles generated from Ni transmutation reaction than ferritic martensitic steels. The alloy development thus shifted to high strength Fe-Cr-based steels with 2¼Cr to 12Cr steels with different alloying elements for purpose of microstructure strengthening (Klueh and Harries, 2001). The strengthening mechanism was the formation of carbides of V, Cr, Nb, etc. at the prior austenite grain boundaries and within the grains (on lath boundaries). Typical composition for ferritic martensitic alloys being developed in India for fusion reactor applications is listed in Table 5. Elements with long half-life transmutants such as Ni, Mo, Nb, Cu, Co, Al, N, etc. have been replaced by low activation counterparts viz. Mn, W, Ta and C so that the steels can be safely handled after a shorter cooling period as against cooling time of 1000 years required for conventional Cr-Mo-Ni-Nb containing ferritic martensitic steels (Saroja *et al.*, 2011). Such steels are produced by vacuum induction melting (VIM) followed by vacuum arc refining (VAR) method. Vacuum techniques are used since undesirable elements having high vapour pressure are readily

Table 5: Composition of Indian RAFM steel [Ref: Saroja *et al.* (2011)]

Element/ steel	Indian RAFM	Eurofer 97	Element/ steel	Indian RAFM	Eurofer 97
Cr	9.04	8.5-9.5	B	0.0005	<0.001
C	0.08	0.09-0.12	Ti	<0.005	<0.01
Mn	0.55	0.2-0.6	Nb	0.001	<0.001
V	0.22	0.15-0.25	Mo	0.001	<0.005
W	1.00	1.00-1.20	Ni	0.005	<0.005
Ta	0.06	0.05-0.09	Cu	0.001	<0.005
N	0.0226	0.015-0.045	Al	0.004	<0.01
O	0.0057	<0.01	Si	0.09	<0.05
P	0.002	<0.005	Co	0.004	<0.005
S	0.002	<0.005	As+Sb+ Sn+Zr	<0.03	<0.05

volatilized during vacuum melting. A typical RAFMS microstructure as indicated in Fig. 6 involves lath martensite boundaries packed in a prior austenite grain. The M₂₃C₆ type carbides are observed to be segregated on prior austenite grain boundaries while the MX type precipitates are present on lath boundaries within prior austenite grains, and such precipitates render strengthening effect to the steel structure. An advancement of this alloy is the oxide dispersion strengthened (ODS) ferritic martensitic steels (Paúl *et al.*, 2005). Particle reinforcement is one of the reliable strengthening mechanisms of FM steels. In such steels, particle reinforcement is provided by addition of minor quantities of nano-sized yttria (Y₂O₃) powders. Such ODS steels can be manufactured by

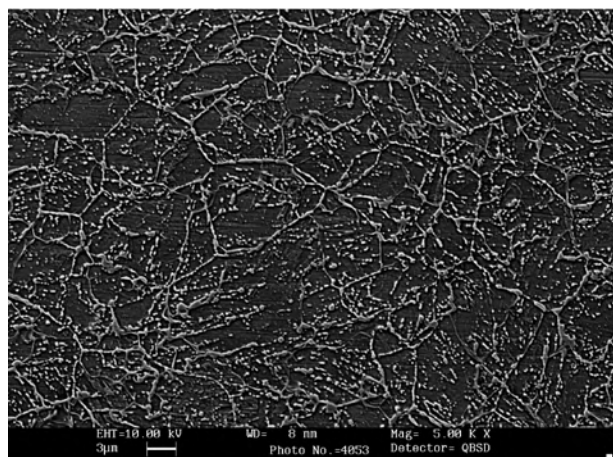


Fig. 6: Microstructure of RAFM steel observed under SEM. Note the carbide precipitation around prior austenite grain boundaries. Minor precipitates within prior austenite grains are indicative of lath martensite boundary

powder metallurgical route followed by hot isostatic pressing to compact shapes.

2.3.3 Vanadium Alloys

In a blanket module, liquid metal flow through structural material and presence of ceramic breeder and neutron multiplier need to be handled through the right choice of candidate material. Vanadium alloys are such that they not only have excellent compatibility with Li, but also provide room for high operating temperatures and eliminate the need of ceramic breeders or neutron multipliers (Chen *et al.*, 2011). Vanadium alloys are one of the candidate materials for structural components of blanket modules in the fusion reactor owing to their high temperature strength, high thermal stress factor, low long-term activation, excellent compatibility against Li, etc. The vanadium alloy with V-4Cr-4Ti type composition has been developed for fusion blanket applications by US, Japan, Russia and China (Muroga *et al.*, 2002; Chen *et al.*, 2011). There are two ways to improve the strength of V-alloys; one of the methods involves increase in amount of alloying elements such as Cr, etc. Addition of Al and W as alloying elements in V-4Cr-4Ti alloy has also been known to enhance the mechanical properties of the alloy. The other strengthening mechanism is to produce fine-grained and particle-dispersed V-alloys using mechanical alloying.

It is important to note that the V-Cr-Ti alloy will endure severe hardening and loss of strain hardening capability by neutron irradiation below 400°C. Also the mechanical strength of reference V-4Cr-4Ti alloy is not as high as FM steels at <~600°C, although it has higher strength at higher temperature up to ~750°C. Efforts are being made to expand the operating temperature window and improve the mechanical properties as well. Such V alloys are specifically considered candidates for Li-V blanket concepts where liquid Li is flowing up to 700°C in V-alloy channels with corrosion rates as low as 7.5 µm/year. V-alloys are thus an attractive candidate for advanced self-cooled fusion blanket concepts such as Li/V. However, issues such as irradiation creep and He embrittlement behaviour still remain unsolved.

3. Status of Materials Development in India

Institute for Plasma Research (IPR), Gandhinagar initiated the plasma physics programme in 1982 and developed “Aditya” which is India’s first tokamak system. Subsequently, IPR started developing a steady state tokamak (SST-1) which is under final stages of completion. With passage of time, as India participated in ITER programme (November 2006), the activities towards technological development for fusion reactor were accelerated. Many activities pertaining to development of fusion reactor materials have been initiated at Indira Gandhi Centre for Atomic Research (IGCAR), Bhabha Atomic Research Centre (BARC) and Institute for Plasma Research (IPR).

Research on first wall and divertor development activities at IPR involves materials development and processing studies of W, W-based alloys, CFC, CuCrZr alloy, their joining studies and the performance tests such as high heat flux testing (Khirwadkar *et al.*, 2011; Singh *et al.*, 2011; Patil *et al.*, 2013). Reduced activation ferritic martensitic steels have been developed for the Indian TBM programme as per the composition specified in Table 5 (Saroja *et al.*, 2011). Physical metallurgy of the developed Indian RAFMS has been reported by a few studies (Raju *et al.*, 2009; Raj *et al.*, 2010). Studies related to the development of blanket relevant materials such as RAFM steels, ceramic breeders (Li₂TiO₃),

compatibility studies of liquid breeder with structural materials under magnetic field, neutronics studies and development of simulation codes, welding and joining techniques, etc. have been reported (Rajendra Kumar *et al.*, 2012). Activities related to development of alumina-based coatings ($\text{Al}_2\text{O}_3 + \text{FeAl}$) for blanket applications have been extensively studied and developed by the authors (Jamnapara *et al.*, 2012a; 2014a). Attempts have been made to explore the insulation properties of alumina films grown by thermal and plasma processing. Plasma grown alumina films on FeAl surfaces had been found to yield improved dielectric properties as compared to thermally grown alumina films (Jamnapara, 2015a). In continuation to this, $\alpha\text{-Al}_2\text{O}_3 + \text{FeAl}$ -based coatings on P91 steels have been successfully generated using hot dip aluminizing followed by normalizing and tempering treatments using plasma oxidation process. A novel patented concept of using plasma as an oxidation tool has been developed so as to accelerate the transformation of metastable $\theta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ (Jamnapara *et al.*, 2015b). The compatibility of such alumina coatings generated by thermal processing and plasma oxidation treatment against Pb-17Li have been conducted at 550°C for 1000 hours under static mode (Jamnapara *et al.*, 2014b). The plasma processed stable $\alpha\text{-Al}_2\text{O}_3$ has been found to be immune against Pb-17Li for 1000 hours duration with no weight loss, while the bare P91 substrate revealed 7.23 mg/cm² weight loss which was $\sim 7\text{ }\mu\text{m}$ of substrate degradation as confirmed by SEM-EDS. Further tests under dynamic Pb-17Li conditions are being planned in near future. FeAl-based coatings for welded areas of blanket structures using electrospray deposition technique have also been explored on a preliminary level by the authors (Jamnapara *et al.*, 2012a). Interesting features of a quasi-amorphous interface without any grain boundary has been observed which could be a potential barrier for hydrogen permeation. The electrospray deposition technique can also be explored as a possible coating process for first wall applications needing W coatings.

Materials development activities for extreme environments such as nuclear fusion would not be possible without nuclear grade materials testing, characterization and validation facilities. Neutron

irradiation sources equivalent to 14.1 MeV are not available and need to be set up. An International Fusion Materials Irradiation Facility (IFMIF) is being conceptualized (Garin and Sugimoto, 2008) and planned for validation trials of materials to be qualified for fusion environment. The IFMIF is being planned by EU, Japan, Russia and USA; and being managed by the International Energy Agency. The primary mission of IFMIF is to generate a materials database to be used for design and construction of various components of DEMO-type reactors. IFMIF will be an accelerator-based, high-energy neutron source mainly composed of two 125 mA deuteron accelerators and a flowing liquid Li target (Baluc *et al.*, 2011). In the high flux test module of the IFMIF, the irradiation conditions will be very close to the ones expected in a DEMO type reactor at the level of first wall, at least in terms of damage rate (22-55 dpa/year) and rates of He production (10-12 appm dpa⁻¹) and hydrogen (40-50 appm dpa⁻¹). In addition to static material interaction in the high flux test module, more sophisticated *in situ* creep-fatigue tests on structural materials and *in situ* tritium release experiments on different tritium breeding materials are foreseen in medium flux test module, where a damage rate of 1-20 dpa/year will be reached (Baluc *et al.*, 2011). India will need to actively participate in such international facility to build a domestic fusion reactor.

4. Indian Fusion Reactor Programme

The energy requirement of India is expected to grow by almost 10 times of the present requirement in the next 50 years. Out of the installed capacity of 120 GWe power, 95.5% is produced through thermal and hydro while just 2% is produced through nuclear energy. With the introduction of the new concepts of fission technology in India viz. prototype FBR and thorium reactors for near future, fusion is viewed as natural advanced successor technology to fission for producing large amounts of electricity (Srinivasan and Deshpande, 2008). The Indian plasma physics programme started in 1982 resulting in the inception of the Institute for Plasma Research (IPR) at Gandhinagar, Gujarat, India. India's first tokamak device "Aditya" was demonstrated in 1989. Later on, the Steady State Tokamak-1 (SST-1) programme was

initiated at IPR. The SST-1 machine (designed for hydrogen plasma) is mainly focused on studies related to plasma physics and supporting instrumentation and subsystems. With India's participation in the ITER project, the D-T fusion reactor technology will be enhanced and would be useful for India's domestic fusion reactor programme. The Indian TBM programme has aggressively progressed with the joint efforts of IPR, IGCAR, BARC and other organizations in India. The Indian TBM concept is to be tested in one half port of ITER reactor at Cadarache, France.

As a roadmap towards the Indian fusion programme (Rajendra Kumar, 2012), India has proposed a next stage of SST-1 machine: a D-T machine named Stead State Tokamak-2 ('SST-2'). SST-2 will be a medium-sized tokamak reactor with D-T operation. SST-2 operation will enable the testing of various indigenously built subsystems of the fusion reactor, specifically addressing tritium breeding and handling issues, robotics and remote handling, alpha particle issues, fusion materials development, etc. Further, the SST-2 will address the availability of a machine for breeding blankets and testing and validation of novel materials developed for DEMO applications. The SST-2 will become the stepping stone towards realization of a DEMO reactor.

5. ITER Project and India's Role

The first conceptual design of ITER device was started in April 1988. A revised design was finalized in 2001 by the ITER Council. Owing to the domestic steady state tokamak programme, India joined ITER in December 2005 and the ITER agreement between seven partners was signed in November 2006. Thereafter, the ITER design and construction work has been in progress. It was projected (Holtkamp, 2009) that ITER would initiate its first plasma shot in 2018. The divertor which was initially a carbon-based (CFC) divertor has now been confirmed as full tungsten-based divertor (Merola *et al.*, 2014). This is because carbon is not permitted during nuclear use owing to the potential risk of rapid generation of tritium dust. Thus, the replacement of a CFC divertor by a full W divertor is due to safety reasons as well as

cost reduction and maintenance. In 2009, the ITER Council created a high-level advisory body, "The TBM Programme Committee", was appointed to ensure the on-time delivery of the test blanket systems at the ITER site (Giancarli *et al.*, 2012). The test blanket module system concepts proposed by the seven partners of ITER underwent a final design review in 2013 and is now entering the engineering and procurement phase (Merola *et al.*, 2014).

India is one of the seven partners and shares some cost of components of ITER. A schematic view of the in-kind contributions of the seven partners is shown in Fig. 7, wherein India's contribution has also been indicated (Kaname, 2010). 'ITER India', is a project governed by an empowered board under the Department of Atomic Energy, Government of India, and is committed to the delivery of the components to be provided by India as "in-kind contribution". The contribution to TBM for ITER excludes the contributions shown in Fig. 7.

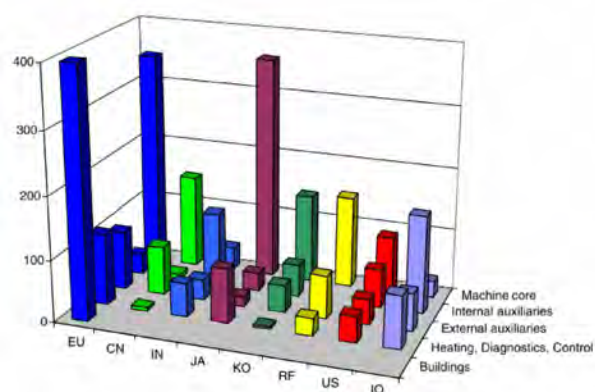


Fig. 7: Contribution of ITER partners to ITER [Ref: Kaname (2010)]

Conclusions

The fusion reactor programme has taken a large leap owing to the increasing energy demands and the limited reliability of energy sources. The extreme environments in fusion reactors pose a challenge to the materials research and development community, which is being worked upon aggressively. Without appropriate materials, we cannot expect a fusion reactor. While most of the materials research is being focused on first wall, divertor, breeder and structural

materials, appropriate thrust is also being made on setting up of fusion grade testing and validation facilities. With India's domestic power demand, it would need to strengthen its domestic fusion programme as next generation energy source. Materials research and development activities are thus inevitable for a better tomorrow.

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Review Article

High Temperature Fuel Cell

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In our country, about 60% of the power generated in India is from fossil fuels such as coal, oil and gas, which are eventually responsible for generating large quantities of greenhouse gases. Fuel cell is an electrochemical device and potential technology to generate power in an environmentally benign manner. This chapter of the monogram deals with high temperature ceramic fuel cells, popularly known as solid oxide fuel cell (SOFC). In the beginning, a generalized discussion has been made about fuel cells with particular emphasis on SOFC which is followed by a detailed description of the progress of research related to the development of planar anode-supported SOFC technology that is being pursued at CSIR-Central Glass & Ceramic Research Institute, Kolkata under CSIR-New Millennium Indian Technology Leadership Initiative (NMITLI) programmes over the last few years. Under these technological developmental activities, large numbers of anode-supported single cells of dimension up to $10\text{ cm} \times 10\text{ cm} \times 1.5\text{ mm}$ have been fabricated that show reasonably good power output of $\sim 1.0\text{ W/cm}^2$ at a cell voltage of 0.7 V and at an operating temperature of 800°C . In parallel, this contribution also describes the indigenous development of high temperature glass-based sealant, an essential component for SOFC stacking. Using the developed 10×10 single cells, glass-based sealants, indigenously designed and fabricated metallic interconnect and gas manifolds, several SOFC short stacks (up to 10 cells) have been fabricated and demonstrated for the first time in our country.

Keywords: Solid Oxide Fuel Cell; Anode; Cathode; Electrolyte; Interconnect; Anode-Supported Planar Design; Electrochemical Performances; Stack

Background

Although the invention of fuel cells (FC) as a renewable energy conversion system was initiated in the mid of 19th century, the discovery of the underlying principle was owned by Prof. Christian Friedrich Schonbein (Bossel, 2000) at the University of Basle (1829-1868). However, Sir William Grove has attributed primarily towards the electrical energy conversion system using the science behind the fuel cell. At the beginning of 20th century, the journey of the fuel cell science and the technology has turned out positively because of significant increase in population around the globe and the depletion of natural resources for energies. During the same time, the initiation of distributed power generation plant has been started with an intention of reducing capital cost for the installer and thereby improving the overall

efficiency due to the possibility of co-generation of heat and electricity. Technologically viable fuel cell is expected to facilitate mankind to reduce dependence on conventional energy sources and in addition diminish poisonous emissions into the atmosphere. A simplistic view of fuel cell is that it is a cross between a battery (chemical energy converted directly to electrical energy) and a heat engine (a continuously fuelled air breathing device). Therefore, fuel cell is also referred as “electrochemical engines”. The range of fuel cell applications and the size of potential markets are enormous which includes, battery replacement in small portable electronic devices, prime movers and/or auxiliary power units in vehicles, residential combined heat and power (CHP) and large-scale megawatt (MW) electrical power generation. Fuel cells share the effectivity of its operation with

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high efficiency (>60%), no moving parts, quiet operation and low or zero emissions during application.

The system efficiency of a fuel cell, independent of Carnot's limitation, can be derived from Gibb's free energy (ΔG) and the enthalpy change (ΔH) of the electrochemical reaction in terms of electrical work (W_e) as:

$$(\varepsilon_\gamma)_{FC} = \frac{W_e}{-\Delta H} = \frac{nFV_o}{-\Delta H} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H}. \quad (1)$$

Practically, majority of reactions are associated with negative entropy change that causes increase in temperature thereby reducing the thermodynamic efficiency of fuel cell. Regardless of all the polarization factors contributing towards reducing efficiency, the overall system efficiencies of fuel cells are high in comparison to internal combustion engine (ICE) which is discussed in reputed fuel cell handbooks (Blomen and Mugerwa, 1993; Appleby and Foulkes, 1993) and a comparative representation of different systems is shown in Fig. 1. Apart from system output, the fuel cells are superior pertaining to the co-generation of heat and electricity. Efforts are being pursued over the globe to enhance the efficiency of fuel cells and

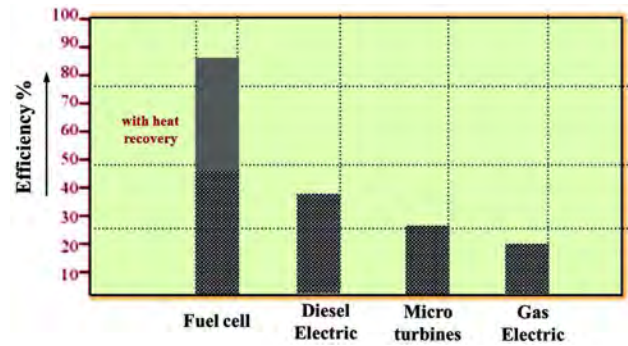


Fig. 1: Comparative system efficiencies of Carnot-dependent and independent energy conversion systems

coupling with devices to utilize the waste heat for energy conservation. Therefore, owing to the advantages associated with fuel cell technology, security of electricity can be ensured in future which is also expected to induce a new era of 'hydrogen economy'.

High Temperature Fuel Cell

Fuel cell is usually being categorized in terms of electrolyte employed except direct methanol fuel cell (DMFC), in which classification is made with respect to the methanol fuel, fed directly to the anode. An overview of the fuel cell types is provided in Table 1

Table 1: Characteristics of fuel cell systems

Types of fuel cell	Alkaline (AFC)	Polymer electrolyte membrane (PEMFC)	Direct methanol (DMFC)	Phosphoric acid (PAFC)	Molten carbonate (MCFC)	Solid oxide (SOFC)
Operating temperature (°C)	<100	60-120	60-120	160-220	600-800	800-1000 or 500-600
Fuel	H ₂	H ₂	CH ₃ OH	H ₂	H ₂ , CO	H ₂ , CO
Oxidant	O ₂	O ₂ /Air	O ₂	O ₂	O ₂ + C O ₂	O ₂
Anode	Ni, Pt	Pt	Platinized Carbon (Pt/C)	Pt	Ni	Ni-YSZ
Cathode	Ni	Pt	Pt	Pt	Li-doped NiO	Sr-doped LaMnO ₃
Charge carrier in Electrolyte	OH ⁻	H ⁺	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Applications	Transportation, space, Military, Energy storage systems			Combined heat and power for decentralized stationary power systems		Combined heat and power for stationary decentralized systems and for transportation
Realised power	Small plants, 5-150 kW modular	Small plants, 5-250 kW modular	Small plants, 5 kW	Small-medium sized plants 50kW-11 MW	Small power plants, 100 kW to 2 MW	Small power plants, 100-250 kW

(Dufour, 1998; Carrette *et al.*, 2000; Chalk *et al.*, 2000). The available high temperature fuel cell is primarily known as solid oxide fuel cell (SOFC) where all the components are in solid state. High temperature fuel cell employs a solid oxide electrolyte material and is more stable with no leakage problems compared to other classes of fuel cell.

Additionally, being a two-phase gas-solid system, SOFC does not suffer from the problems of water management, slow oxygen reduction reaction rate (ORR), etc. It is considered to be one of the most promising power generation technologies for the future due to its high efficiency, zero or extremely low pollution level and fuel flexibility. The concept of such a ceramic fuel cell started long before in 1911 but the perception of stationary SOFC was presented in 1937 (Baur and Preis, 1937) and significant development started around 1960. A detailed review in this context is presented by Mobius (1997). The power and the voltage of SOFC is increased by connecting individual cells in series to form a 'stack', with each cell connected to its adjacent cell using an electrically conducting interconnect which also serves to distribute the reactant across the surface of the electrodes using the designed flow channels. Working temperature of SOFC is dependent on the activity and application of the associated components. SOFC can be divided into three major categories viz. (a) low temperature SOFC (LT-SOFC) which operates within the working temperature of 500-650°C, (b) intermediate temperature SOFC (IT-SOFC) that operates within 650-800°C and (c) high temperature SOFC (HT-SOFC) which operates in the range of 800-1000°C. If a high temperature fuel cell is integrated with a gas turbine in a hybrid arrangement, then, overall efficiency in excess of the individual efficiencies of the fuel cell and heat engine in isolation can be achieved. The characteristic of high temperature operating SOFC constitutes one of the toughest criteria for the dimensional and chemical stability of anode material in reducing atmosphere (Basu, 2006). Similar to MCFCs, internal reforming in SOFC is possible over anode catalyst and both partial and direct oxidation of fuel has been found to occur (Boder and Dittmeyer, 2006; Ren *et al.*, 1996; Hamakawa *et al.*, 2000; Park *et al.*, 2000; Park *et al.*, 1999). SOFC

offers advantages of using different fuels, e.g., hydrogen, CO, natural gasses, bio gas, any light hydrocarbon, etc. However, the cell functioning is highly prone to the presence of sulphur (<60 ppm).

SOFC is therefore a class of electrochemical cell through which free energy of a chemical reaction is converted to electrical energy. Correlation between change in Gibbs free energy (ΔG) and cell voltage is given as (Carrette *et al.*, 2000):

$$\Delta G = -nF\Delta U_0 \quad (2)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant and ΔU_0 is the voltage of the cell at thermodynamic equilibrium in the absence of a current flow. The schematic of SOFC is given in Fig. 2, where an oxygen ion conducting solid electrolyte is sandwiched between anode and cathode.

Even under no load condition, the open circuit voltage (OCV) can be lower than the thermodynamic Nernst value due to mixed potential formation or other parasitic processes. Under load condition, a deviation from OCV occurs corresponding to the electrical work performed by the cell termed as 'overpotential or polarization (η)'. The several losses that are being encountered during the operation of high temperature fuel cell are given in Fig. 3.

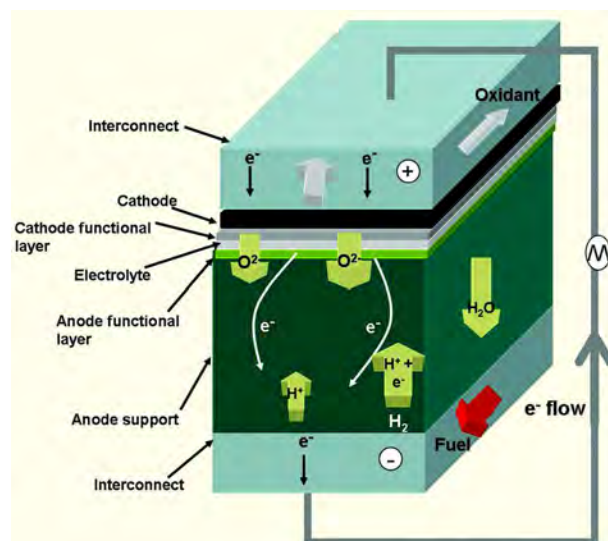


Fig. 2: Schematic of solid oxide fuel cell

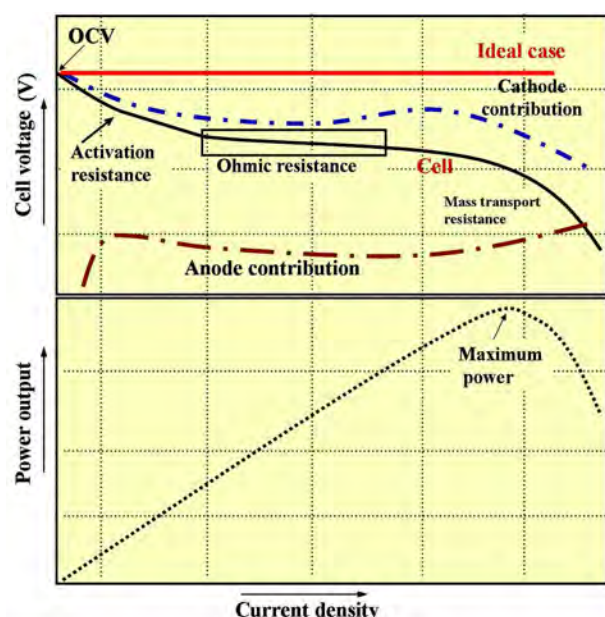


Fig. 3: Several polarization factors towards cell performance and trend of cell voltage vs current density (top) and power output vs. current density (bottom)

Cell Components

Solid oxide fuel cell essentially consists of two porous electrodes; cathode and anode, separated by a dense ion conducting electrolyte material. Ceramic fuel cell is fabricated in several designs (discussed in subsequent sections), but the basis of the material selection is based on the following criteria:

- Sufficient electrical conductivity values
- Matching thermal expansion among the cell components
- Minimal reactivity and interdiffusion among the components to avoid degradation
- Adequate chemical and structural stability at high temperature

The components for SOFC are discussed in brief as follows:

Cathode

The state-of-the-art cathode material satisfying the SOFC operating criteria is the electronically conductive ceramic oxide based perovskite e.g. lanthanum manganite (Basu, 2006; Song *et al.*, 2009).

In general, substituted lanthanum manganite is used in which 'La' is partially substituted by strontium (i.e. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, commonly termed as LSM). These perovskite are electronic p-type conductors for which the electrical properties are determined by the La/Sr ratio. Formation of $\text{La}_2\text{Zr}_2\text{O}_7$ and SrO upon interaction with adjacent 8 mol% yttria stabilized zirconia (YSZ) electrolyte is inhibited by incorporating an excess of Mn (1-10 %) in the composition and keeping the sintering temperature below 1300°C (Stochniol, 1995). The side products as mentioned above impair the cathode performance. The function of cathode in SOFC is based on the capability to reduce oxidant viz. air and oxygen, etc. It is generally assumed that oxygen reduction is a multistep reaction involving adsorption and surface diffusion in a region around the triple phase boundary (TPB) as shown in Figure 4. Mixed ionic and electronic conductor (MIEC)-based perovskite cathodes such as $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ (LSF), $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ (LSCF), and $\text{Ba}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ (BSCF) are also being used as SOFC cathode materials for some specific advantages over prior ones e.g., the conventional LSM cathode. Significant reduction in the cost of air electrode is possible by utilizing composition that has low rare earth content.

Electrolyte

The solid electrolyte for SOFC application needs to be a fast ion conductor and should simultaneously confront both reducing and oxidizing environment. Among innumerable oxygen ion conductors viz. ceria, La-gallate (Ishihara *et al.*, 1998); zirconia stabilized in conductive phase with up to 10 mol% of either yttria or scandia, can be used either as tetragonal zirconia polycrystals (TZP) (3YSZ: ZrO_2 doped with ~3 mol% Y_2O_3) or cubic stabilized zirconia viz. CSZ (8YSZ: ZrO_2 doped with ~8 mol% Y_2O_3) (Manner and Ivers-Tiffée, 1991) are the promising candidates. Fully stabilized zirconia offers the best choice of electrolyte having satisfied criteria of conductivity, chemical stability, durability, etc. Although the oxide ion conductivity of TZP is relatively lower than the fully stabilized zirconia, this material is advantageous because of its outstanding mechanical stability. Significant efforts are also put in to study the traditional zirconia material in terms of appropriate co-dopants

(Hirano *et al.*, 1999; Batista and Muccillo, 2011) for improved bulk and grain boundary conductivity. Activities for alternative electrolyte compositions are generally concentrated on doped CeO_2 or doped LaGaO_3 materials (Steele, 2000). In the absence of suitable materials, minimizing the thickness of YSZ layer effectively reduces the polarization losses and thus reduces the cell operating temperature to 800°C .

Anode

Under reducing atmospheres at anode, metals are stable over a wide range of operating conditions. Among various experimental metals, 'Ni' has been selected due to its high electrochemical activity for hydrogen oxidation reaction, low cost and acceptable compatibility with other cell components (Singhal and Kendall, 2003; Daniel *et al.*, 2008). However, the usual practice is to unify Ni with ceramic component, viz. YSZ (yttria stabilized zirconia), ScSZ (scandia stabilized zirconia), etc. The prime function of the ceramic phase is to prevent Ni from agglomeration, and thereby retain the porous and highly disperse microstructure of the anode. However, the ratio of Ni:YSZ needs to be optimized on basis of the requirement of conductivity and minimization of ambipolar resistance. Although Ni-YSZ has advantages as mentioned above, the high susceptibility of Ni to coking, re-oxidation in case of fuel loss and sensitivity to poisoning of the electrode by sulphur are the main concerns regarding the durability and degradation of Ni-YSZ anodes (Singhal and Kendall, 2003). Experiments have shown that performance of SOFC starts degrading upon increasing the sulphur content beyond ~ 5 ppm (Zhang *et al.*, 2010). As alternative anodes, focus is on the development of fluorites, pyrochlore, perovskite, tungsten and bronze-based materials (Tao and Irvine, 2004). With regard to the competitive performance of Ni-YSZ, only ceria-based, $\text{Ce}_{0.6}\text{Gd}_{0.4}\text{O}_{1.8}$, (Mogenson, 2005) Ni-CGO and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{0.3}$ (LSCM) (Tao and Irvine, 2004; Mogenson, 2005) have been developed. With respect to compatibility with YSZ electrolyte, yttria-titania-modified zirconia (Y2T) is also found to be a promising mixed conducting fluorite-based anode material (Verbreken *et al.*, 2005). From the aforementioned research, it can be mentioned that

SOFC has the potential of using variable fuels viz. H_2 , CO, CH_4 , etc. based on the possible cell component materials.

Other Components

Selection and fabrication of interconnect material is another important concern for fuel cell development. The interconnect should fulfill the prime requirements of being electrically conductive and act as a separating component for restricting fuel/oxidant gasses to intermix at either electrodes. Additionally they should be dense, chemically and dimensionally stable in dual oxidizing and reducing atmosphere. Bipolar plates based on ceramic materials viz. LaCrO_3 offer better thermal compatibility with other cell components. However, sufficient conductivity is observed upon formation of Cr_2O_3 layer on the surface of LaCrO_3 -based interconnect. (Casteel *et al.*, 2009; Ghosh *et al.*, 2006). A new metallic-ceramic alloy is developed by Plansee (Austria) which shows high corrosion resistance, good thermal conductivity, high mechanical strength and low expansion coefficient. The alloy is based on a CrFe stainless steel metallic component mixed with an yttrium oxide ceramic (Carrette *et al.*, 2001). In addition; Fe-Cr ferritic steel alloys are also used as effective materials applicable for IT-SOFC (Yasuda *et al.*, 2009). Commercialization of SOFC is limited by the development of suitable sealant material capable of working at high operating temperatures. Sealants are required for preventing the intermixing of fuel and oxidant gases in the electrode compartments. (Steele, 2001; Mogenson *et al.*, 1992) Promising candidates for sealing purpose could be 'glass (SiO_2)' or 'ceramic-foams'. Normal glasses are proved to be ineffective sealants, as they often evaporate and soften with a likelihood of leakages. Pyrex seals are used and proved to have sufficient stability at high temperature and pressure so that leakages can be avoided (Momma *et al.*, 1997). Ceramic foams consisting of Co-doped LSM materials have been found to have high electronic conductivity and a reasonable compressive strength, but these do not exhibit creep behaviour (Will and Gauckler, 1997). SOFC seals can be broadly classified into two major categories, for e.g., composition specific sealants that include compressive and rigid seals and

bond-specific seals (ceramic-ceramic, ceramic-metal and metal-metal). Additionally, rigid seals consist of: (a) glass ceramic, (b) self-healing type, (c) composite and (d) brazing seals (Furgus, 2005; Reis and Brow, 2006). The application of sealant type is entirely dependent on the nature of its application.

Fuel Cell Research in India

In India, fuel cell research has primarily been catered by the academic institutions and government R&D organizations. However, there is growing interest among many private and PSU organizations which are initiating their own R&D programmes on fuel cell (Reis and Brow, 2006; Confederation of Indian Industry, 2010). The R&D activities have been primarily focused on PAFC, PEMFC and SOFC. India's policy on fuel cells and financial support is driven largely by three agencies, viz. Ministry of New and Renewable Energy (MNRE), Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR). So far as ceramic fuel cell is concerned, CSIR-Central Glass & Ceramic Research Institute, Kolkata has the strongest R&D group for technology development where the related research activities were initiated in the mid-90s. Besides CGCRI, some other R&D laboratories and academic institutes are also carrying out R&D on SOFC. Fuel Cell Lab at IIT Delhi is trying to develop SOFC that operates directly on hydrocarbon feedstock. Similarly, efforts are being made at the CSIR-Institute of Minerals & Materials Technology, Bhubaneswar, to develop high-performance intermediate-temperature SOFC by low-cost ceramic processing technique. IIT Bombay and IIT Kanpur have also recently initiated activities on new materials development for SOFC along with simulation and modelling for planar SOFC. Bhabha Atomic Research Centre (BARC), Mumbai is mainly engaged in tubular SOFC technology development. International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad has started working on SOFC that is based on a typical design of honeycomb structures for specific application. In addition to R&D establishments, multinational companies such as GE (India), Bangalore and Bloom Energy (India) Pvt. Ltd., Mumbai have

ventured into this area, primarily to assemble imported parts supplied by their principals. Bharat Heavy Electricals Limited, CTI, Bangalore has initiated the research with SOFC single cell testing using their own developed glass-based seals. Gas Authority India Ltd (GAIL) and National Thermal Power Corporation (NTPC) have also planned to initiate activities on SOFC. With respect to gasification of Indian coal, Thermax Limited, Pune is involved in building a gasifier for coal and biomass for quite some time and is now looking for application of biogas in SOFC in collaboration with IIT Bombay.

Development of anode-supported SOFC technology: Activities in CSIR-CGCRI, Kolkata

Among the various designs, the planar anode-supported thin film electrolyte design, introduced by Forschungszentrum Jülich, Germany as one of the pioneering organizations of the design, is followed by many of the SOFC developers because of several advantages associated with this design (Ishihara, 2003). Generally, electrolyte-supported cells and electrode-supported cells are the two possible configurations of planar design that are available in the market. In case of electrolyte-supported design, it is practically possible to achieve a mechanically stable structure only when the electrolyte thickness is greater than 200 μm . However, for such a high thickness of the electrolyte, the ohmic loss across the same is appreciably high and the cells have to be operated at a very high temperature of around 1000°C in order to have sufficient conductivity through the electrolyte to be useful for practical device application (Steele, 2000). This hinders the commercialization of SOFC due to the necessity of using costly construction materials to withstand such a high temperature. These problems can be overcome if a thin electrolyte layer is fabricated over a thick and porous electrode-support which is the basis of anode-supported design. In this design, while the porous anode provides the mechanical support, the thinness of the electrolyte helps in lowering the ohmic losses across it. The thinness of the electrolyte helps in reducing the internal resistance of the electrolyte, thereby making it possible to lower the temperature of operation and consequently, to use metallic interconnects which are

much easier to fabricate than their ceramic counterpart. As the resistance of the electrolyte is proportional to its specific resistance and thickness, the total resistance of the electrolyte layer can be reduced by reducing its thickness to such a level that it more than compensates the increase in specific resistance caused due to a lowering in operating temperature. Thus, for an anode-supported SOFC, the operating temperature can be lowered down to about 800°C or even less (depending on the thickness of the electrolyte film) without compromising with the power output. This allows the device to be made of less expensive materials. However, in such a configuration, the major technical challenge involves fabricating a pinhole and crack-free dense layer of YSZ electrolyte of thickness 50µm or less on NiO-YSZ (anode) substrates of high porosity. The YSZ film must be well-bonded to the NiO-YSZ substrate without excessive infiltration into the electrode porosity and there must be minimal interface polarization. However, for such a configuration, the major technical challenge involves fabricating a dense and gas-tight YSZ electrolyte layer of thickness 50 µm or less supported on a porous NiO-YSZ (anode) substrate. Several studies describe the performance of such anode-supported SOFC (Basu *et al.*, 2005; Kim *et al.*, 1999; Yoon *et al.*, 2007). Under the CSIR-New Millennium Indian Technology Leadership Initiative (NMITLI) projects in two different phases (initiated in 2004), CSIR-CGCRI Kolkata is engaged in the development of anode-supported SOFC technology using inexpensive, simple and up-scalable processing techniques, such as tape casting and screen printing. All the processing parameters have been optimized to fabricate single cells of dimension up to 10 cm × 10 cm × 1.5 mm. The fabricated cells have been characterized through microstructural, electrical and electrochemical performance studies using LSM-based conventional cathode. While, in the technology mode, CSIR-CGCRI is engaged in the development of kW-level SOFC power pack based on such single cell using their own novel patentable design and CGCRI developed high temperature glass sealants, CSIR-CGCRI is also engaged in the research and development of several material component developments, viz. new class of doped lanthanum

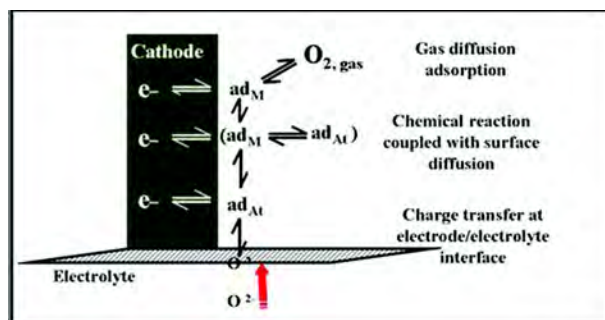


Fig. 4: Possible reaction steps at air electrode in SOFC

ferrite based mixed ionic and electronic (MIEC) cathodes, spinel-based protective coating, new cathode-electrolyte interface interlayer materials, new anode materials by electroless technique, etc.

Component material synthesis

a) Cathode

Strontium-doped lanthanum manganite and lanthanum ferrite cathodes by soft chemical route:

CSIR-CGCRI is engaged in the synthesis of nanocrystalline lanthanum strontium manganite (LSM) and various lanthanum ferrites (LSF)-based cathode materials by combustion technique using L-alanine as novel fuel. The nanocrystalline nature of these cathode materials can play significant role on the ORR kinetics. Details for choosing L-alanine as a novel fuel are provided in studies by Pal *et al.* (2007) and Dutta *et al.* (2009a). Several compositions that were synthesized by this soft chemical route and studied are provided in Table 2. The synthesis procedure adopted for all the compositions is schematically shown in Fig. 5 (Dutta *et al.*, 2009a). Owing to the presence of the oxidant and reductant group in a definite ratio in the solution, an instantaneous burning

Table 2: Cathode compositions and their corresponding sample IDs (Dutta *et al.*, 2009a)

Cathode Composition	Sample ID
$\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$	LS1
$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	LS2
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	LS3
$\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	LS4

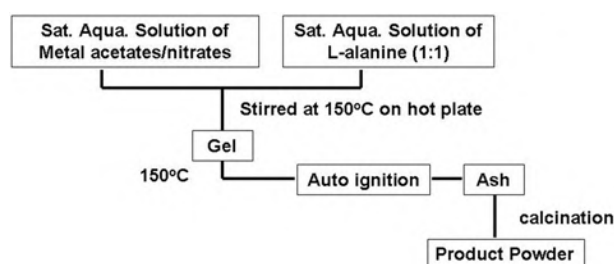


Fig. 5: Schematic for synthesis of cathode powders by soft chemical route (Dutta *et al.*, 2009a)

of the precursor gels leads to the autocombustion synthesis producing finer precalcined ash. The as-synthesized powders (ash) are then calcined at 700° and 825°C for 4 h in air.

Strontium-doped lanthanum manganite cathode by spray pyrolysis technique

CSIR-CGCRI has successfully synthesized Sr-doped lanthanum manganite ($\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$) cathode composition using an indigenously designed spray pyrolysis technique. The main motivation behind the synthesis is not only to prepare powders in larger quantity but also to control the particulate size and morphology which was not feasible by the soft chemical auto-combustion technique. For this purpose, metal nitrate salt solutions with definite ratio of citric acid are prepared with variation in molarity with respect to the metal salt. The precursor solution is sprayed into the reaction zone of an indigenously made pyrolyser using a peristaltic pump and the two-fluid nozzle assembly. The inlet temperature of the spray unit is maintained at 400°C. The ashes generated as a result of the auto-combustion reaction is collected in cyclonic separators. A schematic of the spray pyrolysing process is provided in Fig. 6. For sufficient particulate growth during the pyrolysis reaction, batches are also formulated with a definite amount of addition of precalcined ashes derived from the previous pyrolysis into the precursor solution as the seeding agent. Details of the synthesis procedure, mathematical modelling related to the nucleation and growth process during *in situ* pyrolysis and the effectivity of such materials for the use as cathode functional layers (CFL) and cathode current collection

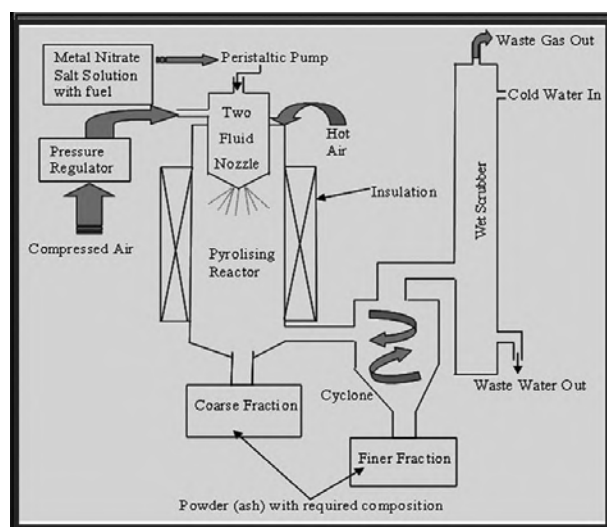


Fig. 6: Schematic for synthesis of cathode powder by spray pyrolysis route (Mukhopadhyay *et al.*, 2013a)

layer (CCCL) are reported in literature (Mukhopadhyay *et al.*, 2013a; Mukhopadhyay *et al.*, 2013b).

b) Anode

NiO-YSZ anode by liquid dispersion technique

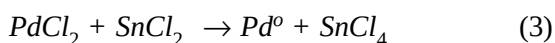
In order to have a homogeneous distribution of the Ni particles in the YSZ matrix of the Ni-8YSZ cermet, a liquid dispersion technique is adopted by CSIR-CGCRI to synthesize the precursor NiO-YSZ powder (Pratihari *et al.*, 1999). In this technique, 8YSZ powder was dispersed in a solution of nickel nitrate hexahydrate dissolved in methanol. The slurry was then heated under stirring and evaporated to dryness. The dried mass was calcined in air at 900°C for 2 h. The calcined powder thus obtained, was ground to fine powder which was used for further characterization and processing. The volume fraction of metallic nickel in the cermet powder varied from 0.1 to 0.6.

Ni-YSZ functional anode materials by electroless technique

Preparation of in-house Ni-YSZ anode powder using a novel electroless technique by CSIR-CGCRI involves two important steps:

- Initial sensitization of YSZ particulates by surface adsorption of metallic palladium (Pd^0)
- In situ* reduction of Ni^{2+} from its salt solution to metallic nickel (Ni^0) and its subsequent deposition onto sensitized YSZ powders.

For the sensitization process, the required amount of YSZ powder is added into a redox bath containing palladium chloride solution and stannous chloride solution where metallic palladium (Pd^0) is produced *in situ* by the equation as mentioned below:



Pd^0 formed due to such redox reaction, gets adsorbed on YSZ surface upon placing the redox bath in a high energy ultrasonifier. The sensitized bath was then kept to attain equilibrium for effective adsorption of Pd^0 and complete precipitation of sensitized YSZ powder. An electroless bath containing aqueous solution of nickel nitrate hexahydrate is prepared for the deposition of Ni particulates onto sensitized YSZ particulates. The reduction is carried out using hydrazine hydrate in an ammoniacal pH of ~ 10 . A process flow chart for the synthesis of Ni-YSZ cermet by electroless technique with YSZ sensitized by ball milling is reported in literature (Mukhopadhyay *et al.*, 2008) and shown in Fig. 7.

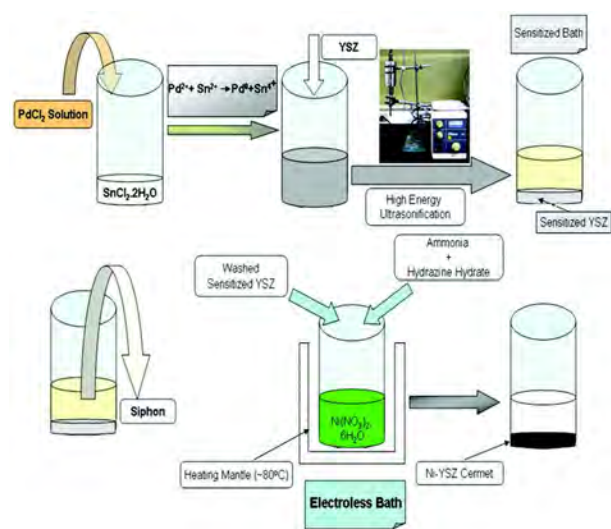


Fig. 7: Process flow chart for ball mill assisted electroless technique (Mukhopadhyay *et al.*, 2008)

c) Ceramic interconnect and protective coating:

Doped lanthanum chromite-based powders by soft chemical route

Efforts have been made by the group for the cost-effective synthesis of perovskite-based lanthanum chromites by doping alkaline earth metal ions or transition metal ions at 'A' site (La) and 'B' site (Cr), respectively. From the viewpoint of thermal expansion compatibility with other cell components, strontium is the most preferred element as a substituent in the La-site of LaCrO_3 -based perovskite, whereas calcium is responsible for enhancing the electrical conductivity when substituted in the same position. Both pure and doped lanthanum chromites have been developed using combustion synthesis technique wherein ammonium dichromate has been used as the source of chromium that has several advantages over the conventionally used chromium nitrate (Ghosh *et al.*, 2006; Ghosh *et al.*, 2007). Several compositions having the general formula $\text{La}_{1-x}\text{Ca}_x\text{Cr}_{1-y}\text{M}_y\text{O}_{3-\delta}$, where M is Al/Mg/Co, $0 \leq x \leq 0.3$ and $0 \leq y \leq 0.1$, have been prepared.

MnCo_2O_4 Based Spinel Powders by Soft Chemical Route

Nanocrystalline powders of $\text{MnCo}_2\text{O}_{4-\delta}$ spinel have been synthesized in-house by the group through combustion synthesis technique (Das Sharma *et al.*, 2011). In order to optimize the fuel to oxidant ratio the combustion reaction was carried out under varying fuel to nitrate ratio using different fuels viz., citric acid and glycine. While a single fuel (either glycine or citric acid) is used for maintaining stoichiometric fuel to nitrate ratio, a mixture of glycine and citric acid has been used for the fuel lean and fuel rich batches. Aqueous solutions of the metal nitrates, taken in a glass beaker in stoichiometric amounts, were mixed with the fuel (dissolved in water). The clear solution was then heated under stirring. The liquid turned viscous and began to set into a deep black gel which finally auto ignited to produce a light and fragile ash. The ash, thus obtained, was calcined between 600° and 750°C for 4 h in air to obtain the powder.

Electrolyte/Interlayer Materials

In the research on low temperature SOFC (LT-SOFC), CSIR-CGCRI, Kolkata has successfully synthesized gadolinium-doped ceria (CGO) using fuel-assisted combustion technique: 20 mole% gadolinium has been successfully doped into the ceria matrix. In order to reduce the sintering temperature for normal CGO, doped transition metal ion (Co^{2+}) has been co-doped with gadolinium during the synthesis (Dutta *et al.*, 2009b). This attempt is in conjunction with the development of co-fired CGO-based interlayer compatible with new class of lanthanum ferrite based mixed ionic and electronic conductor (MIEC) cathode.

Characterizations of Component Materials

a) Structural, Thermal and Microstructural Characterization

Cathode: Fig. 8a and b shows a typical X-ray diffractogram of the as-synthesized and calcined LSM powder, respectively. No significant differences in the diffractograms are observed for the powders prepared either by soft chemical route and spray pyrolysis (SP) techniques. Rietveld analysis of the same shows a phase purity of about 50% and 70% without any significant amount of LaMnO_3 and Mn_3O_4 as secondary phases for cathode synthesized either by soft chemical route (Pal *et al.*, 2007) or spray pyrolysis (Mukhopadhyay *et al.*, 2013b) respectively. After calcinations at 950°C , irrespective of precursor

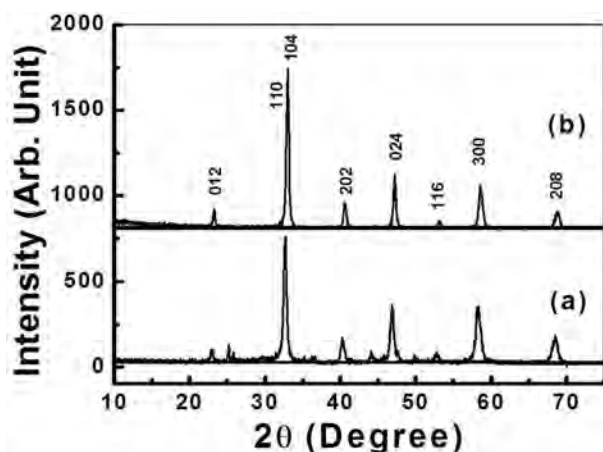


Fig. 8: X-ray diffractograms for LSM cathode prepared by soft chemical and SP routes (Dutta *et al.*, 2009a)

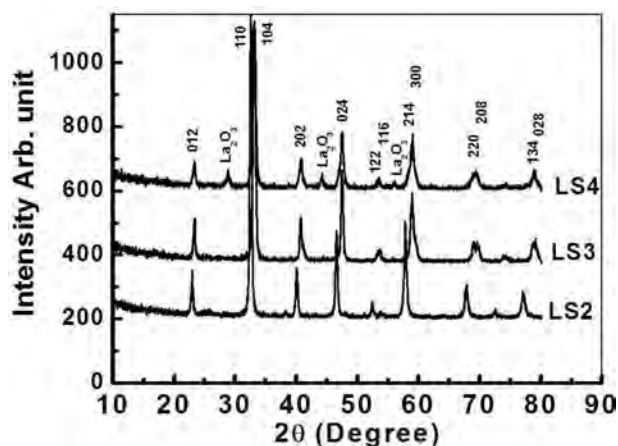


Fig. 9: X-ray diffractograms for LSCF cathode prepared by soft chemical and SP routes (Dutta *et al.*, 2009a)

solution concentration phase purity improves to more than 99% with the formation of a single-phase rhombohedral $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ (LS1). The calculated lattice parameters are found to be $a = b = 5.467\text{\AA}$ and $c = 13.494\text{\AA}$. The average crystallite size of the calcined LSM prepared by SP is found to be $\sim 30\text{ nm}$. Fig. 9 shows X-ray diffractograms of the various doped lanthanum ferrite based cathode powders (LS2, LS3 and LS4) calcined at 825°C . Phase analysis of the diffractograms reveals that LS2 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$) consists of a predominantly rhombohedral phase together with an orthorhombic phase. For LS3 ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$), on substitution of Fe with Co, the structure becomes completely rhombohedral with no other secondary phase. However, for LS4 ($\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$), along with the rhombohedral phase, presence of a small amount of La_2O_3 is observed. The average crystallite sizes are found to be 23, 24 and 19 nm for LS2, LS3 and LS4, respectively (Dutta *et al.*, 2009a).

Coefficients of thermal expansion (CTE) of these cathodes measured at 800°C are given in Table 3. It is observed that CTE increases with

Table 3: Coefficients of thermal expansion (CTE) (Dutta *et al.*, 2009a)

Cathodes	LS1	LS2	LS3	LS4
CTE ($\times 10^{-6}$) K^{-1} (sintered at 900°C)	12.99	10.11	19.26	18.31
CTE ($\times 10^{-6}$) K^{-1} (sintered at 1100°C)	13.05	12.11	19.32	19.23

increase in sintering temperature for all the cathode materials. However, CTE values are quite high enough for 'Co' doped samples (LS3 and LS4) even in the lowest sintering temperature (900°C) which is not at all compatible with other SOFC cell components.. However, electrochemical performances of single cells with doped ceria as an interlayer in between these cathodes and YSZ electrolyte do not show any microcracks which seems that this interlayer compensates some mismatch of CTE for these cathodes with YSZ electrolyte. A typical FESEM micrograph for LSM and LSCF powders prepared by soft chemical route calcined at 700°C is shown in Fig. 10. All the micrographs reveal agglomerated nature of the particles with an estimated size of ~50

nm (Dutta *et al.*, 2009a). FESEM micrograph for LSM cathode powders prepared by spray pyrolysis technique synthesized by *in situ* particulate growth is given in Fig. 11A and B (Mukhopadhyay *et al.*, 2013b).

Anode: Detailed XRD peak profile analysis suggests that on sintering at high temperature in air atmosphere, NiO starts diffusing into the zirconia grains in the samples prepared by solid state and liquid dispersion techniques (Pratihari *et al.*, 1999). This is reflected by the lattice parameter change of the Ni/YSZ cermets. The lattice parameters of YSZ and Ni/YSZ system have been determined from the profile fitting of the (400) reflection. The change in lattice parameters caused by dissolution of Ni^{2+} into cubic

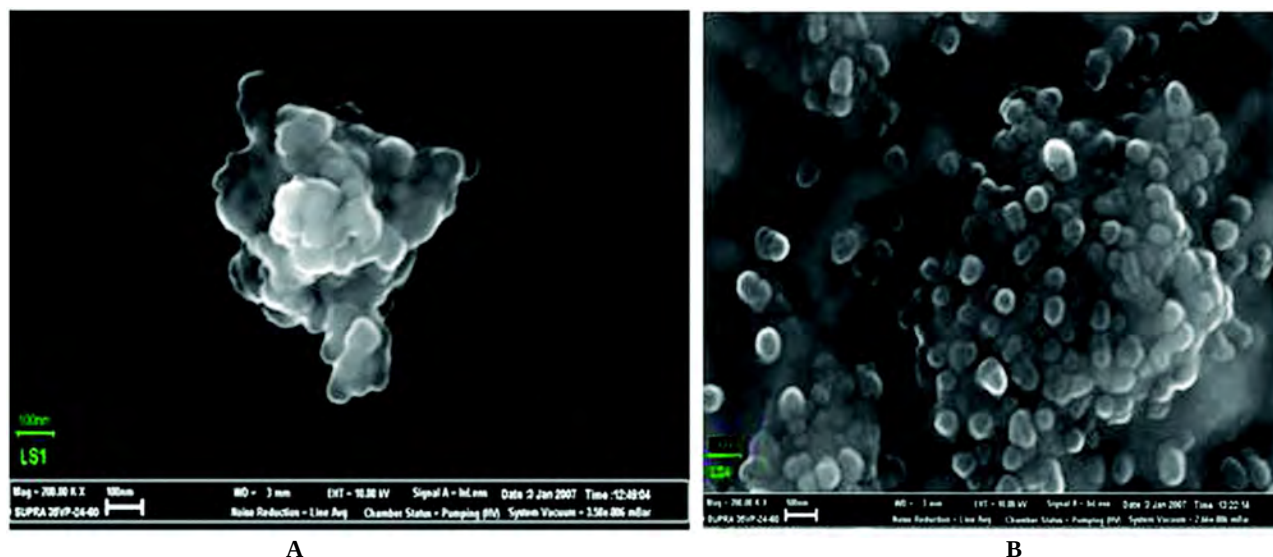


Fig.10: FESEM micrograph for LSM and LSCF prepared by soft chemical route (Dutta *et al.*, 2009a)

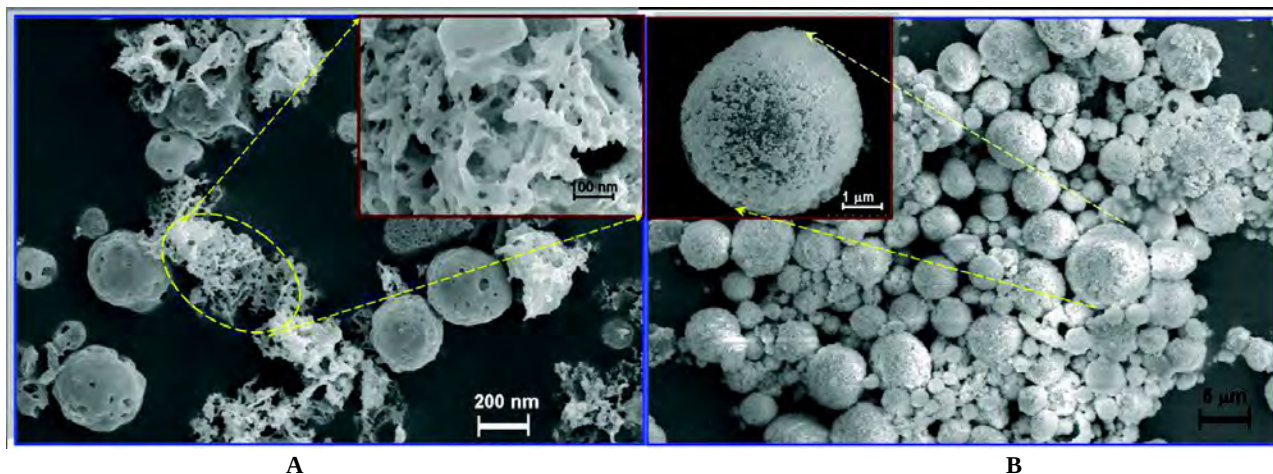


Fig. 11: FESEM micrograph SP-synthesized LSM prepared for (A) cathode functional layer and (B) current collection layer (Mukhopadhyay *et al.*, 2013b)

Table 4: Measured lattice parameters of YSZ and Ni/YSZ

Specimen	Lattice Parameter	Reliability Indices	
	a_c (Å)	R_p %	R_{WP} %
YSZ	5.4103 (3)	2.767	3.478
Ni/YSZ	5.0525 (3)	4.042	5.144

YSZ is shown in Table 4. The X-ray diffraction pattern of as-synthesized Ni-YSZ cermet prepared by electroless technique is shown along with the XRD pattern of precursor YSZ powder in Fig. 12.

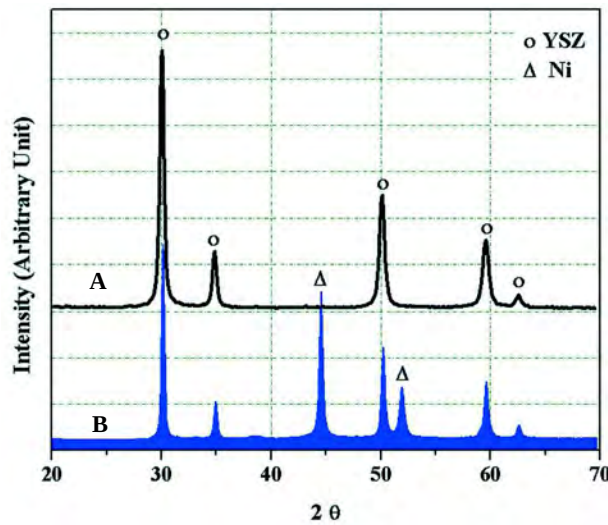


Fig. 12: X-ray diffraction pattern of: (A) precursor YSZ powder and (B) Ni-YSZ cermet prepared by electroless technique (Mukhopadhyay *et al.*, 2009)

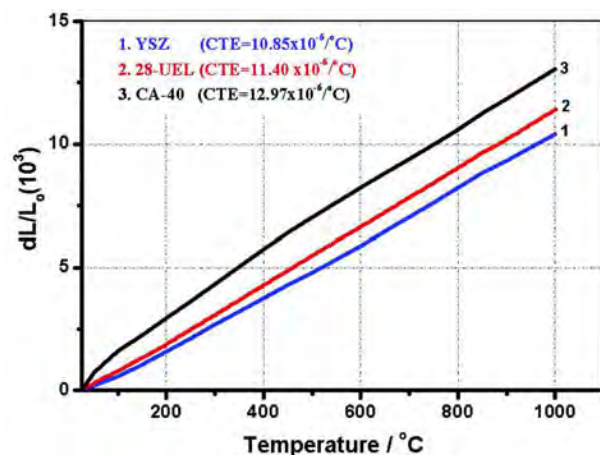


Fig. 13: Comparative plots for coefficients of thermal expansion (CTE) for electroless and conventional anode in conjunction with YSZ electrolyte

Comparison of Fig. 12A and B clearly indicates the formation of phase pure biphasic matrix of Ni-YSZ cermet prepared by electroless technique (Mukhopadhyay *et al.*, 2009). For application in high temperature ceramic fuel cell, the prepared anode happen should enable similar expansion behaviour with the adjacent YSZ electrolyte. Fig. 13 describes comparative expansion plots among electroless and conventional anode in conjugation with the YSZ electrolyte. It can be observed that, electroless anode having only 28 vol% is found to be thermally compatible with adjacent YSZ electrolyte ($10.85 \times 10^{-6} \text{ K}^{-1}$). Completely distinct microstructures are observed in the functional anodes prepared by electroless technique that forms core-shell microstructures with Ni in grain boundary region and YSZ in the core. In comparison, conventional anode prepared by solid state technique comprises uniform dispersion of Ni and YSZ phases. Fig. 14A and B show optical micrographs of the anode synthesized by electroless and solid state techniques (Mukhopadhyay *et al.*, 2008).

Ceramic Interconnect and Protective Coating

The developed LCR materials have been thoroughly analyzed using different techniques such as XRD, SEM-EDX, TEM and particle size analysis for their bulk characterization. Owing to very fine crystallite size (ranging from 10 to 50 nm) as observed from XRD and the high reactivity of the powders (surface area as high as $25 \text{ m}^2/\text{g}$), the sintering temperature reduces drastically (1300°C). TEM micrograph of LCR materials reveals particles as fine as 50-70 nm synthesized by soft chemical route (Ghosh *et al.*, 2006; Das Sharma *et al.*, 2011). Fig. 15 shows the X-ray diffractograms of phase pure MnCo_2O_4 spinel-based protective coating materials that are obtained upon calcination of the ash at a temperature as low as 650°C . It is observed that phase purity of $>99\%$ is achieved upon calcination of the powder at 650°C . Spinel phase of Mn_2CoO_4 is identified with crystallite size of $\sim 38 \text{ nm}$. Transmission electron microscopic (TEM) images of such calcined powders confirm the nanocrystallinity within the synthesized particulates. The size range of such synthesized powders is found to be within 40-50 nm (Fig. 16), (Das Sharma *et al.*, 2011) Upon consolidation, it is possible to sinter the

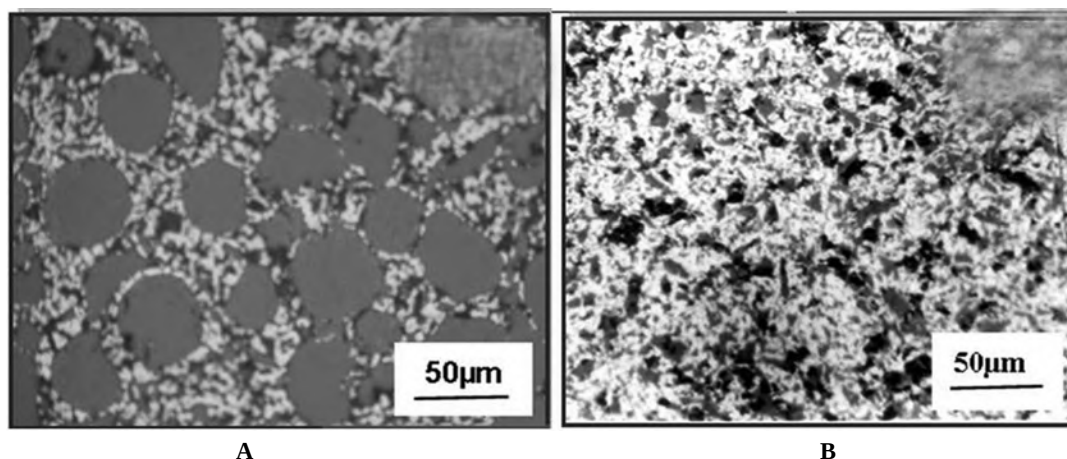


Fig. 14: Optical micrographs for anode synthesized by (A) electroless and (B) solid state techniques (Mukhopadhyay *et al.*, 2008)

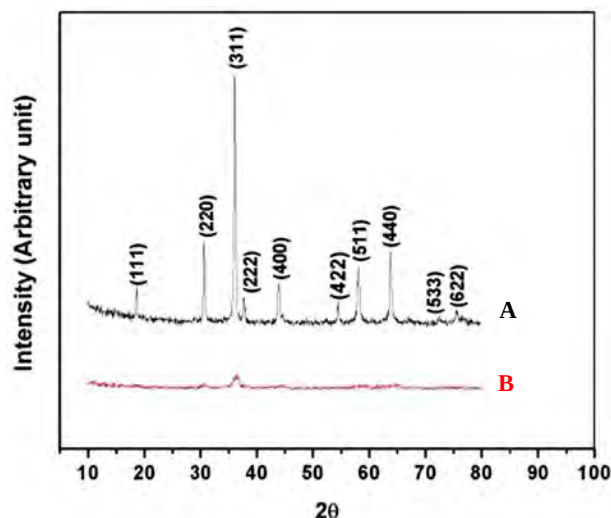


Fig.15: X-ray diffraction pattern of (A) as-synthesized and (B) calcined powder (700°C/4 h) of $\text{MnCo}_2\text{O}_{4-\delta}$ Spinel (Das Sharma *et al.*, 2011)

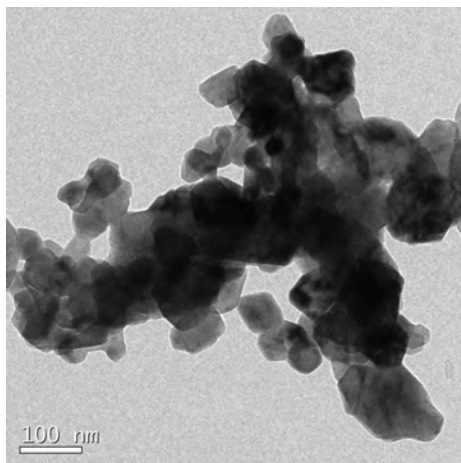


Fig. 16: TEM image of $\text{MnCo}_2\text{O}_{4-\delta}$ calcined powder (Das Sharma *et al.*, 2011)

bulk samples at a temperature of only 1100°C with a density more than 95% of theoretical value. Linear thermal expansion behaviour with an average coefficient of thermal expansion (CTE) of $13.1 \times 10^{-6} \text{ K}^{-1}$ (from 30-1100°C) is obtained. Thus, the CTE is found to be quite close to that of commonly used metallic interconnects such as Crofer22APU (CTE: $\sim 12 \times 10^{-6} \text{ K}^{-1}$).

Electrolyte/Interlayer materials

Due to the nanocrystallinity of the synthesized Co-doped CGO, it has been possible to reduce the sintering temperature of these electrolytes to 1100°C. The sintered microstructure of the Co-doped CGO along with the synthesized powder is given in Fig. 17.

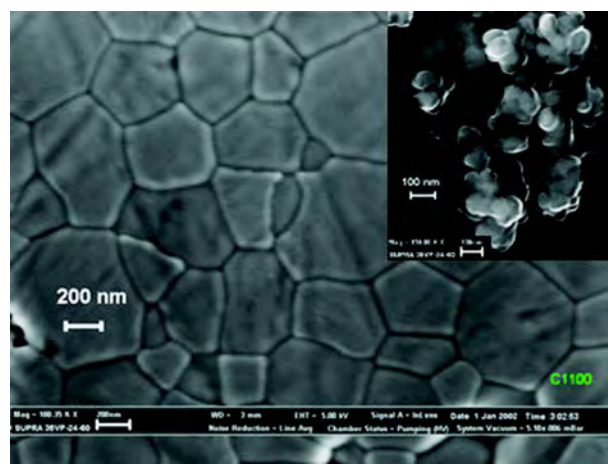


Fig. 17: FESEM of sintered Co-doped CGO with nanocrystalline powders of calcined powder (inset) (Dutta *et al.*, 2009b)

b) DC Electrical Conductivity Characterization

Cathode: The electrical conductivity of LSM (LS1), and doped lanthanum ferrites (LS2, LS3 and LS4) materials synthesized by soft chemical route are measured in the sintered conditions (Fig. 18). For all the materials except LS1, the increase of conductivity is significant. In case of LS1 and LS3, conductivity decreases with the increase of temperature from 500°C to 900°C in all the samples sintered at 900–1100°C showing a metallic behaviour (Dutta *et al.*, 2009a). For spray pyrolysed LSM cathode, similar trend of linear semiconducting type behaviour within the measurement temperature range of 500–800°C is observed. Smaller particulates having average particulate size of ~0.24 μm for cathode functional layer promote sintering at a lower temperature and results in higher electrical conduction of 195 S cm^{-1} at 800°C having open porosity <2% when sintered at 1100°C (Mukhopadhyay *et al.*, 2013b).

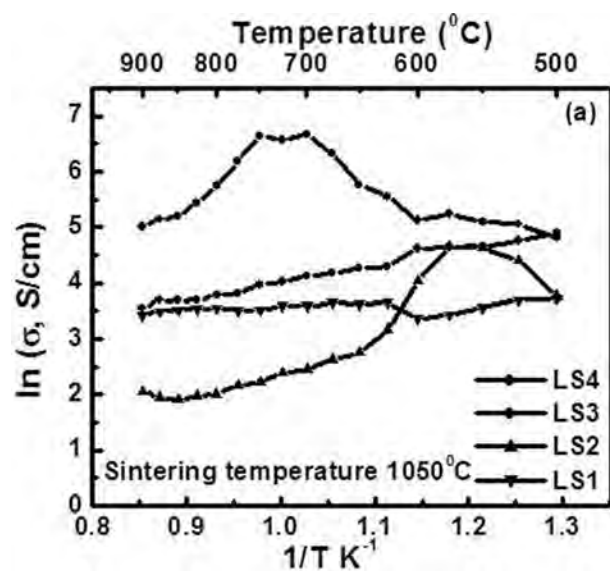


Fig. 18: Electrical conductivities for perovskite cathodes (Dutta *et al.*, 2009a)

Anode: Fig. 19 shows the comparative electrical conductivity values at 800°C of SOFC functional anodes (prepared at transient and non-transient equilibrated sensitized bath) with conventionally prepared anode. The conductivity percolation threshold is brought down to ~28 vol% of Ni in

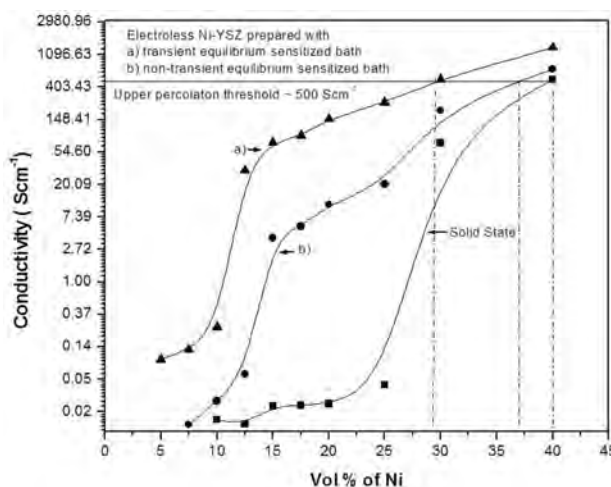


Fig. 19: Electrical conductivity percolation plot for anodes prepared by various techniques (Mukhopadhyay *et al.*, 2008)

functional anode prepared with transient equilibrated sensitized bath in comparison to ~40 vol% Ni for conventionally prepared samples. Reduction in metallic phase in the cermet not only helps in matching the thermal coefficient of the cell components but also reduces the changes of Ni coarsening due to long-term operation of cells (Mukhopadhyay *et al.*, 2008; Mukhopadhyay *et al.*, 2007).

Ceramic Interconnect and Protective Coating

For LCR materials prepared by combustion synthesis, a dramatic improvement in densification (nearly theoretical density) is observed for aluminum substitution, when sintered at as low a temperature as 1300°C. Depending on the substituent, the electrical conductivities of the sintered samples in air, at 1000°C, were found to be in the range of 10–45 S cm^{-1} , and are more than that of the values required for SOFC application (Ghosh *et al.*, 2006). Four probe electrical conductivity measurements for the developed spinel-based materials show a high enough conductivity (>100 S cm^{-1} at 800°C) to be suitable for protective coating application. Semiconducting behaviour with average activation energies of 0.25 and 0.33 eV, respectively is obtained for the various redox systems (i.e. fuel lean and fuel rich) (Das Sharma *et al.*, 2011).

Electrolyte/interlayer Materials

Doping of metallic cobalt in CGO helps in reducing the sintering temperature to $\sim 1100^\circ\text{C}$ which results in co-sintering of Co-CGO and lanthanum ferrite or cobaltite based cathodes. A reasonably high ionic conductivity of $\sim 0.01 \text{ S}\cdot\text{cm}^{-1}$ is achieved at a temperature $\sim 750^\circ\text{C}$. Arrhenius plot of the electrical conductivity for Co-doped CGO as a function of temperature is shown in Fig. 20. Reasonably low activation energies of 0.47 and 0.79 eV are found for the material when sintered at 900°C . The same is found to be 0.43 and 0.75 eV for the materials sintered at 1100°C .

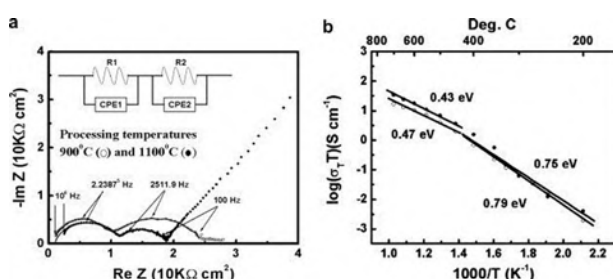


Fig. 20: Temperature dependent electrical conductivity for Co-doped CGO (Dutta *et al.*, 2009b)

c) Electrochemical Impedance Spectroscopic Studies

Cathode: Spray pyrolysed LSM cathode is characterized by impedance spectroscopic studies using symmetric cell configuration onto YSZ electrolyte substrate. Associated polarizations of symmetric cell fabricated by combining the cathode current collection layer (CCCL) and cathode functional layer (CFL) having variable micro to nano porous particulates is found to be the lowest. Fig. 21 shows the impedance spectra of such symmetric cell in the temperature range of 700–800°C. It is also vivid from the impedance spectra that the incorporation of CCCL reduces the diffusion polarization occurring at the lower frequency, thereby enhancing the formation and dissociation of peroxide ion observed at the middle frequency range of the applied AC field (Mukhopadhyay *et al.*, 2013b). In addition, the mutual union of CFL and CCCL tends to reduce the charge transfer polarization through proper inter-connectivity between YSZ and YSZ ionic phases, diffusion

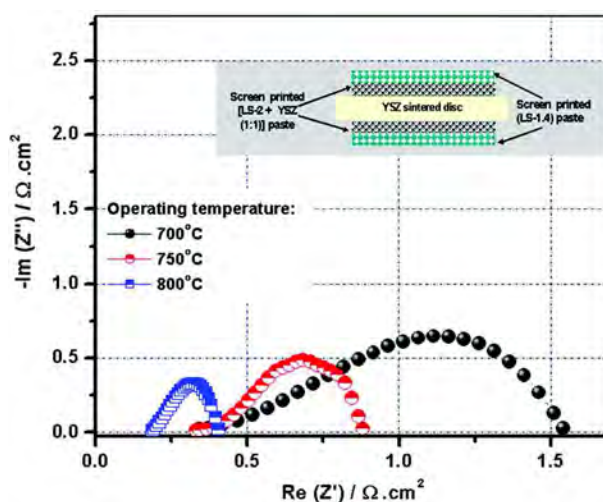


Fig. 21: Impedance spectroscopy of SP-synthesized cathode (Mukhopadhyay *et al.*, 2013b)

polarization of molecular oxygen and polarization related to formation of oxide ion. Such a composite cathode is found effective having a total cathode thickness of $\sim 50 \text{ nm}$ with minimum polarization resistance of $\sim 0.18 \text{ W}\cdot\text{cm}^2$ at 800°C (Mukhopadhyay *et al.*, 2013b).

Anode: Electroless anode in the form of the thin anode active layer (AAL) having dense microstructure and higher charge conduction possesses better electrocatalytic activity at the anode/electrolyte interface and thereby causes lesser charge transfer polarization (Mukhopadhyay *et al.*, 2013c). Additionally, thinner electroless AAL in conjugation

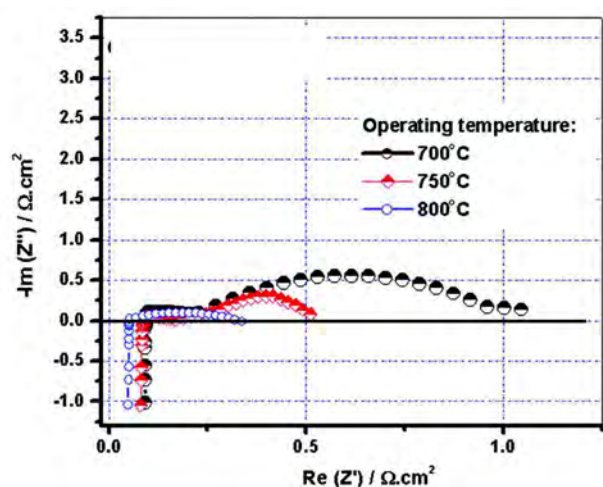


Fig. 22: Impedance spectroscopy of cell with electroless Ni as AAL (Mukhopadhyay *et al.*, 2013c)

with conventional anode support helps in gas diffusion in the porous conventional anode layer, which enumerates lower concentration polarization. Anode of such configuration also helps in lowering the resistance of electronic flow path by minimizing the intra anodic stratum (Mukhopadhyay *et al.*, 2011). Consequently, the single cell with 32 vol% Ni in AAL and conventional anode cermet exhibits least polarizations ($\sim 0.3 \text{ W-cm}^2$) as observed from the impedance spectra (Fig. 22).

Single Cell Fabrication

a) Fabrication of Anode-supported Half-cell by Tape Casting and Lamination Technique

For the development of anode-supported single cells, the major technical challenge involves fabricating a dense and gas-tight 8 mol% YSZ electrolyte layer of thickness $50 \mu\text{m}$ or less that should be well-adhered to the porous NiO-YSZ (anode) substrate so as to minimize the interfacial polarization. Under the NMITLI programme, simple and up-scalable techniques such as tape casting and screen printing have been used to fabricate anode-supported single cells of dimensions up to $10 \text{ cm} \times 10 \text{ cm} \times 1.5 \text{ mm}$ (Basu *et al.*, 2008; Basu *et al.*, 2010). The whole fabrication process is shown schematically in Fig. 23.



Fig. 23: Flow chart of the single cell fabrication (Basu *et al.*, 2008)

A cost-effective and up-scalable processing technique viz., tape casting has been used to fabricate a dense YSZ electrolyte layer on porous anode support (40 vol% Ni + 60 vol% YSZ). The production of ceramic tapes by this process requires the use of significant amounts of organic compounds (e.g., solvents, binders, plasticizers, dispersing agents, etc.). The mechanical and physical characteristics of the green tapes are very important for further processing and the final properties of the material.

b) Screen Printing of Cathode Layers for Single Cell Fabrication

Processing parameters have also been optimized for screen printing of LSM-based cathode functional layer (CFL) and cathode current collector layer (CL) onto the co-sintered flat dense electrolyte surface of the half-cell to produce SOFC single cell. Utilizing the optimized parameters, large numbers of single cells of dimensions $5 \text{ cm} \times 5 \text{ cm} \times 1.5 \text{ mm}$ and $10 \text{ cm} \times 10 \text{ cm} \times 1.5 \text{ mm}$ were fabricated, photographs of some of which are shown in Fig. 24. The right kind of microstructure is obtained in the developed cells (Fig. 25) with $\sim 10 \text{ mm}$ thin, gas-tight YSZ electrolyte sandwiched between a porous anode (Ni-YSZ) support on one side and a LSM-based layer

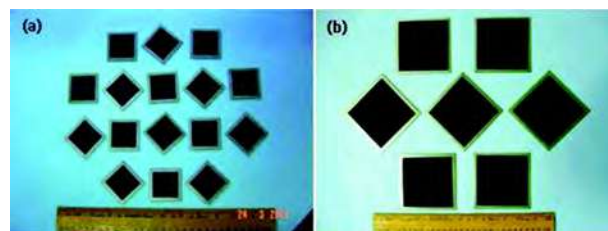


Fig. 24: Fabricated single cells: (a) $5 \text{ cm} \times 5 \text{ cm}$ and (b) $10 \text{ cm} \times 10 \text{ cm}$ (Basu *et al.*, 2008)

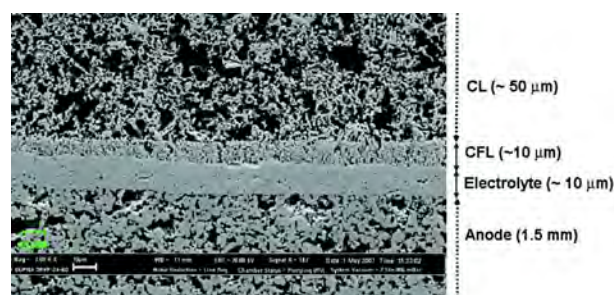


Fig. 25: SEM micrograph of a cross-section of the developed single cell (Basu *et al.*, 2008)

(comprising ~10 mm CFL and a ~50 mm porous CL layer) on the other side.

Electrochemical Performance Evaluation of Single Cells

a) Electrolyte Thickness Dependent Cell Performance

Table 5 shows the comparative electrochemical performance of 5 cm × 5 cm single cells having different YSZ thicknesses (20–40 μm) at 800°C at 0.7V. As expected, the performance of the cells improves with a decreasing electrolyte thickness and for the optimized thickness of 20 μm, a high current density of 1.35 A/cm² is achieved. The electrochemical performance curves for the coupon cells as well as the 5 cm × 5 cm cells (having optimized YSZ thickness of 20 μm) are shown in Fig. 26. It can be seen from Fig. 26 that for both the coupon cell (dia ~15 mm) and square cells (5 cm × 5 cm), current-voltage (I-V) and current-power density (I-P) are similar in nature. For a cell voltage of 0.7V, the current density and power density for 5 cm × 5 cm cell is found to be 1.35 A/cm² and 0.94 W/cm² respectively;

Table 5: Electrochemical performance of SOFC single cells (at 800°C, 0.7 V) with variable YSZ thickness (measured at Forschungszentrum, Jülich)

Electrolyte thickness (μm)	Current density (A/cm ²)	Power density (W/cm ²)
20	1.35	0.95
30	1.2	0.84
40	1.0	0.70

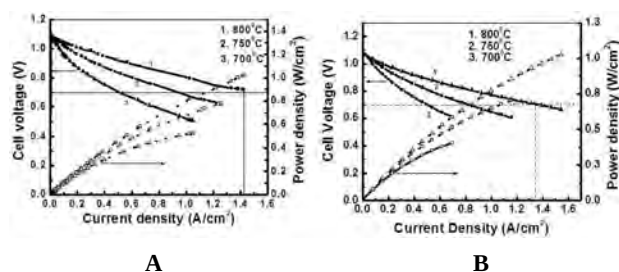


Fig. 26: Electrochemical performance of single cells at different operating temperatures: (A) coupon cell (dia ~15 mm) (B) 5 cm × 5 cm square cell (thickness for each cell: 1.5 mm) (Basu et al., 2008)

while for the coupon cell the values are 1.42 A/cm² and 1.0 W/cm², respectively. Thus, the cell performances are size-independent, establishing the fact that the processing technology followed is up-scalable (Basu et al., 2007; Basu et al., 2008).

b) Performance Evaluation with Doped Lanthanum Manganite Synthesized by Soft Chemical Route and by Spray Pyrolysis Techniques

Fig. 27A shows a typical performance of SOFC consisting of cathode functional and current collection layer (CFL and CCCL) synthesized by conventional SP route [cell configuration: Ni-YSZ/YSZ/CFL (conventional SP-synthesized LSM + YSZ)/CCCL (conventional SP-synthesized LSM)]. Fig. 27B exhibits the performance of SOFC fabricated using optimized spray pyrolysed LSM both for CFL and CCCL. Significant enhancement in single cell performance is observed for the single cells with cathode synthesized by spray pyrolysis technique. Thus, at 0.7 V and 800°C, much higher current density of 3.2 A.cm⁻² is observed for single cells with cathodes synthesized by spray pyrolysis technique compared to single cells having cathode synthesized by soft chemical route (2.0 A.cm⁻²) (Mukhopadhyay et al., 2013b). Furthermore, the induced functionality within SP-synthesized cathode layers (CFL and CCCL) is well-justified from the reduced area specific resistance (ASR) of ~109 mW.cm² at 800°C for cells with SP-synthesized cathode compared to that of 184.8 mW.cm² at 800°C for cells having cathodes prepared by soft chemical route.

c) Single Cell Performance with Lanthanum Ferrite Based Cathodes Synthesized by Soft Chemical Route

The electrochemical cell performance using optimized lanthanum ferrite as cathode La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (LS4) is conducted in the temperature range of 700–800°C. The approximate thickness of CGO coating was 10 μm and that of LS4 cathode was 50 μm after the heat treatment. The CGO coating was sintered at 1200°C for 6 h while LS4 cathode coating was finally fired at 1100°C for 4 h. The cell performance increases with the increase of operating temperature and at

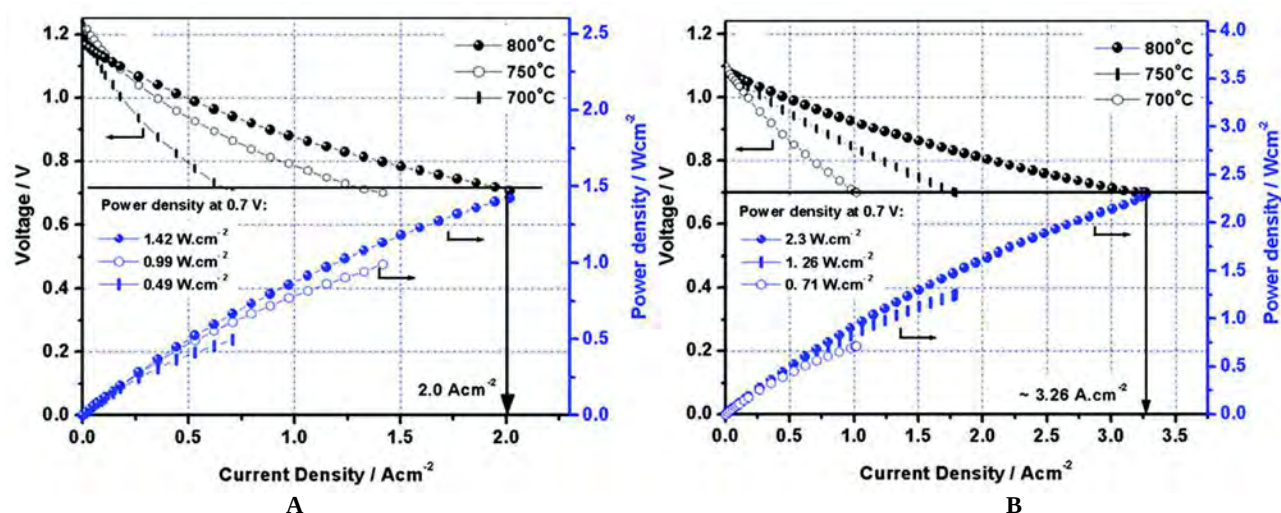


Fig. 27: Electrochemical performance of single cells at with cathode prepared by: (A) soft chemical route and (B) spray pyrolysis techniques (Mukhopadhyay *et al.*, 2013b)

800°C the current density is ~ 1.7 A/cm² at 0.7 cell voltage (Dutta *et al.*, 2009a). The I-V characteristics at different temperatures clearly indicate that the activation polarization exists (below 100 mA/cm² cell current) i.e., at lower temperature oxygen reduction reaction at the cathode/electrolyte interface is kinetically limited. Further systematic research on the optimization of cell fabrication, especially the cathode firing temperature and interlayer composition has been in progress.

High-temperature Glass-based Sealant

For planar SOFC stacks, gas-tight seals must be applied along the edges of each cell and metallic interconnect plates in order to avoid intermixing of fuel gas (on anode side) and air (on cathode side). For such a design, two types of sealing viz., metal-metal and ceramic-metal, are of particular importance. The seals must be stable in a wide range of oxygen partial pressure (in air and fuel) and be chemically compatible with adjoining cell components, while minimizing thermal stresses during high-temperature operation. They must also have high electrical resistivity to avoid short circuiting between different layers of the stack. Generally, glass and glass-ceramic-based sealants meet most of these requirements and therefore, have found widespread application as high temperature sealants. However, these sealants are required to be developed indigenously as they are not

easily available in the market. Hence, major emphasis was given to development of glass-based sealants for planar anode-supported SOFC stack application. At CSIR-CGCRI, efforts have been made towards the development of several glass-based sealing materials based on BaO-Al₂O₃-SiO₂ (BAS), BaO-CaO-Al₂O₃-SiO₂ (BCAS), MgO-Al₂O₃-SiO₂ (MAS) and MgO-BaO-Al₂O₃-SiO₂ (BMAS) systems and their extensive characterization for ultimate use as sealant for SOFC (Ghosh *et al.*, 2008a; Ghosh *et al.*, 2008b; Ghosh *et al.*, 2010). To estimate the applicability of these glasses as sealants, their thermal properties (e.g., glass transition temperature T_g , coefficient of thermal expansion, CTE and softening temperature T_s), crystallization behaviour, electrical resistivities, microstructure upon different heat-treatment schedule and the overall bonding characteristics with ceramic electrolyte (YSZ) and high chromium ferritic steel (e.g., Crofer 22APU) have been investigated. Fig. 28 shows a complete process flow chart of the detailed sample preparation of the glass-based sealants and the different characterizations as performed using such samples.

The prime requirement of matching the CTE both with the electrolyte and interconnect have been achieved by tailoring the compositions in the BCAS and BAS systems. The compositions have been tailor made in such a way that even after prolonged heat-

treatment at the SOFC operating temperature (800°C), the resultant glass-ceramics have compatible CTE with YSZ and the interconnects. Table 6 shows the list of different systems and compositional ranges extensively studied along with their physical properties in order to find out the best possible system and compositions.

A distinctly new approach of “*bi-layered sealing*” was introduced for the first time during this investigation which has been successfully applied to make crack-free joints between the metal-glass-YSZ interfaces (Ghosh *et al.*, 2008b, Ghosh *et al.*, 2008c) (Fig. 29). In addition, the extent of chemical interaction during long-term heat-treatment of the developed sealants with the metal (Crofer 22APU) and the ceramic interconnects, particularly under the oxidizing environment, has been investigated in detail. Electrical conductivity of the sealants has also been investigated under sandwiched condition between two metal plates, especially under the oxidizing environment. Gas tightness of the sealants has been assessed by performing leak/permeability test in presence of helium using an indigenously fabricated helium leak test set-up. In order to lower the extent of chemical interaction between the sealant and adjoining SOFC components, the Crofer22APU interconnect in particular, a novel glass sealant within the BaO-La₂O₃-SiO₂ (BLS) system with relatively low content of BaO has been developed (Ghosh *et al.*, 2008c). These sealants were found to be significantly effective in reducing the chemical interaction while joining with the metallic and ceramic interconnects. Using the developed sealants, near theoretical open circuit voltages (OCV)

of ~1.15 V per cell have been observed during stack testing at 800°C without any appreciable degradation of the OCV, which confirmed the perfect hermetic sealing during such experiments.

Fabrication and Demonstration of Short SOFC Stack

The overall voltage output from a single cell is very low which is neither sufficient to use in any practical device nor is the same significant for use as stationary power. Therefore, several numbers of such single cells need to be stacked thorough interconnects for voltage build up. For intermediate temperature SOFC (IT-SOFC) operating in the range of 700-850°C, ferritic steel based metallic interconnects (Crofer 22 APU) are widely used. CGCRI's SOFC stack is based on counter flow design of the fuel and the air/oxidant. Based on this design, different stack components viz. cell holders, bi-polar and current collector plates have been fabricated with ferritic steel (Crofer 22 APU). Using the indigenously developed 10 cm × 10 cm × 1.5 mm single cells, glass-based high temperature sealants and metallic stack components, several numbers of short SOFC stacks (up to 10-cell level) have been fabricated and tested for their performance evaluation using hydrogen as fuel and air/oxygen as oxidant. At 800°C, the open circuit voltage (OCV) per cell is ~1.1 V which is quite close to the theoretical value (1.15 V). A characteristic 3-cells stack result under different constant current loads of 2.5 Amp, 5 Amp and 7 Amp is shown in Fig. 30A. Demonstration of 10-cell stack resulted in a total power output of ~100 W. Thus, CSIR-CGCRI has successfully

Table 6: Different systems and compositions range for high-temperature glass-based sealants

System	Compositions in mol%	Minor additives (<5 mole %)	Thermal properties			
			T _g (°C)	T _s (°C)	T _c (°C)	CTE (x 10 ⁻⁶ /K)
MAS	MgO:18-20, Al ₂ O ₃ :10-15, La ₂ O ₃ :10-15, SiO ₂ :10-30	B ₂ O ₃ ZnO Co ₃ O ₄ La ₂ O ₃ TiO ₂ ZrO ₂	635-725	670-780	765-825	8-9
BMS	BaO:5-30, MgO:16-20, SiO ₂ :5-50		560-680	625-710	680-750	9.5-11
BAS	BaO:35-40, Al ₂ O ₃ :8-10, SiO ₂ :30-40		610-630	660-680	735-760	10-11
BCAS	BaO:28-35, CaO:5-15, Al ₂ O ₃ :0-6, SiO ₂ :8-30		600-665	665-700	730-780	9.5-12.5

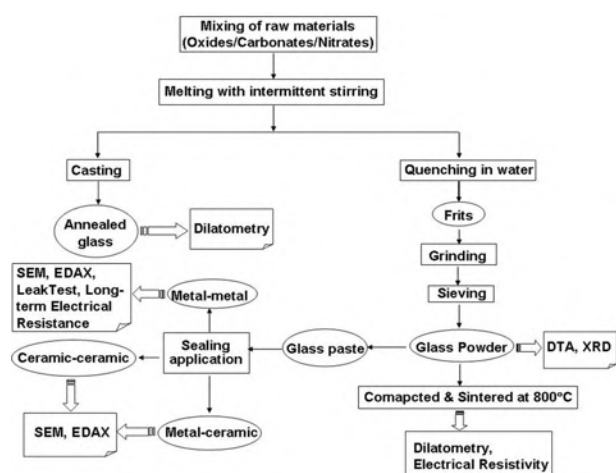


Fig. 28: Schematic of sample preparations and characterizations (Ghosh *et al.*, 2008b)

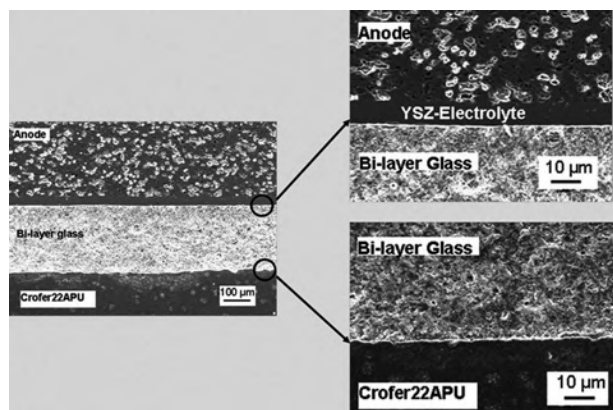


Fig. 29: SEM of polished cross-section of Crofer22APU-YSZ samples sealed at 850°C/1 h, using bilayer glass; closure view of the YSZ-glass interface (top side) and glass-Crofer22APU interface (bottom side) (Ghosh *et al.*, 2008b)

demonstrated working of SOFC stacks for the first time in India. Fig. 30B shows a close view of the CSIR-CGCRI-developed 10-cell SOFC stack.

Material and Design Challenges and Commercialization of SOFC Technology

The fuel cell component materials face significant challenges for redox cyclability with respect to conventional anode materials such as Ni-YSZ, cathode degradation, especially for doped lanthanum cobalt ferrite or barium cobalt ferrite based MIEC compositions under high current during long-term operation. Apart from the cathode and anode, owing

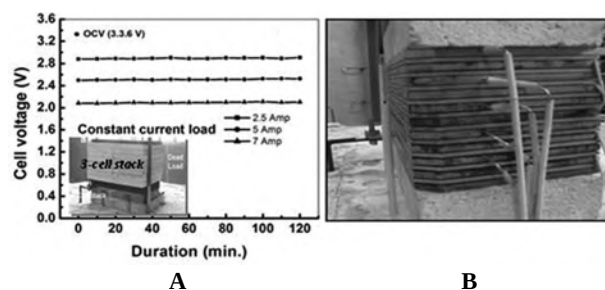


Fig. 30: (A) Stack testing under constant current load (3-cell stack) and (B) CSIR-CGCRI developed 10-cell SOFC stack

to processing defects, formation of hot spots in the impervious YSZ-based electrolyte layers may create internal crossover of fuel and oxidant during long-term operation under electrical load. These cause cell and stack degradation after a reasonable period of time and percentage of degradation are found to be higher based on the materials composition and microstructural aspects. Evaporation of Cr_2O_3 vapour from either LaCrO_3 -based or commercial SS 430 grade ferritic steel also causes significant deterioration in the cathode by blocking active sites for the electrochemical reaction (Casteel *et al.*, 2009; Ghosh *et al.*, 2006). High-temperature glass-based sealant also faces significant challenges with respect to its thermal cyclability and long-term endurance under the SOFC operating conditions. The application of these high-temperature glass-based sealants also imposes significant problems while developing SOFCs in planar design in the level of several kW. While power density of the planar SOFC design overpowers the same for the other famous tubular design, the latter faces challenges for fabrication of longer tubular support with stricter process optimization for depositing thin impervious electrolyte film onto a large dimension substrate.

In the global scenario, the research on SOFC has reached a reasonably mature stage, particularly in advanced countries such as USA, Canada, Germany, UK, Denmark, Australia, Japan, etc., where commercialization of the technology seems to be viable through prototype demonstration as well as installation of systems, particularly for residential and transport applications. However, high costs, issues

related to reliability and degradation during continuous operation are some of the major bottlenecks that are preventing commercialization of SOFC technology and need to be resolved. The technology development so far has been realized through major programmes such as SECA (USA), Framework programme on SOFC (Europe), NEDO (Japan), etc. One of the key features of all such programmes has been the strong industry-institute participation with clear-cut objectives and deliverables. As an outcome of these programmes, several industries have enhanced their capabilities to develop the technology. An excellent review on the present status of these developments is available in a recent report on this subject (McPhail *et al.*, 2013).

Conclusions and Future Direction

Ceramic fuel cell commonly known as solid oxide fuel cell (SOFC) is one of the most promising technologies emerging out as an alternative source for generating power in an environmentally benign manner. The technology is in an advanced stage of development in many of the developed nations of the world such as USA, Germany, Australia, Canada, Japan, UK, etc. and is on the verge of commercialization after successful demonstration of prototype stacks and systems of different capacity (1-10 kW level). However, in India, research on high temperature ceramic fuel cells was initiated in the early 90s with pioneering contribution from CSIR-Central Glass & Ceramic Research Institute (CSIR-CGCRI), Kolkata.

Till date, most of the other research organizations/academic institutions engaged in SOFC research in India have focused on material development. At CSIR-CGCRI, an attempt is being made to develop an indigenous technology that is based on the planar anode-supported design for a national project under CSIR-NMITLI programmes. The research in this area so far has led to the successful development of planar anode-supported single cells of dimension 10 cm x 10 cm x 1.5 mm, suitable high-temperature glass-based sealants along with design and fabrication of ferritic steel (Crofer 22APU) interconnects with various flow fields for reactant gases. Using the indigenously developed cells, high temperature sealants and fabricated metallic interconnects; demonstration of working SOFC stacks has successfully been made for the first time in our country.

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*Review Article***Proton Exchange Membrane Fuel Cell Technology: India's Perspective**

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India, with over a billion people and a growing economy, is one of the countries, which will shape the energy supply and demand scenario in the 21st century. With high growth rates of the Indian economy, energy needs are also growing rapidly. A growing global concern over environmental issues and the need for energy security of the country requires India to pursue all options for diversification of fuels and energy sources. In the coming decades, hydrogen is poised to become a major component in India's energy mix for meeting the growing energy needs of the economy. India's national energy policies acknowledge hydrogen as a promising energy storage option, which will provide clean and efficient energy to meet the requirements in power and transportation sectors. A National Hydrogen Energy Roadmap, setup by National Hydrogen Energy Board, India for the development of hydrogen energy related technologies including fuel cells, has been covered in detail. The most promising of all fuel cell technologies developed is proton exchange membrane fuel cell (PEMFC), which operates at a lower temperature. The variant of PEMFC is direct alcohol fuel cell (DAFC), which is direct fed with methanol and ethanol as fuel instead of hydrogen. The road map is an industry-driven planning process that offers long-term hydrogen energy based solutions to India's energy sector. A section of this article provides detailed information about the R&D activities on PEMFC, DAFC and high temperature PEMFC in India. This covers developmental work carried out by the government research institutes, universities and private sector organizations. A majority of organizations are involved in fundamental research, for e.g. polymer membranes electrolyte, anode and cathode catalysts and membrane electrode assembly and hydrogen storage with very few involved in manufacturing and technology. Some institutions are involved in more application-oriented research such as stack and balance of plant development and fuel cell bus demonstration program. The market potential for fuel cell based applications in India is discussed at the end. India, with a growing economy and a suitable national energy policy is a huge prospective market for fuel cell based applications. Stationary markets for fuel cells in India range from backup power for residential applications to captive power generation for industrial applications. This article includes discussion on potential of fuel cell based power generation in luxury hotels, process industries, chlor-alkali and dairy industry and telecommunication and information technology industry. Fuel cell applications in the Indian automotive sector are of great prospects. Initial penetration in this sector will be in buses due to their centralized operation, maintenance and refuelling. Light duty vehicle market also shows potential for fuel cell technology implementation. India has a large number of organizations in the light duty vehicle category, i.e. passenger car sector.

Keywords: Energy Scenario; Hydrogen Energy; Fuel Cell; Proton Exchange Membrane Electrolyte; Anode; Cathode and Catalyst; Fuel Cell Application

Introduction

In recent years, global energy shortage and ecological pollution problems have created opportunities for fuel cells to replace the existing technologies in a variety of applications. Some common areas of application

of fuel cells include power for stationary, portable and transport applications. They are used to provide electricity and heat in large stationary applications. They are also used to provide power in areas that are difficult to serve by the national grid. In sectors such

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as telecom, they find use in providing backup power. Another promising area of application is their use in portable devices such as mobile phones. Due to their light weight and higher operating times, they are seen as a good alternative to solid batteries. Their application in transport finds its roots in their ability to meet the stringent emission norms. As far as the world fuel cell industry is concerned, most of the activities are concentrated in regions of North America, Europe, Japan and Korea. The areas of expertise range from R&D to component manufacture and system integration. Fundamental and applied R&D is carried out in universities as well as by commercial players. A large number of corporations are involved in component manufacturing and system integration. The governments in these regions provide strong funding for the development of the fuel cell sector.

India's fuel cell industry is not quite developed as compared to the above mentioned regions. Even then, it can be considered a very important and emerging market. An economy growing at a fast pace and a country in need of energy to sustain the growth are the factors that strengthen India's position as a prospective market for fuel cells. New national energy policies of the country that promote the growth of hydrogen and fuel cell technologies add to the market potential of fuel cells in India.

India – A Growing Economy

India is the second most populous country in the world and the fourth largest economy by purchasing power parity. India has seen dramatic economic growth over the last decade with GDP growth rates going as high as 9% in 2007-08 (Fig. 1). Although due to the global economic slowdown, Indian economy has also slowed (GDP growth rate of about 6.1 %) down from its high performance; it was one of the few economies where impact of this downturn was minimum. India's growth rate was among the highest in the world along with China.

This high growth rate essentially signifies upliftment of large number of population from poverty to India's growing middle class. This growing middle class is causing a consumer boom in Indian market which is contributing to India's growth.

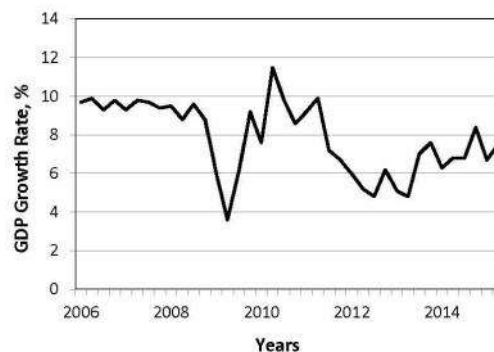


Fig. 1: India's GDP growth rate over the years (WWW.TRADINGECONOMICS.COM | MINISTRY OF STATISTICS AND PROGRAMME IMPLEMENTATION (MOSPI))

Agricultural sector still employs about 60% of the population. A growing service industry is the largest contributor to India's GDP followed by industrial and agricultural sectors. Despite robust economic growth, India continues to face many major problems. One of the major challenges that India is facing to sustain its high levels of economic growth is lack of an effective infrastructure that can support its large population. A provision for reliable power supply and a network for energy supply to India's industrial and transportation sectors are the two key issues that need to be addressed.

Energy Landscape

India is the world's sixth largest energy consumer, accounting for almost 3.4% of the global energy consumption. Due to continuous high growth rates seen over the last few years, the demand for energy has been constantly growing in the economy. To sustain the growth rate for the next 20 years, India needs to increase its primary energy supply to 3-4 times. By 2030, the power generation capacity must increase to about 8,00,000 MW from the current levels of about 1,60,000 MW (Planning Commission Report, 2006). A look at the current energy landscape shows India's dependence on fossil fuels for its energy needs.

About 76% of the electricity produced in India is generated by thermal power plants, 21% by hydroelectric power plants and almost 2-3% by nuclear power plants. India's fuel mix is heavily dependent on hydrocarbons. Fig. 2 shows the

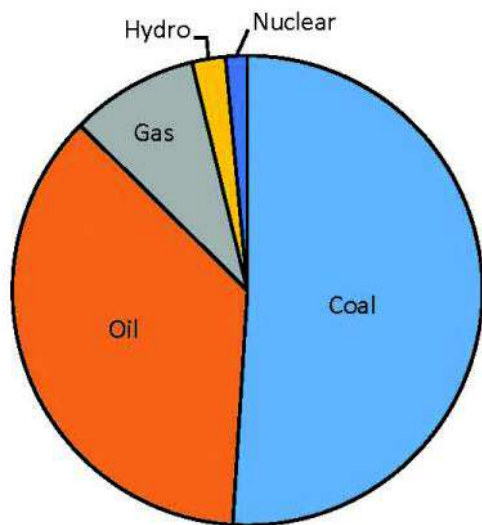


Fig. 2: India's fuel utilization for electricity generation

contribution of various fuels in the supply of energy. This heavily fossil fuel dependent fuel mix of India raises concerns over the energy security of India, particularly regarding imported oil. The main challenge facing India's energy sector is to increase and improve the delivery of energy services to various sections of the economy. A problem of disparity in demand and supply of energy is another big issue that needs to be addressed.

Electricity Demand Supply Situation

Access to electricity is limited in India, even after rural electrification programme and increased power generation capacities are put in place. Even though the electricity line is provided to 80% of the Indian villages, electricity is available to merely 44% of rural households. There is a huge gap between electricity demand and supply in India, amounting to 16% (according to government figures) and 25% (according to industry estimates). Planning Commission of India estimated that around 600 million people are not even on the national grid. This number is even higher than the population of the European Union. Some states are even facing a worse situation. For example, 90% of the rural households in poverty-hit Jharkhand have no electricity and still use oil lamps for light.

India's industry incurs a direct loss of nearly 9 billion USD due to shortage of power. The loss amounts to 1% of India's GDP. The power-intensive

sectors suffer the highest losses. Manufacturing sector alone accounts for 35% of the total loss. The other main sectors include small and medium enterprises at 16%, hospital and hotel, retail at 12%, real estate and infrastructure at 10%.

According to KPMG estimates, India will face a rise in demand of power to 90 GW by 2012 (Fig. 3) and there will be only 65 GW increase in the installed capacity. To sustain the GDP growth rate of 8%, India would need to increase its installed capacity to 220 GW by 2012 from around 130 GW in 2007. Apart from high levels of disparity in demand-supply situation, India has other challenges in its overall energy landscape. These include pollution and growing concerns over energy security. Air pollution in particular is a concern in India's some big cities such as New Delhi, Mumbai, Kolkata, Chennai, Bangalore, Hyderabad and some other urban cities. Measures such as restraining the use of gasoline and diesel vehicles had been adopted to address the environmental degradation problems. New Delhi has converted its public transport system including city buses and 3-wheelers to CNG. This CNG is derived from domestic natural gas, providing energy security. Similarly, cities of Kolkata and Chandigarh have also converted their large auto rickshaw fleets to run on LPG. Still, measures to build a more sustainable energy infrastructure should be adopted and this has been realized by the Indian government.

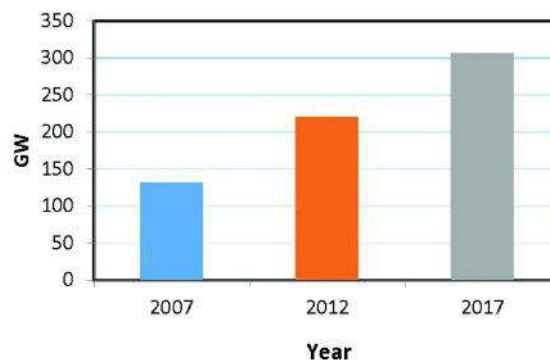


Fig. 3: Installed capacity requirement for power (Planning Commission)

Policy Landscape

The Ministry of New and Renewable Energy (MNRE) largely govern India's policy regarding fuel cells and

hydrogen technology development. The authority being quite active has set up a National Hydrogen Energy Board and a roadmap in 2006. The board set up five expert groups on hydrogen production, storage, power, transport and systems integration. It provided an integrated blueprint for the long-term public and private efforts required for hydrogen energy development inside the country. This roadmap was one of the measures taken in a series to improve the energy supply situation in India. The 2003 Electricity Act was responsible for developing an overall framework for renewable energy. The 2005 National Electricity Policy recognized renewable energy as a key option for areas where national grid is not feasible or cost effective.

The broad objectives of India's National Hydrogen Energy Program are as follows:

1. Reduce dependence on imported petroleum products
2. Promote use of diverse, domestic and sustainable new and renewable energy sources
3. Provide electricity to remote, rural and far flung areas
4. Promote hydrogen as a fuel for transport and power generation
5. Reduce carbon emissions from energy production and consumption
6. Increase reliability and efficiency of electricity generation

The National Hydrogen Energy Roadmap proposed two major initiatives in its Vision 2020 – Prioritized Action Plan (Table 1). The Green Initiative for Future Transport (GIFT) aims to develop hydrogen-powered IC engine and fuel cell vehicles ranging from small (cars, 3-wheelers) to big vehicles through different phases of development and demonstration. The Green Initiative for Power generation (GIP) was to develop hydrogen-powered turbine and fuel cell based decentralized power generating systems.

What is a Fuel Cell?

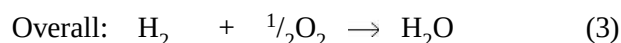
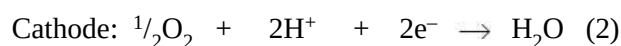
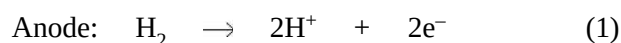
Before going into details of fuel cell technology development in India and its further scope, let us first discuss the science of fuel cell technology. The fuel cell is an electrochemical device that converts the chemical energy of the reactants directly into electrical energy. The free energy of the chemical reaction is converted into electrical energy by redox reaction. The essential difference between a fuel cell and a battery is that the fuel cell can continuously generate power as long as the fuel is supplied. Further, the electrode material in fuel cell works as catalyst to facilitate redox reaction and the electrodes do not take part in the reaction or they do not get exhausted. Fuel cell has two electrodes, cathode and anode, which act as current collector as well as catalyst and thus they are also called electro-catalyst. Every fuel cell has an electrolyte in between the electrode, which carries ions from one electrode to the other. Electrons are produced at anode through fuel oxidation reaction.

Table 1: Initiative due to National Hydrogen Energy Roadmap: Vision – 2020

Green Initiative for Future Transport (GIFT)	Green Initiative for Power Generation (GIP)
Hydrogen Cost at delivery point at Rs. 60-70 per kg Hydrogen storage capacity to be 9 weight % Development of safety regulations, legislations, codes and standards	Hydrogen bulk storage methods and pipeline to be in place Support infrastructure- large number of dispensing stations 1000 MW hydrogen based power generating capacity setup
1, 000, 000 hydrogen-fuelled vehicles on road	- 50 MW small IC engine standalone generators
- 750,000 two/three wheelers	- 50 MW standalone fuel cell power packs
- 150,000 cars/taxis	- 900 MW aggregate capacity centralized plants
- 100,000 buses and vans	

Source: NHERM (2006) Report, Ministry of New and Renewable Energy

These electrons take the least electrical resistive path and move from anode to outer circuit to do useful work such as powering an electric motor or illuminating a light bulb. The electron after traversing through the load or outer circuit reaches the cathode and participates in the reduction reaction to complete the process. Similarly, ions produced at the anode takes the least ionic resistive path for the ion and move from anode to cathode via electrolyte and participate in the reduction process to complete the reaction (Basu 2007). To make it clear, if we assume that hydrogen gas is fed at the anode and oxygen gas at the cathode of a fuel cell, with an acidic electrolyte in between the anode and cathode, the following individual and overall reaction would occur:



There are several types of fuel cells, and each operates differently based on different redox reactions, fuels, electrode materials, electrolytes and operating temperature. A brief description of different types of fuel cells is given in Table 2 (Basu, 2007). The table

shows the different types of fuel cells along with the details of their vital components, application, system output, efficiency, and advantages, etc.

In this article, low temperature fuel cell, namely, polymer electrolyte or proton exchange membrane fuel cell based on hydrogen and alcohol fuels (methanol and ethanol) are discussed in detail in subsequent sections.

Proton Exchange Membrane Fuel Cells (PEMFC)

The proton exchange membrane (PEM) fuel cell shown in Fig. 4 uses a solid polymer electrolyte (perfluorosulphonic acid membrane, Nafion®) in the form of a thin, permeable sheet for the transport of proton (H^+) (Basu, 2007). Generally, platinum (Pt-black or Pt/C catalyst) is used as anode and cathode catalysts.

The perfluorosulphonic acid membrane (Nafion®, Dupont USA) is sandwiched between anode and cathode catalysts, which are supported on gas diffusion layer made of carbon cloth or carbon paper. The composite structure is known as membrane electrode assembly (MEA) and it is the heart of the PEMFC. Gas diffusion layers work as substrate for

Table 2: Different types of fuel cells and their attributes

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Primary applications	Automotive and stationary power	Portable power	Space vehicles and drinking water	Stationary power	Stationary power	Vehicle auxiliary power
Electrolyte	Polymer (plastic) membrane	Polymer (plastic) membrane	Concentrated (30-50%) KOH in H_2O	Concentrated 100% phosphoric acid	Molten carbonate ceramic matrix of LiAlO_2	Yttrium-stabilized Zirconia
Operating Temp. Range	50-100°C	0-60°C	50-200°C	150-220°C	600-700°C	700-1000°C
Charge carrier	H^+	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Prime Cell Components	Carbon-based	Carbon-based	Carbon-based	Graphite-based	Stainless Steel	Ceramic
Catalyst	Platinum	Pt-Pt/Ru	Platinum	Platinum	Nickel	Perovskites
Primary Fuel	H_2	Methanol	H_2	H_2	H_2 , CO, CH_4	H_2 , CO
Start-up Time	Seconds-minutes	Seconds-minutes		Hours	Hours	Hours
Power Density kW/m^3	3.8-6.5	~0.6	~1	0.8-1.9	1.5-2.6	0.1-1.5
Combined cycle fuel cell Eff.	50-60%	30-40% (no combined cycle)	50-60%	55%	55-65%	55-65%

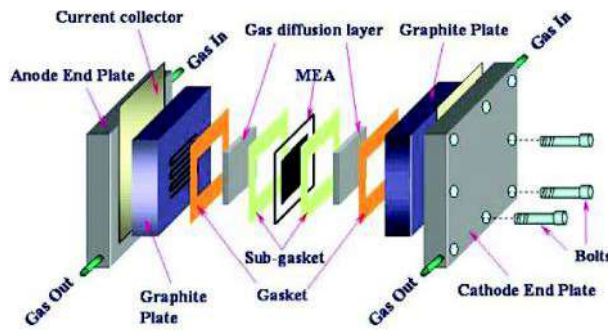


Fig. 4: Schematic of Polymer Electrolyte Membrane Fuel Cell showing different components (Basu, 2007)

catalyst and ensure the proper distribution of reactants over the catalyst. MEA is sandwiched between two bipolar plates (graphite), one in the anode side and the other one at the cathode side. Hydrogen molecules are stripped at the anode by the electro-catalyst into electrons and protons (H^+). Electrons generated at the catalyst-carbon paper (GDL) interface are conducted through GDL, having high electron conductivity, to the bipolar plate and to the outer circuit. The bipolar plate, made of graphite, also has channels to supply the reactants over the diffusion layer. The protons permeate through polymer electrolyte membrane and reach the cathode side, where it reacts with conducted electrons from the outer circuit and oxygen from air to produce water. The continuous flow of electron from the outer circuit through a load is nothing but the generation of electricity, which performs electrical work. The polymer electrolyte membrane allows protons to pass through it and restricts the passage of electrons as it is not a conductor. The migration of proton in membrane is promoted by sulphonate group present in the membrane structure through the formation of hydronium ion. The membrane needs to be hydrated for efficient transport of proton in the form of hydronium ion. Hence, the PEM fuel cell cannot be operated above $90^\circ C$ because of water loss from the membrane and subsequent poor conduction of proton. The reaction scheme for proton exchange membrane fuel cell is shown by Eqs. (1-3). In Fig. 4, one single cell is shown, which generates reversible voltage equals to 1.23 V. The reversible voltage is related to change in Gibbs free energy of the overall reaction

(Eq. 3) by the following expression:

$$\Delta G = -n F E \quad (4)$$

where, ΔG is the Gibbs free energy change due to fuel cell reaction (Eq. 3), n is the number of electron transfer per mole ($n = 2$) of hydrogen reacted, E is the reversible potential and F is the Faraday constant. The hydrogen-oxygen fuel cell reaction (Eq. 3) has a Gibbs free energy change of -237 kJ/mole under standard condition. The change in Gibbs free energy for any electrochemical or chemical reaction is calculated from definition of the Gibbs free energy at constant temperature, which is given in difference form as:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

Where, ΔH is the change in enthalpy during the reaction and T is the temperature and ΔS is the change in entropy during the reaction and the product formation; ΔH and ΔS of reaction can be determined from the difference in enthalpy and entropy of formation of the products, less the formation of enthalpy and entropy of the reacting species at the reaction temperature. Using Eq. (4), at the standard state condition, one can determine reversible voltage,

$$E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{-237,000 \frac{J}{mole}}{2 \text{ mole electrons/mole of reactants} \times 96500 \frac{C}{mole}} = 1.23 \text{ V}$$

The superscripted 'o' denotes the standard state (298 K and 1 bar). Although each cell is capable of generating standard state reversible voltage (also known as standard state open circuit potential) equal to 1.23, in actual operation due to Nernst loss (to incorporate the effect of reacting and product species concentration and temperature) and during fuel cell operation, when current is drawn, due to presence of overpotentials, for e.g., activation, ohmic and mass transport, the operating voltage is much less than that of 1.23 V. Normally, estimate of voltage generation at reasonable current density (700 mA/cm^2) in PEMFC is 0.5-0.7 V volt. The fuel cell operation typically

characterized by current-voltage characteristics, which is explained in fig. 5, with dominant regions of losses identified. The current is specified in terms of unit area of electrode, which essentially signifies the reactor area. The power out may be calculated by, $P = V \times I = 0.6 \times 700 \text{ mA/cm}^2 = 420 \text{ mW/cm}^2$. To increase output voltage (or wattage), several MEAs in between bipolar plates are stacked in replicated fashion in a fuel cell unit. The schematic of such a fuel cell stack is shown in Fig. 6. It shows the alternative hydrogen and oxygen (air) in flow into the channels of the bi-polar plates. When cells are stacked in series, the total voltage may add up to 40-80 V depending upon the number of unit cells stacked. In parallel and series stacking combination, both voltage and current can be increased. The details are available in O'Hayre *et al.* (2006) and Larminie and Dicks (2003). It may be noted that from fuel cell, DC voltage is generated, which needs to be conditioned to change it to AC at higher voltage using DC-DC and DC-AC converter using electronic circuits.

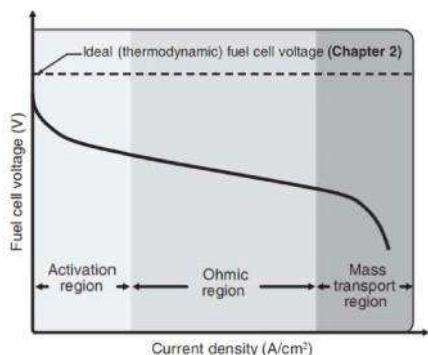


Fig. 5: Typical V-I characteristics of fuel cell showing various losses

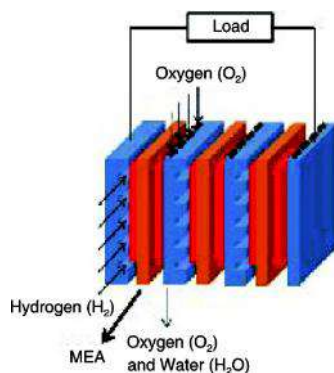
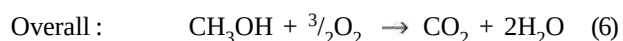
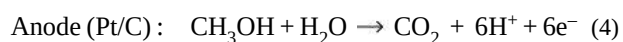


Fig. 6: Schematic of fuel cell stack showing repetition of unit cell with MEA and inflow of hydrogen and oxygen

Direct Methanol Fuel Cell (DMFC)

Direct alcohol fuel cell (DAFC) is a variant of PEM fuel cell. In case, methanol is used as fuel, it is called direct methanol fuel cell (DMFC); and similarly in the case of ethanol, it is called direct ethanol fuel cell (DEFC). In general, when a fuel cell uses PEM as electrolyte, it is termed as DAFC; and in the case of anion exchange membrane electrolyte, it is called direct alcohol alkaline fuel cell or direct alcohol AEM fuel cell (DAAFC). It is well-known that fuel oxidation and oxygen reduction kinetics is faster in the presence of alkaline medium than acidic medium (Basu 2007). In the recent past, AEM-based DAFCs have become popular as fuel crossover is absent, which is predominantly present in PEM-based DAFCs.

As mentioned earlier, DMFC uses methanol instead of hydrogen gas. The methanol dissociates into electrons, protons and carbon dioxide at the anode. The protons diffuse from anode to cathode through the polymer electrolyte membrane and electrons migrate toward the cathode through an external circuit. At the cathode, the electrons, hydrogen ions and oxygen from the air react to form water. The reactions involved in direct methanol fuel cell are shown here (Basu 2007):



Methanol is a readily available and a low-cost liquid fuel that has an energy density comparable to the gasoline. If methanol can be used as a fuel, then all the problems of storing or generating hydrogen for fuel cell may be solved. The fuel cell system would be simpler to use and very quick to refill. These are the main advantages of DMFC. However, the main problem associated with DMFC is that the methanol electro-oxidation reaction at the fuel electrode (anode) is very slow as compared to hydrogen. This leads to a far lower power for a given size of fuel cell. The second major problem is the methanol crossover from anode compartment to cathode compartment through the polymer electrolyte membrane. Both these problems markedly reduce the performance of the DMFC compared to PEMFC.

Equation (4) shows the methanol oxidation reaction in which 6 electrons are generated by electro-oxidation of a methanol molecule. The reversible cell potential at standard condition of a DMFC is calculated as 1.199 V. The methanol electro-oxidation reaction is a complex multi-step process. It is a very slow reaction and the reaction may proceed through many routes. Fig. 7 shows the possible routes of the complete oxidation of the methanol (Larmine and Dicks 2003). In one of the routes, first, the methanol is oxidized to formaldehyde, which is further oxidized to formic acid. In the final step, formic acid is oxidized to carbon dioxide. Some of the methanol may take another route, which forms carbon monoxide as an intermediate product. The carbon monoxide acts as a poison to the generally used platinum catalyst at the anode of the DMFC. Therefore, to reduce platinum catalyst poisoning, ruthenium (Ru) is used along with the platinum catalyst in a 2:1 ratio. Ruthenium helps to oxidize carbon monoxide into carbon dioxide.

Methanol solution, which is used as fuel at anode

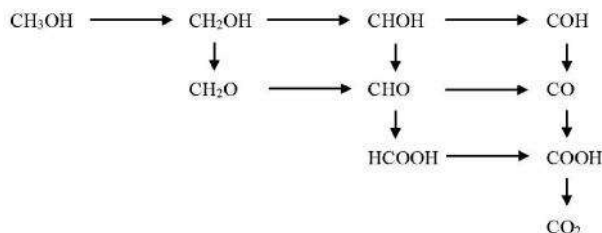


Fig. 7: Possible routes of methanol electro-oxidation

side of DMFC permeates through the electrolyte to the cathode side and this short-circuits the fuel cell, i.e., methanol oxidation at Pt cathode. There have been significant efforts towards the development of polymer electrolyte membranes for DMFCs in order to reduce the methanol crossover and increase their operating temperature (Kerres 2001). There are a few standard approaches for reducing the methanol crossover: (a) use of active anode catalyst results in complete methanol oxidation and not being available to diffuse through the electrolyte; (b) controlled use of methanol to the anode so that at the time of low current there is no excess methanol available, which can diffuse through the membrane; (c) use of thick electrolyte, that may reduce the fuel crossover but it should not be at the expense of the electrolyte

resistance; (d) use of composite polymer electrolyte membrane that may reduce the methanol crossover.

The development of polymer electrolyte membrane with reduced methanol crossover is an active area of research for DMFC. Efforts to develop the desired membrane for DMFC include modification of the conventional polymer electrolyte membrane (Nafion®) properties by incorporating organic or inorganic materials (composite Nafion® membrane) or by developing alternative PEM (Savadogo 1998). In an effort to modify the existing Nafion® membrane properties, inorganic solid acids have been incorporated with the objective of serving the dual functions of improving water retention as well as providing additional acidic sites (Malhotra and Datta, 1997). Composite membranes containing finely dispersed hygroscopic inorganic oxides (zirconium phosphate) effectively show decrease in methanol permeability with increasing (upto a certain extent) infiltrated oxides with a simultaneous increase in proton conductivity at a higher temperature (Daiko *et al.*, 2006). Yang *et al.*, (2001) demonstrated that composite Nafion®/Zr(HPO₄)₂ membrane reduced the methanol crossover for DMFC operating at temperature close to 150°C. Hygroscopic oxides such as SiO₂, Zirconium phosphate, and TiO₂ have been used for Nafion® modification (Watanabe *et al.*, 1996). Moreover, different composite membranes such as PVA/MMT, ErTfO/Nafion®, SPEEK with silicotungstic acid, etc., are under study for DMFC and DEFC. Recently, Barбора *et al.* (2009) produced ErTfO/Nafion® composite membranes, which showed higher proton conductivity and lower methanol or ethanol permeability than those of pure Nafion® membrane. The permeability was reduced by 77 % and 80 % for ethanol and methanol using 1% ErTfO/Nafion® composite membrane. The tensile strength and oxidation stability of 1% ErTfO/Nafion® was the highest among all the membranes under study. The results showed that the ErTfO/Nafion® composite may be a suitable membrane for direct alcohol fuel cells; exhibiting decreased fuel permeability, increased tensile strength and chemical stability, and decreased membrane swelling, without compromising proton conductivity.

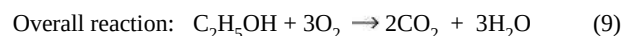
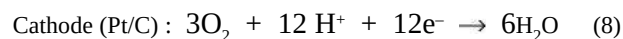
Direct Ethanol Fuel Cell

During the last decade, many studies have been conducted on the electrochemical oxidation of alcohols, especially methanol, in DMFC. However, recently it has been shown that ethanol is more advantageous and convenient compared to methanol and other higher alcohols. The focus of researchers has shifted from methanol to ethanol in the recent past, mainly due to its low toxicity and volatility as compared to methanol. Moreover, methanol is not considered as primary fuel. Ethanol is renewable owing to the fact that it can be produced in large quantity by fermentation of sugar-containing biomass resources. There exists a strong distribution network for ethanol in most of the countries. Also, ethanol as a fuel has higher theoretical mass energy density than methanol (8 versus 6.1 KWh/kg). All these advantages make ethanol more favourable as fuel in DEFC (Basu 2007, Pramanik and Basu 2007).

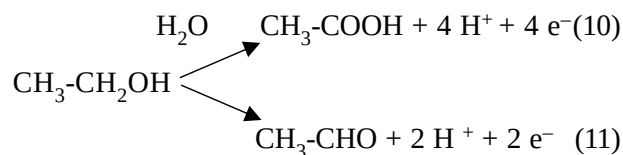
Different platinum-based electrodes, for e.g., Pt-X alloys (with X = Ru, Sn, Mo, Ir, Re, and W) have been investigated by Lamy *et al.* (2001) to study the electrocatalytic oxidation of ethanol. Among these, the most effective electrocatalysts were found to be Pt-Ru and Pt-Sn for DEFC. Since complete oxidation of ethanol requires breaking of C-C bond, its electro-oxidation is more difficult than that of methanol. It was confirmed in the review of the infrared reflectance spectroscopy and gas chromatography experimental data that electro-oxidation of ethanol leads to the formation of intermediate products with C-C bonds and adsorbed CO poisoning species (Lamy *et al.*, 2001). Analysis of the detailed electro-oxidation reaction mechanism of ethanol and the role of catalyst, for e.g., bi-functional mechanism of Pt-Ru/C, at the anode was first proposed by Lamy *et al.* (2002, 2004). Recently, ethanol electro-oxidation on carbon-supported Pt, Pt-Ru and Pt₃Sn electrocatalysts in the temperature range of 70-120°C was studied by Colamati *et al.* (2006). They pointed out that Pt-Ru and Pt₃Sn show about the same performance in a DEFC at 70°C.

In order to attain maximum energy from electro-oxidation of ethanol, it is necessary that the oxidation

reaction goes to completion. The complete oxidation of an ethanol molecule involves release of 12 electrons at the anode, as given by



The reversible cell potential at standard condition of a DEFC is calculated as 1.145 V. At a higher operating temperature (>100°C), DEFC gives enhanced performance with an increased CO₂ formation. Below 100°C, product analysis by differential electrochemical mass spectrometry (DEMS) or by chromatographic techniques (HPLC and GC) provided a detailed reaction mechanism of ethanol oxidation on Pt electrodes in acidic medium. The ethanol oxidation involves parallel and consecutive reactions as follows:



Reaction (10) occurs at higher electrode potentials ($E > 0.8$ V vs. RHE), where the water molecule is activated to form oxygenated species at the platinum surface. Reaction (11) occurs mainly at lower potentials ($E < 0.6$ V vs. RHE) (Hitmi *et al.*, 1994). There have been considerable efforts to develop bi-metallic and tri-metallic anode catalysts such that the complete electro-oxidation of ethanol to CO₂ at low temperature is possible and that there is no crossover ethanol from anode to cathode (Pramanik *et al.*, 2008, Tayal *et al.* 2011, 2012, 2014, 2015). The single direct ethanol fuel cell (DEFC) test at 90°C, 1 bar with catalyst loading of 1mg/cm² and 2M ethanol as anode feed showed an enhancement of catalytic activity in the following order. Pt-Re-Sn (20% Pt, 5% Re and 15% Sn by wt) and Pt-Ir-Sn/C (20% Pt, 5% Ir and 15% Sn by wt) exhibited highest performance among all the catalysts prepared with power density of 33 and 29 mW/cm² in DEFC, respectively, operating at 90°C (Tayal *et al.*, 2011, 2012). Basu *et al.* (2008) showed that improvement in cell performance may be achieved by adding

sulphuric acid in ethanol feed and using Ni-mesh as current collector at the anode. Goel *et al.* (2014, 2015) showed that performance of DEFC increases to 61.2 mW/cm² by using Pt-Ru on mesoporous carbon nitride (MCN) support at the anode. Andreadis *et al.* (2006) and Pramanik and Basu (2010) developed mathematical model for anode of DEFC and complete model for DEFC to estimate the overpotentials, respectively. The model predicted the experiment data on current-voltage characteristics with reasonable agreement. The influence of process parameters such as ethanol concentration and temperature on the cell performance is reflected in the model prediction.

In recent years, the interest in the direct alcohol alkaline fuel cell (DAAFC) rose again because of its better oxygen reduction kinetics in alkali than in acidic environment, simplicity, low cost and comparable efficiency compared to other types of fuel cell. Verma and Basu (2005, 2007a, b) developed direct alkaline fuel cell with liquid potassium hydroxide solution as an electrolyte for the direct use of methanol, ethanol or sodium borohydride as fuel. The typical power density achieved using Pt-Ru (40%: 20% by wt.)/C catalyst at 1 mg cm⁻² is 15.8 mW cm⁻² at current density of 26.5 mA cm⁻² for methanol and 16 mW cm⁻² at 26 mA cm⁻² for ethanol. The typical power density achieved for NaBH₄ is 20 mW cm⁻² at 30 mA cm⁻² using Pt-black as anode. A mathematical model of DAAFC predicted the experimental data well. Oxygen reduction reaction at manganese oxide cathode in alkaline medium is studied using cyclic voltammetry and by measuring volume of oxygen consumed at the cathode (Verma *et al.*, 2005). Single peak in cyclic voltammogram suggests that 4-electron pathway mechanism prevails during oxygen reduction at MnO₂ cathode in alkaline medium. This is substantiated by calculating the number of electrons involved per molecule of oxygen reacted at MnO₂ cathode from the oxygen consumption data for different fuels. A simple DAAFC stack has been developed, which consists of a series of flow channels in anode and cathode chambers (Gaurav *et al.*, 2010). Anode and cathode electrodes used were platinum black and MnO₂, respectively. The open circuit voltage of the stack made of four cells was nearly 4.0 V. The maximum power density obtained from such a stack

(25°C) was 50 mWcm⁻² at 20 mA cm⁻² for methanol and 17 mA cm⁻² for ethanol.

Approaches to PEMFC and DAFC Challenges

Proton exchange membrane fuel cells and direct methanol fuel cells currently use platinum-based catalysts at the anode and cathode. It would be difficult for the fuel cell technology to become competitive with other energy conversion technologies unless the overall materials cost is reduced significantly. For example, (Gasteiger *et al.*, 2004) reported that approximately one-fifth of the platinum loading is needed in PEMFC stack for mass commercialization of fuel cell powered automobiles. One method to decrease the cost of the materials in the catalytic layers of a membrane electrode assembly is to engineer catalysts with ultra-low precious metal loadings that still meet performance specifications. Researchers are currently engineering nano-structured supports such as carbon nano-tubes to increase the dispersion of the precious metal catalyst and enhance transport in the active layer (Jeng *et al.*, 2007; Priyanka *et al.*, 2009; Kannan *et al.*, 2009; Gao *et al.*, 2010). Others are attempting to reduce the catalyst cost. Two approaches to reduce catalyst cost are being actively pursued: one is to reduce Pt loading, and the other is to explore non-noble catalysts. In the short-term, catalysts containing low amounts of Pt are the priority and also practical, but in the long term, non-noble metal catalysts would be the better solution. Tremendous efforts have been made towards the finding out low Pt loading anode catalysts and non-noble metal catalysts (Vojislav *et al.*, 2007, Lim *et al.*, 2009). While Vojislav (2007) developed low metal loading nano-scale Pt-bimetallic catalyst for anode of a PEMFC with much higher power density, Lim *et al.*, 2009) developed Pd-Pt bimetallic nanodendrites PEMFC cathode with high activity towards oxygen reduction reaction. A team of scientists at the U.S. Department of Energy (DOE), Brookhaven National Laboratory, in collaboration with researchers from the University of Delaware and Yeshiva University, have synthesized a ternary PtRhSnO₂/C electrocatalyst by depositing platinum and rhodium atoms on carbon-supported tin dioxide nanoparticles that is capable of oxidizing ethanol with high efficiency and holds great

promise for resolving the impediments to developing practical direct ethanol fuel cells (Kowal *et al.*, 2009). This electrocatalyst effectively splits the C–C bond in ethanol at room temperature in acid solutions, facilitating its oxidation at low potentials to CO₂, which has not been achieved with existing catalysts.

Analysis of literature shows that over the last few years, tremendous progress towards improvements of activity and stability of non-platinum catalysts has been achieved. Some of the notable catalysts are tabulated in Table 3.

Thermal and water management issues should be handled with great care in the case of new types of gas diffusion layer (GDL), for e.g., metallic/carbon cloth or carbon paper for better electron conductivity and mass transfer of the reactants and products. A well-defined electron transfer through solid metallic structure and fluid flow path in GDL would reduce polarization losses. GDL is the key component of membrane electrode assembly (MEA). It should be such that activation polarization at anode and concentration polarization at cathode are minimal. GDL should keep a balance between water drying condition (decrease of proton conductivity in membrane) and water flooding condition (increase of mass transport resistance hence loss in voltage). Designing of thinner bipolar plate of low resistive

material or highly conductive material for excellent stack performance is the key to success for higher efficiency and minimization of cost of fuel cell. In general, investigators have been focusing on efficient development membrane and electrode-catalyst development. Following Fig. 8 on cost components of a typical PEMFC stack, it becomes obvious that commercialization of PEMFC highly depends on the development of GDL with high conductivity and high surface area with uniform distribution of pores and cheaper, efficient, highly conductive bipolar plate (Kamarudin *et al.*, 2006; Jayakumara *et al.*, 2006). Investigators are working on development of carbon fibre doped with metals, new carbon material and carbon nano-tubes and mesoporous carbon nitride.

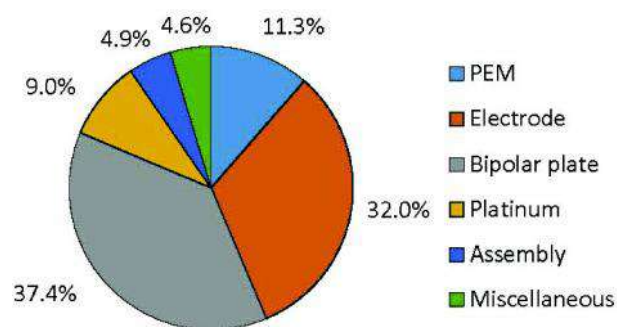


Fig. 8: Percentage share of PEMFC cost components

Table 3: Few Pt and non-Pt metal catalysts of interest to PEMFC and DAFC

Purpose	Catalyst	References
Hydrogen electro-oxidation	WC; WMC (where M= Co, Ni); Ir; IrO _x ; IrM (where M=Ru, Mo, W,V)	Wiesener 1989; Zagal <i>et al.</i> , 1992; Faubert <i>et al.</i> , 1996; Alves <i>et al.</i> , 1999; Lefevre and Dodelet 2003; Schulenburg <i>et al.</i> , 2003; Olson <i>et al.</i> , 2008; Serov and Kwak, 2009
Methanol electro-oxidation	Pd/C; Pd/Ni/C; Fe-MnO _x ; Ni-MnO _x	Hwu <i>et al.</i> , 2001; Zellner and Chen 2005; Liu <i>et al.</i> , 2003; Ganesan and Lee 2005; Weigert <i>et al.</i> , 2007; Serov and Kwak, 2009
Ethanol electro-oxidation	RuNi; Pd/C, PdAu/C; PtSn/CeO ₂ -C; (PtSnPd)/SnO ₂ ; PtSn/C-Rh; PtSn/C-CeO ₂ ; IrSn/C; Pt-Sn-W/C; CuNi, CuNiPt	Tarasevich <i>et al.</i> (2005); Xu <i>et al.</i> 2010; Neto <i>et al.</i> 2008; Antolini <i>et al.</i> 2009; De Souza <i>et al.</i> 2010; Cao <i>et al.</i> (2007); Ribeiro <i>et al.</i> 2008; Gupta <i>et al.</i> (2004)
Oxygen electro-reduction	Fe-N/C; Co-N/C; MnO ₂	Wasmus and Kuver 1999; Batista <i>et al.</i> , 2001; Shobha <i>et al.</i> , 2003; Savadogo <i>et al.</i> , 2004; Atwan <i>et al.</i> , 2005; Verma <i>et al.</i> (2005); Lima <i>et al.</i> , 2005; Wang <i>et al.</i> , Mustain <i>et al.</i> , (2007)

It has been found that the development of non-noble metal catalysts and GDL is comparatively simpler when they are used at higher temperature. However, with the present technology and use of PEM in the PEMFC and DAFC, it is not possible to use the fuel cells at an operating temperature above 90°C. Therefore, development of high temperature PEMFC and DAFC is being studied. A brief discussion on high temperature polymer electrolyte membrane is provided in the subsequent section.

High-temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFC)

The interest in development of high temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) has risen due to the numerous advantages of PEMFC technology operating above 100°C (Lobato *et al.*, 2007; Scott *et al.*, 2007; Li *et al.* 2008): (i) kinetics of both the electrode reactions are enhanced, (ii) tolerance of the Pt electrodes to carbon monoxide is increased, (iii) non-noble metal catalysts may be used, (iv) the integration of reformer technology is simpler, and (v) the cooling system for facilitating heat dissipation is simplified.

A suitable polymer electrolyte membrane is an important step for the development of HT-PEMFC. So far, perfluorosulphonic membranes such as Nafion® (DuPont), Dow (Dow Chemicals), Aciplex (Asahi Chemicals), and Flamion (Asahi Glass Co.) are the most widely used in fuel cell research and development. However, these membranes are not suitable for temperature higher than 100°C due to insignificant proton conductivity of the membrane for fuel cell purpose as the water content of the membrane at higher temperature, required for the conductivity, reduced appreciably. Therefore, three different types of membranes have been investigated for the fuel cell at temperature higher than 100°C: (i) modified perfluorosulphonated membranes, (ii) alternative sulphonated polymers and their composite and (iii) acid-base polymer membranes and their composites.

It is necessary to prepare polymer structure with higher glass transition temperatures, which can solvate the mobile cations in a polar phase containing the anions and the solvation groups. The solvation groups being

developed worldwide include imidazoles, which are tethered to the polymer matrix (Schuster *et al.*, 2005). Phosphoric acid doped polybenzimidazole, which is an alternative to Nafion® membrane, and works at a higher temperature suffers from leaching problem in water environment. It is therefore required to carry out investigation to provide a solid-state membrane with no leachable components. PolyFuel offers a new membrane, which works at a higher temperature (175°C) without much deterioration to reactants and by-products forms (Ashley 2005). Other new membranes such as sulphonated poly-(arylene thioether sulfone) (PATs), sulphonated poly (arylene ether sulphonate) (BPSH), and sulphonated poly (imide) (SPI) copolymers are found to be as good as Nafion® in many respects (Hickner and Pivovar 2005). Recently, high temperature proton exchange polyimide electrolyte membranes having sulphopropoxy and fluorenyl groups with higher proton conductivity are tested by Zhou *et al.*, (2005).

The polybenzimidazole (PBI) doped with phosphoric acid is a serious candidate for being used in HT-PEMFC. This acid-base membrane has low-cost and can work efficiently at high operational temperature of fuel cell. PBI membrane doped with phosphoric acid works at temperature up to 180°C without humidification and making it possible for the fuel cell to tolerate the use of H₂ having impurity of CO up to 3% with only small power loss. There are various other membranes for the HT-PEMFC such as PBI/PTFE, PBI composite membrane, SPEEK/PBI, pyrophosphate-based inorganic membrane, etc. on which active research is being conducted (Wu *et al.*, 2008; Verma and Scott, 2010).

The question is whether ceramic membrane can be developed as in solid oxide fuel cell (SOFC) as substitute for PEM, which operates at a temperature range of 150-200°C. Normally, ceramic material and metal oxides are used in high temperature SOFC. Impregnation of nano-metals in perfluorosulphonic acid membrane may help in proton transport. The membrane should have the following characteristics: chemical and mechanical stability for higher durability, control over undesired side reactions, greater tolerance to contamination caused by impure fuel or

by-products, low electro-osmotic drag and high proton conductivity.

Most of the points covered for PEMFC are also true for DAFC. Some additional issues are discussed further. Normally portable electronic equipment work at room temperature. However in some extreme cases at outdoor conditions, for e.g., sub-zero temperature or very high temperature, electronic equipment are used. In such conditions, the start-up time for the stack should be a few seconds such as 5–10 s. In DAFC, the main hurdle to be overcome is the development of membrane such that it does not allow crossover of fuel, for e.g., methanol and ethanol, through the membrane restricting fuel oxidation at cathode and minimizing over voltage loss.

PEMFC stack engineering and control is the next biggest hurdle once the component level improvements are achieved. The biggest challenge is in the computer controlling of fuel cell stack with load variation, minimum response time, better heat removal, less fuel flow resistance, by-products removal, decrease in stack mass per volume and weight and cyclic endurance.

Commercial Development of PEMFC

In 1955, W. Thomas Grubb of General Electric (GE) introduced the concept of using a sulphonated polystyrene ion-exchange membrane as the electrolyte in a PEMFC. Three years later, another GE chemist, Leonard Niedrach, devised a method of depositing platinum catalyst directly onto the polymer electrolyte membrane. Both these technologies were used by GE to develop the fuel cell system for Gemini Spacecraft. This can be considered as the first commercial use of fuel cell. In 1959, British engineer Francis Thomas Bacon successfully developed a 5 kW stationary fuel cell. During the same time, a team led by Harry Ihrig built a 15 kW fuel cell tractor for Allis-Chalmers and it was demonstrated across the United States. Pratt and Whitney, in late 1960, licensed Bacon's U.S. patents for use in the U.S. space program to supply electricity as well as drinking water.

United Technologies Corporation Power (UTC Power) was the first company to manufacture and

commercialize 2kW stationary fuel cell system (PureCell 200) to use as a powerhouse for hospitals, universities, and large buildings. They are also the sole supplier to NASA till date. UTC Power supplies (PureCell 400 model) complete fuel cell system to Coca-Cola Enterprises, CT Science Center, Fujitsu America, Hilton New York, Mohegan Sun, New York Power Authority, NYPD, Saint Helena's Hospital, Samsung Everland, South Windsor High School, Verizon, Whole Foods Market, etc. In 1983, Ballard Power Systems started development of a PEMFC system. Now, Ballard develops different type of fuel cells both for stationary power generation (FCgen™) and automotive application (FCvelocity™). Ballard fuel cell systems are used by ACME group, BAXI Innotech, FutureE Fuel Cell Solutions, H₂ Logic, Heliocentris Fuel Cells AG, IdaTech, ISE Corporation, New Flyer Industries, Plug power, etc. In January 2007, Daimler AG, with thirty-six experimental units powered by Ballard fuel cells, completed a successful three-year trial in European metropolitan cities. The cities included in that project were Amsterdam, Barcelona, Berlin, Chicago, Hamburg, London, Luxembourg, Madrid, Perth, Porto, Reykjavik, Stockholm, Stuttgart, and Vancouver. Similarly, NedStack has an ongoing project with Akzo Nobel at Delfzijl, Holland. Its 50 kW system recently reached the milestone of 4000 running hours and has delivered over 200 MWh to the grid. Plug Power Inc. has been involved, since 1997, in the design, development, and manufacturing of fuel cell systems for industrial off-road and stationary power markets. The company develops and sells a range of fuel cell products and services, including PEMFC systems for mobile (GenDrive) and stationary power (GenSys). They also develop a high temperature fuel cell system for residential and light commercial co-generation. In 2008, they received full certification to the American National Standards for Stationary Fuel Cell Power Systems (ANSI/CSA FC-1) requirements. Recently, various power requirements in the Oscars red carpet ceremony (2010) were successfully fulfilled by Freedom Power fuel cell systems.

R&D in the fuel cell sector in Europe (Germany, United Kingdom, France, Russia) and Asia (Korea, Japan, China, Taiwan) has progressed as much as in

North America (USA and Canada). In Japan, PEMFC and MCFC technologies are already in the market, PEFC systems for vehicular and mobile applications as well as for standalone systems in residential use are ready for applications. PEMFC technologies started in 1980s, which led to their early commercialization as compared to other fuel cell technologies. Several hundred units including prototype have been sold. Non-noble catalysts based on C, N, O, H alloys and proton exchange membrane based on poly (paraphenylene)s are used leading to higher PEMFC efficiency and durability. Based on this technology, several companies are working on development of FC-based light duty vehicles and back-up power with heating facility for household use. Honda FCX car with twin 100 kW PEMFC stack claiming lifetime of 5000 h, cruising range of 620 km and 60,000 start-stop cycle is one of the finest example of development of FC-based vehicle in Japan. Toshiba, Eneos-Celltech, Ebara-Ballard, Toyota Motors, Panasonic installed 3307 units of 1 kW PEMFC stack work on LPG and LNG using reformer. The 1 kW PEMFC stack works with 40% electrical efficiency, produces hot water with claimed lifetime of 40,000 h and 4000 times start-stop cycles. The cost of both PEMFC operated FCX Honda car and 1 kW PEMFC system is exorbitantly high. The number of 1 kW PEMFC stationary systems sold and installed by different companies are shown in Table 4.

Table 4: 1 kW PEMFC stationary systems installed in Japan

Manufacturer	LPG	LNG	Kerosene	Sub total
ENEOS Caltech	1062	191	0	1253
Ebara Ballard	0	396	314	710
Toshiba	554	194	0	748
Panasonic	0	520	0	520
Toyota Motors	0	76	0	76
Total	1614	1379	314	3307

Considerable commercial activity has been seen in the last decade on the development of DMFC as a power source for portable electronic equipment such as laptops and mobile phones. Toshiba and Motorola

demonstrated DMFC-powered laptop and mobile phones in different international exhibitions on fuel cell technology. In a similar manner, DEFC and direct glucose fuel cell development have been undertaken by many investigators (Basu *et al.* 2010, 2011) and Sony Corporation.

However, their commercial viability *vis-a-vis* Li-ion battery in mobile phone and other handheld devices application is not known, but it holds much promise.

Fuel Cell and Its Application

PEMFC is used for motive power i.e., vehicle application, power generation for portable application as well as powering a building complex and block of houses i.e., utility market in the form of combined heat and power. Hydrogen is the fuel for PEMFC, which can be produced through different pathways, for e.g., utilizing solar and wind power to electrolyse water to produce hydrogen, biomass to synthesis gas and further converting to hydrogen, coal to hydrogen with carbon dioxide sequestration, natural gas to hydrogen with separation of unwanted (CO) gases, nuclear and thermo-chemical reaction route to produce hydrogen. In the initial stage in North America, Europe and Japan, fixed route vehicles, busses, trucks, and delivery vans have been tried to create effective hydrogen dispensing facility and gain experience from it. Internal combustion vehicle, fuel cell vehicle (ICE-FCV) or fuel cell hybrid vehicle (FC-HEV) has been the starting point in these countries to have a smooth transition from ICV to FCV in terms of economy, infrastructure and technology development. India may follow a similar strategy.

DAFC is constructed on basis of proton exchange membrane (PEM) or anion exchange membrane (AEM) technology. DAFC is suitable as a power source to portable electronic equipment, for e.g., laptops, mobile phones, pads, and camcorder replacing the use of Li-ion batteries with possible commercialization in near future. The market for portable application is increasing by leaps and bounds with advancement in microelectronics technology, for e.g., micro-fluidics devices, micro-chemical plants, lab-on-a-chip, etc. Thus, demand for micro Watts to Watt ranges of miniature to portable power packs

will increase and portable fuel cell is a good option as the duration of power supply by fuel cell is much higher than Li-ion battery. The primary candidates as fuel for direct fuel cell technology are methanol, ethanol, formic acid, esters and sugar with improved catalysts and membrane electrolyte technology for the fuel cell.

Fuel Cell Research in India

The last few years have seen considerable activity in the area of fuel cell research in India. Most of the basic research is done by India's reputed academic institutions and very few industrial organizations are involved in research. A vast majority of this research is funded by the government under new energy policies of the Ministry of New and Renewable Energy. These research institutions are involved in more fundamental research such as catalysis and MEA development. Some institutions are also involved in more application-oriented research such as stack development and Balance-of-Plant(BoP)-related work. Table 5 presents a summary of fuel cell related activities of key R&D institutions in India.

Although, Indian companies are generally regarded as only manufacturers and service providers with less emphasis on R&D, some big corporate houses of India have entered the area of fuel cell research. Most of these industrial houses are carrying out applied research which is concerned with the adaptation of fuel cell technologies in the Indian scenario. Car makers such as Tata and Mahindra & Mahindra are involved in making fuel cells a part of the Indian automobile industries.

Apart from these, several foreign companies have also entered the Indian market since the market is still in a nascent stage. Some of these organizations are focusing on bringing the technologies developed in other countries to India, while some have focused on using Indian expertise and resources to develop a strong R&D base. Some local players are also involved in collaborations with these companies. In the last few years, India has seen a steep growth in fuel cell research activities with several national and international conferences and workshops organized locally. Both academic institutions and private sector

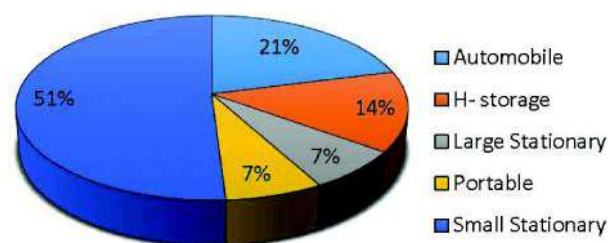


Fig. 9: Distribution of fuel cell organization application-wise in India

companies are actively participating to organize these events. These events have provided a good platform to Indian researchers to interact among themselves and also with researchers from other countries. This is quite important, as no active network of Indian researchers exists in the area of fuel cell research.

A large percentage of organizations involved in fuel cell activities are working on small stationary units (Fig. 10). Power distribution is a big problem in both domestic and industrial sectors in India and fuel cells are being considered as a good option to provide stationary backup power. Several programmes related to stationary applications of fuel cells are being promoted by the government.

Apart from stationary power, automotive sector is also an important focus area for fuel cell research institutions in India. Some of the big industrial organizations are involved in development of fuel cells for automobile applications. Hydrogen storage, portable and large stationary applications of fuel cells are some other important areas of fuel cell research in India (Table 5).

Markets for Fuel Cells in India

A fast growing economy, with a large gap in demand and supply of power, makes India a good potential market for various power generation technologies including fuel cells. Favourable national energy policies for hydrogen and fuel cell technology development in stationary power and automotive sectors strengthen India's position as a future market for fuel cell based applications. This section of the report describes some of the markets for fuel cells in stationary power and automotive sectors.

Table 5: Summary of fuel cell R&D organizations in India

Institute/Organization	Main Focus Area(s)	Achievements/Remarks
CECRI, Chennai	PEMFC, DMFC, DBFC, Hydrogen Generation	Developed a 1 kW PEMFC stack, Developed a 5 kW PEMWE
CFCT, Chennai	PEMFC, Hydrogen Generation	Developed PEMFC stacks- up to 5 kW, Grid independent power systems (3 kW), Fuel cell systems for transport applications with Mahindra Rise and Reva
CGCRI, Kolkata	SOFC	Developed electrode and membrane materials for high performance SOFCs and Low Temperature SOFC. 400 W SOFC stack developed. SOFC technology is discussed elaborately in a separate chapter.
SPIC SF, Chennai	PEMFC, DMFC, Hydrogen Generation	Developed 5 kW PEMFC stacks, 250 W DMFC Stack, PEM-based water and methanol electrolyzers, fuel cell based stationary applications such as UPS
IIT Bombay, Mumbai	PEMFC, DMFC, IT-SOFC, hydrogen generation	PEMFC system development, Catalysts for PEMFC, Working on HT-PEMFC and IT-SOFC, Hydrogen storage in complex hydrides
IIT Delhi, Delhi	PEMFC, DAFC, Hydrogen Generation, SOFC	Developed DEFC with power density of 70 mW/sq.cm, electrode-catalysts, Developed Direct Glucose fuel cells. Non-PGM ORR catalyst and micro fuel cell for MEMS. Anode materials for hydrogen generation using PEM water electrolyzer, working on anode material for Direct Hydrocarbon SOFC and low temperature SOFC.
IIT Madras, Chennai	PEMFC, DMFC, SOFC, Hydrogen Storage	Developed a DMFC with non-noble cathode catalyst with 340 mA/sq.cm (0.6 V) at 80-°C. Non-PGM catalyst for PEMFC, SOFC material research
NCL, Pune	PEMFC	Prepared thermally stable PBI membranes, Demonstrated a 350 W (15 cell) PBI-based PEMFC stack
NMRL, DRDO, Mumbai	PAFC, PEMFC, Hydrogen Storage	Developed and demonstrated 700-1000 W capacity PAFC-based UPS/generators. 1.2 kW PAFC system integrated in an electric vehicle developed under DRDO-REVA joint project. Development work on PEMFC and SOFC and hydrogen generation by autothermal reforming
BARC, Mumbai	SOFC, PEMFC	SOFC material and tubular SOFC under development
BHU, Varanasi	Hydrogen Storage, Hydrogen IC Engines, Hydrogen Production	Developed AB ₅ and AB ₂ type storage materials with improved storage capacity. Converted existing petrol-driven IC engines to operate with hydrogen as fuel
IISc, Bangalore	PAFC, DMFC, PEMFC	Developed PAFC with power density value of about 560 mW/sq.cm.
Mahindra Rise	Hydrogen IC engines	Developed hydrogen powered Alfa 3-wheeler vehicle. Developing battery-powered electric hybrid vehicle
TATA Motors	Fuel cell technology for transport applications	Developing a fuel cell based city bus, Projects on using hydrogen blends as fuels. TATA teleservices involved in demonstration of fuel cell technology for mobile tower backup power
Indian Oil Corp. Ltd.	Hydrogen infrastructure, hydrogen for transport sector	Setup hydrogen dispensing stations. HCNG usage in 3-wheeled vehicles and light duty buses.
Reliance Industries Ltd.	PEMFC for stationary applications, SOFC	Joined the NMITLI project for Indigenous PEMFC Technology Development as the industrial partner. Established a fuel cell R&D lab in Mumbai
REVA (Own by Mahindra Rise)	Fuel cell based small cars	Developed a car with NMRL with 1 kW PAFC stack on board. Involved in a similar project with CFCT.
BHEL	PAFC, PEMFC,SOFC	Developed a 50 kW PAFC power plant, developed 1 kW PEMFC modules and a 3 kW PEMFC power pack. Partner institute in the development of a 5 kW PEMFC system under the NMITLI project

Nissan India	PEMFC technology for automobile applications	Working on membrane development for PEMFC technology. Studying membrane degradation
ACME Telepower	Fuel cells for backup power	Joint venture with Ballard power systems Inc. and Ida-Tech to set up a high volume low cost fuel cell systems for mobile tower back-up power
Eden Energy (India) Pvt. Ltd.	Hhydrogen for transport sector	Involved in production of Hythane, agreement was signed with Ashok Leyland for the supply of Hythane to be used in natural gas powered buses
Gas Authority of India Limited	Hydrogen Infrastructure	Main player for supply of suitable fuels, including hydrogen, natural gas, propane, butane and methanol
Bloom Energy (India) Private Limited	SOFC	Working on testing and characterization of SOFC technology
Daimler Research Center (DMRC), Bangalore	Fuel cell for transport applications	Setup an outsourcing R&D centre in Bangalore. Considering launching a commercial fuel cell vehicle in India. Final outcome of DMRC is not known to author
Indian Space Research Organization	Application of PEMFC powering automatic weather station. PEMFC use future space station and man mission	100 W PEMFC system is developed for automatic weather station

Stationary Power

Stationary power generation sector in India can be considered to have the most near term potential market for fuel cells. The rapid growth in Indian economy demands for a growth in infrastructure facilities and energy supply. India is suffering from severe power shortages which can affect the growth levels of economy as it affects both the domestic and industrial sectors. In India, several industrial and commercial enterprises use some form of captive power and are potential customers for fuel cell based stationary power plants. An unreliable grid system and prolonged power blackouts in urban areas in India add to the market potential for fuel cell applications in stationary power sector. A study conducted by TERI, Delhi, on the market assessment of fuel cells in India, identified several key markets for fuel cell stationary power plants in India. These include chlor-alkali industry, luxury hotels, paper and pulp industry, dairy industry, telecommunication industry and stationary backup power. The study identified availability of fuel for fuel cell power plant as one of the key factors in selection of potential consumers. Also, potential use of waste heat from fuel cell power plant was another important factor considered in the selection of consumer. Table 6 presents some of the key niche areas for stationary power generation identified from the study.

Another market application for fuel cell base power plants could be in distributed power generation in Indian rural areas. Due to the unavailability of grid connected power supply, these areas can be seen as a potential market for distributed power generation systems. Government incentives and support in this area can be seen as an advantage for the market players.

Telecommunication Industry

India has emerged as one of the fastest growing telecom markets in the world. Mobile services in telecom industry have been growing at a much faster pace mainly in urban areas. Still, the total wireless tele-density remains at around 40.3% which shows a huge untapped potential for market growth. The main future market for these services lies in non-urban areas where penetration of these services remains low.

A growing telecom industry presents itself as a potential market in mobile towers backup power. There are around 2,80,000 mobile telecom sites and it is estimated that about 5,00,000 sites will be required by 2018. One of the main infrastructure requirements for mobile towers is the provision of backup power which is a necessity due to frequent power cuts in both urban and rural areas. The issue of irregular

Table 6: Summary of key niche markets for stationary power generation in India

Potential Markets	Power requirement, MW	Potential fuel cell types	Remarks
Luxury Hotels	0.5 -5	PAFC, SOFC, MCFC	Availability of natural gas or LPG a big advantage
Chlor alkali	5-45	SOFC, MCFC, PEMFC	Hydrogen available as a by-product
Pulp and Paper	2-50	SOFC, MCFC	Availability of natural gas is required
Dairy Industry	<5	AFC, PAFC, PEMFC	Use of biogas from rural areas will be economical
Telecom & IT	<5	AFC, PAFC, PEMFC	Fuel availability, a big issue
Weather station	<5	PEMFC, DMFC	Hydrogen and methanol fuel

power supply is more pronounced in the rural sector, where a number of Indian villages either do not have an electricity grid connection or face limited power availability. Mobile towers use backup power in the form of diesel-powered generators. Although the start-up costs for diesel based power generators are low, the operating costs are quite high due to high costs of crude oil in recent times. It is estimated that over 35% of rural cell site's network operating expenses are due to costs associated with electricity and diesel.

Fuel cells are being offered as a viable option to telecom customers in place of diesel generators. Telecom infrastructure companies are willing to pay a premium for reliable power, especially in remote rural areas. Fuel cells offer clean, noise-free and most importantly, they can be run on a variety of fuels. These fuels can be cheap biogas which is available in remote rural areas and thus can provide a solution to telecom companies looking for a replacement to diesel-based generators.

In May 2008, agreement was signed between Ballard Power Systems and ACME Telepower for supply of fuel cell stacks to the telecom's backup power. A development and supply agreement was signed between ACME, Ballard and IdaTech for supply of 5 kW natural gas PEMFC stack 30,000 systems to be delivered by 2013. A minimum order of 10,000 systems is to be completed by 2010, rest of the order after evaluation of this unit. In August 2008, Plug Power demonstrated a LPG-fuelled telecom power backup unit in partnership with Hindustan

Petroleum Corp. Ltd. and Tata Teleservices. However, outcome of the above agreement is not known to the public.

Chlor-alkali Industry

Chlor-alkali industry in India mainly comprises manufacturers of caustic soda and soda ash. In the process of manufacturing caustic soda, some valuable by products are produced. A tonne of caustic soda produces 860 kg of chlorine and 25 kg of hydrogen. Chlorine and hydrogen produced can be combined to prepare hydrochloric acid. These basic chemicals are used by many industries. Table 7 shows the hydrogen-producing capacity of various chlor-alkali plants in India.

The manufacturing process of caustic soda is quite energy intensive (5-45 MW). The load requirements are met by grid supply as well as captive power plants. Hydrogen as a major by-product of the manufacturing process finds little usage in the chemical industry (Table 7). Although some hydrogen is used in the manufacturing of hydrochloric acid and some is sold after compression and storage in bottles, a significant amount does not find any use. Compression of hydrogen and storage into cylinders is a labour and energy intensive process. Also, market for HCL is limited; so, conversion of hydrogen to HCL is restricted by demand. Caustic soda is transported to long distances after it is converted to caustic flakes by an evaporation process, which consumes fuel. Use of hydrogen in this process is also difficult as it requires sophisticated burners and controls. It has also been

estimated that all the hydrogen produced as by-product in the plant cannot meet the energy requirements of the flaking process. So, use of additional fuel is necessary in any case. Due to these factors, use of hydrogen in fuel cells presents itself as a promising option. In recent times, due to liberal import policies of Government of India, domestic chlor-alkali industry is facing stiff competition from overseas manufacturers which sell caustic soda at a significantly lower price. So, domestic manufacturers are looking for technologies which can give them an advantage in terms of overall cost reduction inside the plant. Several domestic manufacturers have switched to more efficient technologies of production namely membrane cell processes and are incurring large capital investments. For fuel cell technology adoption in this market, economics of fuel cell power plant and particularly the capital investment would be of utmost importance. Thus, fuel cells which also generate waste heat in the form of steam can be thought of as a good option as they can satisfy some of the energy needs of the plant. SOFC and MCFC power plants could be the ideal fit in these cases. Steam from the fuel cell power plants can be used in the flaking process of the caustic soda. Benefits of the fuel cell power plants depend on how effectively the waste heat is utilized in the plant.

Table 7: Hydrogen producing capacity of some chlor-alkali plants in India

Manufacturer, State	H ₂ , Nm ³ /day	Excess H ₂ , Nm ³ /day
Century Rayon, Maharashtra	11000	11000
Hukumchand Jute Industries Ltd., M.P.	23100	11100
DCW Ltd., Tamil Nadu	48160	16800
Indian Petrochemicals Corporation Ltd., Gujarat	120000	50000
Grasim Industries. Ltd.	112000	50000
Tata Chemicals, Gujarat	29500	4720
Punjab Alkalies & Chemicals	84000	11866
DCM Sriram, Kota	91000	19000

Luxury Hotels

There is a need for reliable primary and backup power in large commercial premises. The five star hotels of India can be viewed as a prime candidate for the adoption of fuel cell technology in stationary power generation. The load requirements range from 500 kW to 5 MW depending upon the capacity of the hotels. The load is distributed lighting requirements, kitchen load, operation of lifts and mainly space conditioning.

These hotels require heat for various purposes which include hot water for guests, kitchen, and laundry. Some hotels also have sauna baths and health clubs which also require steam. The hotels are well-connected by grid, but due to frequent power cuts, they also maintain some form of captive power generation which can meet the energy requirements. Most commonly diesel-based generators are used as captive power plants in the hotel. Fuel cells which can simultaneously supply electricity, steam and hot water will be an attractive option to hotel owners. PAFC, MCFC and SOFC power plants are best suited for this case. A clean and noise-free energy generation process with ease of operation can be considered as factors which will drive fuel cells entry in this market.

Availability of fuel for such plants will be another important factor in this market. Some of the cities in India, mainly metropolitan cities such as Delhi and Mumbai have a good infrastructure for natural gas distribution. This infrastructure is being extended to commercial hotels in these cities. These large hotels also have a good supply of LPG gas for their cooking requirements. So, availability of fuels is another advantageous factor for the adoption of fuel cell technology in this market.

Other Stationary Power Generation Markets for Fuel Cells

The pulp and paper industry in India have electricity requirement in the range of 2-50 MW. The industry also requires low and medium pressure steam in the chemical processes of cooking raw material for making pulp, drying of paper and evaporation processes. The bleaching plants also require saturated steam at around

200°C. The industry uses captive power generation systems mainly in the form of diesel generators. Sometimes, gas turbines or steam turbines are used for power generation.

Fuel cell system with the capacity to produce heat (PAFC, SOFC and MCFC) can be useful in the industry. Again, the capital cost of the fuel cell systems would be critical in their entry into this market. Another area of fuel cell application in stationary power sector is in the dairy industries most of which are in the western and north-western parts of the country. These industries use diesel generators or gas turbine based captive power generation systems. The dairy industries in western India have easy access to natural gas. Other fuels such as biomass and biogas are also available in these areas. Thus, fuel availability is a major advantage for fuel cell applications in these industries.

Power cuts in the urban area have created a market for standby/back up power generation systems used by domestic users. The backup power load ranges from 0.3 to 5 kW depending upon the requirements of the domestic user. Diesel, petrol and kerosene generators and battery banks (DC to AC inverters) are the most commonly adopted power generation systems used by domestic users. The problem with diesel, petrol and kerosene based generators lies in the pollution and noise caused by these systems. The inverters are also not very efficient while charging and discharging cycles. PEMFC-based systems can be good alternative for domestic users but they face stiff competition from conventional generators in terms of their costs.

Fuel cell power systems designed and developed by Indian Space Research Organization (ISRO) were installed (Fig. 10) at Shillong and Thiruvananthapuram for powering Automatic Weather Stations (AWS). In a first of its kind in the country, the first unit was installed during April 2013 and it has completed one year of operation, successfully. The power systems are based on a 100W class PEM fuel cell stack that operates on hydrogen and air and deliver 12V DC required for the functioning of AWS. The systems are designed to work in fully unmanned and autonomous mode with very simple architecture with



Fig. 10: Fuel cell power system installed by ISRO for powering automatic weather station at Shillong

minimal subsystems, especially, dynamic components. The systems make use of hydrogen from standard gas cylinders and ambient air, directly, and deliver stable electrical output. The work was done as a spin-off application of the systems under development at ISRO, after specific design adaptations. More such installations, which have the potential to enhance our remote sensing and disaster mitigation capabilities, have been planned.

There are a large number of automatic weather stations (AWS) all over the country and these acquire regional weather data, which is then pooled into a common data base, automatically, through a satellite uplink. The AWSs work in fully outdoor conditions and are many of them are located in remote areas without grid power. The units are configured to operate in fully autonomous mode and are normally powered by solar panel-battery combination. The AWSs located in areas with long spells of rain and winter, generally, suffer from insufficient solar intensity for certain periods. This renders them non-functional since the battery tends to run out of charge due to insufficient recharging. Similarly, those located in high altitudes and latitudes are also prone to chronic low solar intensity resulting in under performance of the power system.

Fuel cell power system operates on the stored hydrogen gas and is fully free of all the constraints mentioned. Also, when the system operation is configured in such a way that the refilling of gas

cylinder would be needed once in 3-4 months, it becomes quite manageable. The system provides a fully clean power generation cycle and water is the only by-product. The system thus offers an alternative power system option for AWSs. The new solution based on fuel cells enables AWSs, which provide crucial data on regional weather forecasting and now-casting, to operate free of adverse weather conditions.

Fuel Cell Markets in Automotive Sector

The automobile industry in India is one of India's fastest growing industrial sectors. Still, the penetration in this sector is quite low which indicates a huge potential for growth. The Indian automobile industry can be classified as follows:

Light duty 2- and 3-wheeled vehicles, passenger car

Heavy duty vehicles including buses and trucks

The following section discusses the market potential of fuel cells and recent market developments in both these categories.

Light Duty Vehicles

Majority of light duty vehicles in India belong to 2- and 3-wheeler vehicle categories. Two-wheeled scooters and motorcycles are the main mode of transport for the Indian middle class homes which constitute a large market. As per the NHERM, activities related to adoption of hydrogen-based technologies in this vehicle segment have already started. The focus is on the development of hydrogen-powered IC engines rather than adoption of fuel cells. Domestic manufacturers such as Mahindra Rise have developed a hydrogen IC engine based vehicle 'HyAlfa' (Table 5). Bajaj has developed a hydrogen-powered three-wheeler vehicle. Companies are involved in developing hybrid versions of 2- and 3-wheeled vehicles. However, lack of hydrogen infrastructure in majority of Indian cities has kept these vehicles from coming into entering the market. Most of such vehicles are in the demonstration stages in Delhi, where they have developed a hydrogen/CNG infrastructure. Fuel cell application in this area would not be possible in the near term. This is due to high

capital costs associated with fuel cell systems, which makes it hard for the consumers in this category to adopt this technology. Indian middle class consumers would find it hard to invest a substantial amount on a two-wheeler when gasoline-based vehicles are available at substantially cheap prices. Similarly, fuel cell costs may be prohibitively high for an Indian autorickshaw operator. With huge skilled labour force in India for maintenance, it is possible that fuel cell applications in India may not be as sophisticated as that of the developed world, where labour force is dwindling and costly. This may bring down the cost of fuel cell and become competitive with the IC engine based vehicles. Another important issue will be the durability of fuel cell based vehicles given the near continuous operation of 3-wheelers and the bad condition of Indian roads which are often filled with potholes. So, market potential for fuel cell based 2- and 3-wheelers is quite limited in India.

Passenger car market in India presents an interesting picture. This sector is growing at a very rapid pace which has led to many international automobile manufacturers entering the Indian market. Apart from a number of large domestic players, the Indian automobile sector now has several world-known automobile manufacturers, which sell their products in the premium segment of the market. The domestic manufacturers in this market are looking for alternative fuelling options. Various activities regarding the development of alternative fuelled vehicles are being carried out by these car companies.

Again a look at the hydrogen fuel infrastructure condition in India tells us that commercialization of fuel cell based passenger cars is not an immediate-term option. Also, the capital costs related to these systems make it hard to commercialize such vehicles in Indian markets. Although, fuel cell based vehicles can be a good option to battery-based electric vehicles as range extenders which have a very small market in India at present. Delhi government gives tax sops to manufacturers and users of battery-operated vehicles, which is a good sign to start with. Such benefits may be extended to fuel cell operated vehicles in future during implementation stage.

Heavy Duty Vehicles

Buses in India show a promising future for the adoption of fuel cell technology. A number of manufacturers in this industry in India are showing much interest for the development of fuel cell based demonstration units. Operation of buses in many cities is by state-run enterprises. Also, in many metro cities, the government is planning to impose some environmental constraints on public transport systems of which buses are an integral part. A good example of this is the conversion of city buses in Delhi to CNG-fuelled buses in 2001. In near future, buses seem to be the most promising option for fuel cell technology implementation. Although, high capital costs will still hinder this technology from entering the market, but fuel cell buses for demonstration purposes have sufficient scope.

Two of the biggest manufacturers (Tata and Ashok Leyland) in this sector have started developing buses based on hydrogen technologies. Tata and ISRO are jointly developing a PEMFC-powered bus for demonstration purpose. While they are using Ballard PEMFC stack as power source along with a battery, the system engineering is completely developed by Tata and ISRO. Ashok Leyland is working with Society of Indian Automobile Manufacturers on guidelines of NHERM towards development of low cost hydrogen IC engine technology. In detail, they are discussed here.

Tata Motors Ltd. (TML) is developing a hydrogen-fuelled fuel cell bus which is in line with its corporate policy of designing and developing environment-friendly, sustainable transport solutions. In this endeavour, Tata Motors is developing a fuel cell power train technology to power buses which will be fuelled with hydrogen (Fig. 11). As part of this initiative, Tata Motors has set up a Research Centre, in Society for Innovation and Development at Indian Institute of Science, Bangalore Campus and has created a fuel cell power system test facility there.

A typical low floor Tata Motors Starbus running on CNG-based electric traction was used for the purpose. The CNG electric generator was replaced with a fuel cell power system. The power system



Fig. 11: Tata Motors designed fuel cell Starbus which was displayed during AutoExpo 2010 at Delhi

consisted of a FCvelocityTM-1100 Ballard stack capable of 120 kW and a Li-ion battery pack. The battery is placed in the front-end so that it powers the motor and the fuel cell keeps charging the battery. This way, the battery was made to handle the transients. Hydrogen gas was stored under high pressure up to a permissible level of 350 bar on the roof of the bus in a composite high pressure vessel. An air compressor delivered the required quantity of air into the system based on a proprietary control logic evolved for the purpose. Development of a robust gas humidification system by TML was indeed a highlight of the programme. The prototype realized does not envisage recovery of the product water which is exhausted into the atmosphere. However, future vehicles are expected to include water recovery as well. Cooling radiators in bus are mounted on the roof top. The total power system was mounted in the rear module of the vehicle. The bus being developed comprises fuel cell power system, electric traction, hydrogen storage system and controls. Hydrogen is used as fuel, which will be stored on-board in compressed form in light weight composite cylinders. ISRO has provided some of the technology-related hydrogen handling. Electric power is generated by fuel cell power system on-board bus by indirect combustion of hydrogen. Surplus power required during transients is met by the lithium ion traction battery which also absorbs power generated by traction system during braking. Power generated is regulated and controlled by using traction controller. The motive power for the bus is provided by electric traction. Tata Motors has already developed two

prototype buses and trials are being carried out at test facilities. Several cities around the world, consider the fuel cell and battery hybrid bus as the most promising technology to facilitate decarbonisation of public transport.

The other kind of heavy vehicles in India, trucks, show very little scope for fuel cell adoption. These trucks are mostly operated by private owners. Fuel cell operated trucks should be affordable and operation-wise less expensive so that the owners do not incur loss. These owners would not be willing to invest in this technology unless the capital costs become low. Also, the operation of these trucks is very rough and runs for long hours. The fuel cell systems in such vehicles should be rugged and reliable with low maintenance costs. These factors impose further restrictions for the fuel cell technology to be implemented in such vehicles. The only option is to use fuel cells in the auxiliary power unit of trucks with the present state-of-the-art FC technology.

There is a small window for the entry of fuel cells in the niche vehicle market. These vehicles can

be forklift trucks in the warehouses of the industries such as food processing and microelectronics manufacturing. Such industries require zero emissions vehicles and mostly use battery-run electric vehicles to which fuel cell based vehicles will be a good alternative. Also, some airports in the country can switch to fuel cell operated vehicle fleet to decrease noise and air pollution inside the airport premise. Some monumental sites such as Taj Mahal in Agra impose severe restrictions on the use of fossil fuel based vehicles near the premise. Sites such as these can be a good market for fuel cell operated vehicles as they are already using electric vehicles.

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Review Article

Electrochemical Energy Storage Devices

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Increasing reliance on renewable energy sources, and technological advances in areas such as electric traction, smart grids and portable electronic gadgets have catalysed renewed interest in electrochemical energy storage options, of both miniature and large scale. The electrochemical mode of energy storage offers flexibility and scalability as well as candidate systems with a range of energy densities. With their low costs and low rates of self-discharge, they are particularly suitable for stationary applications as in power grids that are connected to intermittent renewable energy sources such as wind and solar. In this study, we assess the suitability of both mature and emerging electrochemical storage technologies that can meet the energy requirements of India.

Keywords: Energy Storage; Batteries; Electrochemical Capacitors; Energy Sustainability; Renewable Energy

Introduction

With the world electricity consumption expected to grow at 3.6% annually (engineeringnews.co.za, 2009), increasing emphasis is placed on more efficient technologies with low or zero-carbon footprints for both generation and use of energy. Since a key requirement of the grid distribution system is a balance of the amount of electricity fed into it and the demand, electrical storage technologies are called upon for both storing excess power and for meeting peak demands. The balancing act between supply and demand needs a re-look as we prepare to move from conventional power plants that depend, for example, on the fast-depleting oil to renewable energy sources such as those based on the wind and the sun. However, energy production by renewable technologies is weather-dependent and, therefore, unpredictable. Storage and release of electrical energy is critical for uninterrupted and non-fluctuating supply with increasing penetration of intermittent renewable power sources. However, there is only a handful of back-up storage technologies

that are efficient and at the same time economical. If additional requirements such as sustainability and low-carbon emissions are to be factored in, the choices narrow down to such technologies as pumped hydro storage (pumped storage hydroelectricity), which, however, comes with the burden of location, environmental conservation and social problems. Other leading energy storage technologies include flywheels, superconducting magnetic energy storage, compressed air energy storage, water electrolysis and methanation, and electrochemical energy storage devices such as batteries and electrochemical capacitors.

Several of these technologies have a fast response time, which is essential if power blackout during peak demand is to be avoided. However, high installation costs and poor efficiency (as with water electrolysis and methanation) can hamper their widespread use. Most importantly, they must also have low rates of self-discharge. Flywheel and superconducting magnetic energy storage

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technologies suffer from self-discharge rates of 3–20% per hour and about 12% per day, respectively. In contrast, the self-discharge loss in lead-acid batteries, for example, is only about 5% per month. Batteries and electrochemical capacitors can be cost-effective and allows for flexibility in deployment, which can in turn facilitate widespread use and networking of intermittent renewable energy technologies. Electrochemical storage technologies are ideal for transportation where instant power should be available to the vehicle for reasonable lengths of time. They are mature, inexpensive and ensure high levels of safety, reliability and durability. They are also ubiquitous, available in various sizes and capacities, suitable for stationary and portable applications in a broad spectrum of human activity.

Electrochemical Energy Storage Systems

Two types of electrochemical energy storage systems can be recognized: (i) batteries that store energy as chemical energy in their active materials (chemical storage) and (ii) electrochemical capacitors that store energy as charge (capacitive storage). Currently available electrochemical storage technologies fall short of projected everyday requirements, for example, electric vehicles, in terms of their energy and power densities, and even in terms of the time they take to get recharged. Our understanding of the fundamental

processes that govern their operation, performance, safety limits and failure is poor even after two hundred years of the demonstration of the first galvanic cell by Alessandro Volta. Much needs to be researched before we can translate our understanding of the fundamental molecular processes into practical devices. Here, we review the current status of electrochemical energy storage technologies and their limitations, and address key directions and new materials that can lead to high-performance energy storage devices. The individual systems chosen for discussion are considered both mature and emerging (European Parliament's Committee on Industry, Research and Energy, 2008; Soloveichik, 2011; Pollet *et al.*, 2012), suitable for a sustainable future, and adequate enough to meet the needs of the Indian populace. Table 1 compares the features of select battery systems.

Battery Systems

Lead-acid Batteries

Lead-acid batteries are unrivalled in terms of cost-effectiveness with less than \$150/kWh. It commands more than half of a whopping \$60 billion world battery market, with India's share of the market being \$4 billion. The most common use of these batteries is for starting-lighting-ignition (SLI) in automobiles. The

Table 1: Features of select battery systems

System	Cell voltage (V)	Energy density (Wh/kg)	Cycle life	Self-discharge/month (%)	Major issues/limitations
Lead-acid	2.04	25–40	200–300	5	Low energy density
Nickel-cadmium	1.2	45–80	1000	15–20	Cadmium toxicity
Nickel-metal hydride	1.2	70	300–500	20–30	Cost of rare earth metals
Nickel-iron	1.37	30	3000	30–50	Gassing; low charging efficiency
Lithium-ion cobalt	3.6	150–190	500–1000	5–10	Safety
manganese	3.8	100–135	500–1000	5–10	Poor performance above 55°C
phosphate	3.3	90–120	1000–2000	5–10	
Sodium-sulphur	1.78–2.08	140–170			

Note: Cycle life is defined here as the number of complete charge-discharge cycles that a battery can sustain before its capacity drops below 80% of its original capacity

battery operates on the double sulphate reaction in which both the active materials, spongy lead in the negative plate and lead oxide in the positive plate, are reversibly converted into lead sulphate. Their cycle life and deep discharge capability depend on the type of construction.

A mature technology, the lead-acid battery is backed by 150 years of development. Contrary to what some believe, scientists have come to recognize that there is more to be expected from lead-acid batteries. In fact, until not long ago, they were stereotyped with the common SLI batteries, whose performance expectations are limited. The entry of high-energy batteries such as nickel-metal hydride and lithium-ion batteries triggered research on tapping deeper into the performance capabilities of lead-acid batteries. Electrode reactions in lead-acid batteries give rise to several products with differing morphologies. Deep-discharges, as expected in applications such as electric vehicles, would mean maximizing volume and morphological changes in the active materials, a consequence of which is shedding of the active mass. Deep discharge can also lead to corrosion of the positive plate. High-rate recharge and failure to routinely return to full state-of-charge can lead to sulphation of the negative plate. In stationary applications such as power grids and rooftop photovoltaic installations, less taxing regimes may be expected.

Commercially available lead-acid batteries have energy densities of 25-45 Wh/kg. Their discharge-charge efficiencies lie between 60% and 95%. Although their current energy densities are rather low and their cyclability only of the order of a few hundreds of cycles, they are the choice workhorse for a variety of applications where weight and bulkiness are secondary. The flooded-electrolyte lead-acid batteries are the traditional types used in stationary applications although the valve-regulated lead-acid batteries (VRLABs) are now increasingly being used. The VRLABs use a recombination mechanism by which the oxygen evolved at the positive plates combine with the hydrogen evolved on the negative plates to form water; this provision eliminates the need for periodical 'topping' and allows a sealed construction. These

batteries use an absorbent-glass-mat or a gelled mass as the electrolyte and have a compacted stack construction. VRLABs exhibit specific energies of 35-40 Wh/kg and 70-80 Wh/l, and energy and power efficiencies of 95% and 75%, respectively. Their self-discharge rates are only 2-5% per month. Improvements in design and use of alloying additives have resulted in VRLABs with a shelf-life of 8 years and a cycle-life of over 1,000 cycles.

As noted earlier, the science and technology of lead-acid batteries is undergoing a tremendous change, opening up possibilities in higher energy density applications. For example, both mechanical properties and corrosion resistance of lead grids have been improved by the use of alloying additives. A debilitating phenomenon in lead-acid batteries is sulphation, which is now sought to be mitigated by use of a thin layer of carbon in the negative plate (Kelley and Taylor, 2006). The results have been so dramatic that Honda replaced the nickel-metal hydride batteries in its Insight HEVs with these batteries. Other recent developments include 3D polysiloxane-based gel electrolytes as well as separators and light weight current collectors. Lead-acid batteries continue to cater to emerging demands for portable or reserve energy sources by novel technological innovations and/or design solutions for their production. Other advantages include an operation temperature of -20°C to $+50^{\circ}\text{C}$, and availability of technologies to recover 99% of lead from spent batteries. Key disadvantages such as relatively poor cycle-life and limited specific energy have, however, restricted their wider commercial adaptability.

Alkaline Batteries

Alkaline batteries-based invariably on the nickel oxyhydroxide cathode – are superior to the lead-acid battery in terms of energy turnover, ability to deliver continuous power, fast recharge capability and long service life. The nickel-iron battery, invented by Thomas Alva Edison in the USA as early as 1901, was extensively deployed in the railway carriages of the erstwhile Soviet Union. The instability of the iron electrode in alkaline medium and the lead-acid battery lobby put the lid on the nickel-iron battery technology.

However, in recent years, interest in nickel–iron batteries is being revived since these batteries are reliable and inexpensive. They can be subjected to high discharge rates, exhibit good low- and high-temperature behaviour with long cycle life, undergo two-step charge-discharge and provide reserve charge during the second step of discharge. These batteries are electrically and mechanically rugged, and, above all, environment-friendly. The nickel-cadmium system, developed by Waldemar Jüngner, and made maintenance-free and sealable by Neumann *et al.* (Varta Batterie, 1982), dominated the market for several decades. SAFT Batteries have commissioned the world's biggest nickel-cadmium battery bank (40 MW; 13,760 cells) for stationary applications in Alaska. An undesirable characteristic of nickel-cadmium batteries, especially those with sintered-type cadmium electrodes, is the memory effect. (Memory effect is a self-conditioning, reversible phenomenon by which nickel-cadmium cells appear to adjust their electrical properties to a certain duty cycle to which they have been subjected to for extended periods of time. It leads to a temporary and partial loss in capacity. In other words, the cells deliver less capacity than they are designed for. Memory effect is observed in cells with sintered-type cadmium negative electrodes.) Furthermore, their ability to recharge is limited by their substantial negative temperature coefficient. Their self-discharge rates are also high. These, together with the toxicity of cadmium, have led to a waning of the production of nickel-cadmium batteries worldwide. Advances in the technology of the nickel-zinc system are hampered by the poor cyclability of the zinc anode, primarily due to non-uniform zinc deposition upon recharge. In contrast, nickel-metal hydride batteries have shown promise in hybrid electric vehicles albeit being expensive and prone to heavy self-discharge.

Nickel-iron Batteries

In hibernation for decades, due to euphoria generated by rapid strides in competing battery systems, the nickel-iron system has begun to catch the attention of policy makers. The resurrection of the system rests heavily on its techno-economic feasibility for a number of applications arising out of recent technological developments. Two problem areas that have now been

successfully addressed are (i) catalytic recombination of hydrogen and oxygen gases that are evolved in the battery, with possibilities of a sealed battery and (ii) electrolyte/electrode additives that can shift the overvoltage for the hydrogen evolution reaction. Latching on to the new developments should propel nickel-iron battery for applications wherefrom lead-acid and nickel-cadmium batteries have been withdrawn. Its cost competitiveness is a given considering its longevity (typically 3000 cycles, corresponding to a calendar life of about 20 years). Particular areas of application should include stationary ones as in photovoltaic installations, where its mechanical robustness and long life even under adverse operational conditions such as over-charge, over-discharge, charge-stand, discharge-stand and inadequate maintenance would be very attractive.

Nickel-metal Hydride System

Cadmium being toxic, alternatives to the nickel-cadmium system began to be explored, which resulted in the nickel-metal hydride system (Willems, 1984; Ogawa *et al.*, 1988). The nickel-metal hydride battery uses alloys of AB_2 composition (A: drawn from Ti, V, Zr, etc.; B: Ni, Co, Cr, Mn, Al, Sn, etc.) and AB_5 compositions (A: La, Ce, Pr, Nd, or misch metal; B: Ni, Co, Mn, Al, etc.) as the anode. Improvements in the technology include use of a new A_2B_7 composition and PEO-KOH-gelled electrolyte that ensure 80% coulombic efficiency (Vassal *et al.*, 1999). Although nickel-metal hydride batteries have been popular power sources for consumer electronics, particularly in portable gadgets such as cameras, cell phones and laptops, and for electric traction, it is only recently that they began to be considered for uninterrupted power systems and telecommunication (Zelinsky *et al.*, 2010). However, the discharge-charge efficiency is only about 70%. Perhaps the one factor that stands against this system is its cost, which is about twice that of lithium-ion batteries. However, if the metals, especially the rare earths can be sourced locally, defunct nickel-cadmium manufacturing plants can be re-activated to suit this system. The metal components in these batteries must be recycled for sustaining this metal-rich technology as recovery procedures for nickel from spent batteries are already established.

A major disadvantage of nickel-metal hydride batteries is their high rate of self-discharge (typically 30% per month). Both nickel-metal hydride and nickel-cadmium systems have similar cell voltages, although the former does not exhibit memory effect. They have moderately high specific energies and tolerate temperatures up to 70°C, a trait that not many other systems can boast of. Despite its superior performance characteristics over the nickel-cadmium system, nickel-metal hydride batteries are up against lithium-ion batteries in competing for a share of the market. Today, the use of nickel-cadmium batteries is limited to special applications where nickel-metal hydride batteries would be found unsuitable. India is blessed with huge deposits of rare earth elements all along its southern coastal belt. Therefore, cost considerations that have prevented its widespread use may not be much of a constraint for India. This sharply contrasts with the scenario for lithium-ion technologies that depend entirely on imports for lithium metal and lithium chemicals.

Vehicular traction is one single application area where alkaline batteries hold promise due to high power capability and long endurance both in terms of cyclability and service life. For example, these batteries have been demonstrated to endure ten year service in automobiles and more than 200,000 running kilometres. Developments in this direction include replacement of the sintered nickel electrode with a foam electrode, bringing about ~50% improvement in volumetric capacity. Recent adoption of highly porous foam electrodes and new varieties of high-density nickel hydroxides has helped raise the volumetric charge density from 450 Ah/l for the sintered electrode to 700 Ah/l for the foam electrode. Similarly, a 30% increase in volumetric charge density has been achieved by simple replacement of the sintered cadmium electrode with a cadmium slurry electrode. Other developments include use of thin separators, new electrode designs and electrolyte compositions, all of which have brought about substantial improvements in the performance of the battery.

Metal-air Batteries

A clear advantage of rechargeable metal-air batteries

over conventional systems is that only one reactant, namely, the anode material, needs to be contained within the battery, while oxygen, the active material for the cathode, is sourced from the atmosphere. Thus, the energy densities of metal-air batteries can be high, between 110 and 420 Wh/kg (itpower.co.uk). A notable disadvantage of metal-air batteries, however, is their poor energy efficiency (around 50%). Research emphasis today is to move from the mechanically rechargeable version to the electrically rechargeable version. The latter version may have a lower specific energy, but has the advantage of lower life-cycle costs. The electrically rechargeable version may have a bi-functional cathode or an auxiliary (third) electrode, which is used only for recharging the battery. Metal-air batteries based on aluminum are purely mechanically rechargeable, while those based on zinc and iron are potentially electrically rechargeable. Considerable efforts are in progress to develop lithium-air rechargeable batteries with an open-circuit voltage of 3.86 V.

Recharging of the zinc electrode is fraught with problems of non-uniform deposition and shape change associated with precipitation, crystallization and grain growth. Two companies have in the recent past claimed to have developed a technology for long-cycling zinc-air cells and are planning large-scale production (phys.org, 2012; treehugger.com). While they are in common use in a variety of portable applications (e.g., earphones, wrist watches), zinc-air batteries are projected as ideal low-cost options for grid storage and for vehicular traction. They are safe to use and their constituents recyclable.

Unlike the zinc electrode, the iron electrode does not suffer problems of redistribution of active materials or gross shape change upon prolonged electrical cycling. The theoretical specific energy density of the iron-air system is 955 Wh/kg, which is about thrice that of nickel-iron batteries. The realization of such batteries rests heavily on the development of a bi-functional oxygen electrode and oxygen-selective membranes for mitigating carbonation of the electrolyte. Besides their low cost, their environment-friendliness is a rallying point for developmental activities in metal-air systems.

Lithium-ion Batteries

Lithium-ion batteries in commerce contain a variety of cathode materials such as layered lithiated transition metal oxides, lithium-manganese spinel oxide and lithium iron phosphate, although the anode-active material is usually carbon. The working principle of the lithium-ion battery is unlike that of conventional batteries, and is schematically described in Fig. 1. These batteries represent the cutting edge of electrochemical science and technology today. Bestowed with the highest energy densities (150 Wh/kg and projected to reach 200 Wh/kg with the introduction of nanocomposite electrodes (ntrc.itrc.org, 2004)), low self-discharge rates and nearly 100% discharge-charge efficiency, they have already captured a sizeable and niche market in portable gadgets. Although considered very expensive for applications such as transportation and grid storage, they are expected to vie for these markets once their costs are reduced by mass production. A major portion of the cost arises from specialized processing and assembly lines as well as from the adoption of safety measures. As for environmental impact, technologies are available for recovering transition metals such as cobalt from spent batteries. Lithium oxides and salts can also be recycled although their content in lithium-ion batteries is below 1% by weight (Shukla and Kumar, 2013a).

Current technologies aim at replacing the toxic and expensive cobalt in the electrodes with low-cost and environment-friendly metals such as iron, manganese, titanium, etc. Low-cobalt alternatives include $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, spinel electrode materials such as the high-

voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and olivines such as LiFePO_4 and $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$. A major breakthrough was made by the introduction of LiFePO_4 as the cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the anode. Systems based on the above two materials have lower voltages, which render them safer. On the anode side, much headway has been made in realizing practical specific capacities much above that of the conventional graphite. The new anode-active materials include alloy anodes, conversion electrodes and silicon. Replacement of the carbon anode with high-capacity silicon, especially in nanowire form, is attracting much attention. More stable and non-flammable electrolytes, including ionic liquid-based ones, are being investigated. Lithium-ion batteries have now become commonplace and are the choice systems for grid storage, telecommunication and photovoltaic applications.

New chemistries based on lithium are emerging, which include the lithium-sulphur and lithium-air systems. A practical energy density of 350 Wh/kg has already been demonstrated for the lithium-sulphur system (Mikhaylik *et al.*, 2008). The lithium-sulphur system could potentially double the specific energy of lithium-ion batteries and offer competitive cost. Much ground needs to be covered before problems associated with cyclability of the positive and negative electrodes are solved. Safer and long-lasting solid electrolytes are also being investigated. If integrated in a lithium-air battery, they should give an energy density of 1,000 Wh/kg (Kumar *et al.*, 2010). The realization of a practical lithium-air battery is even more formidable. There are a multitude of technical challenges to its realization including cyclability of the lithium anode, bi-functional electrodes for the rechargeable cathode, charge-discharge rate capability of the cathode, identifying electrolyte compositions, and designing membranes permeable to the electrolyte but impermeable to water and carbon dioxide.

Safety has been a recurring theme in lithium-ion batteries. The several recalls of products, especially by manufacturers of laptops and automobiles, and more recently, the grounding of Boeing's Dreamliner fleet, have not helped penetration of this technology into large-scale applications. While lithium-ion batteries come with built-in safety

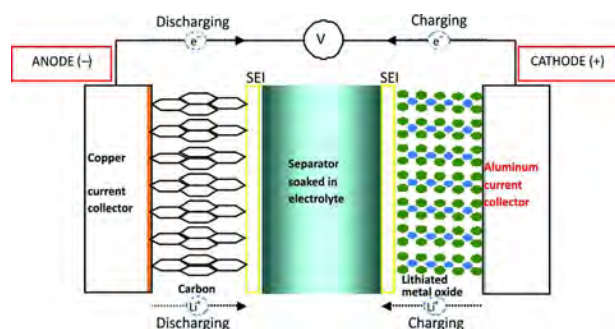


Fig. 1: Working principle of a lithium-ion battery

methodologies based on shutdown separators and electrical/pressure interrupts, manufacturers depend mainly on the expensive and more reliable safety circuitry for ensuring safety of the batteries. A complicating factor is the absence of uniform, standardized regulations for large batteries. This arises from the very nature of lithium-ion battery technologies that rely on a variety of active materials for their electrodes and even on a variety of electrolyte formulations.

Redox Flow Batteries

Redox flow batteries consist of two electrolytes each with a redox couple. The solutions, stored in separate tanks, are pumped through a cell in which chemical energy associated with the redox couples is converted to electrical energy. The most common of these redox couples are based on vanadium-vanadium, vanadium-bromine, sulphur-bromine, zinc-bromine, cerium-zinc, iron-chromium, and lead-lead. They have energy densities of about 35-50 Wh/kg only. However, they have a long operational life of about 40 years or tens of thousands of discharge cycles. Their energy and power can be increased independently of each other: energy by increasing the size of the electrolyte tank and power by increasing the size of the cell. Several commercial plants are in operation for grid storage. As flow cells operate for decades on end and generate hardly any waste product, their environmental impact is zero except probably during installation and dismantling. The vanadium-vanadium redox flow battery (with V^{5+}/V^{4+} and V^{3+}/V^{2+} redox couples), the iron-chromium flow battery (with Cr_{3+}/Cr_{2+} and Fe_{3+}/Fe_{2+} redox couples) and the soluble lead-acid flow battery are among candidate systems that must be pursued. The electrode reactions in the soluble lead-acid flow battery are the same as in the lead-acid battery. However, unlike in the other redox flow systems, one needs to employ only an undivided cell here. This is because both charged products (Pb and PbO_2) are insoluble while soluble discharge product (lead methanesulphonate) is common for both the electrodes.

Sodium-sulphur and ZEBRA Batteries

The key to success of the molten sodium-based

batteries is a solid membrane of $\beta-Al_2O_3$ (often doped with Li^+ or Mg^{2+}) with excellent sodium ion conductivity at elevated temperatures. Operating at 300-350°C, the sodium-sulphur battery gives an energy density of 140-170 Wh/kg at an average voltage of 1.78-2.208 V. The battery was originally developed for electric vehicle applications, but fell behind in the mid-1990s with the emergence of competing technologies such as the nickel-metal hydride. However, mega-watt installations still operate for power grid applications, the largest being a 34-MW/238-MWh (7 h) unit for the Rokkasho wind farm in Japan.

Replacement of the sulphur electrode in sodium-sulphur batteries with a cathode made of porous metal/metal halide impregnated with molten $NaAlCl_4$ results in ZEBRA (Zeolite Battery Research Africa) batteries. The replacement renders it safer than the sodium-sulphur battery. The usual metal halides are $NiCl_2$ and $FeCl_2$, yielding voltages of 2.58 and 2.35 V, respectively. The higher voltages translate to higher energy densities than that for the sodium-sulphur system. They also tolerate overcharge and over-discharge. ZEBRA batteries have been demonstrated for transportation and stationary applications. The capital cost of these batteries is around \$500-600/kWh.

Electrochemical Capacitors

Electrical Double Layer and Pseudo-Capacitors

Energy and power play against each other. Therefore, increasing one will lead to a loss in the other. This means that if we require high power from the battery, we will extract less total energy than when we require low power. Capacitors complement battery power by allowing very rapid charge and discharge cycles. Accordingly, capacitors will gel well with batteries into the emerging energy-storage landscape. As the capacitance mode allows storage of electricity directly as electrical charges, electrical double layer capacitors can have efficiencies close to 100%. Carbon-based electrochemical double layer capacitors exhibit high power densities (100-2,000 W/kg) but low energy densities (1-5 Wh/kg). Their typical discharge periods are between 1 s and 1 min. Because the charge and

discharge processes are purely physical phenomena and involve no chemical changes, wear is low; they sustain hundreds of thousands of cycles and last for more than 15 years. They are especially suitable for instantaneous voltage compensation. Thus, batteries and electrochemical capacitors are complementary power sources. For example, in electric vehicles, batteries can provide power for continuous drive while electrochemical capacitors can provide sudden bursts of power for acceleration and hill-climbing. The latter are also amenable to energy storage by regenerative braking. (In regenerative braking, the kinetic energy of a slowing vehicle is converted into electricity by recharging the car's battery. In conventional cars, the brake pads clamp down on the wheels and let the kinetic energy dissipate as heat. In regenerative braking, an electric motor is used to slow the car slow down. In other words, the flow of power through the electric motor is reversed to slow the car down, effectively converting the motor into an electric generator to charge the battery).

Charge storage by the pseudo-capacitance mode is another method of capacitive storage. A combination of faradaic and non-faradaic storage, as in supercapacitors, should, therefore, result in high pulse power with continuous energy (Ravikumar *et al.*, 2009). Noble-metal oxides with capacitance of about 700 F/g are now employed in supercapacitors. Owing to their prohibitive cost, they are sought to be replaced with transition metal oxides and non-oxides. Nano-structures of Ni(OH)_2 , MnO_2 , PbO_2 , etc. are also being investigated (Choi *et al.*, 2006; Naoi and Simon, 2008; Banerjee *et al.*, 2012). Targeted research goals include increased lifetime, higher rated voltage, wider range of operating temperatures, higher combined power/energy density, and capacitance of the order of 1000 F/g. Non-aqueous lithium-ion hybrid supercapacitors with operating voltages as high as 3.5 V are also on the horizon. Polymer-based supercapacitors such as those based on bithiophene-triarylamine, are attractive as they provide a peak specific capacitance of more than 990 F/g, but problems of swelling and contraction (leading to mechanical degradation and failure) as well as chemical degradation over repeated cycling must be addressed. Incorporation of CNTs in these electrodes

can mitigate degradation caused by volume changes by reducing diffusion lengths. For example, a PANI/CNT composite electrode with a hierarchical porous nanostructure provided a specific capacitance of 1030 F/g.

Lead-carbon Battery-supercapacitor Hybrid

The recognition that carbon added in small amounts (0.15-0.25 wt.%) into the negative paste of lead-acid batteries has been known to resist accumulation of lead sulphate (Shiomi *et al.*, 1997), led to a new class of energy storage devices: the lead-carbon asymmetric supercapacitors (Lam and Louey, 2006; Lam *et al.*, 2007). The new configuration not only ensures higher cycle life, but also reduced corrosion of the positive electrode because of diminished swings in acid concentration during charging and discharging. This system is also sealable similar to a VRLAB, with oxygen recombination efficiently supported by the carbon negative electrode. Moreover, it can be operated over a wider depth-of-discharge window than conventional lead-acid batteries and can be charged and discharged at higher rates. The new technology can replace the conventional lead-acid system in applications such as those of power grids. Its penetration is expected to be facilitated by the fact that essentially the same manufacturing infrastructure required for lead-acid batteries could be used for the new hybrid system.

Multi-functionality

Technological advances in areas as disparate as portable electronic gadgetry, electric vehicles and the electrical grid are often hindered by limitations of the power pack. Moreover, modern devices come with increasing multi-functionality. For example, today's mobile phones are transceivers of textual, voice and visual content with added capabilities for voice recording, photography, data storage and transmission, and multi-media entertainment. Furthermore, the power-on-demand profiles of applications become unpredictable, stretching over a large time scale as well as a large swathe of the energy/power spectrum. This requires power packs to be algorithm-controlled, multi-capable units with a balanced mix of batteries and electrochemical capacitors. Such battery-

electrochemical capacitor combinations should effectively wrap up the entire energy-power-time range, helping to blur the restrictions imposed by Ragone plots (Fig. 2). Such a judicious technology mix will also guarantee supply security and cost efficiency for a range of applications. Naturally, an area of research that is gaining momentum is asymmetric supercapacitor configurations that address the energy-power gulf between batteries and conventional capacitors. Specifically, these devices are based on large-area transition metal oxide electrodes that support rapid and reversible faradaic reactions in non-aqueous media that can operate at voltages much above 1.2 V.

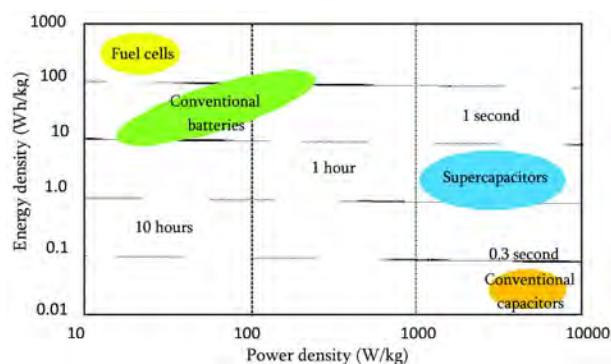


Fig. 2: Ragone plots for batteries, capacitors and fuel cells

New Materials, New Tools

Approaches to battery systems with higher performance should focus on (i) new materials and new chemistries, and (ii) improving the performance of existing systems (Shukla and Kumar, 2008). The push for batteries with higher energy and power densities would mean pushing the active materials and electrolytes to their stability limits. This also would mean a penalty in terms of safety, reliability and charge-discharge cyclability, three crucial factors that determine the acceptability of the device. While higher energy densities would require any new battery-active material to possess higher specific capacities and/or to form galvanic couples with higher cell voltages, cell safety and durability would require more stable electrode-electrolyte interphases. Batteries exhibit high energy densities, but their power densities are low. In contrast, electrochemical capacitors have low energy densities, but high power densities. Thus,

batteries and electrochemical capacitors complement each other in the energy-power equation. In addition, the latter deliver high pulse currents and sustain extended cycling. One way to enhance the energy densities of electrochemical capacitors is to resort to new materials with enhanced capacitive properties. However, a key priority in both the cases is the identification of highly conducting electrolyte solutions with wide electrochemical stability windows and capable of forming stable interphases with the active materials.

Nano-architectures, An Answer?

There is increasing evidence that electrochemical energy storage devices stand to gain from the rapidly strengthening nexus between electrochemistry and nanoscale science. A notable feature of this nexus is that a number of materials that have hitherto been dismissed as electrochemically inactive are now emerging as hot favourites to replace existing active materials in batteries. Particular mention must be made of demonstration of nano-SiO₂ (Chang *et al.*, 2012) and nano-SiC (Kumari *et al.*, 2013) as potential low-cost and high-capacity anode materials in lithium-ion batteries. Conversion electrodes are another class of such materials that hold promise as anodes that can deliver multiple electrons per molecular unit of the active material (Poizot *et al.*, 2000; Tarascon *et al.*, 2005). Such discoveries have opened the floodgates for systems that are projected as “beyond lithium” and “beyond intercalation chemistry”. The combination of electrochemistry and nanoscale materials chemistry has also triggered research into pseudo-capacitance charge storage materials. Studies with nanostructured materials have led to the possibility of moving towards the upper right quadrant of the Ragone plot, which erases the demarcation of “batteries for energy” and “capacitors for power” model.

Tailored, multi-functional nano-architectures can enhance performance through improved electronic and ionic conductivities, diffusion and mass transport, and electron transfer and electrocatalysis (Shukla and Kumar, 2013b). Due to their high surface areas, nanostructured materials can support high electrode reaction rates, which should translate to high power

capabilities. Moreover, because such structures present reduced diffusion lengths, the time constant for diffusion of active species can be brought down considerably. Although the high porosity of such materials should facilitate ingress of electrolyte into the interior of the electrode structure, it can reduce volumetric energy densities. Another disadvantage of nanostructured electrode materials is that due to higher surface energies, they facilitate undesirable reactions with the electrolyte, leading to extensive passivation, self-discharge, and truncated cycling/calendar life. While nanoscopic materials do promise high-performing devices, their suitability for energy storage hangs on our understanding of phenomena that occur at the nanoscale.

It is clear that the ability to control matter at the nanoscale is becoming an additional functional variable in our search for high-performance materials for electrochemical devices. However, that introduces more questions particularly relating to co-existence of nanoscale phases, role of surface energy on electrochemical properties, electrolyte structure in confined spaces, structure of surfaces at the nanoscale, effect of nano-dimensions on electronic properties, delineation of pseudocapacitive behaviour from faradaic reactions at the nanoscale, and inter-relationships between electron and ion transport in nanostructures.

Theory and Modelling

In contrast to their simplicity in appearance, batteries and electrochemical capacitors are complex systems with a multiplicity of reactive and passive components and interfaces. The performance of the device is thus limited by their properties. A theoretical understanding of the charge transfer phenomena in correlation with experimental results remains a large gulf that must be bridged. There are also limitations brought about by mass and charge transport, and their dependence on design and structural parameters. For example, the interplay of pore size, pore morphology and pore distribution on mass/charge transport, and electrolyte behaviour in confined spaces are poorly understood. Modern analytical and characterization tools, including *in situ* microscopic and spectroscopic tools, can help

unravel the complex molecular-level phenomena that underlie individual charge-transfer processes and the nature and properties of dynamically changing solid electrolyte interphases. Any insight thus gained on the working and failure mechanisms, backed by sound computational modelling simulation can lead to electrode materials, electrode architectures and system designs for next-generation storage devices.

The Road Ahead

It is necessary to introduce a policy on sustainable energy with stakeholders drawn from the academia, industry and government. The academia and R&D institutions should lay the seeds of technology independently or in partnership with industrial houses. Their research programs should specifically focus on high-risk basic technologies and platform technologies. The industry should focus on technologies for commercialization, allocating a part of its funds into research. In addition to devising business strategies for its growth, the industry should advise the government on emerging trends in the application sector. As a general enabler, the government should provide directions and funds for basic research, platform technologies, and infra-structure building, and even disruptive and tangential research.

India will need to establish the necessary expertise in carrying out transformational research and for absorbing imported technologies. A careful revamping of the syllabi at the university level is thus called for. Another strategy would be to establish centres of excellence in electrochemical power systems across the country, where services of people with proven/potential expertise can be tapped.

Conclusions

Given their critical role in energy security and in reducing greenhouse gas emissions, electrochemical energy storage should be a prime objective for policy makers. Large-scale economical storage of electrical energy for applications ranging from portable gadgets to transportation, power grid and beyond remains a great challenge and our weakest link to the future. Electrochemical storage technologies provide solutions for both decentralized units as well as for stationary

use. While their portability guarantees a niche market for them, competition can arise from other energy storage technologies for large-scale, stationary applications. It is thus necessary to reduce capital cost and enhance the service life and reliability of electrochemical energy storage systems. Mature technologies such as those of lead-acid and nickel-metal hydride batteries may soon be replaced by those of advanced lead-acid and lithium-ion batteries in the near term. Second-generation nickel-iron, lead-carbon hybrid and flow batteries should be able to meet the storage requirements in the mid-term. Emerging

technologies such as lithium metal polymer batteries, lithium-sulphur and lithium-air systems are expected to blossom only in the long term. In order to ensure that such technologies measure up to the demands of a developing nation such as India, cross-cutting research must be undertaken with special emphasis on the synthesis and characterization of multi-functional and nanostructured materials, and high-performance electrolytes, backed by sound theory of the physico-chemical phenomena and processes that occur at the molecular scale in these systems.

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Review Article

Advances in Thermoelectric Materials and Devices for Energy Harnessing and Utilization

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The emerging global need for energy generation, conservation, and utilization has intensified interest in more efficient, cost-effective and pollution-free means of power generation. Thermoelectric materials can generate electrical energy from waste heat and can play an important role in a global alternative energy solution. Recently, there have been significant advances in direct thermal-to-electrical energy conversion materials development and this has generated increased interest in the field of chemistry, physics and materials engineering. This article highlights a combination of new high performance materials, new device concepts and future directions to improve material efficiencies and cost effectiveness. Here, I have first presented a brief introduction to thermoelectrics followed by the reason for the importance of the research and development in this field for India. I have discussed about the main criteria for good thermoelectric materials and provided important examples of state-of-the-art materials followed by future direction and conclusions.

Keywords: Energy Conversion; Waste Heat Recovery; Thermoelectrics; Thermal Conductivity; Seebeck Coefficient; Earth Abundant Materials

Introduction

Driven by the demand for clean and sustainable energy sources, thermoelectricity has become a significant part of research portfolio seeking to identify new and efficient energy materials for power generation (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003). Thermoelectric materials can directly and reversibly convert heat energy into electrical energy (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003). The heat can be generated from the combustion of fossil fuels, from sunlight, or as a byproduct of various processes (e.g. combustion of coal and petroleum, chemical reactions, nuclear decay, etc.). Therefore, thermoelectric materials can play a pivotal role in both primary power generation and energy conservation (i.e., waste-heat harvesting). An important topic of discussion is how big this role is likely to be and the answer to this

question depends exclusively on how efficient these materials are. It is hoped and expected however that thermoelectrics will play a more increasing role than it has in the past and will be one of the several technologies working together to address energy efficiency issues.

Thermoelectric modules are solid-state devices that directly convert thermal energy into electrical energy (Fig. 1). This process is based on the Seebeck effect, which is the appearance of an electrical voltage caused by a temperature gradient across a material. The inverse of this, that is the appearance of a temperature gradient upon the application of voltage is known as the Peltier effect. For power generation, the thermoelectric efficiency (η) is defined by combining the Carnot efficiency ($\Delta T/T_{\text{hot}}$) and the figure of merit (ZT) as shown in the equation (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003).

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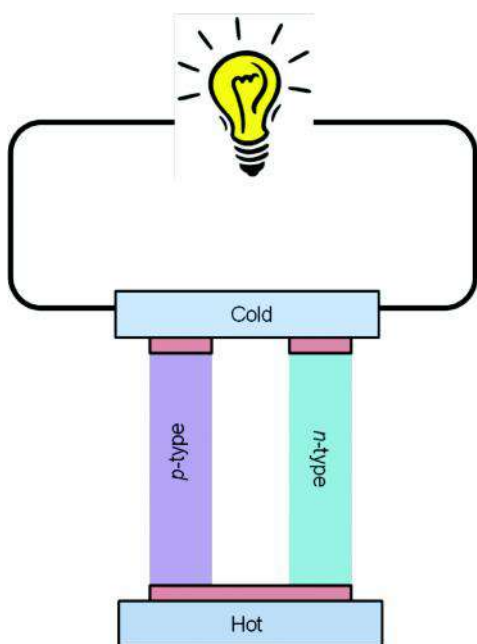


Fig. 1: Generic module diagram of a thermoelectric couple made of *n*-type and *p*-type materials in power generation mode

$$\eta = \frac{\Delta T}{T_{\text{hot}}} \left(\frac{\sqrt{1 + ZT_{\text{av}}} - 1}{\sqrt{1 + ZT_{\text{av}}} + \frac{T_{\text{cold}}}{T_{\text{hot}}}} \right)$$

where T_{hot} and T_{cold} are the temperatures of the hot and cold ends in a thermoelectric device and ΔT their difference. This equation indicates that increasing efficiency requires both high ZT values and a large temperature difference across the thermoelectric materials. Market-based thermoelectric devices currently available have a ZT of ~ 1 and operate at an efficiency of only around 6–8%. By increasing ZT by a factor of 4, and depending on ΔT , the predicted efficiency increases to 30%, a highly attractive prospect. The challenge to create high ZT thermoelectric materials lies in achieving simultaneously high electronic conductivity (σ), high Seebeck coefficient (S) and low thermal conductivity (κ) in the same solid. These properties define the dimensionless thermoelectric figure of merit $ZT = (S^2\sigma/\kappa)T$, where T is the temperature (Snyder and Toberer, 2008; Sootsman *et al.*, 2009; Chen *et al.*, 2003; DiSalvo, 1999; Trit, 2011; Li *et al.*, 2010; Biswas *et*

al., 2011; Biswas *et al.*, 2012). The quantity $S^2\sigma$ is called the power factor and is the key to achieving high performance. A large power factor means that a large voltage and a high current are generated. The thermal conductivity κ has a contribution from lattice vibrations, κ_{latt} , called the lattice thermal conductivity. Thus, $\kappa = \kappa_{\text{el}} + \kappa_{\text{latt}}$, where κ_{el} is the electronic thermal conductivity. Naturally, the thermal conductivity must be low as a large temperature gradient must be maintained; a large thermal conductivity will short the thermal circuit.

The field of thermoelectrics presents an important challenge to synthetic chemists, physicists, as well as the materials scientists. The main challenge in this field is to develop highly efficient, stable, environment-friendly and inexpensive solid state materials. The discovery of new promising materials requires a combination of theoretical direction, intense chemical intuition, synthetic chemistry skill, materials processing, and good measurement expertise. This powerful combination can be effectively achieved by reaching across scientific disciplines.

Why is Thermoelectrics Important to India?

In the last decade, Indian economy has shown incredible growth. Steadily and slowly, India is gaining strategic importance globally owing to the impressive economic growth pattern and market attractiveness. With growing economy, there will be more energy consumption in the country. India is the world's 5th largest energy consumer accounting for about 4.1% of the world's total annual energy consumption and moving fast enough to become the third largest consumer by 2025 after USA and China (Source: India Energy Book, 2012). The per capita energy consumption of India is 0.5 toe (tonnes of oil equivalent) as compared to the world average of 1.9 toe, and this indicates a high potential for energy consumption (Source, 2012). Fig. 2A shows the graph of total energy consumption by type for India in 2011 (Source: US Energy Information Administration, 2012). It can be seen that major percentage of the energy was consumed in terms of the use of coal, petroleum and gas. In general, main share of the electricity is generated from coal, hydro and nuclear fuel. On the

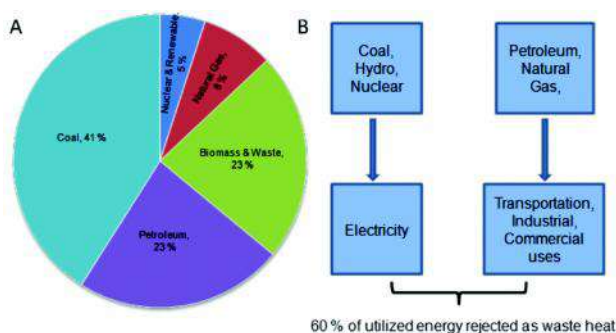


Fig. 2: (A) Total energy consumption by type for India in 2011. Source: U.S. Energy Information Administration, International Energy Statics, Indian Central Electricity Authority (2012). (B) Schematic shows partly the utilized energy being lost as waste heat

other hand, combustions of petroleum and gas are used to run the industrial and transportation sector in India. If we carefully observe that after the use of this enormous amount of energy in terms of electricity or combustion process, $\sim 60\%$ of the utilized energy is being lost as waste heat (Fig. 2B) (Biswas *et al.*, 2012). Could it be possible to make use of this untapped heat energy? The answer is yes, and 10-20% conversion to the useful form can have significant impact on overall energy. Thermoelectric materials allow the direct conversion between thermal and electrical energy. Different sectors of application include automobiles, heavy trucks and vehicles, coal burning electric utilities, and nuclear reactor facilities. Anything that uses an internal combustion engine (moving or stationary) can use these thermoelectric materials to convert waste heat to electrical energy for enhanced energy-efficiency. Basic research and extensive academic-industrial collaboration are essential to improve the existing thermoelectric efficiencies further to make it usable for major applications.

Criteria for a Good Thermoelectric Material

Primary object to the field of thermoelectric materials is the need to optimize a variety of interdependent properties. To maximize the thermoelectric figure of merit (ZT) of a material, a large Seebeck coefficient, high electrical conductivity, and low thermal conductivity are required. As these transport

characteristics depend on interrelated material properties, a number of parameters need to be optimized to maximize ZT . As high ZT requires high electrical conductivity but low thermal conductivity, the Wiedemann-Franz law reveals an inherent materials conflict for achieving high thermoelectric efficiency. Electrical part of the thermal conductivity (κ_{el}) is directly related to electrical conductivity (σ) by the relation, $\kappa_e = L\sigma T$, where L is the Lorenz number (Snyder and Toberer, 2008; Sootsman *et al.*, 2009). Ideally, a good thermoelectric material should have low thermal conductivity (property of glass), high electrical conductivity (property of metal) and large Seebeck (property of semiconductor). Challenge lies in the field to optimize all these important properties to achieve high thermoelectric performances.

Reduction of the Thermal Conductivity

A successful approach to increase the ZT value has been introduced to modify an already promising compound by introducing point defects through the synthesis of solid solutions. The solid solution provides an environment of the atomic mass fluctuation throughout the crystal lattice (disorder), which gives rise to strong phonon scattering and generally can lead to the significantly lower thermal conductivity and a high ZT value. For example, solid solutions of $\text{PbTe}_{1-x}\text{Se}_x$ and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ have lower thermal conductivity than that of pure PbTe (see Fig. 3) (Kanatidis, 2010). Nanoscale inclusions in bulk materials can dramatically suppress lattice thermal conductivity by scattering the longer mean free path

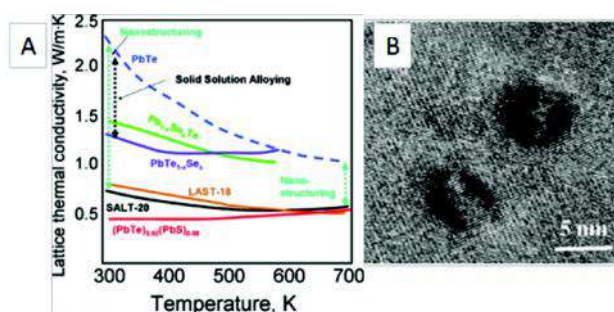


Fig. 3: (A) Lattice thermal conductivity as a function of temperature for various PbTe-based alloys and nanostructured samples. (B) High resolution transmission electron microscopy of a LAST-m sample. Source: Kanatzidis (2010)

heat-carrying phonons, as in $\text{AgPb}_m\text{SbTe}_{m+2}$ (LAST-m) (Fig. 3), which resulted in high ZT of 1.8 (Hsu *et al.*, 2004). Calculations predict that a wide size distribution of nanoparticles is preferable since it can effectively scatter different phonon modes and reduce thermal conductivity. However, the power factor is also reduced because the nanoprecipitates increase carrier scattering, which in turn unfavourably affects the carrier mobilities.

An interesting idea to achieve high ZT was proposed by Slack and is referred to as the “phonon glass electron crystal” (PGEC) approach (Slack, 1995). A PGEC material features cages in its crystal structure inside which massive atoms can reside. These big atoms are small enough relative to the cage to rattle. This situation produces a phonon damping that can result in significant reduction of the lattice thermal conductivity. In the PGEC picture, a glass-like thermal conductivity can in principle coexist with charge carriers of high mobility. The PGEC approach has inspired a significant amount of new research and has led to significant increases in ZT for several compounds such as the multiple filled skutterudites (Shi *et al.*, 2011).

Cubic AgSbTe_2 and AgBiSe_2 compounds are renowned for their intrinsically low κ_{lat} due to the strong anharmonicity of the bonding arrangements in these compounds (Morelli *et al.*, 2008). Recent theoretical and experimental studies on a series of cubic bulk I-V-VI₂ compounds have shown that the lone pair on the group V element plays an important role in deforming the lattice vibration, which results in strong bond anharmonicity (Nielsen *et al.*, 2012). Valence electronic configuration of Bi/Sb is ns^2np^3 , where only np^3 electrons are involved in the bond formation with chalcogen valence electrons while the beguiling ns^2 electrons of Bi/Sb form a lone pair. The origin of strong anharmonicity in Bi/Sb-X (X = S/Se/Te) bond is the electrostatic repulsion between the stereochemically active lone pair of Bi/Sb and the valence bonding charge of the chalcogen (Guin *et al.*, 2013).

Increment of the Power Factor

The important challenges in current thermoelectric

research are how to increase the thermoelectric power (S) of a material without depressing the electrical conductivity (σ) and to predict precisely which materials will have a high power factor ($S^2\sigma$). Generally, the thermoelectric power and electrical conductivity change in opposite directions with doping (Sootsman *et al.*, 2009) and thus there is a compromised set of values that must be achieved. Generally, multiple pockets in valence or conduction band extrema give rise to high Seebeck coefficient (Snyder and Toberer, 2008). When the system is highly doped, more valleys are populated, thus resulting in high power factor. Convergence of multiple charges carrying electronic band valleys has virtually no detrimental effects on the carrier mobility (μ). Multiple degenerate valleys (separate pockets of Fermi surface with the same energy) have the effect of producing large effective mass (m^*) without explicitly reducing μ (Pei *et al.*, 2012). Flat/broad valence band maximum also gives rise to high m^* (Guin *et al.*, 2013, 2014a, b), thus resulting in enhanced S as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{3/2},$$

where k_B is the Boltzmann constant, e is the electron charge, h is the Planck constant and n is carrier concentration.

Boltzmann transport theory describes both electronic and thermal transport in the vast majority of solids. This theory provides a general understanding of the thermopower (S) that is expressed by the Mott equation (Sootsman *et al.*, 2009):

$$\left[S = \frac{\pi}{3} \frac{k_B T}{e} \frac{d \ln \sigma(E)}{dE} \right]_{E=E_f},$$

$\sigma(E)$ is the electronic conductivity determined as a function of the band filling of Fermi energy, E_F . If electronic scattering is independent of energy, then $\sigma(E)$ is just proportional to the density of states (DOS) at E . Fig. 4 shows two hypothetical electronic DOS diagrams; one in which the DOS varies rapidly near E_F , and the other in which it does not. Based on the above equation, the system in Fig. 4A with sharp

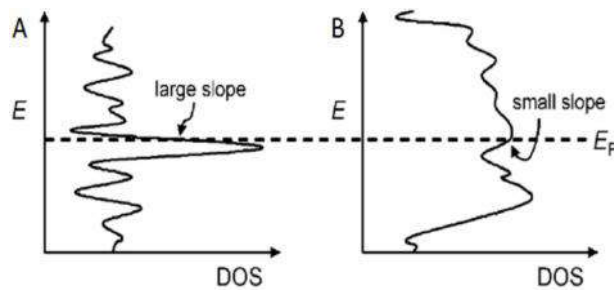


Fig. 4: Hypothetical density of state (DOS) with (A) a large slope and (B) a small slope near Fermi energy (E_F). Source: Sootsman *et al.* (2009)

changing DOS is expected to have a larger thermoelectric power (Sootsman *et al.*, 2009).

Thus, important parameters to consider when selecting or designing material systems are the band gap values, the shape and width of the bands near the Fermi level (E_F), and the carrier effective masses and carrier mobilities. The band gap is important because, in general, it is the temperature at which the ZT maximizes scales with band-gap size (Snyder and Toberer, 2008). This is because for a given band gap energy (E_g), there is a temperature at which thermally induced cross-gap carrier excitations occur to generate carriers of opposite sign which decrease the thermopower. Thus, for cooling applications, lower band-gap (0.1-0.2 eV) materials are best; whereas for high-temperature power generation, slightly larger band gaps (0.3-1 eV) are well-suited.

State-of-the-art Thermoelectric Materials

Various thermoelectric materials have been prepared and are present as device form in the mass market. My goal herein is to provide a brief overview about the most recent progress in thermoelectric materials. The thermoelectric figure of merit of the best recent thermoelectric materials is compared in Fig. 5 (Kanatzidis, 2010). Here onwards, a few of them are discussed case-by-case.

Bismuth Chalcogenides

Bi_2Te_3 is a narrow-gap semiconductor with an indirect gap of ~ 0.15 eV (Sootsman *et al.*, 2009). Bi_2Te_3 crystallizes in the rhombohedral space group $R\bar{3}m$ and the structure is made up of quintuple layers (Te1-

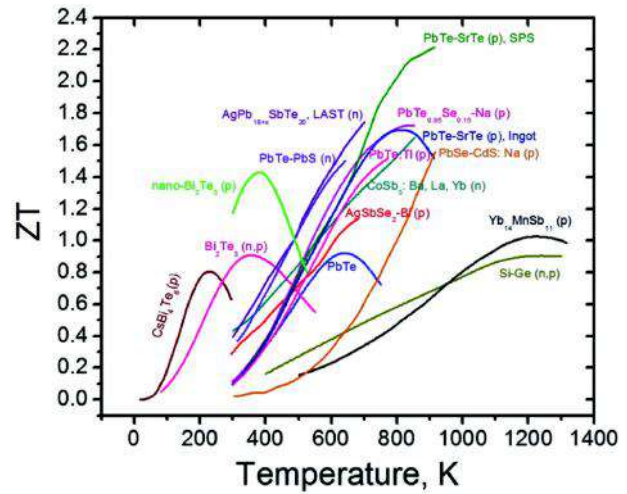


Fig. 5: Current state-of-the-art in bulk thermoelectric materials. Plot shows the temperature-dependent thermoelectric figure of merit (ZT) vs T . Note: Data obtained from recent literature and Kanatzidis (2010)

Bi-Te2-Bi-Te1), stacked by van der Waals interactions along the c -axis in the unit cell (Fig. 6A). The state-of-the-art Bi_2Te_3 materials with $ZT = 1$ are synthesized by alloying with Sb for p -type and Se for n -type materials. In actual devices, the p -type “legs” are

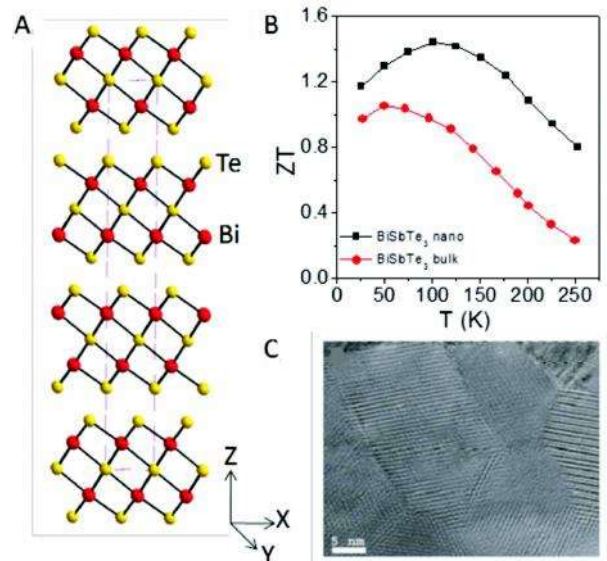


Fig. 6: (A) Layered crystal structure of Bi_2Te_3 . (B) Temperature-dependent ZT of hot-pressed nanostructured and market-based ingot bismuth antimony telluride. (C) Transmission electron microscope (TEM) image showing nanocrystalline grain of high performance bismuth antimony telluride. Note: (B) and (C) from Poudel *et al.* (2008)

generally hot-pressed and annealed pellets of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, which have good mechanical properties. The *n*-type counterpart is typically an ingot form of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ grown by zone melting techniques. Melt spinning followed by spark plasma sintering (SPS) yielded *p*-type Bi_2Te_3 ingots with a *ZT* value of 1.35 at 300 K (Tang *et al.*, 2007). This material features 25 nm wide ribbons composed of nanostructured layers of Bi_2Te_3 crystals with 1 nm interplanar distance. The highest *ZT* value for a bulk *p*-type Bi_2Te_3 material was reported recently (Poudel *et al.*, 2008). The material with *ZT*~1.4 at 100°C was prepared by ball milling followed by hot pressing (see Fig. 6B) (Poudel *et al.*, 2008). The *ZT* enhancement for this system arises from reducing the lattice thermal conductivity while maintaining a comparable power factor to that of the bulk *p*-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$. This material is called “nanobulk” $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ and it is a single-phase material composed of nanograins and micrograins mixed together (see Fig. 6C). Devices made of these nanostructured materials have shown superior thermoelectric efficiency than that of the devices from commercially available *p*-type Bi_2Te_3 . Promising thermoelectric performance has been achieved in nanostructured Bi_2Te_3 , Sb_2Te_3 and their alloys synthesized by bottom-up solution-based microwave-assisted synthesis (Mehta *et al.*, 2012).

CsBi_4Te_6 is a promising material for low-temperature thermoelectric applications (Chung *et al.*, 2000). The presence of Bi-Bi bonds in the structure is responsible for the very narrow energy gap (~0.08 eV), nearly half of that of Bi_2Te_3 . The narrower band gap is responsible for the maximum *ZT* value in CsBi_4Te_6 being at lower temperature than that of Bi_2Te_3 . A *ZT* value of 0.8 at 225 K was obtained for 0.06% SbI_3 -doped CsBi_4Te_6 .

Lead Chalcogenides

PbTe is the champion thermoelectric material for mid-range temperature (600–800 K) applications. It crystallizes in the NaCl crystal structure with Pb atoms occupying the cation sites and Te forming the anionic lattice. A band gap of 0.32 eV allows it to be optimized for power-generation applications and can be doped in either *n*- or *p*-type with appropriate

dopants.

Significant enhancement of the Seebeck coefficient was achieved by introducing resonance level (sharp changes in density of states) in the valence band of PbTe by doping 2 mol% thallium, which resulted in the doubling of *ZT* to 1.5 at 773 K (Heremans *et al.*, 2008). The *p*-type Na-doped $\text{PbTe}_{1-x}\text{Se}_x$ also exhibits high performance thermoelectric properties (*ZT*~1.8 at 850 K) arising from convergence of the multiple valence bands (Pei *et al.*, 2011).

Nanoscale inclusions in bulk materials can dramatically suppress the lattice thermal conductivity (κ_{latt}) by scattering the longer wavelength heat-carrying phonons, as shown for the first time in $\text{AgPb}_m\text{SbTe}_{m+2}$ (Hsu *et al.*, 2004). In all these cases, however, the power factor ($S^2\sigma$) is also reduced because the nanoinclusions increase carrier scattering which in turn adversely affects the carrier mobilities. Recently, it was observed that by embedding endotaxial SrTe nanocrystals at a concentration as low as 2% in *p*-type bulk PbTe, the heat flow can be greatly inhibited without affecting the carrier mobility, thereby allowing a large power factor to be maintained (Biswas *et al.*, 2011). The insensitivity of carrier scattering was attributed to valence band alignment of SrTe and PbTe allowing facile hole transport. The crystallographic alignment of SrTe and PbTe lattices and associated strain at interfaces decouples phonon and hole transport leading to a thermoelectric figure of merit of 1.7 at ~800 K (Biswas *et al.*, 2011). Later, similar research has been extended to PbTe–MgTe/CaTe/BaTe (matrix–nanoprecipitate) system, where promising thermoelectric performances have also been achieved (Biswas, He *et al.*, 2011; Ohta *et al.*, 2012; Lo *et al.*, 2012). Recently, Biswas and Kantzidis have demonstrated the substantial suppression of lattice thermal conductivity at high temperature in the PbTe–SrTe system that leads to a record high *ZT* of ~2.2 at 915 K in spark plasma sintered-processed samples (Biswas *et al.*, 2012). This is the result of introducing phonon scattering at all-length scales in a hierarchical fashion from atomic scale doping and endotaxial nanostructuring to mesoscale grain boundary engineering (Fig. 7). With this new advance in the maximum *ZT*, average ZT_{avg} values of ~1.2 and

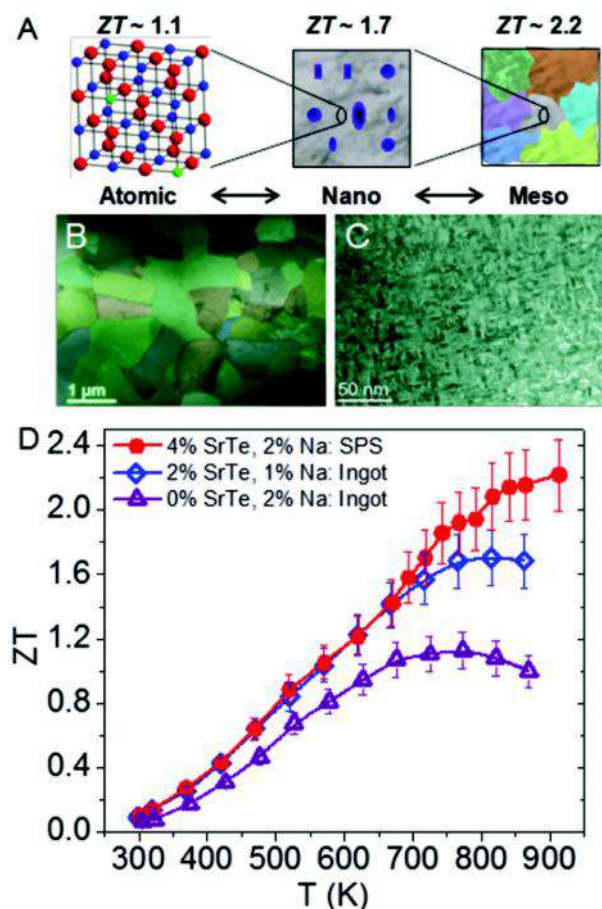


Fig. 7: (A) Maximum achievable ZT values for the respective length scales: the atomic scale (alloy scattering), the nanoscale (PbTe matrix, grey; SrTe nanocrystals, blue) to the mesoscale (grain-boundary scattering). (B) and (C) TEM images show the micro and nanostructures in spark-plasma-sintered PbTe-SrTe doped with Na. (D) Temperature-dependent ZT for an ingot (atomic scale), endotaxial nanostructured PbTe (atomic plus nanoscale) and spark-plasma-sintered PbTe (atomic + nano + mesoscale). Source: Biswas *et al.* (2012)

~ 1.7 were obtained for non-segmented and segmented thermoelectric devices, respectively (segmentation with BiSbTe, $ZT \sim 1.2$ at 350 K). Considering a cold side temperature of 350 K and hot side temperature of 950 K for such devices, waste heat conversion efficiencies, respectively of $\sim 16.5\%$ and $\sim 20\%$ were predicted (Biswas *et al.*, 2012).

Silver Antimony Chalcogenides

Fifty years earlier, Rosi (Rosi *et al.*, 1961) recognized AgSbTe₂ to be an efficient p -type thermoelectric

material with ZT of 1.3 at 720 K. In the recent years, AgSbTe₂ compound has been repeatedly studied to improve performance further by optimization carrier concentration through various doping. Interestingly, AgSbTe₂ alloys with GeTe (TAGS) (Lee *et al.*, 2014; Salvador *et al.*, 2009; Zhang *et al.*, 2013) and PbTe (LAST-m) (Hsu *et al.*, 2004) showed extraordinary ZT values ~ 1.5 at 750 K and ~ 1.8 at 800 K, respectively. Recently, we have shown from India that enhanced electrical transport and ultra low thermal conductivity resulted in high thermoelectric performance of Pb or Bi doped bulk p -type AgSbSe₂ which is Se analogue of AgSbTe₂ (Guin *et al.*, 2013). The maximum ZT achieved is 1.2 at 685 K for 2 mol% Bi-doped sample, which is 190% higher than pristine AgSbSe₂ sample (Fig. 8). With this advance in the maximum ZT values of this Te-free material, we can expect an average ZT value of ~ 0.75 (considering a hot side temperature of 700 K and cold side temperature of 350 K), which is higher than leading metal selenide-based thermoelectric systems reported recently in literature (Fig. 8) (Guin *et al.*, 2013). Considering a cold side temperature of 350 K and hot side 700 K for such devices, waste heat conversion efficiencies, respectively of $\sim 9\%$ was predicted, which is comparable to market-based metal telluride devices. We have also shown that by introducing second phase nanostructures and proper carrier engineering, high ZT can be achieved in AgSbSe₂ (Guin *et al.*, 2014a, b).

Skutterudites

Skutterudites are a extremely promising class of compounds for thermoelectric power generation (Shi *et al.*, 2011). They crystallize in the cubic CoAs₃-type structure with the space group $Im\bar{3}$. The structure is composed of eight-corner-shared XY₆ (X=Co, Rh, Ir; Y=P, As, Sb) octahedra. Linked octahedra gives rise to a void at the centre of the (XY₆)₈ cluster, where the void space occupies a body-centered position of the cubic lattice. This void is large enough to accommodate large metal atoms to form filled skutterudites. Since the void-filling atoms can act as electron donors or acceptors, partially filling the void space of skutterudites could lead to an optimum electron concentration. At the same time,

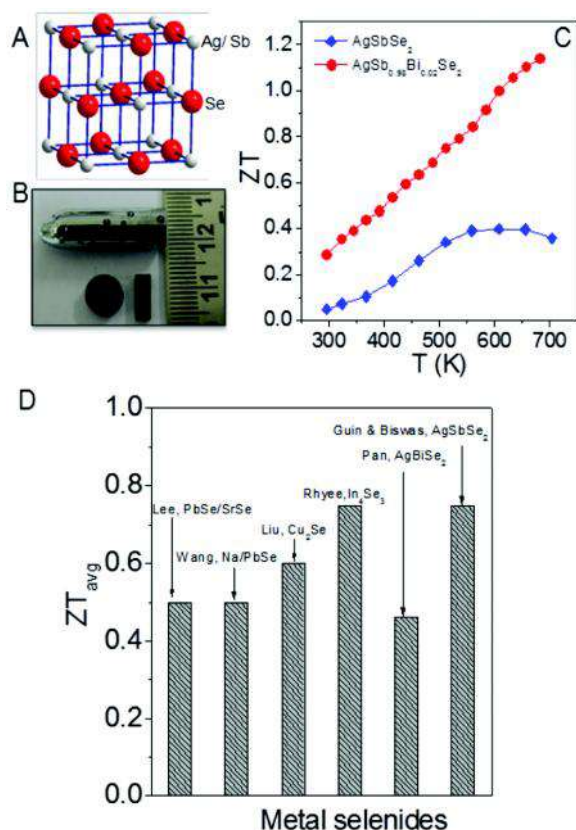


Fig. 8: (A) Crystal structure of cubic rocksalt AgSbSe₂ with disordered Ag/Sb positions. (B) Photograph of as-synthesized ingot. Bar- and coin-shaped samples are used for electrical and thermal transport measurements, respectively. (C) Temperature-dependent ZT of Bi-doped and pristine AgSbSe₂. (D) Average ZT of present AgSb_{0.98}Bi_{0.02}Se₂ and leading metal selenides reported in recent literature, considering a hot side temperature of 690 K and cold side temperature of 350 K. Source: Guin *et al.* (2013)

these atoms can also act as strong phonon-scattering centres to greatly reduce the lattice thermal conductivity. The “rattling” effect of these void-filling atoms has resulted in improvements in the thermoelectric properties of skutterudite. High ZT values of partially filled skutterudites with a small amount of Ni doping for Co, Ba_{0.30}Ni_{0.05}Co_{3.95}Sb₁₂ (ZT~1.25 at 900 K) were reported (Tang *et al.*, 2005). Further improvement in the ZT was achieved by filling up multiple atoms in the void of CoSb₃ (Shi *et al.*, 2011).

Half-Heusler Compounds

Another class of compounds of considerable interest

as potential thermoelectric materials for high-temperature applications are the half-Heusler (HH) compounds (Snyder and Toberer, 2008; Sootsman *et al.*, 2009), given by the composition MNiSn (M=Ti, Hf, Zr). HH phases have the MgAgAs crystal structure which consists of three filled interpenetrating face centered cubic sublattices and one vacant sublattice. The general formula is XYZ, where X and Y are transition metals and Z is a main-group element. Another advantage of these compounds is their high melting points of 1100-1300°C as well as their chemical stability with essentially zero sublimation at temperatures near 1000°C. The Heusler intermetallic compounds with fully filled sublattices are metals (full-Heusler alloys), whereas the vacant Ni atom sites in half-Heusler compounds give rise to narrow bands resulting in d-orbital hybridization and substantial semiconducting character of the compounds. Notable progress was reported with ZT ~0.7 at 800 K for n-type Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01} (Shen *et al.*, 2001). Sakurada and Shutoh (2005) reported a ZT value near 1.4 at 700 K for n-type (Zr_{0.5}Hf_{0.5})_{0.5}Ti_{0.5}NiSn_{1-y}Sb_y. A study by Indian researchers shows enhanced thermoelectric performance (ZT ~ 1.1 at 773 K) in nanostructured Zr_{0.25}Hf_{0.75}NiSn was prepared by ball milling followed by spark plasma sintering (Bathula *et al.*, 2012).

Future Outlook and Conclusions

The development of new materials and complex composites over the last 5-10 years has significantly increased the ZT values. It has been occurred through better theoretical understanding, development of new synthesis techniques, and state-of-the-art measurements that the field has progressed so far and promises to move forward further. For a long time, it was thought that there was a practical barrier at ZT = 1; however, new mechanisms for increasing the power factor and reducing the thermal conductivity in thermoelectric materials continue to emerge and increase the ZT value. The newest generation of bulk materials has ZT ~1.6-2.2 at approximately 700-900 K (Biswas *et al.*, 2011, 2012; Pei *et al.*, 2011). It is hoped that ZT ~3 will soon be achieved, which will provide a new generation of thermoelectric power generators with thermoelectric efficiency of ~25%.

Future efforts in understanding these mechanisms promise to increase the ZT value further and enable more practical application. The discovery of advanced thermoelectrics poses a challenge to chemists, physicists, materials scientists and engineers.

Further reductions in the thermal conductivity alone may be sufficient to raise ZT values to 2.5; however, to reach values of 3-3.5 or greater, we also need dramatic enhancement in the power factor. This can be achieved with innovation of some new and unexpected single-phase materials. What is needed now are new physical concepts on how the power factor can be enhanced 2-4-fold in the existing leading materials.

For realistic applications, the cost of power generation – as governed by material, manufacturing, and heat exchanger costs – is also a critical factor which is not captured in ZT alone (Yee *et al.*, 2013). Among the high performance materials, PbTe is the most efficient for power generation application at high temperature, whereas Bi_2Te_3 -based materials are well-known for refrigeration near room temperature. These leading high performance materials are mainly

based on tellurium which is enormously scarce in the earth's crust (Hu *et al.*, 2008). Hence, the cost of Te is likely to rise sharply if Te-based thermoelectric materials reach the mass markets. Therefore, it would be desirable to develop alternative materials which minimize the use of rare and toxic elements such as Te and involve cheaper and abundant elements. S and Se are much more earth abundant and less expensive than Te. Highly promising thermoelectric performance was observed in optimized bulk PbS (Zhao *et al.*, 2012), PbSe (Zhao *et al.*, 2013) and Bi_2S_3 (Biswas, Zhao *et al.*, 2012), which can replace expensive PbTe and Bi_2Te_3 based thermoelectric materials. We have also observed high thermoelectric performance in Te-free bulk AgSbSe_2 (Guin *et al.*, 2013, 2014a, b).

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Review Article

Hydrogen Energy in India: Storage to Application

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It is well-known that the evolution of society is guided by several environmental strains. One of the important strains existing at this point of time is climate change due to pollution. Other issue of paramount importance is “energy”. One of the comparatively new energy vectors which is typically suited for India is “hydrogen”. Hydrogen is an indigeneous fuel since it can be produced by dissociating water with a variety of input energies, out of which solar energy is of particular importance. India has both of these in plenty. Hydrogen produced from water burns back to water after use. It is thus climate-friendly, inexhaustible, clean and indigenous fuel. Hydrogen must first be produced, afterwards stored, and then used, particularly in vehicular transport. Hydrogen storage is the crucial issue of hydrogen economy, cutting across production, distribution and applications. Finding efficient materials capable of storing hydrogen with high gravimetric and volumetric efficiencies is the central issue for harnessing hydrogen to replace fossil fuel oil (petroleum). We have brought out the relevance of hydrogen, particularly its storage aspect. The study then focuses on various aspects of hydrogen storage materials. The article describes some hydrogen-fuelled devices with particular emphasis on vehicular transport (three-wheelers and small cars).

Keywords: Hydrogen Energy; Hydrogen Storage; Hydrides; Hydrogen-Fuelled Vehicle

Introduction

Energy is an important component of our life. It needs paramount attention with regard to its availability, in ever increasing amounts. As we attempt to improve the quality of our lives and enhance our efficiency for doing work, more and more energy is going to be needed. For India, increase in population is another reason for increasing required quantity of energy. Solar energy can safely be considered as the source of most forms of energy that we use. The commercial forms of energy, the fossil fuels, i.e. coal and oil are indirect manifestation of stored solar energy, which was formed several millions of years ago. Solar cells, both dry (producing electricity) and wet, producing hydrogen are manmade devices and directly convert solar energy to fuel.

With regard to oil, India is an energy-starved country. We have only 0.9% of total oil deposits, the Middle East has about ~60%, China ~5% and USA 15% (bp.com/statistical review, 2012). Owing to emergence of new oil resources and also highest oil sales, it is predicted that USA may surpass Saudi Arabia’s oil production. Several other countries such as Russia, Norway, and Libya also have large amount of oil deposit. It is estimated that the indigenous oil supply will last only about 23 years in India. The instability which oil imports create for our economy is well-known. Owing to increasing population and increase in vehicular transport for better comfort and efficiency, we need more and more oil. However, the depletion of oil is fast. We ought to remember that our main source of oil supply “Bombay High” peaked in 1998 and it is rapidly decreasing. We are thus in a paradoxical position.

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Another aspect which is at present comparatively more important is the issue of global warming/climate change. The Stern Report (2006) for the first time quantified the effect of global warming in economic terms. The temperature must not rise more than 2°C by 2050. Many countries are required to reduce their CO₂ remission to achieve the 2°C rise in temperature cap. For developing countries, there are no binding targets; but for developed countries, there are binding targets to reduce CO₂ emissions ([p://unfccc.int/files/kyoto_protocol/status_of_ratification/application/pdf/kp_ratification.pdf](http://unfccc.int/files/kyoto_protocol/status_of_ratification/application/pdf/kp_ratification.pdf)).

One aspect which is often forgotten is the fact that global warming climate change affects different countries differently. For example, global warming/climate change arising out of few degrees change in temperature will initially help cold countries such as USA. On the other hand, rise in temperature by few degrees will produce calamitous difficulty for warm countries such as India. Global warming/climate change produces detrimental effect on agriculture. For USA, the contribution of agriculture to GDP is only 0.9%; whereas for India, it is 22% (The World Fact Book, 2012). Thus, it is obvious that climate change will affect Indian economy drastically, in fact, it has already started affecting.

There are various ways in which global warming/climate change effects are quite different for India as compared to USA.

All the detrimental effects typically affecting India suggest that unlike USA, our country has to take the global warming/climate change much more seriously. Since oil (petroleum) is one of the most dominant sources of CO₂ emission, we have to switch over even if slowly to a renewable fuel for vehicular transport which does not produce CO₂. The urban air pollution resulting from use of petroleum deserves to be mentioned here. This is a serious problem emanating from the use of petroleum for vehicular transport. The air quality of not only Delhi, but many other cities, particularly metropolitan cities is quite bad. This aspect again demands, the gradual replacement of petroleum by a clean fuel. The above facts and figures suggest that for India, we not only need a clean and renewable fuel but also a fuel which is

source regenerating and indigenous. The following lists the motivations which should induce India to switch over to renewable fuel.

- Deficit between oil demand and supply
 - Huge imports ~170 MT (Ariga *et al.*, 2013)
- Economic burden (depletion of indigenous resources)
 - Irreversible climate changes (It could be the first priority.)
 - Air pollution

Decades of researches clearly led to the conclusion that out of the various renewable fuels, hydrogen is the best option for India. Hydrogen can be produced from water and hydrocarbons in a variety of ways. However, the most plausible and long-term sustainable mode is “solar hydrogen”, which is the hydrogen produced from dissociation of water by employing solar energy. India has solar irradiation next only to Africa (India ~800 watts/m², Africa ~1000 watts/m²). India has huge water resources such as the Indian Ocean, Arabian Sea and Bay of Bengal. Hydrogen produced from water burns back to water after use (cold combustion in fuel cells and hot combustion in IC engines). Thus, hydrogen is inexhaustible, indigenous, clean and climate-friendly. It thus solves the triple problems of gap in production consumption, supply, climate change effects and air pollution (Hudson *et al.*, 2009).

We will proceed to deal with hydrogen energy with particular emphasis on its use in vehicular transport. For harnessing hydrogen, its production, storage (including related effect of safety) and applications should be taken care of. It should be pointed out that as far as hydrogen production is concerned, it is already being produced to the tune of 57 MT per annum, which is equivalent to ~170 MT of oil (bp.com/statistical review, 2012). The methods of hydrogen production most commonly used are steam reformation of naphtha or methane. These processes even though practised widely produce CO₂ and hence result in global warming/climate change. Sustainable methods of production are those which employ solar energy to dissociate water or water-containing

species. These are photo-catalytic, photo-electrochemical and photo-biological routes of hydrogen production (Hudson *et al.*, 2009).

It may be pointed out that the search for viable hydrogen production routes takes into account the cost of hydrogen. In fact, the cost of hydrogen is possibly the top consideration in testing the viability of hydrogen as a fuel. However, it should be realized that the real cost of hydrogen takes into the account the costs involved in damages caused by use of fossil fuel. This is presented in Table 1 and Fig. 1.

Table 1: Enviromental and health damages by fossil fuels (after Prof. T.N. Veziroglu, private communication) (\$/GJ)

Type of damage	Coal	Petroleum	N. Gas
On Humans	5.84	4.51	3.33
On Animals	0.82	0.67	0.48
On Plants and Forests	2.15	1.74	1.29
On Aquatic Systems	0.29	1.68	0.18
On Man-Made Structure	1.78	1.43	1.07
Other Pollutant Costs	1.56	1.26	0.94
By Strip Mining	0.79	-	-
By Climatic Change	2.22	1.80	1.34
By Sea-Level Rise	0.51	0.41	0.31
Total Enviromental Damage	15.66	13.50	8.94

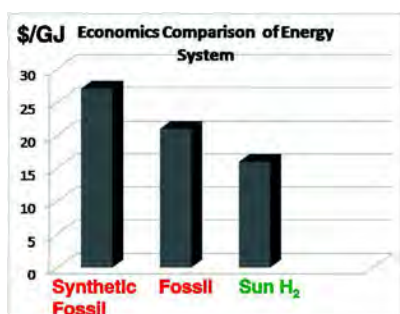


Fig. 1: Comparison of economics of hydrogen and fossil fuel systems (after T.N. Veziroglu private communication)

Hydrogen Storage

Hydrogen storage is considered to be the crucial issue for hydrogen economy, cutting across production,

distribution and applications. It is generally believed that storage in the form of hydrides is an efficient and safe storage mode with high hydrogen density (Hudson *et al.* 2009). Earlier, the emphasis was on hydrogen fill-in and take-out type hydrides typified by intermetallics, for e.g. FeTi, LaNi₅ (Züttel *et al.*, 2003), etc. The emphasis has recently shifted to take-out and regenerate type of built-in hydrides such as MgH₂, NaAlH₄, LiNH₂, etc. Out of these, MgH₂ appears to be a promising material because of its high storage capacity (7.6 wt.% H₂), better reversibility and plentiful availability of Mg in the earth's crust. It satisfies most of the requisites for a viable hydrogen storage system for mobile as well as stationary hydrogen devices. Slow hydriding and dehydriding are the major drawbacks of magnesium hydride as hydrogen storage material. Different studies also reveal that carbon-based nano-structures may also be used as effective hydrogen storage materials (Rao *et al.*, 2009).

Studies at Hydrogen Energy Center (HEC), Banaras Hindu University (BHU) are focused on hydrogen production, hydrogen storage and demonstration of hydrogen-fuelled vehicles. In this article, we will focus on storage and applications of hydrogen. For storage, the studies focus on Mg, Li-Mg-N-H and NaAlH₄ systems, with respect to the lowering of desorption temperature and enhancement of desorption kinetics by synthesizing these materials with alternative routes and deployment of various new effective catalysts. Here, we describe some important results on hydrogen storage materials which were studied recently at our centre.

Intermetallic Metal Hydrides

Intermetallic metal hydrides are often obtained by combining an element forming a stable hydride with an element forming an unstable hydride. The general formula for the intermetallic hydride is AB_xH_n. The A element is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. The B element is often a transition metal and forms only unstable hydrides. Some well-defined ratios of B to A in the intermetallic compounds are $x = 0.5, 1, 2, 5$ have been found to form hydrides with a hydrogen to metal ratio of up to two. The maximum amount of

hydrogen in the hydride phase is given by the number of interstitial sites in the intermetallic compound for which the following two criteria apply. The distance between two hydrogen atoms on interstitial sites should not be less than 2.1 Å (Switendick, 1979) and the radius of the largest sphere on an interstitial site touching all the neighbouring metallic atoms is at least 0.37 Å (Westlake, 1983). Usually, upon hydrogenation, binary alloys will experience lattice expansion and distortion, but the crystal structure will stay the same. On the other hand, for some hydrides, the crystal structure changes with hydrogen content.

Research on intermetallic compounds for hydrogen storage has already been attempted more than 20 years ago. Sakintuna *et al.* (2007) summarizes the results of different studies/investigations on hydrogen storage characteristics of different intermetallic compounds. The different families of intermetallic compounds are classified on the basis of their crystal structures. AB₂-type (Laves phase), AB₅-type phases and Ti-based body centered cubic (BCC) and quasicrystalline alloys are well-known intermetallic hydrogen-storage system. These are reviewed as follows.

AB₅-Type Hydrogen Storage Materials

LaNi₅ is the most studied compound belonging to this series. Several investigations have already been devoted to the crystal structure, thermodynamic and electrochemical properties. The hydriding properties of this material were first reported by Vuchet *et al.* (1970). LaNi₅ crystallizes in the hexagonal structure of a CaCu₅ type (space group P6/mmm with La in 1a (0 0 0) and Ni in 2c (1/3 2/3 0) and 3g (1/2 0 1/2)). The crystal structure of the metal host-lattice is generally preserved upon hydrogenation. Several types of tetrahedral interstices can be identified within the structure with different metal co-ordination: A₂B₂, AB₃ (2 types) or B₄ (Latroche *et al.*, 1998). Upon hydrogenation, the A₂B₂ sites are filled first, followed by the AB₃ sites. Occupation of the B₄ sites remains low, even for a fully loaded hydride. LaNi₅ absorbs about 1.0 H/LaNi₅ (1.5 wt%) and is easy to activate (5 bar at *T* = 100°C after a few cycles, to achieve the maximum hydrogen capacity). It has small absorption/desorption pressure hysteresis and the plateaus are

rather flat. The enthalpy of formation of LaNi₅H₆ is -30.9 kJ/mol-H₂ and desorption plateau pressure at 25°C is 1.6 atm. So far, the multi-component La_{1-x}RE_xNi_{5-x}M_x system has also been extensively studied (M = Mn, Cr, Fe, Co, Cu, Al, Sn, Ge, Si and RE = Mischmetal, Ce, Nd). LaNi₅ has very useful properties, but is rather expensive due to the presence of expensive elemental La.

AB-Type Hydrogen Storage Materials

FeTi is a well-known hydrogen-storage compound. This belongs to the class of intermetallic compounds with a total hydrogen capacity of around 1.90 wt% with inexpensive elements. However, the activation process of FeTi is troublesome due to the formation of Ti oxide layer. Both high-pressure and high temperature is required to achieve a reproducible absorption/desorption of the maximum amount of hydrogen in the compound (Bououdina *et al.*, 2013). Hydrogen capacity of FeTi can be accomplished to 1.90 wt% by the catalytic effect of 1 wt% Pd addition (Zaluski *et al.*, 1995 a, b). The application of mechanical alloying under different atmospheres with the use of catalytic elements, for e.g., Pd, dramatically enhances the activation process and the hydriding/dehydriding kinetics of FeTi (Zaluski *et al.*, 1996). Ball milling under pure argon atmosphere (20-0 h) of FeTi with small amount of Ni can readily absorb H₂ without activation (Bououdina *et al.*, 1999). Drastic improvement of the kinetics is due to the formation of a fine powder of FeTi covered by nanocrystalline Ni particles, which act as catalytic centres for the decomposition of H₂ molecules into H atoms.

AB₂ Laves Phases

AB₂ Laves phases have attracted great attention as potential hydrogen-absorbing materials. The potential AB₂ types are obtained with Ti and Zr on the A site. The B elements are represented mainly by different combinations of 3d atoms, V, Cr, Mn and Fe. AB₂ exists in three types of crystal structure: cubic C15 (MgZn₂, such as ZrV₂, low-temperature TiCr₂ and high-temperature ZrCr₂), hexagonal C14 (MgCu₂, such as ZrCr₂ low temperature, TiCr₂ high temperature and ZrMn₂) and double hexagonal C36 (MgNi₂). Laves phases show relatively high storage

capacities ($\text{ZrV}_2\text{H}_{5.3}$, $\text{ZrMn}_2\text{H}_{3.6}$, $\text{ZrCr}_2\text{H}_{3.4}$), faster kinetics, longer life and a relatively low cost. However, their hydrides are too stable at room temperature. In general, the AB_2 -type compounds seem to be more sensitive to gaseous impurities than the AB_5 -type compounds.

BCC Solid Solution

It has been reported that Ti-based Laves phase alloys of AB_2 type are multiphase alloys consisting of BCC and Laves phases. Both these phases are responsible for hydrogenation (Yang *et al.*, 2011). In fact, the BCC and Laves phase showed the same equilibrium pressure. For this reason, these new classes of alloys are called as Laves phase-related BCC solid solutions. Earlier studies on $\text{Zr}_{0.5}\text{Ti}_{0.5}\text{VMn}$ have shown that this alloy is composed of three phases. In subsequent studies on the Ti-V-Mn system, microstructure analysis by TEM revealed that the BCC phase consisted of two nanoscale phases with a fine lamellar structure of 10nm thickness (Cote *et al.*, 2005). Hydrogen storage capacity was found to be higher than 2 wt% for the system Ti-Cr-V. Furthermore, this system has a smaller hysteresis than Ti-V-Mn and needs only one activation cycle. Usually, BCC solid solution alloys form two types of hydrides: the first (approximately a monohydride) is very stable and usually cannot be desorbed under practical conditions; and the second (dihydride) is mainly responsible for the reversible capacity. Therefore, the challenge is to destabilize the first hydride or increase the intrinsic reversible capacity of the dihydride. Recently, many groups have reported BCC alloys of various compositions which could store hydrogen with a maximum capacity close to 4 wt% and with reversible capacities of more than 2 wt% (Murray *et al.*, 2009).

We proceed further to discuss the other types of hydrides. Here, these hydrides will be elucidated by describing and discussing the research done in our laboratory.

Elemental hydride

Magnesium Hydride; Co-catalysed with Ti, Fe and Ni

MgH_2 is one of the promising materials for reversible

hydrogen storage application due to its light mass, high hydrogen storage capacity (both volumetric and gravimetric) and abundance in nature. However, there are some key issues which need to be addressed for using MgH_2 as a practical onboard candidate. The issues associated with MgH_2 are high dehydrogenation temperature, slow kinetics of de/rehydrogenation and thermodynamics limitation. Details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2013). The starting materials: pure MgH_2 (500-1000 μm), Ti (150 μm), Fe (120 μm) and Ni (100 μm), were taken in various compositions. These powders (5 wt% each of MgH_2) were mechanically milled to obtain the desired compositions: $\text{MgH}_2\text{-Ti}_5$, $\text{MgH}_2\text{-Fe}_5$, $\text{MgH}_2\text{-Ni}_5$ and $\text{MgH}_2\text{-Ti}_5\text{-Fe}_5\text{-Ni}_5$. The container with samples was flushed through hydrogen to avoid the effect of residual oxygen. In order to investigate the structural modification of mechanically milled MgH_2 separately and together with Ti, Fe and Ni, XRD is performed for different samples. It is found that the grain size of milled MgH_2 is ~ 15 nm, whereas the grain size for as-received MgH_2 is found to be ~ 199 nm. It is also worth noticing that the XRD patterns of MgH_2 mechanically milled separately with Ti, Fe and Ni give the XRD peaks which correspond to TiH_2 , Mg_2FeH_6 and Mg_2NiH_4 hydride phases shown in Fig. 2A, respectively. On the other hand, when Ti, Fe and Ni are used together with MgH_2 , the alloys Mg_2NiH_4 and Mg_2FeH_6 do not get formed. This is likely since Ti has very little solid solubility. Hence, the presence of Ti may cover the surface of Mg particle due to which there is very less possibility for the diffusion of Fe and Ni in Mg particles for the formation of alloys. This may hinder the formation of Mg_2NiH_4 and Mg_2FeH_6 when Ti, Fe and Ni are used together as catalysts. Fig. 2G represents the decomposition temperature (peak at maximum decomposition temperature) of different samples. From Fig. 2G, it is clear that the maximum decomposition temperature of the received MgH_2 is 410°C and this is reduced to 370°C for nano MgH_2 . However, the decomposition temperatures for nano $\text{MgH}_2\text{-Ni}_5$, $\text{MgH}_2\text{-Ti}_5$, $\text{MgH}_2\text{-Fe}_5$ and $\text{MgH}_2\text{-Ti}_5\text{-Fe}_5\text{-Ni}_5$ are found to be 340, 320, 310, and 280°C , respectively. The effects of transition metals are higher when all these catalysts are used

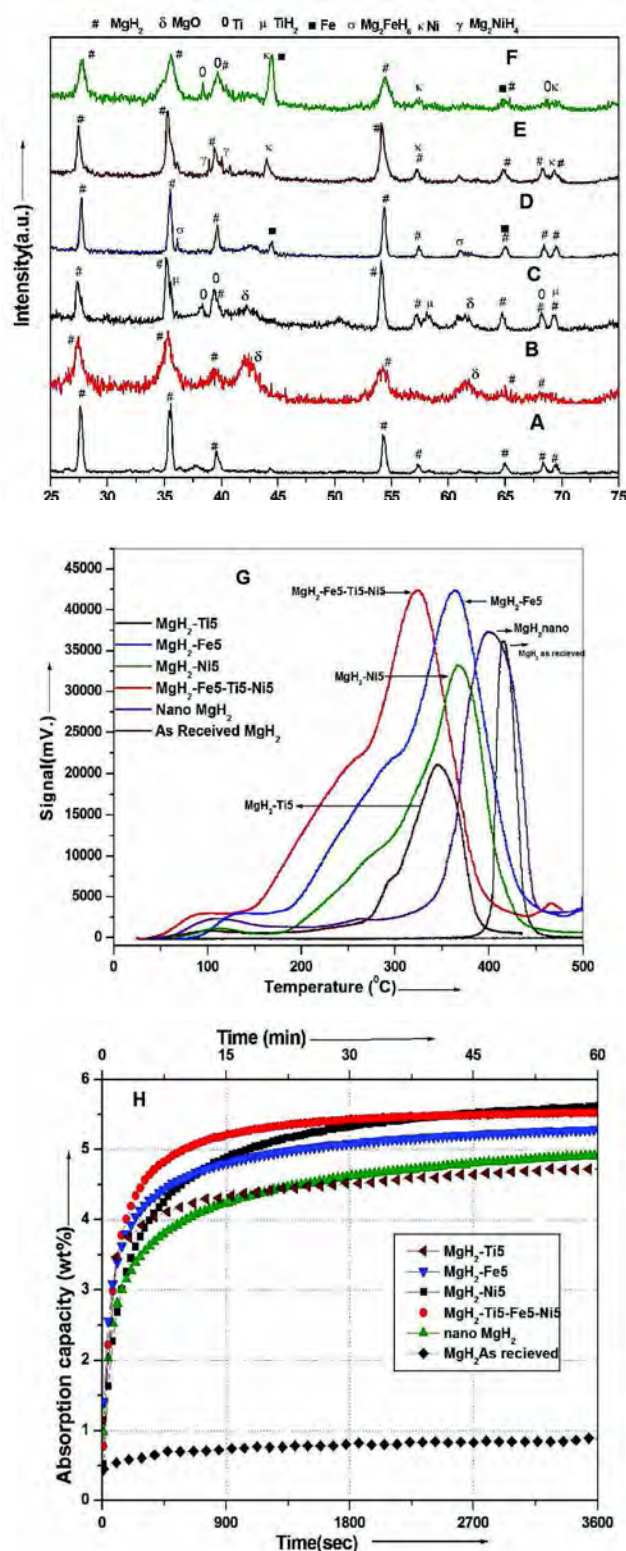


Fig. 2: X-ray diffraction pattern of (A) received MgH₂, mechanically milled (B) MgH₂, (C) MgH₂+5wt% Ti, (D) MgH₂+5wt%Fe, (E) MgH₂+5wt% Ni and (F) MgH₂+5wt% (Ti+Fe+Ni) (G) TPD profile of different samples and (H) absorption kinetics plot of different samples (Figures 1, 2a, 4b; Shahi *et al.*, 2012)

together. This may occur due to the co-catalysed effect of Ti, Fe and Ni (370°C to 280°C for nano MgH₂ to MgH₂-Ti₅-Fe₅-Ni₅).

In order to investigate re-hydrogenation characteristics of different samples, the absorption experiments were performed at 270°C and 15 atm of hydrogen pressure for 1 h. It is found that nano MgH₂ reabsorbs only 4.2 wt%; whereas, nano MgH₂-Ti₅, MgH₂-Fe₅ and MgH₂-Ni₅ absorb 4.3, 4.98 and 5.0 wt%, respectively. However, the absorption capacity for co-catalysed nano MgH₂-Ti₅-Fe₅-Ni₅ is found to be 5.3 wt% within 15 min. The difference in re-absorption capacity of the samples occurs due to the formation of stable hydrides TiH₂, Mg₂FeH₆ and Mg₂NiH₄ when Ti, Fe and Ni are mechanically milled separately with MgH₂. (Liang *et al.*, 1999) have also reported that these hydrides are highly stable and did not decompose under mild desorption condition. The presence of these Ti, Fe and Ni in Mg matrix causes co-catalysed effect of these transition metals and hence the de/re-hydrogenation characteristics of MgH₂ increase appreciably.

Effect of Carbon-based Nanostructures on Hydrogen Sorption in MgH₂

In addition to transition metals, another type of catalysts which has recently caught attention as effective catalyst for de/re-hydrogenation of MgH₂ are the carbon nanostructures. We have synthesized different morphologies of CNSs and investigated their catalytic effect on the hydrogenation behaviour of nano MgH₂ at HEC BHU. The details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2012).

Different CNSs were synthesized through the chemical vapour deposition (CVD) technique. Nanocrystalline MgH₂ (nano MgH₂) was synthesized through the method described previously by the ball milling of as-received MgH₂ (particle size is 50-100 μm) using Retsh PM-400 ball miller. Admixing of CNSs were performed inside the glove box by using locally fabricated mixer (at 4000 rpm) having three chromium nickel stainless steel balls.

In order to explore the effectiveness of CNS as catalyst for improving the de/rehydrogenation

behaviour of MgH_2 , temperature programmed desorption (TPD) (at heating rate $5^\circ\text{C}/\text{min}$) were performed for nano MgH_2 with and without CNS. Fig. 3A shows representative TPD profile for different samples. As seen in figure, desorption temperature is reduced to 346°C from 367°C with admixing of MWCNT (multi-wall carbon nanotube). Desorption temperature for SWCNT (single-wall carbon nanotube) admixed nano MgH_2 is found to be 357°C . Further, it is also found that desorption temperature is $\sim 334^\circ\text{C}$ and $\sim 300^\circ\text{C}$ for the PCNF and HCNF admixed nano MgH_2 . The desorption temperature of nano MgH_2 is reduced to $\sim 300^\circ\text{C}$ from $\sim 367^\circ\text{C}$ with admixing of HCNF (decrease of $\sim 67^\circ\text{C}$). Effectiveness of the catalyst is found to be highest for HCNFs followed by PCNFs, MWCNTs and SWCNTs. The absorption kinetics plots of nano MgH_2 with and without CNS at 300°C and 2 MPa of hydrogen pressure are shown in Fig. 3B. The hydrogen uptake capacity of nano MgH_2 is found to be 4.8 wt%. This gets improved with admixing of MWCNTs, SWCNTs, PCNFs and HCNFs. It is found that the nano MgH_2 admixed with MWCNTs, SWCNTs, PCNFs and HCNFs absorb 5.2, 5, 5.7 and 5.8 wt% of hydrogen within 1 h, respectively. It is also found that HCNF admixed nano MgH_2 absorbs ~ 5.25 wt% within 10 min as compared to pristine nano MgH_2 , which absorbs only ~ 4.2 wt% within the same time and same condition of temperature and pressure. Thus, absorption kinetics of the pristine nano MgH_2 improves significantly with admixing of HCNF.

There are two possible reasons for lowering of desorption temperature and improvement in rehydrogenation kinetics of CNS-catalysed nano MgH_2 . These are (a) type and morphology of carbon nanostructures and (b) presence of synthesis-acquired metallic particles. In order to confirm the catalytic effect of metallic particles, we have also conducted TPD experiments with acid-treated (purified) CNS under previously performed condition and compared the desorption results with that of pristine nano MgH_2 . From these investigations, we can say that the catalytic activity of purified CNS becomes less significant as compared to as-synthesized CNS. The purified MWCNT shows the marginal effect on desorption behaviour of pristine nano MgH_2 ($\sim 16^\circ\text{C}$),

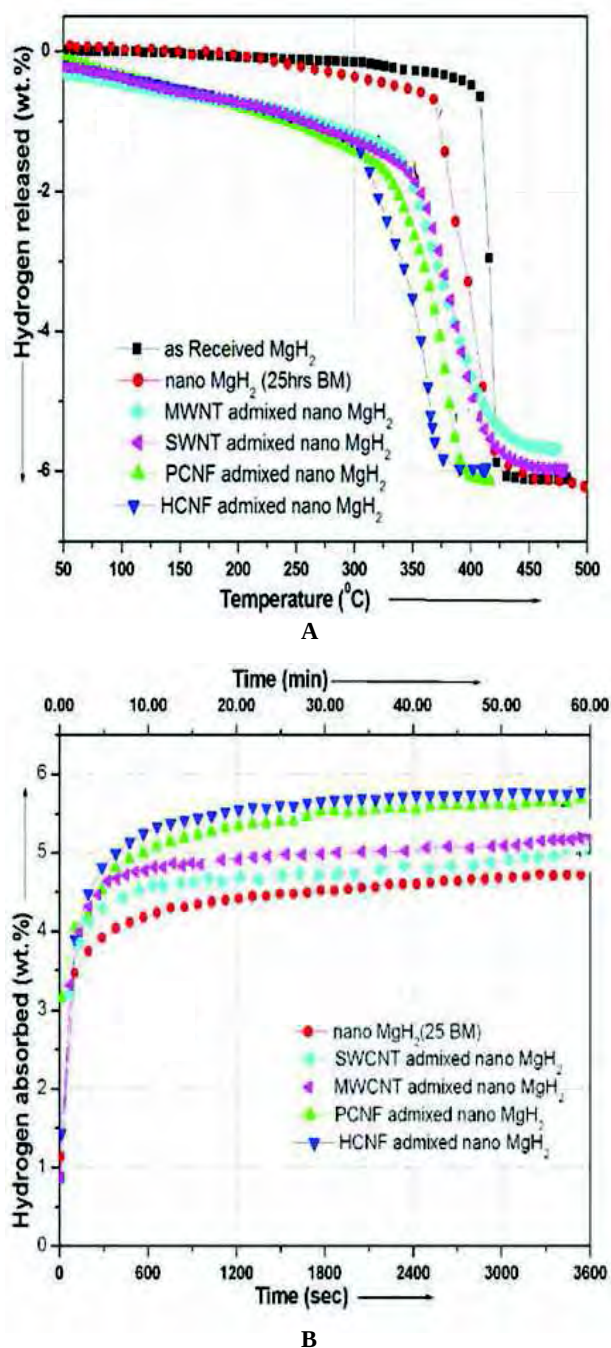


Fig. 3: A: TPD profile and B: absorption kinetics plot of different samples (Shahi *et al.*, 2012)

whereas purified HCNF admixed sample exhibits the significant effect ($\sim 37^\circ\text{C}$). Hence for the present case, we can say that the fibrous morphology shows better catalytic activity than the tubular morphology of carbon nanomaterials. Furthermore, the presence of synthesis-acquired metallic particles enhances the

catalytic activity of CNF. Hence, we can say that the morphology of carbon nanostructures is not the only factor for lowering of the desorption temperature. It is the combined effect of both, morphology and the presence of metallic particles in carbon nanostructures which play a vital role in lowering the desorption temperature of MgH_2 .

Effect of TiO_2 Nanoparticles of Different Sizes on Hydrogen Sorption Behaviour in MgH_2

The effect of variation in concentration of the catalyst on improving the sorption characteristics of MgH_2 has been widely investigated by various researchers (Shahi *et al.*, 2012; Vegge *et al.*, 2005; Magusin *et al.*, 2008; Fernández *et al.*, 2012; Charbonnier *et al.*, 2004; Pandey *et al.*, 2013). However, the effect of variation in size of the catalyst particles on the sorption behaviour of MgH_2 has been studied only sparsely. An important aspect of catalytic activity relates to the size of the catalyst which may lead to uniform distribution over and/or within MgH_2 . This will lead to selection of optimum size of catalyst particle for efficient hydrogen sorption in the case of MgH_2 . Here, we describe the effect of the size variation of TiO_2 nanoparticles (np) and determination of optimum size for improving the hydrogen sorption behaviour of MgH_2 . Details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2012).

Fig. 4A brings out a representative dark field TEM image taken with (211) rutile reflection of TiO_2 nanoparticles. As seen in the figure, the TiO_2 nanoparticles (with bright contrast) are almost uniformly distributed into MgH_2 large particles with the TiO_2 nanoparticles of size 50 nm. The corresponding selected area diffraction pattern is shown in the inset of Fig. 4A. The diffraction pattern (inset) shows spots corresponding to large MgH_2 particles and ring pattern for TiO_2 nanoparticles. In Fig. 4B, the microstructural features of MgH_2 - TiO_2 (50 nm) have also been analysed from secondary electron image employing SEM. At the resolution level of SEM, TiO_2 nanoparticles cannot be visualized. However, the contrast in the SEM picture suggests the presence of large particles together with very small particles on and around the large particles.

Presumably, the large particles are MgH_2 and the smaller ones are TiO_2 nanoparticles. Fig. 4C brings out the representative TPD curves of MgH_2 catalysed with different sizes of TiO_2 nanoparticles as a function of temperature. TPD was carried out at the heating rate of $2^\circ\text{C}/\text{min}$ from room temperature to 450°C . It can be clearly observed from the TPD curves that the dehydrogenation temperature of MgH_2 catalysed with various sizes of TiO_2 (np) has shifted to a lower onset desorption temperature than that of the ball-milled MgH_2 and as-received MgH_2 . The TPD curves can be divided into two broad categories. It is noted that the onset desorption temperatures for the first category is found to be $\sim 335^\circ\text{C}$ for the ball-milled MgH_2 as well as for MgH_2 catalysed with TiO_2 nanoparticles having particle sizes of 250 nm and 100 nm. This temperature is $\sim 55^\circ\text{C}$ lower than as-received MgH_2 , for which the onset temperature is at $\sim 390^\circ\text{C}$; whereas, the onset desorption temperature for the second category is up to 310°C and lower. Thus, for MgH_2 catalysed with TiO_2 (np) of sizes 7, 25 and 50 nm, the onset desorption temperatures are 300, 305 and 310°C , respectively. Fig. 4D exhibits representative re-hydrogenation kinetic curves of Mg and TiO_2 (np) catalysed Mg. The better reabsorption kinetic is achieved for Mg catalysed with 50 nm of TiO_2 . The Mg- TiO_2 (50 nm) reabsorbed 5.1 wt% of hydrogen within 6 min. During the same period, the sample catalysed with TiO_2 (25 nm) could reabsorb only 4.2 wt% of H_2 and the sample catalyzed with (7, 100 and 250 nm) TiO_2 could reabsorb merely 3 wt% of H_2 . In the present sorption studies, MgH_2 catalysed with TiO_2 (50 nm) is annealed up to a temperature of $\sim 340^\circ\text{C}$, the TiO_2 is expected to undergo reduction leading to formation of non-stoichiometric TiO_x . In order to check the reduction of TiO_2 , we have studied temperature-programmed reduction (TPR) under hydrogen atmosphere at the heating rate of 5°C min^{-1} . It is found that reduction of TiO_2 in MgH_2 -50nm TiO_2 system by hydrogen takes place at $\sim 340^\circ\text{C}$. It may be pointed out that even at temperatures lower than 340°C , partial reduction may take place. Considering the observed results in the present investigations, it can be said that TiO_2 can undergo reduction. TiO_{2-x} being more electronegative (Pauling scale electronegativity of TiO_2 is 1.9 and for MgH_2 , it

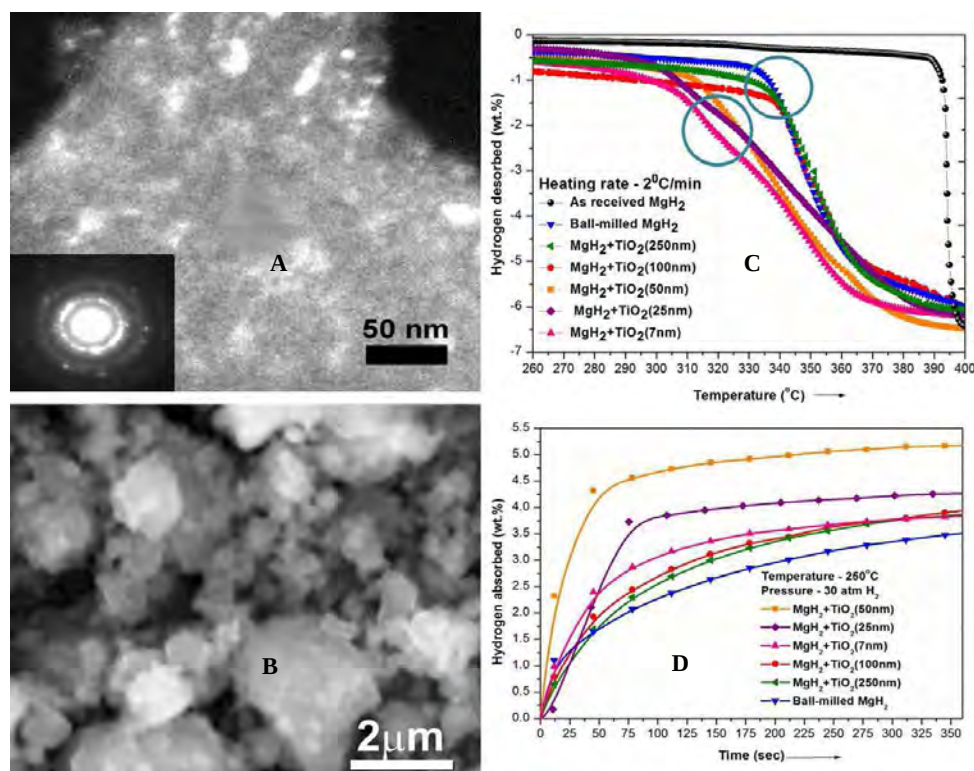


Fig. 4: A: Dark field TEM micrograph and inset represent corresponding SADP, B: SEM micrograph C: TPD profile at 5C/min and D: re-hydrogenation kinetics at 250°C under 30 atm hydrogen of MgH₂ catalysed with different sizes of TiO₂ nanoparticles (Pandey *et al.*, 2013)

is 1.4) (Vegge *et al.*, 2005) will therefore weaken the Mg-H bond by attracting the electrons from MgH₂. As a result, decomposition of MgH₂ will occur at a lower temperature leading to fast desorption kinetics. During absorption, reverse reaction will take place, which leads to lowering of the absorption activation energy.

Li-Mg-N-H System

Chen *et al.* have discovered a Li-N-H system for hydrogen storage in 2002. This discovery added a new material to the class of complex hydrides. In spite of high reversible storage capacity, this system possesses unfavourable thermodynamics (Song *et al.*, 2009; Janot *et al.*, 2007). Numerous other studies reveal that the substitution of Li by Mg provides a system having beneficial hydrogen sorption properties. It has already been described by different research groups that the Mg(NH₂)₂/LiH mixture is much better than those of LiNH₂/LiH (Song *et al.*, 2009; Janot *et*

al., 2007) with respect to thermodynamics and hydrogen uptake and release capacity. This is because Mg(NH₂)₂ is less stable and easily transforms into corresponding imide (MgNH) than LiNH₂ (Chen *et al.*, 2002). Further studies on this system revealed that Li-Mg-N-H system has slow desorption kinetics and the hydrogen uptake and release kinetics of the system is further improved by deployment of suitable catalysts. Some improvement has occurred in the kinetics with tuning, ball-milling of the Li-Mg-N-H system (Chen *et al.*, 2003; Ichikawa *et al.*, 2004; Weifang, 2004; Lohstroh *et al.*, 2007). Till date, no catalyst has been found for improvement in desorption kinetics and/or lowering of desorption temperature of Li-Mg-N-H system.

We have also explored this new class of complex hydrides as a storage material at our laboratory. We have synthesized Mg(NH₂)₂/LiH mixture and investigated the sorption kinetics with and without different catalysts such as vanadium and

vanadium-based compounds and carbon-based nanostructures. Vanadium is one of the typical transition metals which has better affinity towards electrons due to the presence of unoccupied d-orbital. It has been found that desorption kinetics and temperature of $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture gets improved with admixing of V, V_2O_5 and VCl_3 . The VCl_3 has been found to be the most effective followed by V and V_2O_5 (Chen, 2006; Shahi *et al.*, 2010). Here, we will describe the summary of the results obtained with the addition of carbon nanofibres to $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture. The details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2010). The used carbon nano fibres (CNFs) are synthesized by the catalytic thermal decomposition of acetylene (C_2H_2) gas over LaNi_5 alloy (Shahi *et al.*, 2013). The samples for hydrogenation characteristics were prepared by the admixing of 4 wt% different types of a CNFs (planer (P) and helical (H)) in the parent material for 5min, inside the glove box through the high energy (4000 rpm) mixer (Shahi *et al.*, 2013). The decomposition behaviour of mixture with and without CNFs were examined by TPD experiment at heating rate of $2^\circ\text{C}/\text{min}$. The initial desorption temperature of $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture is 90°C and lowered to $\sim 70^\circ\text{C}$ and 50°C for PCNF and HCNF admixed $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture, respectively (Shahi *et al.*, 2013). The maximum decomposition temperature for without catalyst is found to be 250°C , which is lowered to 150°C and 140°C for PCNF and HCNF admixed samples, respectively. TPD experiments indicate that the admixing of CNF reduce the decomposition temperature of 1:2 $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture. The mixture without CNF desorbs ~ 3.5 wt% within 60 min; whereas, desorption of ~ 5 wt. occurs within 50 and 40 min for PCNF and HCNF admixed $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture respectively (Shahi *et al.*, 2013). The hydrogen uptake capacity of pristine and 4 wt% of each PCNF and HCNF admixed $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture after 5h was found to be ~ 1.8 , 3.4 and 3.7 wt%, respectively (Shahi *et al.*, 2013). This may occur due to the presence of carbon fragments having various hybridized orbitals and these hybridized orbitals which can interact with the hydrogen molecule and provide transit site for the hydrogenation. The different catalytic effect of these CNFs is attributed to the fact

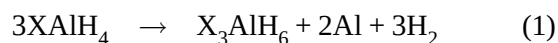
that these CNFs (PCNF and HCNF) have the same synthesis-acquired metallic particles. Hence, these different levels of improvement arise due to the morphological differences in CNFs.

Complex Hydride

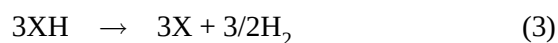
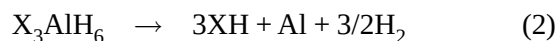
Complex hydrides consist of hydrogen atoms which are covalently bonded to a central atom in an anion complex (e.g. $[\text{AlH}_4]^-$, $[\text{AlH}_6]^{3-}$, $[\text{AlH}_4]$, $[\text{BH}_4]^-$, $[\text{NH}_2]^-$) and stabilized by the cation, particularly alkali metal complex hydrides (e.g. NaAlH_4 , NaBH_4 , NaNH_2) or alkaline earth metal complex hydrides (e.g. $\text{Mg}(\text{AlH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$) (Li, 2013). All these materials are known as “complex hydrides”, although only the alanates contain anionic metal complexes. In case of amides and borohydrides (saline materials), the hydrogen atom is covalently bonded to central atoms in “complex” anions (in contrast to interstitial hydrides). These materials offer high hydrogen gravimetric densities. After the pioneering research of Bogdanovic’ and Schwickardi (1997), the complex hydride (particularly, NaAlH_4) was considered as viable candidate for application as practical, onboard hydrogen storage material. Bogdanovic and Schwickardi show that, upon doping with selected titanium compounds, reversibility can be achieved in NaAlH_4 under moderate conditions (Bogdanovic *et al.*, 1997).

Complex Hydrides: Sodium Aluminium Hydrides

Hydrogen desorption in complex aluminium hydride (Alanates) containing alkali atoms takes place in three sub-steps as follows (Bhatnagar *et al.*, 2013).



(X denotes alkali element)

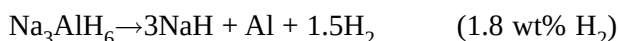


The decomposition of hydride in step 3 takes place at high temperature. Therefore, step 3 is generally omitted, while considering complex aluminum hydride for hydrogen storage. Many experiments have been carried out on alanate, with an objective to improve the thermodynamics of steps 1 and 2. Among

complex aluminium hydrides, NaAlH_4 , the prototype alanate is a widely studied hydrogen storage material (Jensen *et al.*, 2001; Sandroock *et al.*, 2002; Bogdanovic *et al.*, 2000,2007; Hassel *et al.*, 2012; Wang *et al.*, 2004).

Sodium aluminum hydride (NaAlH_4), would seem to be a possible candidate for application as a practical on-board hydrogen-storage material due to the theoretically reversible hydrogen-storage capacity of 5.6 wt%, low cost and its availability in bulk. The group of complex hydrides that have received the most attention over the last decade are the alanates (Bogdanovic *et al.*, 2007; Hassel *et al.*, 2012; Wang *et al.*, 2004).

Alanates are remarkable due to their high storage capacities; however, they decompose in two steps upon dehydriding.



Theoretically, NaAlH_4 and Na_3AlH_6 contain large amounts of hydrogen, 7.4 and 5.9 wt%, respectively. Reversibility of the above two reactions is a critical factor for practical applications. Although they have good hydrogen-storage capacity, complex aluminum hydrides are not considered as rechargeable hydrogen carriers due to irreversibility and poor kinetics, until Bogdanovic and Schwickardi (1997) showed that titanium-doped NaAlH_4 can reversibly be dehydrogenated and rehydrogenated. The addition of Ti-based compounds (such as TiCl_3 or $\text{Ti}(\text{O}i\text{Bu})_4$ to NaAlH_4) was found to lower the first decomposition temperature of the hydride. A quantity of 3.7 wt% is released at 353 K, but at the expense of lowering the hydrogen content from 5.5 wt% in the hydride without a catalyst (Jensen *et al.*, 2001; Bogdanovic *et al.*, 2000). Furthermore, the reaction is reversible; a complete conversion to product was achieved at 270°C under 175 bar hydrogen pressure in 2-3 h (Bogdanovic *et al.*, 2000).

The operating temperatures are between 185°C and 230°C for the first and the second reaction, respectively. Finally, the decomposition of NaH occurs at a much higher temperature, with the total hydrogen

release of 7.40 wt%. For hydrogen storage, only the first two reactions need to be considered, because the decomposition of NaH occurs at too high temperature of 425°C for practical storage systems (Bogdanovic *et al.*, 2007). With 2 mol% TiN as doping agent, cyclic storage capacity of 5 wt% H_2 is achieved after 17 cycles (Hassel *et al.*, 2012; Bogdanovic *et al.*, 2003). However, decrease in hydrogenation rate with number of cycles is observed (Srinivasan *et al.*, 2004). This clearly indicates that the addition of titanium species enhances not only the dehydrogenation kinetics, but also the rehydrogenation reaction of NaAlH_4 (Bogdanovic *et al.*, 2003; Sun *et al.*, 2002; Balema *et al.*, 2000), which demonstrates reversible hydrogen cycling in Ti-catalysed sodium alanate over 100 cycles with a measured capacity of nearly 4 wt% H_2 at 160°C.

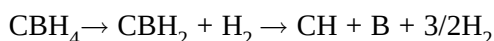
The van't Hoff plot of Ti-doped NaAlH_4 revealed that the enthalpy of the dehydrogenation of NaAlH_4 to Na_3AlH_6 and Al has been determined to be 37 kJ/(mol of H_2). This value is in line with the predictions of the studies discussed earlier. In accordance with this value, the temperature required for an equilibrium hydrogen pressure of 0.1 MPa has been determined as 33°C and highly practical hydrogen plateau pressures of 0.2 and 0.7 MPa have been found at 60°C and 80°C, respectively (Sun *et al.*, 2003). Unfortunately, the equilibrium hydrogen plateau pressures of the $\text{Na}_3\text{AlH}_6/\text{NaH} + \text{Al} + \text{H}_2$ equilibrium in the 70-100°C temperature range are insufficient for utilization in a PEM fuel cell system in which the heat of the steam exhaust would be used to drive hydrogen release for the storage material.

In addition to NaAlH_4 and Na_3AlH_6 , there are a number of other alanates capable of rehydrogenation under moderate pressures and temperatures including $\text{Na}_2\text{LiAlH}_6$, KAlH_4 , K_3AlH_6 , K_2LiAlH_6 and K_2NaAlH_6 . However, all these compounds have lower gravimetric hydrogen densities and are more stable than sodium alanate. On the other hand, there are a few alanates that are known to be less stable than sodium alanate, which also exhibit high gravimetric hydrogen densities such as LiAlH_4 , Li_3AlH_6 , $\text{Mg}(\text{AlH}_4)_2$, $\text{Ca}(\text{AlH}_4)_2$, $\text{Ti}(\text{AlH}_4)_4$ among others. Despite their promising capacities, these

materials are not known to be irreversible under moderate pressure conditions.

Complex Hydride: Borohydride

Hydrogen atoms in the borohydrides are positioned at the corners of the tetrahedral $[\text{BH}_4]^-$, where boron coordinates the hydrogen atoms located at the centre. The charge transfer from alkali or alkaline earth or by few transition metals helps in additional charge localization for the stabilization of the complex boron-hydrogen tetrahedron (Orimo *et al.* 2007). General dehydrogenation reaction of alkali metal tetrahydroborates can be represented by the following equation.



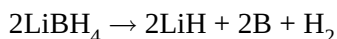
(C: alkali metals)

However, for alkaline earth metal tetrahydroborates, the dehydrogenation reaction can be written as:



(D: alkaline earth metals)

Recently, the hunt to find a high capacity reversible hydride has shifted to borohydrides. The most well-known borohydrides are lithium borohydride, LiBH_4 , and sodium borohydride, NaBH_4 . They are promising materials owing to their high gravimetric hydrogen contents up to 18 wt%. However, very high temperatures are required for the release of hydrogen from borohydride. Substantial effort has gone into finding ways of thermodynamically destabilizing the materials. LiBH_4 , one of the well-known borohydrides decomposes at temperatures 438°C to LiH and B and releases 13.5 wt% H_2 through the following reaction:



Since, borohydrides are thermodynamically very stable material; research efforts are mainly focused on reducing the decomposition enthalpy by destabilizing the LiBH_4 . Moreover, creating nanoscale powders and incorporating the hydride into nanoporous scaffolds or frameworks which inhibit agglomeration and sintering during cycling are some

efforts which are being made to improve the reaction kinetics of borohydrides. Researchers around the globe show considerable interest in the alkaline earth and transition metal borohydrides ($\text{Mg}(\text{BH}_4)_2$ (Matsunaga *et al.*, 2008 ; Ronnebro *et al.*, 2007; Nakamori *et al.*, 2006), which are much less stable than Group 1 borohydrides. These materials have demonstrated promising capacities at reasonable decomposition temperatures, but similar to less stable alanates, reversibility is the main issue. However, due to their higher hydrogen gravimetric capacity of storing hydrogen than aluminohydrides, they are at present considered appealing candidates for hydrogen storage. Detailed study on borohydride can be found in the review report of Enis *et al.*, 2004.

Quasicrystal: Materials for Hydrogen Storage and Catalytic Application

Quasicrystal

Quasicrystals (QCs) are orientationally ordered structures, which may often possess classically forbidden rotational symmetries (e.g. five-fold, eight-fold, ten-fold and twelve-fold). For the revolutionary discovery of QC, the 2011 Nobel Prize in Chemistry has been awarded to Professor Danny Shechtman. Before Shechtman's 1982 discovery of the first quasicrystal (QC), it was universally accepted, though never proven, that the internal order of crystals was achieved through a periodic filling of space. Crystallography treated order and periodicity synonymously, both serving equally to define the notion of a crystal. With that came the so-called "crystallographic restriction," stating that crystals cannot have certain forbidden symmetries such as 5-fold rotations. Shechtman *et al.* (1984) discovered the first icosahedral quasicrystal (IQC), formed under rapid solidification conditions in binary Al-Mn, quasicrystals have sparked debate over their atomic structure, stability, and other basic scientific issues. Quasicrystals are of great interest due to their potential for creating unusual structural form of matter having extraordinary physical properties. During the last three decades, significant progress has been made in the preparation, characterization and application of quasicrystals. Quasicrystal was discovered initially in

Al-based alloys (Shechtman *et al.*, 1984; Chattopadhyay *et al.*, 1985) and later in other binary Al-TM-based alloys containing Cr (Inoue *et al.*, 1987), V (Inoue *et al.*, 1986), and different ternary alloys (Rabe *et al.*, 1991; Kelton, 1995). Additionally, the icosahedral phase was observed in Ga-, Ti-, Mg-, and Pd-based alloys (Louzguine-Luzgin *et al.*, 2008) as well as in Cd- (Guo *et al.*, 2000), rare-earth (RE)- (Fisher *et al.*, 2000), and Zn-based (Kaneko *et al.*, 2001) alloys.

Similar to many intermetallics, QCs are expected to exhibit properties different from conventional metallic materials, which can be exploited for industrial applications (Somekawa *et al.*, 2011; Dubois, 2011). Quasicrystalline materials are characterized by a combination of such properties, as low friction, high hardness, low surface energy, and thermal expansion comparable to that of the metals (Dubois *et al.*, 2011; Lifshitz *et al.*, 2011; Hu *et al.*, 2011). Moreover, Ti/Zr-based QCs seem to be good candidates for hydrogen storage applications (Viano *et al.*, 1995).

Hydrogen Storage in Quasicrystal

The large free volume associated with quasi-periodicity and the high density of tetrahedral interstitial sites displayed by metallic alloys with quasicrystalline structure makes them materials of potential technological interest in the field of hydrogen storage and such structural features may indeed result in improved hydrogen storage capabilities (Wang *et al.*, 2004). The Ti-3d transition metal-Si icosahedral phases can absorb hydrogen from the gas phase and by electrolytic methods (Bahadur *et al.*, 1989; Viano *et al.*, 1993). The Ti-Zr-Ni icosahedral phase may contain interstitial sites for hydrogen and therefore, it is considered to be a new, promising hydrogen storage material (Taksaki *et al.*, 2006). The substitution of chemical elements in the Ti-based icosahedral phase powders may control hydrogen desorption properties. Both Ti-Hf-Ni and Ti-Zr-Ni alloys were reported to absorb hydrogen without the formation of a detectable crystal hydride phase (Molokanov *et al.*, 1990). The maximum hydrogen concentration of Ti-Zr-Ni phase powders is approximately 60 at %, which can be attained by either gaseous-phase or electrochemical

loading of hydrogen (Gibbons *et al.*, 2004; Tsai *et al.*, 1995; Wehner *et al.*, 1997). The two different absorption methods, one at room temperature and another requiring elevated temperature, successfully introduce hydrogen into Ti-Zr-Ni alloys (Viano *et al.*, 1998). The Ti-Zr-Ni alloys are good candidates for hydrogen storage because they contain two elements, Ti and Zr, which have high affinities for hydrogen and presence of Ni is beneficial in that it often creates a pathway for H diffusion through a surface oxide layer (Sawa *et al.*, 1990; Stroud *et al.*, 1996). The hydrogen storage capability of the quasicrystal compares to or exceeds those of the Ti-Zr-Ni crystal and amorphous phases and a complete determination of the absorption curves with a varying number of days prior to hydrogen exposure has been discussed in Fig. 5.

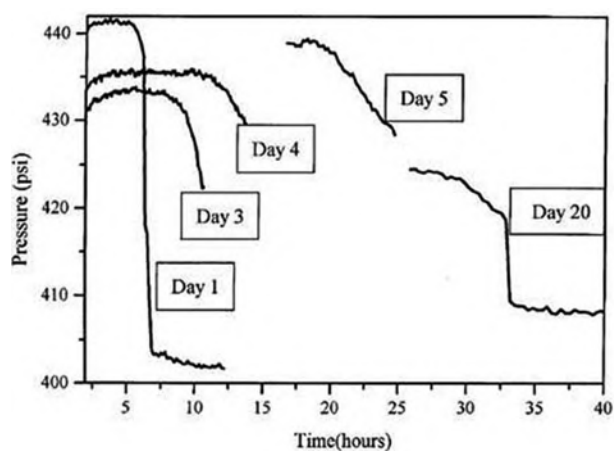


Fig. 5: Absorption curves for samples of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ stored in air for a varying number of days prior to hydrogen exposure. The drop in pressure corresponds to hydrogen absorption. For clarity, the data for days 5 and 20 are clipped to show only the part corresponding to absorption (Viano *et al.*, 1998)

The high-resolution synchrotron-radiation powder diffraction experiments were performed to observe structural changes induced by hydrogen loading in rapidly-quenched Ti-Zr-Ni alloy ribbons with dominant icosahedral character (Nicula *et al.*, 1998). It was suggested that moderate strains generated by hydrogen absorption was accommodated by the icosahedral structure at the cost of increasing phason disorder only, both quasilattice parameter and phonon disorder coefficient being unaffected (Nicula *et al.*,

1998). The formation of quasicrystalline phase in Ti-Zr-Ni system by mechanical alloying (MA) has revealed better hydrogenation than bulk (Takasaki *et al.*, 2002). The maximum amount of hydrogen that could be loaded into the amorphous and the QC phase powders, at a temperature of 573K and an initial hydrogen pressure of 3.8 MPa, were almost the same, about 60 at.% (M/H = 1:5) indicating that there was no dependence of the hydrogen solubility on the atomic structure (Fig. 6). The QC was retained after hydrogenation, with no formation of hydrides. Activation energy for hydrogen desorption was 127 kJ mol⁻¹ for the QC powder and 168 kJ mol⁻¹ for the amorphous powder (Takasaki *et al.*, 2002, 2006). For a rapidly quenched Ti₄₀Hf₄₀Ni₂₀ alloy, there exists a high-order approximant 3/2 phase, whose structure is very similar to the QC phase, absorbing hydrogen up to H/M=1.2 (Kelton *et al.*, 2006). Hydrogen storage behaviours were also compared in rapidly quenched Ti-Zr-Ni and Ti-Hf-Ni alloys in details (Kelton *et al.*, 2006). Although Ti₄₀Hf₄₀Ni₂₀ has nearly identical hydrogenation properties to those of the icosahedral Ti₄₅Zr₃₈Ni₁₇ phase, no evidence of a hydride phase is observed after loading from the gas phase at 250°C, suggesting that Ti-Hf-Ni could have superior cycling properties (Huett *et al.*, 2002). The PCT curves (Fig. 7) measured at 300°C for both samples, i.e. Ti-Zr-Ni and Ti-Hf-Ni show a higher-pressure plateau at higher hydrogen concentrations (Kelton *et al.*, 2006) and both indicate the existence of a pressure plateau beginning at an H/M of about 1.2-1.5 and extending to an H/M of 3.

Hydrogen storage activities were also observed in additional element substituted Ti-based alloys (Baozhong *et al.*, 2006; Liu *et al.*, 2006, 2007, 2008, 2009a, b). Pd-substituted Ti-Zr-Ni alloys were prepared by melt-spinning at different circumferential velocities and a mixed structure of Laves phase, QC phase and a little amorphous phase is formed at $v = 10$ m/s (Liu *et al.*, 2009). Moreover, the hydrogenation characteristics of Ti-Zr-Ni-Pd alloy electrode was better than that of Ti-Zr-Ni-Y and Ti-Zr-Ni-La alloy electrodes, which mainly ascribed to the excellent electrochemical activity of Pd (Liu *et al.*, 2008, 2009). Electrochemical hydrogen storage in Ti-V-Ni alloys comprising icosahedral quasicrystalline phase was also

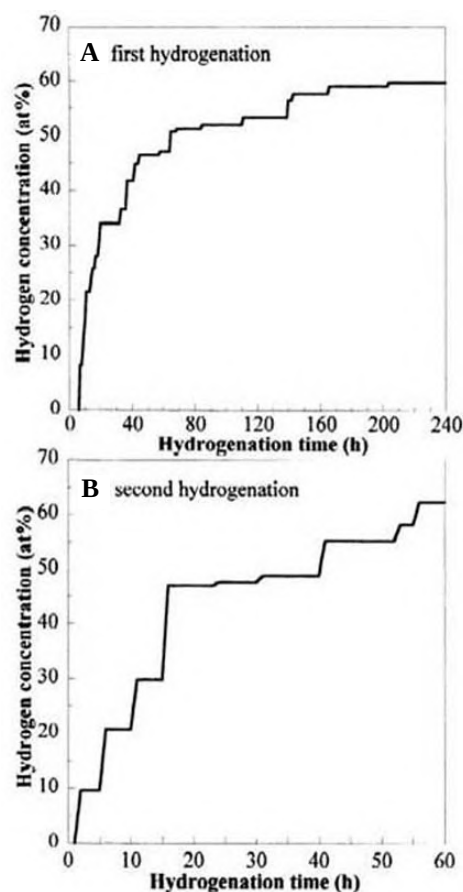


Fig. 6: Hydrogen concentration as a function of time for the i-phase powder during (A) the first, and (B) the second hydrogenation (Figure 2; Takasaki and Kelton, 2002)

investigated in detail (Hu *et al.*, 2009, 2013; Wen *et al.*, 2013; Liu *et al.*, 2013 a, b). The effect of substitution of Zr for Ti on the discharge performance of electrodes consisted of Ti_{45-x}Zr_{30+x}Ni₂₅ ($x = -4, 0, 4$) powders produced by MA subsequent annealing was investigated by a three-electrode cell at room temperature (Ariga *et al.*, 2013). All the powders after MA were amorphous, but a subsequent annealing caused the formation of the icosahedral quasicrystal phase with a Ti₂Ni type crystal phase as the second phase. The discharge capacities of the amorphous electrodes were lower than those of the QC phase ones if the composition levels were alike (Zhao *et al.*, 2012).

The synthesis parameters were also an influence on hydrogen storage behaviour of Ti-Zr-Ni QC alloys (Huogen *et al.*, 2008 a, b; Kocjan *et al.*, 2011; Shahi

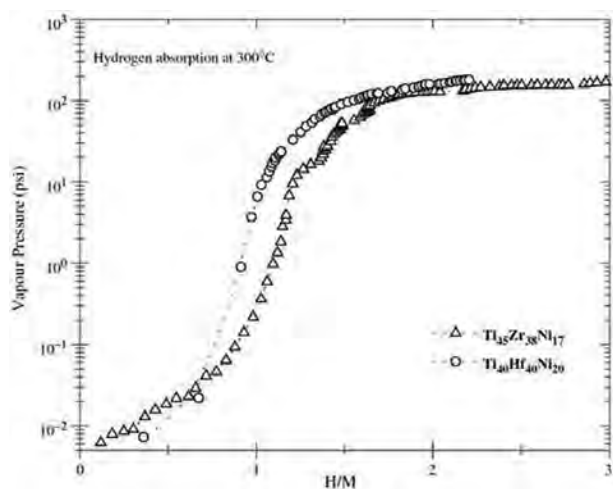


Fig. 7: Equilibrium hydrogen vapour pressure for icosahedral phase ($\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$) and 3/2 rational approximant phase ($\text{Ti}_{40}\text{Hf}_{40}\text{Ni}_{20}$) samples produced by rapid quenching, measured as a function of hydrogen concentration during absorption at 300°C (Kelton *et al.*, 2006)

et al., 2011; Jenk *et al.*, 1998; Takasaki *et al.*, 2013). The effect of solidification rate on phase formation and the microstructure of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ as quenched ribbons are discussed in detail (Figs. 8 and 9). The XRD pattern of the alloy melt spun at 35 m/s (Fig. 8A) reveals the presence of icosahedral quasicrystalline phase and further increased the wheel speed from 40 m/s to 45 and 50 m/s (Fig. 8B-D). The peak broadening occurs due to the formation of finer grains and strain developed at higher wheel speeds. Ribbons of the alloy were synthesized at different quenching rates obtained through different wheel speeds (35, 40, 45 and 50 m/s) and investigated for their hydrogen storage characteristics (Figs. 10 and 11). The lower cooling rate obtained through low wheel speed (35 m/s) produces, i-phase grains whose size ranges from 300–350 nm, whereas higher cooling rates obtained through high wheel speed (45 and 50 m/s) promote the formation of grains with size ranging from 100–150 nm in $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ ribbons. It was found that ribbons synthesized at 35 m/s absorbed ~2.0 wt%, whereas ribbons synthesized at 50 m/s absorbed ~2.84 wt% of hydrogen (Fig. 10). The hydrogen storage capacity of ribbon increases for ribbons produced at higher quenching rate. One of the salient features of the present study is that the improvement of hydrogen storage capacity obtained through higher quenching

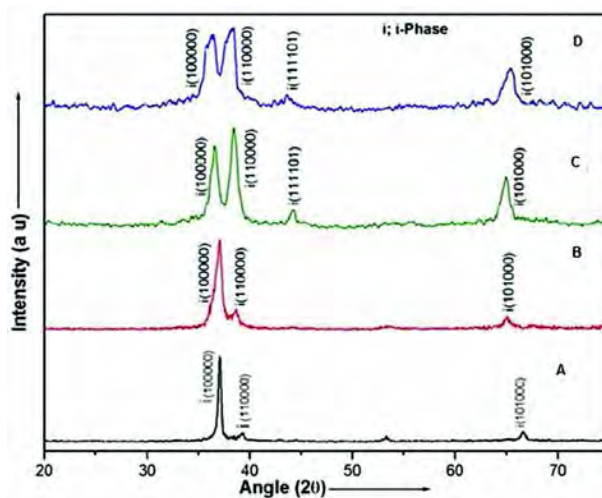


Fig. 8: XRD patterns of as-synthesized ribbon at wheel speed of (A) 35 m/s, (B) 40 m/s, (C) 45 m/s and (D) 50 m/s (Shahi *et al.*, 2011)

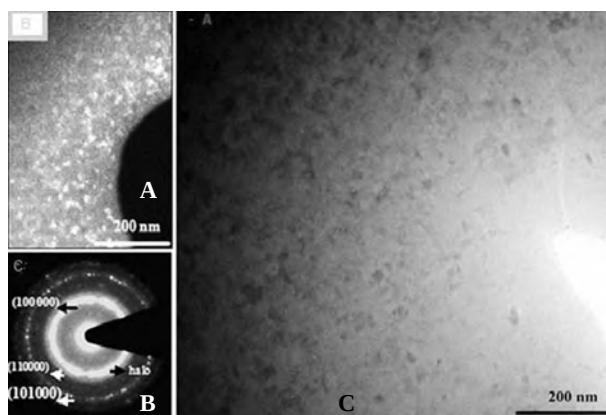


Fig. 9: TEM micrograph of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ as-synthesized ribbons at 50 m/s (A) bright field microstructure, (B) dark field microstructure and (C) corresponding diffraction pattern (Shahi *et al.*, 2011)

rates (~45 to 50 m/s wheel speed) leads to the formation of lower grain size.

Quasicrystals as a Catalyst in Hydrogen Storage

In the methanol decomposition reaction, the quasicrystalline catalyst achieved the highest amount of hydrogen gas generated and the lowest reaction initiation temperature (Li *et al.*, 2013; Tsai *et al.*, 2001; Yoshimura *et al.*, 2002; Ngoc *et al.*, 2008). The powder of thermally stable icosahedral (i) Al-Cu-Fe quasicrystal leached with NaOH aqueous solutions shows excellent activity for steam reforming of

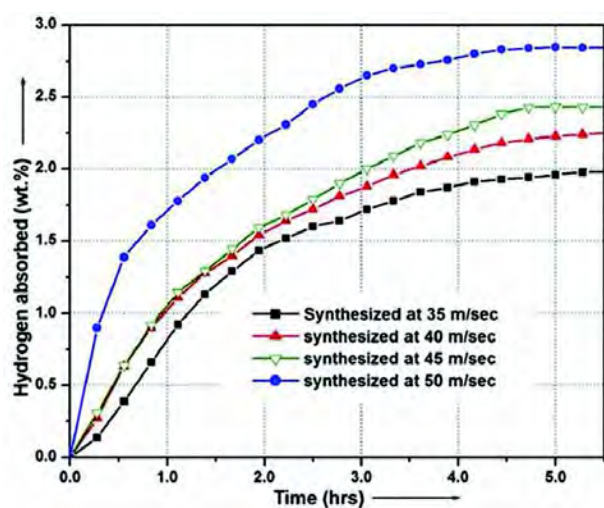


Fig. 10: Hydrogen absorption kinetics curves of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ ribbons synthesized at wheel speed of 35, 40, 45 and 50 m/s. (Figure 4; Shahi *et al.*, 2011)

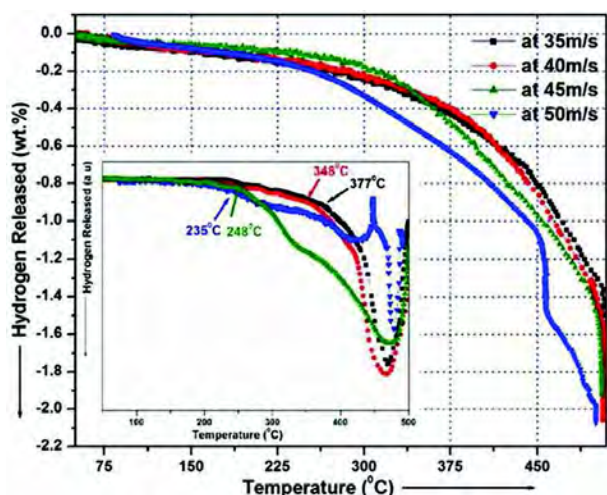


Fig. 11: Temperature-programmed desorption curve of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ as-synthesized ribbons at wheel speeds of 35, 40, 45 and 50 m/s (inset shows the TPD difference curves for each consecutive step) (Figure 6; Shahi *et al.*, 2011)

methanol (Kameoka *et al.*, 2004; Tanabea *et al.*, 2006, 2010). The leaching treatments yield Cu and Fe nanoparticles on the quasicrystalline surface. These nanoparticles are believed to be responsible for catalytic reactions (Tanabea *et al.*, 2011). Recently, the leached (i) Al-Cu-Fe quasicrystal and mechanical activated (i) Al-Cu-Fe quasicrystal were used as a catalyst in hydrogen storage of MgH_2 (Mishra *et al.*, 2007). The scanning electron micrograph (SEM) in secondary

electron image mode of the fractured as well as leached surface of $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy was shown (Fig. 12), where existence of a single-crystal (nearly 10-20 μm size) of icosahedral phase, exhibiting the faceted pentagonal dodecahedral morphology and a homogeneous distribution of particle together with very small particles on and around the large particles, were observed on the leached surface.

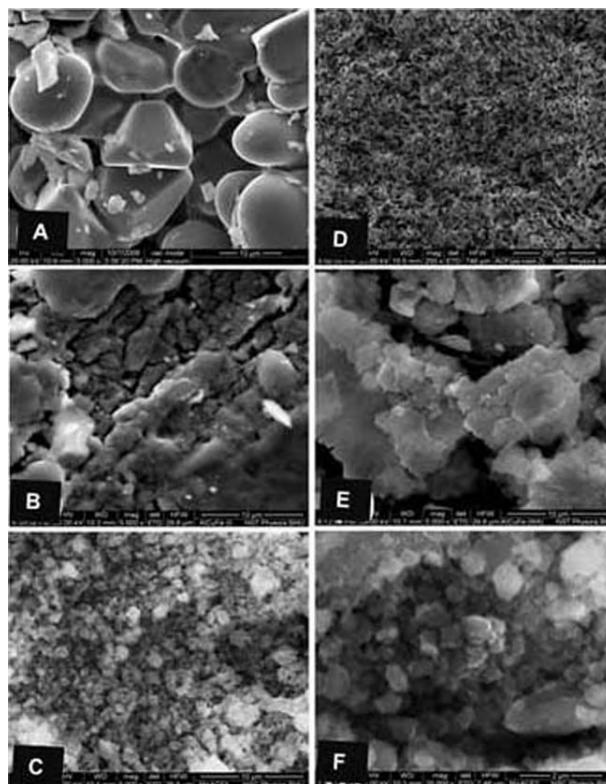


Fig. 12: Scanning electron microscopy of (A-B) as grown (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, (C) leached surface of as-grown (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, (D-F) mechanically activated (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ and (F) leached surface of mechanically activated (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$

The results of TEM investigation on the microstructure of as-cast (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ and mechanically activated QC along with leached powder are discussed in detail (Fig. 13). A rosette and coral-like morphology of the as-cast alloy and corresponding selected area diffraction patterns was demonstrated. The two different types of contrast were observed in the leached as-cast (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ QC alloy, however in the leached mechanically activated alloy, a homogeneous distribution of small

particles was observed (Fig. 13). These particles were identified as Cu and Fe in the leached powder.

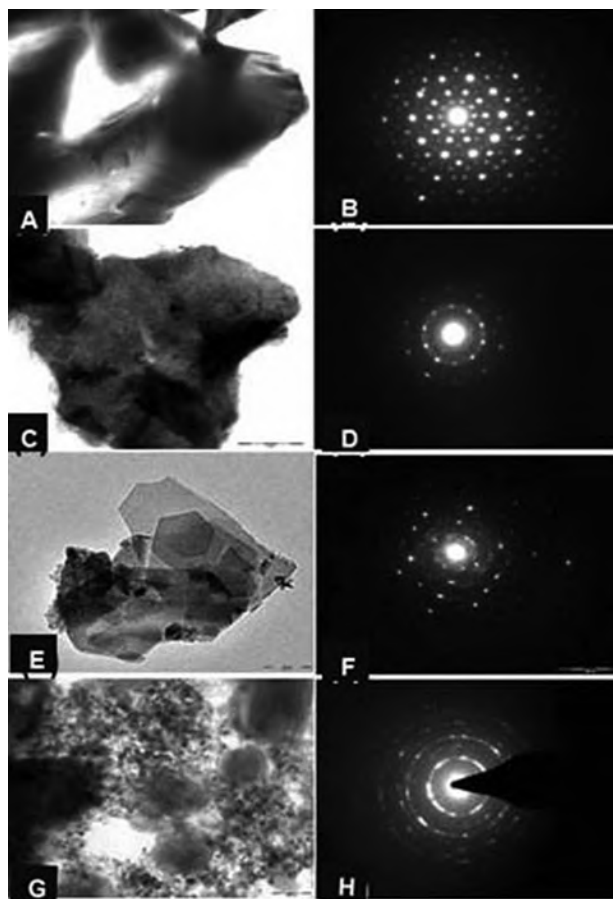


Fig. 13: (A) Transmission electron microscopy microstructure of as-cast (i)-Al₆₅Cu₂₀Fe₁₅, (B) corresponding selected area diffraction (SAD), (C) microstructure of mechanically activated powder, (D) corresponding SAD patterns, (E) microstructure of the leached as-cast (i)-Al₆₅Cu₂₀Fe₁₅, (F) corresponding SAD patterns, microstructure leached mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder and (G) corresponding SAD pattern

In order to explore the effectiveness of leached as-cast (i)-Al₆₅Cu₂₀Fe₁₅ and leached mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder as catalysts (which was abbreviated as LACF and LBACF for the sake of simplicity), these QCs were ball-milled separately with MgH₂ to investigate its hydrogen sorption behaviour. The representative TPD profile for MgH₂ catalysed with LACF and LBACF was shown to be 6.3 and 6.5 wt% hydrogen capacity, respectively (Fig.

14). TPD experiments were carried out under continuous heating rate of 5°C/min. The onset desorption temperature of as-received MgH₂ was found to be 422°C (Vegge *et al.*, 2005), but for MgH₂ catalysed with LACF and LBACF, it was ~225°C and ~215°C, respectively. Therefore, the leached QC alloy showed its catalytic activity by reducing the onset desorption temperature ~200°C of MgH₂. The hydrogen absorption curve of MgH₂+LACF and MgH₂+LBACF charged at 250°C under 20 atm of hydrogen pressure was also discussed (Fig. 15). It was observed that MgH₂+LBACF sample exhibits better rehydrogenation kinetic curve than MgH₂+LACF as well. Desorbed MgH₂+LBACF

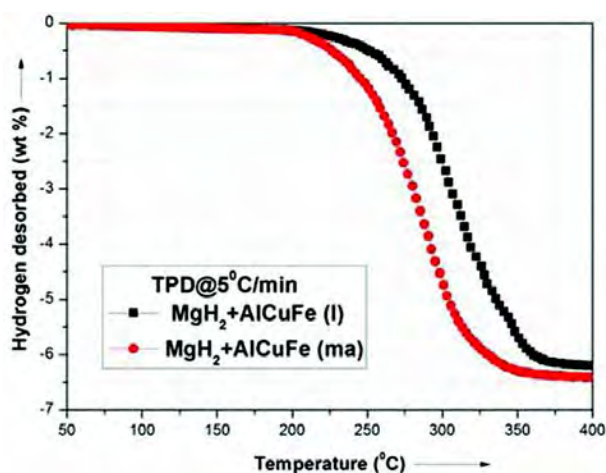


Fig. 14: TPD profile of leached as-cast and mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder admixed with MgH₂ at heating rate of 5°C/min

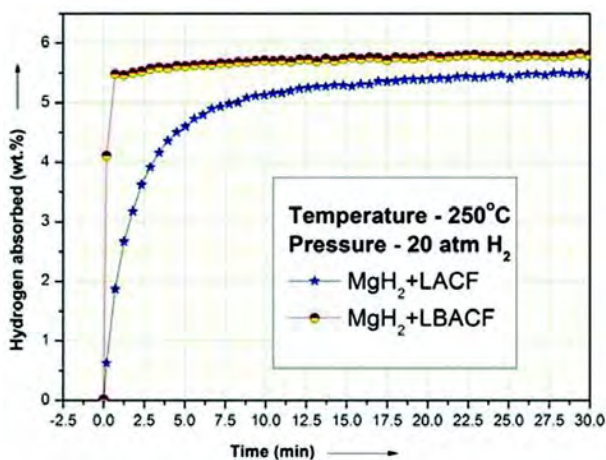


Fig. 15: Absorption kinetics plots of as-cast and mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder admixed with MgH₂ samples at 250°C

absorbed 5.5 wt% of hydrogen in less than 1 min; on the other hand desorbed MgH_2 catalysed with LACF absorbed 5.2 wt% of hydrogen in 10 min. It has been demonstrated that leached QC was an effective catalyst for hydrogen desorption/absorption from MgH_2 .

Applications

There is a wide variety of applications of hydrogen. In fact, hydrogen can be used as replacement for both the fossil fuels: the coal and petroleum. Thus, instead of coal, it can be burned to run turbines to produce electricity. It can also be subjected to cold combustion to produce electricity through fuel cells. Fuel cells are also considered for road transport (electrical vehicles). Hydrogen can substitute for petroleum/diesel/kerosene engine sets. Hydrogen can also be used for cooking (replacement of LPG). In India, road transport consisting of two-wheelers and three-wheelers is the largest in number, followed by cars and trucks. Two and three-wheelers are most petroleum consuming and also most polluting vehicles. About 35% of greenhouse gas (CO_2) is produced by road transport in India. Keeping these aspects in view, we have focused our attention regarding hydrogen application on vehicular road transport. We have carried out R&D and developed hydrogen-fuelled three-wheelers and more recently small cars (Tata Nano, Figs. 16 and 17).

In all the applications of hydrogen in vehicular transport, hydrogen has been stored in hydrides ($\text{MmNi}_{4.6}\text{Fe}_{0.4}\text{H}_x$, BHU-HEC is able to produce this storage material in kilogram level) (Mishra *et al.*, 2007). This is because hydrides are the most efficient storage system for hydrogen. In hydrides, unlike high pressure gaseous and liquid hydrogen storage modes, hydrogen atoms rather than molecules are stored. Thus, the storage capacity is very high. Such efficiencies cannot be reached in the usual high pressure gaseous storage mode. For example, volumetric storage density (which is very important for vehicular transport) of hydride is between ~ 60 and $\sim 100 \text{ kg/m}^3$. In gaseous state, even at 400 bar pressure, this is only $\sim 20 \text{ kg/m}^3$. Hydrides are also the safest storage modes. Here, hydrogen is locked in the lattice and is not free to combine with atmospheric



Fig. 16: Hydrogen-fuelled Nano car developed at HEC-BHU



Fig. 17: Hydrogen-fuelled three-wheeler developed at HEC-BHU

oxygen to burn/explode. It is the above said aspects, which have induced us to use the hydrogen storage mode.

Hydride powder is put in the heat exchanger system. This is coupled to IC engine exhaust gas (which is mostly steam and nitrogen in the case of hydrogen). Quantity of hydride employed is $\sim 18 \text{ kg}$. Exhaust gas coming out at a temperature of $\sim 60^\circ\text{C}$ in

two-wheelers is circulated in the hydride heat exchanger bed. Since thermal conductivity of the hydride is very poor (0.5 to 1.0 W/mk), a hydride heat exchanger tank (HHET) has been designed. To heat the hydride effectively by the exhaust heat of the engine, 20 kg of hydride (storage capacity ~1.8 wt%) is distributed in the HHET by 20 aluminum tubes of 1 inch diameter and 12 inch length. Exhaust heat from the 100 cc two-wheeler engine is able to raise the temperature of hydride to ~60°C. For a Nano car, the temperature rise is about 85°C. We have removed the carburetor and the hydrogen is made to enter the engine during suction stroke through a port near the engine inlet valve. The timing of hydrogen entry is controlled through a cam valve. In a two-wheeler system, the hydride tank is mounted below the driver's seat. In the Nano car, the hydride tank is mounted in the rear above the engine. We have chosen vehicular transport based on IC engine rather than fuel cell. This is because India manufactures high quality internal combustion engines. Also fuel cell technologies have not matured in spite of persistent efforts in the last two decades. Fuel cells capable of being used for vehicular transport require platinum as catalyst which is very expensive (~5 times more expensive than gold). Also, there is rather limited stock of platinum.

The Hydrogen Energy Centre has collaborated with the company Indian Cars and Motors Ltd. (ICML, a sister concern of Sonalika Tractors at Jalandhar, Punjab) to develop the first hydrogen-based three-wheeler for ICML which was demonstrated at Auto Expo Delhi in 2007. At present, we are developing eight hydrogen-fuelled three-wheelers which will be run at Varanasi and Delhi to demonstrate the feasibility of hydrogen-fuelled vehicles. More recently, we have developed a hydrogen-fuelled Nano car. It is planned to develop six more hydrogen-fuelled Nano cars.

It is hoped that the above developments will lead

to the public perception that hydrogen is a viable, clean, climate-friendly, inexhaustible fuel and is typically suited for India.

Conclusion

In this article, we have attempted to bring out the relevance of hydrogen, particularly in the Indian context. India is known to be an energy-starved country, particularly with reference to oil/petroleum. Hydrogen which can be produced from water through a variety of energy inputs including solar energy appears to be a first priority option for India with regard to replacement of oil (and later on coal). Since India has significant solar irradiance and large water resources, and after use the water is returned, hydrogen is definitely a potential energy vector. For harnessing hydrogen, three key ingredients are involved, these are production, storage (safety is mostly related to storage) and applications. We have shown that two equally important factors, namely, large gap between demand and supply of oil and climate change effects make hydrogen a fuel of choice for India. We have provided the necessary input for hydrogen production, some detailed discussion on storage which is possibly the most crucial aspect for the use of hydrogen and applications of hydrogen as replacement for oil in vehicular transport.

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Review Article

Simulation, Modelling and Design of Hydrogen Storage Materials

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In the current renewable energy scenario, one of the thrust areas is hydrogen generation and storage in an environment-friendly and cost-effective fashion. The primary challenge of efficient generation as well as storage of hydrogen has triggered R&D all over the world. Various routes such as solar photovoltaic, solar thermal, nuclear and bio-inspired routes are being vigorously pursued; the costs are still rather high for the hydrogen economy to be viable for renewable energy. There has been a concerted effort in many Asian countries, to push the frontiers of hydrogen energy for automobile and other applications. From the point of view of fundamental research, Hydrogen storage in solid state is a vibrant research area in materials science. Various types of materials, viz. metal hydrides, complex hydrides, chemical hydrides, and new materials such as functionalized nanostructures have been reported as candidate materials for hydrogen storage. However, their storage efficiencies, desorption kinetics and thermodynamics are yet to be optimized for practical applications. The article presents a broad overview of the current status of these materials issues for efficient storage of hydrogen in solid state. In particular, the focus here is on how first-principles computational approach can be gainfully utilized to design various low-Z complex hydrides (along with their decomposition pathways), as well as functionalized nanostructures (H_2 adsorption and desorption processes). Some of the outstanding issues and challenges will be discussed.

Keywords: Hydrogen Storage; Density Functional; Complex Hydride; Functionalized Nanostructure

1. Introduction

Energy, environment and economy are the most crucial global issues for our sustainable future. While energy is the most vital requirement for the progress of our civilization, it is ironic that this progress is what puts maximum load on our natural resources which are getting depleted in an alarmingly narrow window of time. One thing is amply clear that the way we produce and use energy today is not sustainable, and a new direction is needed. Our current global energy need is about 15 Tera Watt and about 85% is being provided by fossil fuels (Smalley, 2005; Abbott, 2010). Apart from the fact that these high density energy sources are not renewable, they are also associated with emission of carbon and greenhouse gases that have an irreversible effect on environment. Even if

we had an unlimited supply of fossil fuels, burning them sends greenhouse gases into the atmosphere, trapping the sun's heat and contributing to global warming (*The Inconvenient Truth*, 2006). The world's energy need is expected to grow by 33% during the next 10 years. The only way to tackle this situation is to use renewable energy sources that are continually replenished by nature, for e.g. (a) solar energy (b) hydro energy (c) bio energy (d) geothermal energy (e) ocean energy (f) wind energy and (g) hydrogen energy. The recommendations for sustainable energy future chalked out by the 18-member Inter-Academy Council Board (*Lighting the Way*, 2007) aptly summarize the road map for energy sources that are abundant secure, renewable, clean, and cost-effective.

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Hydrogen is the universe's most abundant element, exhibits the highest heating value per mass of chemical fuels, and it is pollution-free as water is the only by-product during its combustion. It is this 'clean tag' of non-CO₂-emitting energy carrier, that arguably puts hydrogen as the most potential candidate as the 'fuel of the future' (Jain, 2009)! The question being posed "Is hydrogen-based economy our ultimate destination?" has been posed and addressed in several reports and publications during the last decade (Basic research needs for the hydrogen economy, 2003; The hydrogen economy: Opportunities, costs, barriers and R&D needs, 2003; Fueling the Future: On the road to the hydrogen economy, 2005; Crabtree *et al.*, 2004; 2008). There are numerous hurdles associated with its production, storage and transportation that need to be overcome before it can compete with other conventional sources of energy (leaving aside political issues that invariably get linked with energy). Among these, hydrogen storage is considered to be the biggest challenge in a new hydrogen economy.

As Peter Eklund of Penn State Hydrogen Program explained (*National Hydrogen Energy Road Map*, 2002) "When it comes to energy density, gasoline blows hydrogen away. While hydrogen packs more energy per pound than gasoline — roughly three times more — it fills four times the space". Some prototype hydrogen-powered vehicles solve the problem by using compressed gas in high-pressure tanks. Other hydrogen-powered cars such as the newest BMW model, store hydrogen as a liquid in super-cooled tanks nestled near the driver's seat. Cooling the hydrogen increases its density, but a tremendous amount of energy is required both to keep the tanks cold and, when needed, to turn the liquid back into a gas that can be delivered to an engine or fuel cell. Thus safety, space and cost remain significant concerns in gaseous or liquid storage, for which we have more or less reached the technological limit. In view of this, the most promising alternative is solid state storage of hydrogen, and to find out the right candidate is a challenge faced by materials scientists. In addition to the high gravimetric and volumetric density requirement, an ideal storage medium should be able to operate under ambient thermodynamic conditions and exhibit fast hydrogen

kinetics. The solid state storage of hydrogen is regarded as the best choice, and the families of materials that are being explored for efficient hydrogen storage are light metal hydrides, amides, alanates, ammonia boranes, composite materials, metalorganic frameworks, porous hydrates, etc. (Bhattacharya and Das, 2013)

Hydrogen bonds in various chemical complexes are known to be strong bonds, for e.g., in CH₄ molecule, the binding energy of H is ~4 eV which lies in the regime of chemisorption. On the other extreme, bonding of hydrogen to C and BN nanostructures is weak (~0.1 eV, i.e. physisorption range) and very little hydrogen can be stored under ambient conditions in these materials (Walker, 2008). It is possible to 'weaken' the bonds in the former class, or 'strengthen' the bonds in the latter class in such a way that the binding energy of H lies in the 'right window' between physisorption and chemisorption (Jena, 2011), as will be discussed in more detail in Section 3 of this article. First-principles electronic structure can be gainfully utilized for 'tailoring' such behaviour and thereby designing a suitable material for efficient storage of molecular hydrogen. For example, light metal hydrides are envisioned as novel class of materials that can show a major shift towards more favourable thermodynamics, kinetics and reversibility of the hydriding reaction by tailoring its particle size, physical confinement, and doping with suitable materials (Bhattacharya and Das, 2013; Shevlin and Guo, 2013). On the other hand, doping of nanostructured materials with suitable metal atoms can fundamentally change the nature of hydrogen bonding and hence provide a lightweight material capable of meeting the requirements of an ideal hydrogen storage material (Bhattacharya *et al.*, 2009a). Thus first-principles simulation and design of materials with a desired combination of properties for hydrogen storage can be very much rewarding in this technologically important domain of solid state hydrogen storage.

In this article, we restrict ourselves to the materials' issues for efficient storage of hydrogen in solid state. More specifically, we shall discuss how first-principles computational approach can be

gainfully used to predict the H₂ adsorption and desorption processes in metal nanoclusters, in complex hydrides (along with their decomposition pathways), as well as in functionalized nanostructures. We start with a brief outline of the theoretical-cum-computational tool that is used to handle this problem of hydrogen storage.

2. Theoretical-cum-Computational Approach

Efficient storage of hydrogen essentially requires optimum adsorption as well as desorption, i.e. ‘going in’ and ‘coming out’ of the storage medium. Microscopically, this essentially means that we have to tune the binding energy of hydrogen with the material within the desired window, as discussed earlier. For that, one has to use quantum mechanical calculations taking into account the motion of electrons in the presence of ionic core. This is a many-body problem, which is intractable to solve, and therefore we take recourse to some simplifying but reasonable approximations such as Born-Oppenheimer (BO) approximation, self-consistent field (SCF) approximation, local density approximation (LDA), tight binding (TB) approximation, etc. that are well-documented in the literature (Das, 2003). In the SCF approximation, the electrons interact in the mean field of the other electrons and ions. Thus, the many-body problem reduces to an effective two-body problem consisting of electron-ion and electron-electron interactions. Calculations are usually performed within the so-called density functional theory (DFT), where the exchange correlation potential is treated via some mean field approximation and the problem of solving an inhomogeneous many-electron system is reduced to that of solving an effective one electron Schrödinger equation with an effective potential (Jones and Gunnarsson, 1989; Das, 2002). Such an effective single-particle approach has been embraced by materials scientists, mainly because it provides a reliable computational tool yielding *material-specific quantitative results* with desirable accuracy for the ground state (cohesive, electronic, magnetic, etc.) properties of a large variety of systems. First-principles DFT calculations, based on LDA (local density approximation) and its improved variants such as GGA (generalized gradient approximation) have reached

an unprecedented level of accuracy and reliability such that one can not only explain but also predict material properties and phenomena. Although LDA has its own limitations in treating excited state properties such as semiconductor band-gap and strongly correlated phenomena, it is still the unchallenged workhorse for investigating the physics of materials. Attempts have been made to salvage some of these limitations via better functionals, as aptly described by John Perdew through his famous ‘Jacob’s Ladder’ (Perdew *et al.*, 2009). However, for rigorous treatment of strongly correlated electron systems, one has to invoke many-body techniques such as quasiparticle GW approach (Hedin, 1965; Hedin and Lundqvist, 1969) or the Quantum Monte Carlo (QMC) method (Mitas, 1996; Foulkes *et al.*, 2001).

The most widely used first principles electronic structure method for materials with fixed geometry are based on either plane wave based pseudo potential methods or on localized basis set methods. From the ground state total energy, one can estimate the force acting on the atoms that is essential to do molecular dynamics. For first-principles simulation and design of hydrogen storage materials, we have used state-of-the-art DFT-based methods with plane wave basis set viz., VASP (Hafner, 2007; Kresse and Hafner, 1993; Kresse and Furthmüller, 1996) with PAW potentials (Blöchl, 1994; Kresse and Joubert, 1999) for extended systems and with localized atomic orbital or Gaussian basis set viz., DMol3 (Delley, 2000) or GAUSSIAN03 (Frisch *et al.*, 2004) or GAMESS (Schmidt *et al.*, 1993) for molecular or cluster systems. In all our calculations, the ions are steadily relaxed towards equilibrium until the Hellmann-Feynman forces are converged to less than 10⁻³ eV/Å. Available experimental structural data have been used as input for some of the hydrides whenever they are available. An important breakthrough was the recipe proposed by Car and Parrinello (1985) for *ab initio* MD simulation within the framework of DFT. Such dynamical simulation enables one to determine the so-called “energy landscape”, i.e. how the energy of a system evolves with the position of the atoms, to monitor the making and breaking of chemical bonds, for example, desorption of hydrogen molecule from a host material as a function of temperature. The

calculations carried out for studying the above mentioned materials and phenomena can be broadly classified into the following three categories: (a) ground state geometry, electronic structure and activation barrier estimation (using the so-called nudge elastic band method (Sheppard *et al.*, 2008) for different possible configurations, (b) transition state calculations and reaction pathways and (c) *ab initio* molecular dynamics with Nose thermostat for estimating desorption kinetics.

3. Materials for Hydrogen Storage

We now discuss the various ways for efficient storage of molecular hydrogen in solid state (Walker, 2008; Schlapbach and Züttel, 2001; Züttel, 2003), for which a fundamental understanding of how hydrogen interacts with materials is of utmost importance (Jena, 2011). High storage capacity, satisfactory kinetics, and optimal thermodynamics are some of the essential criteria for a potential hydrogen storage material. Most of the metals in the periodic table, their alloys or inter-metallic compounds react with hydrogen to form metal hydrides. The bonding between hydrogen and the metal can range from covalent to ionic, as well as multi-centered bonds and metallic bonding (Schlapbach and Züttel, 2001; Züttel, 2003). In fact, some metal hydrides can store hydrogen with a density higher than that of liquid hydrogen. It is exciting as well as challenging to probe the possibility of storing hydrogen in a more compact and safer way than pressurized gas and cryogenic liquid. A classic textbook example is palladium hydride (PdH_x) that can retain a substantial quantity of hydrogen within its crystal lattice. At room temperature and atmospheric pressure, palladium can adsorb up to 900 times its own volume of hydrogen in a reversible process. However, Pd is a heavy metal and hence does not yield good gravimetric efficiency, apart from the fact that it is quite costly. Same argument holds for some of the promising intermetallic hydride such as LaNi_5 . Perovskite hydrides of ABH_3 structure (A is a monovalent alkali metal such as K, Sr, Cs, or Rb, while B is a divalent alkaline earth metal such as Ca or Mg), in particular, Mg-based compounds have received particular attention because of their lightweight and low cost production (Banerjee *et al.*, 2009), as will be

discussed in Section 3.1.

Next, we discuss complex hydrides formed by a combination of metals or metalloids, where hydrogen atoms are bonded covalently to a metal or metalloid atom to form an anion. This anion is then bonded ionically to a metal cation present, to form a complex metal hydride (Schlapbach and Züttel, 2001; Züttel, 2003). In general, complex metal hydrides have the formula $\text{A}_x\text{M}_y\text{H}_z$, where “A” is an alkali metal or alkaline earth metal cation or cation-complex, and “M” is a metal or metalloid. Well-known examples feature anions of hydrogenated group 3 elements, in particular, boron and aluminium. Borohydrides such as LiBH_4 and alanes, such as NaAlH_4 are among the most widely studied. The variety in complex metal hydrides is very large. The possibility of forming complex metal hydrides using lightweight elements opens a promising route to achieve very high hydrogen content by weight, for e.g., LiBH_4 contains 18 wt% hydrogen. Accordingly, there is an increasing interest to explore complex metal hydride systems and their subsequent optimization for practical use. Combining several complex hydrides into one storage system might improve the storage characteristics, but the complexity of reaction mechanisms requires further fundamental research on such materials. Further details are available in some recent reviews on complex hydrides (Orimo *et al.*, 2007). While complex hydrides involving light metals show impressive gravimetric efficiencies, the desorption temperature of H_2 turns out to be rather high. Lithium imides, for example, constitute one such promising material showing reversible hydrogenation when reacted with LiH (Chen *et al.*, 2002). Attempts have been made to bring down the desorption temperature close to room temperature by suitable alloying with Ca or Mg (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011) which essentially weakens the effective bonding between the metal M^+ cation and the complex $(\text{NH}_2)^-$ anion. This will be discussed in further detail in Section 3.1. Alanes, borates, and amidoboranes are the other families of complex hydrides that are being extensively studied both experimentally and theoretically.

Apart from complex hydrides, there are other kinds of materials that have been investigated for

hydrogen storage, for e.g., carbon-based materials activated with nano-catalysts (Struzhkin, 2007), clathrate hydrates (Panella, 2007), and metal-organic complexes (Dillon and Heben, 2001). Nano-structured cages with curvature such as single-walled carbon nanotubes, boron nitride nanotubes (BNNT), or B-C-N composite nanotubes and buckyball-like clusters of C or BN are among the most widely investigated nano-materials for hydrogen storage (Barman *et al.*, 2008; Bhattacharya *et al.*, 2008a, b; 2009b; 2010). The presence of a highly specific surface area is promising for physical and chemical optimization of such materials. The storage takes place as hydrogen molecules are adsorbed on the surface of the solids. The possibility of storing hydrogen in molecular form is advantageous over chemical storage in atomic form, which requires dissociation of the hydrogen bond and the formation of a hydride. In order to understand and exploit these materials for H-storage, it is crucial to know the way hydrogen interacts with the surface or the bulk. There are mainly three ways in which hydrogen can be adsorbed on a material (Jena, 2011).

- (a) *Physisorption*, where hydrogen remains in molecular state (H_2) and gets bound on the surface rather weakly (B.E. ~ 10 – 100 meV)
- (b) *Chemisorption*, where H_2 dissociates into H atoms that migrate and gets strongly bound to the material (B.E. ~ 2 – 4 eV range)
- (c) *Molecular chemisorption*, where H-H bonding gets weakened, but not broken (still H_2 molecular state is retained) and the strength of the binding is intermediate between physisorption and chemisorption.

It is this third form of the quasi-molecular bonding that is most suitable for optimal absorption and desorption of hydrogen. The basic quasi-molecular interaction and bonding of hydrogen can be explained via what is known as Kubas interaction (Kubas *et al.*, 1984; Kubas, 1988; 2007; 2009) i.e., donation of charge from H_2 molecule to the unfilled d-orbitals of the transition metal TM atoms and back-donation from the transition metal TM atom to the anti-bonding orbital of H_2 molecule. Kubas interaction has been exploited for designing transition metal decorated

nano materials (Sun *et al.*, 2005; Chandrakumar and Ghosh, 2008; Hoang and Antonelli, 2009), metal organic frameworks (MOF) (Dixit *et al.*, 2009), spillover catalysts (Singh *et al.*, 2009) and other kinds of materials for H-storage. However, it has limitations in explaining the bonding in alkaline earth metal complexes and alkali metal doped nanostructures (Bhattacharya *et al.*, 2012). In case of metal clusters, the way hydrogen interacts is fundamentally different from bulk and the reactivity and adsorption behaviour change drastically with the addition and subtraction of a few metal atoms (Niu *et al.*, 1992; Giri *et al.*, 2011).

In the following subsections, we shall attempt to illustrate how first principles simulation helps addressing some specific issues in designing materials for efficient storage of hydrogen. We consider materials that we have worked on in our laboratory.

3.1 Simple Metal Hydride: A Case Study of Magnesium Hydride

Bulk hydrides of light weight alkaline earth metals such as MgH_2 , contain a large amount (~ 7.7 wt%) of hydrogen (Imamura *et al.*, 2005; Zaluska *et al.*, 1999). However, the chemically strong metal-hydrogen bonding causes a significantly high hydrogen desorption enthalpy (~ 0.8 eV/ H_2 molecule) (Shevlin and Guo, 2013), thereby resulting in an unfavourable hydrogen desorption temperature of $\sim 300^\circ C$ (Liu *et al.*, 2013). Due to this fact, their usage for the practical hydrogen storage application has been retarded. There are already efforts to circumvent these constraints by different processes. Nanostructuring via ball milling process (Liang *et al.*, 1999; Orimo *et al.*, 2007) has been found to be a viable route to ameliorate the adsorption and desorption kinetics of hydrogen and thereby to reduce the hydrogen desorption temperature by tuning the Mg-H bond strength. This happens due to the higher diffusivity of hydrogen and higher surface to volume ratios of the nanoclusters. Eventually, a computational analysis on MgH_2 nanoclusters of different sizes (Shevlin and Guo, 2013) reported that nanostructuring of MgH_2 leads to the improvement of the dehydrogenation characteristics only for smaller size Mg_nH_{2n} ($n = 1$ – 4) nanoclusters.

This is due to the fact that the majority of the earlier studies have been concentrated on the atomic hydrogen adsorption into the Mg nanoclusters. The H-H bond dissociation energy (~ 4.52 eV) of H_2 molecules enhance the desorption enthalpy of the atomic hydrogen adsorbed in these nanoclusters. Hence, an attempt has been made to explore the possibility of interaction of hydrogen in molecular form with neutral as well as cationic Mg nanoclusters (Banerjee *et al.*, 2015) and thereby, overcome the limitations of bulk MgH_2 . Detailed study on the origin of $Mg-H_2$ and Mg^+-H_2 bonding using molecular electrostatic potential (MESP) (Truhlar, 1981) based charge analysis and energy decomposition analysis (EDA) (Su and Li, 2009) reveals that the polarization of H_2 molecules on the surface of these nanoclusters plays an effective role in binding of the H_2 molecules to these nanoclusters. The results show that incorporation of dispersion correction in these weakly interacting systems is essential to accurately estimate the $Mg-H_2$ bond strength. Banerjee *et al.* (2015) illustrated how dispersion corrected interaction energy of the attached H_2 molecules (~ 0.1 eV/ H_2 molecule) lie in the right energy window required for efficient hydrogen storage. The estimated desorption temperature of $\sim 100^\circ\text{C}$ establishes the suitability of these hydrogen ornamented neutral and charged Mg nanocluster systems for practical hydrogen storage application.

3.2 Complex Hydride: A Case Study of Lithium Imide

First we take up a low-Z complex hydride viz. lithium imide. It was demonstrated by Ping Chen *et al.* (2002) how lithium amide ($LiNH_2$) reacts with lithium hydride (LiH) to yield lithium imide (Li_2NH) or lithium nitride (Li_3N) and molecular hydrogen.



The forward reaction results in desorption, while the reverse reaction results in absorption. The reaction is exothermic with $\Delta H \sim -96$ kJ/mol H_2 , while the gravimetric efficiency turns out to be ~ 10 wt%. This dehydrogenation reaction leading to release of hydrogen is reversible, which is an additional attractive feature. Li atoms are ionized as Li^+ cations, while

$[NH_2]^-$ forms a complex anion and it is the strength of the interaction between Li^+ and $[NH_2]^-$ that dictates the enthalpy of reactions and hence the desorption kinetics of H_2 . One way to do this is to alloy the binary hydride with some divalent alkaline earth metal such as Ca or Mg (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011) and these ternary complex hydrides have been synthesized in recent years (Wu *et al.*, 2007).

The electronic structures of each of the constituents of the equations stated above, and its Ca/Mg-doped counterparts, as well as the heats of reactions (exothermic) have been estimated from first principle DFT calculations (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011). The average N-H bond lengths, hydrogen removal energies and the enthalpy of formation of $Li_2Ca(NH)_2$ and $Li_2Mg(NH)_2$ have been estimated and the results compared with the same quantities estimated for the pure Li imides and amides. The enthalpy of formation is the most fundamental and important quantity for hydrogen storage materials, which can be estimated from the difference between the energies before and after the hydriding reaction. The enthalpy change in a reaction at 0 K was calculated from the difference between the total energies of the products and the reactants, as calculated by DFT for their respective bulk geometries. We investigated the thermodynamics of hydrogen release from the mixture of $Li_2Ca(NH)_2$ and LiH , which allows us to draw comparisons with the thermodynamics of hydrogen release from the other Li-N-based compounds, viz., parent imides and amides along with $Li_2Ca(NH)_2$ with LiH . Table 1 summarizes our results for the specific exothermic chemical reactions that take place for H_2 desorption in different binary and ternary hydrides. We observe that ΔH decreases from 108.8 kJ/mol- H_2 in Li-imide to 102.6 kJ/mol- H_2 and to 82.8 kJ/mol- H_2 for Ca and Mg ternary imides, respectively. The corresponding ΔH value estimated by Araujo *et al.* (2007) is 118 kJ/mol- H_2 for Li_2NH assuming *Pnma* space group; and for $Li_2Mg(NH)_2$, it is 84 kJ/mol- H_2 . It is interesting to note that ΔE_H reduces by $\sim 5.5\%$ for the ternary Ca-imide. The H removal energy correspondingly decreases by about 5.5% with a concomitant increase in the N-H bond length by about

Table 1: Estimated bond-lengths, reaction enthalpies (ΔH) and hydrogen removal energies (ΔE_H) for undoped and doped Li-imides (Bhattacharya *et al.*, 2008a)

System	Structure space group (formula unit)	Chemical reaction	Reaction enthalpy (ΔH) KJ/mole H_2	ΔE_H KJ/mol H_2	Average N-H bond length in Å
$LiNH_2$	Tetragonal <i>I-4</i> (4f.u)	$LiNH_2 + LiH \rightleftharpoons Li_2NH + H_2$	68.9	268	1.03
Li_2NH	Orthorhombic <i>Ima2</i> (8f.u)	$Li_2NH + LiH \rightleftharpoons Li_3N + H_2$	108.8	192	1.04
$Li_2Ca(NH)_2$	Trigonal <i>P-3m1</i> (3f.u)	$3Li_2Ca(NH)_2 + 2LiH \rightleftharpoons 4Li_2NH + Ca_3N_2 + 2H_2$	102.6	181	1.05
$Li_2Mg(NH)_2$	Orthorhombic <i>Iba2</i> (16f.u)	$3Li_2Mg(NH)_2 + 2LiH \rightleftharpoons 4Li_2NH + Mg_3N_2 + 2H_2$	82.8	183	1.05

0.01 Å for the ternary Ca imide system (Bhattacharya *et al.*, 2008a; Bhattacharya, 2011), indicating weakening of the N-H bond. The enthalpy of reaction $\Delta H = T\Delta S$ for pure lithium imide decreases on ternary addition. Assuming the entropy change ΔS to remain more or less constant during the reactions, the dehydrogenation temperature T is expected to come down to a desirable range.

3.3 Chemical Hydride: A Case Study on Mono-ammoniated Li-Amidoborane

Next, we take up ammonia-borane (NH_3BH_3) or in short, AB-complexes that have emerged as attractive candidates for solid state hydrogen-storage materials because of their high percentage of available hydrogen (19.6 wt%). However, relatively poor kinetics and high temperature of dehydrogenation as well as release of volatile contaminants such as borazine are posing big challenges for practical application of AB (Staubitz *et al.*, 2010; Chua *et al.*, 2011). When one H atom in AB is replaced by an alkali or alkaline earth metal (M), a new class of materials called metal-amidoboranes (MAB) is formed, which in turn can be used for efficient storage of molecular hydrogen (Wu *et al.*, 2008; Shevlin *et al.*, 2011). These materials were highlighted as some of the best potential hydrogen-storage materials in the 2008 DOE Hydrogen Program annual progress report. For example, LiAB and NaAB provide high storage capacity of 10.9 wt% and 7.5 wt%, respectively (Xiong *et al.*, 2008) at easily accessible temperatures without the unwanted release of borazine. $LiNH_2BH_3$ is environmentally harmless and stable in solid-state at

ambient temperature and normal pressure. The bonds get distorted as compared to those in pristine ammonia-borane, as seen from the ball-and-stick model optimized geometries and corresponding bond-lengths (Bhattacharya and Das, 2013). However, in order to improve the operating properties of these materials such as rapid H_2 release near room temperature, it is vital to understand the underlying mechanism in the release of H_2 .

Recent experimental and computational studies have shown that NH_3 reacts with LiAB to yield H_2 and the dehydrogenation takes place in three different stages (Bhattacharya *et al.*, 2012), each time resulting in an intermediate meta stable product (adduct). We have found a transition state where the hydric B-H bond in the $[NH_2BH_3]$ unit interacts with the protic N-H bond of NH_3 , which in turn leads to H_2 release from the system as a first dehydrogenation process. The reaction pathway with the minimum activation barrier has been estimated using transition state calculations (Bhattacharya *et al.*, 2012; Bhattacharya and Das, 2013). Similarly, we have determined using our first principles approach, the second and the third dehydrogenation processes that result in relatively high activation barriers and H_2 -removal energies (Table 2), while the metastable products left behind are respectively, $Li(NH)NH_2BH$ and $Li(NH)NBH$, the final product matching with the available experimental results (Bhattacharya *et al.*, 2012).

We explored using our computational approach, the possibility of forming a higher order cluster, especially after the first dehydrogenation when the

Table 2: Activation barriers and hydrogen removal energies for 1st, 2nd and 3rd dehydrogenation energies of monoammonated LiAB (Bhattacharya *et al.*, 2012).

Dehydrogenation	Activation barrier (KJ/mol H ₂)	H ₂ -removal energy in eV/H ₂	
Monomer of LiAB+NH ₃			
First	78	0.16	
Second	105	0.27	
Third	353	1.3	
[LiNH ₂ -BH ₂ -NH ₂] ₃			
Second [1]	No Barrier	0.14	
Second [2]	No Barrier	0.20	Average ~0.25
Second [3]	No Barrier	0.40	
Third [1]	230	Average 0.14 ~236	Average ~0.67
Third [2]	236	0.20	
Third [3]	243	0.40	

metastable product LiNH₂—BH₂NH₂ is reached. For the subsequent (i.e. after 1st) dehydrogenation reactions, we have studied the stability of [LiNH₂-BH₂-NH₂]_n clusters with *n* varying from 2 to 6. Our results reveal that as the cluster size goes up from monomer to dimer to trimer (*n* = 3), the relative stability keeps on increasing (i.e. more negative) and tends to saturate for *n* ≥ 6. The detailed reactions and their pathways are provided in Bhattacharya *et al.* (2012). It is this reduction in the activation barrier as a function of increasing cluster size that provides an explanation for the dehydrogenation mechanism in the monoammoniated LiAB system.

4. Nano-structured Materials

As discussed in Section 3, the binding energy of hydrogen molecules to curved nano-structures such as buckyballs or nanotubes are rather low, i.e. in the physisorption range, which needs to be increased. Also the hydrogen coverage densities need to be enhanced. The usual approach to these problems is decorating these nano-structures with suitable metals.

Considering the gravimetric hydrogen density issue, it is only the lightweight metals that are potentially interesting for decoration. The challenge is to find metals that can bind to nanotubes or bucky balls strong enough so that they remain as immobilized on the surface, and resist metal clustering. The density of the metals covering the surface is also important and needs to be adjusted to an optimum value, that is, it should be high enough to capture as much hydrogen as possible, but low enough to preserve the hydrogen gravimetric density by not influencing the total system weight to a great extent. The interaction between the hydrogen molecules and metal atoms deposited on a surface can be electrostatic, chemisorption or of Kubas type (Dillon and Heben, 2001; Barman *et al.*, 2008; Bhattacharya *et al.*, 2008b; 2009b; 2010; Kubas *et al.*, 1984; Kubas, 1988; 2007; 2009).

In the last decade, graphitic materials with planar structures (Patchkovskii *et al.*, 2005; Bhattacharya *et al.*, 2009a) have been investigated for H-storage. Theoretical calculations show that graphene layers spaced 6 and 7 Angstroms apart, store hydrogen at room temperature and 100 bars (Patchkovskii *et al.*, 2005). However, this is only possible if the interplanar distances can be fixed at an appropriate value that maximizes the stored hydrogen content. Spacer molecules can be used for this purpose, although an ideal one has not been reported yet. For graphene to become a strong contender in practical hydrogen storage, thermo-dynamical issues need to be resolved as well. The interaction of hydrogen molecules with the layers needs to be increased in order to enable operating under moderate temperature and pressure conditions. In addition, extending the storage densities to more than monolayer hydrogen coverage would be interesting. Recently, there have been numerous studies in this field. While this is still futuristic, single-walled as well as multi-walled carbon nanotubes (CNT) and their isoelectronic counterparts viz. boron nitride nanotubes (BN-NT) are being considered (Dillon *et al.*, 1997; Sun *et al.*, 2005; Gundiah *et al.*, 2002) for storing hydrogen, although they have their own advantages and shortcomings. This will be discussed in the next section.

4.1 Hydrogen Storage in CNT, BNNT and Beyond

In spite of high expectations, the early experiments on carbon nanotubes are not so encouraging for storing hydrogen because of their sub-critical storage capacities (Gundiah *et al.*, 2002; Kajiura *et al.*, 2003). A recent theoretical study indicates that high hydrogen content in the pure carbon nanotubes cannot be achieved through physical sorption (Blasé *et al.*, 1994). Yildirim and Ciraci (2005) have shown from their first principles calculations that functionalizing the CNT with suitable transition metal atoms could lead to high capacity hydrogen storage (~8 wt%) along with the possibility of some interesting hydrogen desorption of the system. However, tendency of a normal CNT to get oxidized around 600°C is an impediment for the usage of TM-functionalized CNT for high capacity hydrogen storage.

Owing to these shortcomings of carbon nanotube, efforts have been shifted towards non-carbonic materials composed of light elements such as B and N. B-N nanostructures are analogous to their carbon counterparts and offer many advantages. For example, B-N nanotubes are stable up to 900°C. In addition to their heat resistance in air and structural stability, B-N nanotubes are semiconducting with wide band gaps (5.5 eV) that are nearly independent of tube diameter or helicity. Several groups have studied the hydrogen uptake and reversibility issues of B-N nanostructures (Ma *et al.*, 2002; Oku *et al.*, 2004a, b; Oku and Narita, 2004; Narita and Oku, 2002). However, if we look at the practical implementation of these kinds of structures for hydrogen storage, these have limited success. This is because of (a) the stability of most of these cage-like B-N nanostructures at room temperature (Sun *et al.*, 2005) and (b) the abnormally high hydrogen-desorption temperature from the B-N nanotubes for its extra thermal stability (Ma *et al.*, 2002). Is it possible to exploit the thermal stability of BN nanotube, together with the advantages of Ti-functionalized CNT? We have reported (Bhattacharya *et al.*, 2009a) the designing of a Ti-functionalized B-C-N nanocomposite, viz., BC_4N nanotube, as a possible H-storage material. $\text{B}_x\text{C}_y\text{N}_z$ nanostructures have been studied both experimentally and theoretically (Sen *et*

al., 1998; Weng-Sieh *et al.*, 1995). Recently, BC_4N nanotubes have been experimentally synthesized (Raidongia *et al.*, 2008) and found to be semiconducting in nature with very high thermal stability. The local structural unit of BN_3 and NB_3 linked with B-N bonds are responsible for the extra stability, as compared to its host carbon nanotube. While the host carbon nanotube is metallic, the substitutional doping of B and N with a large enough concentration (33%) turns it into a semiconductor. The synthesis, characterization and various properties of BC_4N nanotubes are described in detail by Raidongia *et al.* (2008). What we have done is to explore how to functionalize it for storage of molecular hydrogen (Bhattacharya *et al.*, 2008b). We have addressed several open questions, for e.g.: (1) Does transition metal prefer to stay in exohedral or endohedral position of the nanotube? (2) What is the energy barrier for the transition metal to enter into or escape from the nanotube? (3) What happens when more transition metals are decorated in different hexagonal faces of the nanotube? (4) How does the binding energy of H_2 change during addition of more H_2 in the TM-doped BC_4N nanotube both in exohedral and endohedral positions? (5) As more H_2 is stored, what are the changes in the geometry and electronic structures of the nanotube? (6) Lastly, from the hydrogen storage point of view, what is the effect of temperature on the stability of this kind of B-C-N composite nanotube? We have carried out detailed first-principles investigations to address these questions for this novel BC_4N nanotube, and suggested the means of improving the storage efficiency.

5. Concluding Remarks

In this restricted review, we have discussed how density functional based first-principles simulation has been used to design efficient hydrogen storage materials. While complex hydrides have been subjected to extensive investigation, functionalized nanostructures are becoming the focus of attention. Optimizing the gravimetric efficiency, dehydrogenation temperature and fast kinetics pose a real challenge to the materials scientists. The coming decade is going to witness some breakthrough in this direction. .

As an epilogue, I would like to add that while the developing countries in Asia are sincerely trying to achieve some breakthrough in hydrogen economy; in the western world, particularly in the United States, the euphoria on hydrogen seems to be on low ebb. This may be because of several reasons such as the finding of huge gas reserves and other political reasons. However, the Asian initiative on hydrogen storage is looking forward to an optimistic goal in the foreseeable future.

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*Review Article***Hydro Energy Sector in India: The Past, Present and Future Challenges**

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During the last century, hydropower has made an important and significant contribution to meeting the energy needs of countries. In developed countries, most hydropower potential has been harnessed. However, the situation is not similar in developing countries such as India. It is seen that nearly 3/4 of exploitable hydro energy potential in India is yet to be harnessed for the betterment of growth and welfare of population of the region and boost industrial growth. The estimated economically exploitable hydro potential in India is assessed at 84,000 MW (@ 60% load factor) with a suggested installed capacity of 1,48,700 MW. About 26% of this has been exploited with the existing hydro power plants.

The study is an effort to bring out vividly the past, present and future of hydro energy in India; some relevant aspects of the global situation are also discussed. Relevant policies of the central government have been touched upon as required while discussing the bottlenecks encountered in accelerating hydropower sector development.

India has the capacity to play a lead role in energy security if it were able to harness all the exploitable hydro energy in the region, including Himalayas in collaboration with its neighbouring countries.

With the completion a few world class hydro projects of challenging nature such as the Tehri Dam and power plants, Naptha Jhakri Hydro Project, etc. in recent decades, the engineering community in India is well-poised to focus on the development of hydro energy in challenging sites, mostly in the Himalayas, and accomplish the realization of the balance available energy potential that is sizeable.

Keywords: Hydropower; Historic Scenario in Hydro Development; Water Resources Sector and Hydropower Generation; Government Policies in Energy and Water Sectors; Resettlement Issues; Indian Strength in Hydro Engineering

Historical Glimpse of Hydropower – The Global Scenario

The world's first electrical power generation on a commercial scale is just 130 years old. The first hydropower station was constructed in England in 1881 by utilizing the water potential of river Wey at Godalming Surrey, and put into operation to supply electricity. The world's first electrical power generation for a specific customer however was started in 1879 in Switzerland when a hydropower

generating set was installed for supply of electrical power to a hotel in St. Moritz for its lighting. The old Schoelkopf Power Station No.1 near Niagara Falls in the U.S. side began to produce electricity in 1881. The first Edison hydroelectric power plant – the Vulcan Street Plant – began operating in September 1882, in Appleton, Wisconsin, with an output of about 12.5 kilowatts. Switzerland's first power station on commercial scale started in 1882 at Laussane. Soon other countries of Europe such as Italy in 1884 and Germany in 1891, also commissioned power

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generating stations using water potential. In USA, the first hydropower station was commissioned at Niagara Falls in 1885, having two units of 5500 kW each.

The earlier uses of waterpower could be traced back to Mesopotamia and ancient Egypt, besides peninsular India and Sri Lanka. Through different means of energy conversions, irrigation stood as a practice since the 6th millennium BC. The water clocks had been used since the early 2nd millennium BC. Other notable earlier examples of “water power” include the Qanat system in ancient Persia and the Turpan water system in ancient China. Hydropower had also been in common use since the ancient times for grinding the flour and to perform other similar tasks. However, most of the direct uses or conversion of water power especially from flowing streams using water wheels were mostly of crude nature with little regard to efficiency, output, etc. From the early 19th century, the water wheel designs were being refined and engineered on the basis of principles of fluid mechanics by the French and Americans. In course of time, various types of hydraulic turbines were invented such as Fourneyron, Francis, Kaplan and Pelton. The use of these turbines, located at or close to the water sites, considerably improved efficiency of direct water power use in domestic industries of the day and also proved very handy and was a boon when the possibility of electricity generation from hydropower became feasible for the first time in the world in 1879. It was in the late 19th century, when the electrical generator was developed and coupled with hydraulic turbines.

By 1886, there were about 45 hydroelectric power plants in the USA and Canada. By 1889, there were 200 plants in USA. At the beginning of the 20th century, a large number of small hydroelectric power plants were constructed by commercial companies in the mountains that surrounded metropolitan areas. By 1920, 40% of the power produced in USA was hydroelectric. Hydroelectric power plants continued to become larger throughout the 20th century. After Hoover Dam’s initial 1345 MW power plant became the world’s largest hydroelectric power plant in 1936, it was soon eclipsed by the 6809 MW Grand Coulee Dam in 1942. Brazil’s and Paraguay’s Itaipu Dam

opened in 1984 as the largest, producing 14,000 MW but was surpassed in 2008 by the Three Gorges Dam in China with a production capacity of 22,500 MW.

India did not lag much behind: the commencement of the maiden hydropower generation plant in India began in 1897 with an electricity generating station of 130 kW capacity, named Sidrapong. Using the potential of Teesta river at the site, this facility was constructed and put into service by the Municipality of hill station of Darjeeling in (the present day) State of West Bengal.

Hydropower plants all over the world produce about 24% of the world’s electricity and supply more than 1 billion people with power. According to National Renewable Energy Laboratory, the combined output of the world’s hydropower plants is about 675,000 MW, the energy equivalent of 3.6 billion barrels of oil. More than 150 countries around the world generate hydropower now. About 44% of the world’s hydropower was generated in four countries in 2002, mostly large- and mid-scale plants. Asia accounted for 24% of the world’s hydropower generation, with 618 GWh, followed by North America with 23% (595 GWh) and Europe with 20% (537 GWh). Currently, 808,000 megawatts of hydropower generation capacity are in operation or under construction around the world.

Central and South America generate nearly 70% of their electricity from hydropower, and many countries, including several large countries such as Canada and Brazil, rely on hydropower for more than half of their electricity. Brazil, Canada, Norway, Paraguay, Switzerland, and Venezuela are the only countries in the world where majority of the internal electric energy production is from hydroelectric power. Paraguay produces 100% of its electricity from hydroelectric dams, and exports 90% of its production to Brazil and Argentina. Hydropower makes up 85% of Brazil’s electricity generation with 69 GW of installed capacity. The capacity under construction or planning is more than 25 GW. One of the hydropower plants under construction is the giant 11.18 GW Belo Monte power plant. Hydropower accounts for 57% of the electricity generated in Canada, 7% in USA (USA uses hydropower for peaking and not as

base load) and 12% in Mexico. Canada's economical hydropower potential is second only to that of Brazil in the Western Hemisphere. Canada still has several projects either under construction or planning, amounting to 6.6 GW. In Western Europe and USA, the scope for additional hydropower is limited, as most economic sites have already been developed.

An incredible 99% of all electricity in Norway is produced from hydropower with an average annual production capacity of about 125 TWh (2005). This is achieved through 620 power plants spread along the whole country and utilization of approximately 60% of Norway's accessible hydropower potential.

Norway is the world's sixth largest producer of hydropower and the largest producer in Europe. While the developed countries have harnessed their respective hydro potential, other countries such as Brazil, China and India embarked upon development of their hydropower a little later. Brazil and China had done it in a big way. India is progressing to develop its hydropower potential but due to wide ranging issues such as resettlement of affected people and other environmental concerns is lagging behind some of these developing nations. Smaller countries such as Nepal and Bhutan having huge untapped hydropower potential are also pursuing ambitious plans for development of hydropower. In particular, the importance of hydropower is well-recognized in Bhutan and seeing the immense contribution of hydropower projects developed in the last few decades with Indian co-operation such as Chukha, Tala, etc. to their economy, envisaged in 2011, a target of adding yet another 10,000 MW hydropower in Bhutan by 2020. Many of these would be joint venture operations with several leading Indian public sector power utilities.

China obtained about 17% of its electricity from hydropower during 1990 to 2006. Chinese hydropower generation grew at a compounded annual growth rate of 8% (compared to 1.5% for the rest of the world), thus increase in Chinese hydropower generation over this period accounting for 36% of the global increase in hydropower generation.

Historical Glimpse of the Indian Hydropower Scenario¹

India is fortunate to be endowed with all the primary energy sources such as coal, hydropower, uranium/thorium, etc. However, among these, hydropower is the only renewable source of energy and has been recognized as economical and a preferred source of electricity due to its various benefits. Development of hydropower resources is important for energy security of the country. Hydropower is a renewable, economic and non-polluting source of energy. Hydropower stations have inherent ability of quick starting, stopping and load variations offering operational flexibility and help in improving reliability of power system. Hydro stations are the best choice for meeting the peak demand. The generation cost is not only inflation-free but reduces with time. Hydroelectric projects have long useful life extending over 50 years and help in conserving scarce fossil fuels. They also help in opening of avenues for development in remote and backward areas.

Although hydropower was generated at Darjeeling in 1897, the first major landmark hydropower station, designed to promote industrial development, was set up at Sivasamudrum on the river Cauvery with an initial capacity of 7.92 MW in 1902 and in due course of time, this was increased in stages. The final installed capacity of this powerhouse became 47 MW by 1938. Initially, power was supplied to Kolar Gold Fields for mining development and operations and later to Bangalore and Mysore cities too. Mysore Darbar's second development was in 1940: the Shimsapura hydro power station (2×8.6 MW), also on the river Cauvery.

In the north, in 1905, a 4 MW Mohora hydro station on river Jhelum was the first major hydropower development in the then princely state of Jammu and Kashmir. The maximum contribution to hydro development was made later in the west by the renowned private industrial house of the Tata's who set up three major hydro stations in the Western Ghats in the then Bombay Presidency, namely 40 MW Khopoli (5×8 MW) in 1915, 48 MW Bhivpuri (4×12

¹Please see reference 1

MW) during 1922-25 and 90 MW Bhira (5×18 MW) in 1927.

In 1932, two major hydro development projects, namely 48 MW Jogindernagar (Uhl) hydro station (now in Himachal Pradesh), and 14 MW (initial capacity) Pykara hydro station were taken up and completed by the then provincial governments of Punjab and Madras, respectively. Further notable developments in the then Madras Presidency were Mettur dam hydro station (40 MW) in 1937 and Papanasam (14 MW initial) in 1944. The then Travancore-Cochin princely state (now in Kerala) and the State of United Provinces (now Uttarakhand and Uttar Pradesh) also carried out some significant hydro developments namely the Pallivassal hydro station (with 15 MW initial capacity), and a series of hydro stations on Ganga canal, respectively. A total installed hydro capacity at the time of independence increased to 508 MW in a span of about 50 years since the first development project that surfaced in the British period.

A few notable major projects were undertaken since independence that made significant strides in the subsequent few decades after the 1950s. Prime Minister Pandit Nehru was quite proud to proclaim some of the impressive dams and hydro as “the modern temples of India”. Inter-alia, one can view a few from among a larger list² viz:

- Bhakra Dam multipurpose project complex comprising Bhakra Dam and dam toe powerhouse – 450 MW, and two canal powerhouses – total 154 MW, in the then larger Punjab state (later divided into smaller states, Punjab, Haryana and Himachal Pradesh)
- Rihand Dam multipurpose project – 300 MW in the then United Province, now Uttar Pradesh
- Gandhi Sagar multipurpose project in the then Madhya Bharat, now Madhya Pradesh
- Koyna Dam multipurpose complex project (with first major underground powerhouse) – 540 MW in the then larger Bombay state, now Maharashtra

- Sharavati project – 891 MW in the then Mysore State, now Karnataka
- Periyar project – 140 MW
- Kundah complex project PHs I-60 MW and II-175 MW in the then larger Madras state, now Tamil Nadu
- Machkund – 120 MW, and the famous Hirakud dam multipurpose projects 308 MW in Orissa.

A host of other smaller capacity projects ranging from the minimum of a few MW to 50-60 MW were also undertaken in J&K, UP (now in Uttarakhand), Mysore State, Madras State, Travancore-Cochin now Kerala, Bihar now in Jharkhand, West Bengal and the then Assam State (now in Meghalaya) and in various other states. By 1960, these developments resulted in increasing the hydro capacity to about 1920 MW from 508 MW at the time of independence.

The first systematic and detailed study to assess the hydroelectric power potential of the country was undertaken during 1953-59 by the Government of India in the then Central Water & Power Commission (CW&PC). This was on the basis of the then prevailing technology, available topographical and hydrological data. The study carried out by CW&PC (Power Wing) placed the country's power and annual energy potential, respectively as 42,100 MW at 60% load factor corresponding to annual energy generation of 221 billion units. The subsequent re-assessment studies carried out by the Central Electricity Authority (CEA), Ministry of Power, during 1978-87 have placed the hydropower potential at 84,044 MW at 60% load factor and the economically exploitable hydro potential as 1,48,701 MW. The re-assessment studies undertaken by CEA were to provide an update of hydroelectric potential of the country in order to facilitate a quick follow-up and undertake the development of the country's exploitable hydropower capacity. A total of 845 schemes were identified to yield 442 billion units of electricity. In addition, 56 sites were also identified in various regions of the country for the development of pumped storage schemes with an assessed aggregate installed capacity of about 94,000 MW. The largest potential estimated was

²Central Board of Irrigation and Power Hydropower in India Publication (2012)

37.91% in the north eastern region followed by 35.88% in the northern region. The bulk of potential in the hill states of Jammu & Kashmir, Himachal Pradesh, Uttarakhand, Arunachal Pradesh and Sikkim were then yet to be developed.

Though the country ranks fifth in terms of available hydropower potential globally, much remains to be achieved despite their timely identification. This is a challenge while one takes pride in what could be achieved in a developing country with financial resource limitations soon after gaining its independence. Some 177 hydro power stations with a station capacity above 25 MW (having 617 generating units) provide a total installed capacity of about 38,748 MW that are operational; and, about 50 projects with an installed capacity of 15,065 MW are under execution as of December 2011.

The latest assessment reveals the hydro share percentage to the grid in India as just 19%. The potential harnessed within India remains at about 15%, with yet another 7% in various stages of development. The balance potential of about 78% remains unharnessed due to many issues and barriers, with more and more new challenges creeping in before their development.

Future Prospects – Indian Hydropower

Large Hydropower Potential

The estimated economically exploitable hydropower potential in India is about 84,000 MW at 60% load factor with a suggested installed capacity of 148,700 MW³. The Indus, the Ganga and the Brahmaputra, basins together in the administrative boundary of India could contribute about 80% of the hydropower. The majority of India's hydropower development potential lies in the key basins of Brahmaputra Basin (66 GW), Indus Basin (34 GW), Ganga Basin (21 GW), and the rivers of South India (24 GW). From a total hydropower potential of 149 GW, India can currently develop only 40 GW of the assessed potential.

³Central Electricity Authority official website http://www.cea.nic.in/hydro_wing.html; see the report annex, listing region-wise development in hydropower (above 25 MW)

Small Hydropower Potential

India's small (capacity less than 25 MW), mini (3-25 MW) and micro hydropower schemes (with capacity less than 3 MW) have been assessed at 6781.81 MW of installed capacity. Despite such an amazing opportunity, due to varying reasons, even the small and mini hydropower plants could not make an impressive progress.

Should the development of the regional resources that can be pooled together with cooperation from India's neighbouring countries such as Bhutan and Nepal, the hydropower potential figures (149 GW) could increase further by over 50 GW; this can make South Asia's energy position quite enviable. The share of hydro energy will then really boost the desired grid security of the entire region as a whole even under extreme variations in the load pattern in summer and winter. Efforts by India in this direction under international cooperation mechanism can ensure the overall welfare of the region, which lags behind many others such as South East Asia.

The hydropower sector in India today is considered to be at crossroads as the decline in its share is impacting the energy grid and its stability. The hydropower's share was at a high of 40% in the 1970s and one wonders if the same could ever be reached again in the future. In hindsight, even in 2006, hydropower shared about 26% of the installed capacity of the then total energy generation that stood at 124 GW. The balance is tilting adversely with the passage of time. A mid-course correction in our energy policy for an enhanced focus on hydro energy option with all encouraging policies, as rapidly as possible, is a requisite now and this has to consider several new factors that surfaced after the announcement of liberal policies two decades earlier to bring in the private sector with some encomiums.

What is crucial is that the energy segment too is given an impetus and hydropower potential unique to regional development obtains the requisite support, not only from the national budgets but also from international funding agencies. The role of India is of importance. The challenges that the sector faces are numerous and all pervasive to social, political,

environmental, economic and engineering dimensions with the geological and geotechnical risks that are inherent in Himalayan river valley projects.

India's Power Grid

India's power system is divided into five major regions namely, the northern region, western region, southern region, eastern region and north-eastern region. It is well-known that each of the regions faces distinct issues. While the eastern and north-eastern (NE) regions are power abundant, the northern and western regions are power deficit essentially due to greater power demands. The hydropower potential is largest in the NE region and lies in Brahmaputra and Barak basins but it is a fact that not much could be accomplished in the last seven decades: nearly 98% of the available resources remain to be harnessed in this region. A similar comparison indicates that the northern, eastern, western and southern regions have 79%, 77%, 23% and 33% untapped hydropower potential, respectively.

The CEA and Ministry of Power (MoP) are the nodal agencies involved in power sector planning and development in the Centre for accomplishing the Government of India's "Power Vision". Being a concurrent subject under the Indian Constitution, electricity is generated, transmitted, maintained and the hydro projects are developed by the Central and

State authorities. Since liberalization, independent power producers (IPPs, under private sector participation) were encouraged to participate in the power sector and this segment had also contributed, since the last two decades impressively though not to the expected levels. The primary role continues to be that of the states besides a number of central projects undertaken by the public sector undertakings such as National Hydro Power Corporation (NHPC), Sutlej Jal Vidyut Nigam (SJVN), Tehri Hydro Project Ltd. (THDC), North Eastern Electric Power Corporation Ltd. (NEEPCO) and National Thermal Power Corporation (NTPC) who were also enthused to take up hydro projects. With the central policy providing the overall direction for development, the states decide their needs for power generation, distribution and management systems.

Energy Development and India's Water Resources Sector – Mutual Issues

The development of water resources and its management is equally important when dealing with all forms of energy sector, and particularly hydro power. The subject "water" lies with the states as per the Constitution and the role of the Centre in an effective manner in water issues have been rather persuasive than directive, so far, despite certain available provisions as per River Boards Act 1956. The establishment of the River Boards was left purely as a voluntary measure for the states concerned in a shared river basin and despite differences in water sharing of the basin in several cases, none of the states invoked the provisions to request the Centre to constitute a River Board for the basin issues. The Centre felt that it could only propose a River Board when there is a solicitation to that effect from Basin States which was never the case since 1956.

The funding support for the state-sponsored Water Resources Development (and management) Projects could of course play as a catalyst to the Centre's intervention and this has been used to encourage the project planning and development in a manner that helps avoid conflicts between basin states. Besides, several centrally sponsored schemes are declared as "National Projects"; and, these are so

Table 1: Station-wise installed capacity of H.E. stations (above 25 MW) in the country⁴

Region	No. of Utility/ Stations	No. of Units X size MW	Capacity in MW
Northern	67	228	17487.27
Western	28	101	7392.00
Southern	68	243	11432.45
Eastern	17	61	4078.70
North Eastern	10	29	1242.00
All India Total	190	761	32182.25

⁴Central Electricity Authority official web site http://www.cea.nic.in/hydro_wing.html; see the report annex, listing region-wise (station-wise) installed capacity in the country (above 25 MW)

articulated and shaped to take on board multi-state interests as well as national objectives, at large.

Since hydropower development involves water resources, the responsibility of hydro-project development stayed (*and remains so even now*), primarily with the state agencies; however, in respect of inter-state rivers, the Centre's role in ensuring fairness and acceptability for all parties continues to remain a primary factor for projects to get initiated and this task takes considerable time. This adversely impacts the speedy implementation of several large projects including the long distance water transfer projects that has a hydro component of over 34,000 MW (popularly known as interlinking of rivers or ILR) among other benefits such as irrigated agriculture, flood and drought mitigation, navigation and ensuring reasonable environmental flows.

While the private sector was enthusiastic to step in when private participation in energy generation opened up in 1990s, there were other hurdles that had lessened the initial spirit and enthusiasm of the private sector which looked forward to certain new policy supports from time to time after experimenting with the effects of several liberalization measures announced for their entry, ever since 1992.

The energy sector in India remains largely public with a share of nearly 89% in the total installed capacity, even now.

Risks and Benefits – Hydropower

While the hydropower stands out as a class of its own right, the sector faces several inevitable competition from among other energy options and this is exasperating. Owing to the large quantities of water required to be stored in large dam-based storage projects, hydrologic uncertainties creep in. This is also the case with the 'run-off' type of developments. The other major risks that surface even during the project planning, design and construction are the *geological and geotechnical risks*. The Himalayan projects are particularly complex.

The meeting of ever-growing energy demand cannot be dealt with isolatedly, without also addressing durable and acceptable trade-offs between “water

and energy” and “water, energy and climate change mitigation”.

In terms of electrical power generation, the intermittency of most renewable energy options such as solar and wind, had an inherent problem (i) how could a “*well-secured load balance*” on grids be maintained against the backdrop of ever-increasing demand and (ii) energy storage. Two options are currently more feasible and cost-effective than others – hydropower and natural gas – both having their advantages and disadvantages from water resource and climate change perspectives, as well as broader social, environmental and economic considerations. Hydropower has a well-deserving recognition as the best option in terms of energy storage (with large dam-backed storage option) and quick dispatch power in India's energy development programmes given that the resource itself is renewable. However, the tendencies tilt in favour of opting for quick-fix solutions. These, among others, include (imported) natural gas. This can pose a threat, counterbalancing aspirations for self-reliant sustainable energy security in the light of global economic upswings and downturns and climate change associated threats with regard to bioenergy.

Implementation Challenges in the Hydropower Sector, after Selection of Projects

Hydropower has the following benefits and challenges:

- Abundantly available potential for hydropower development, particularly in the Himalayan river basins
- Hydropower involves no extra foreign exchange outgo year after year and insulates the nation with the relative independence in its price. Unlike gas power that is prone to international market such as oil prices, and energy costs, it is self-reliant energy when developed to a sufficient extent in the country.
- Hydropower is subject to no inflationary trends once construction phase is over as the “raw material” for power generation is free from such effects.

- Hydropower is green energy and hence stakes better claim as an environment-friendly energy option.
- Hydropower development can take onboard a few of the concerns such as submergence-induced involuntary displacement of people through proper “mitigation” measures to ensure that the adverse effects are minimized to affected families and sustainable solutions that provide welfare to their families and successive generations.
- Hydropower projects support socio-economic development of remote areas as the project site is developed and it is a development option that helps to reach areas that remain neglected, otherwise.
- Hydropower is not only cost-effective and a renewable form of energy but also multi objective multi-purpose development option as it extends additional benefits such as irrigated agriculture, secure food production and hence food security on a self-reliant basis, flood control, tourism, etc.

The hydropower development stands retarded in India, especially in recent times. The challenges are many apart from a few mentioned elsewhere, earlier. Hydropower development is unable to face competition from other energy options despite its attractiveness.

National Policy (1998) on Hydropower⁵

With an aim to accelerate the development of hydropower, Ministry of Power (MoP), Government of India, introduced the National Policy on Hydropower Development in 1998. The policy document has identified and responded to the major issues and barriers. The objectives of the National Policy document on Hydro Power Development, 1998 are as follows (*as stated in the document*):

"To ensure targeted capacity addition during 9th Five Year Plan (and subsequent plans) with central, state and private hydropower projects contributing

3455, 5810 and 550 MW respectively, the government at the centre pushed forward all-round efforts. The 11th Five Year Plan aimed subsequently at a capacity addition of 18,781 MW in the hydropower sector with the same vigour. Accordingly, an assurance to speed up steps such as execution of all CEA-cleared projects, update and clear pending detailed project reports of all identified schemes, etc., ensued. Small and mini hydro projects are especially viable for remote and hilly areas where extension of grid system is comparatively uneconomical".

In 2001, the CEA introduced a ranking study which prioritized and ranked the future executable projects. As per the study, 399 hydro schemes with an aggregate installed capacity of 106910 MW were ranked in A, B & C categories depending upon their *inter se* attractiveness. This was followed by a 50,000 MW hydro initiative in which preparation of Pre-Feasibility Reports (PFRs) of 162 projects was taken up by CEA through various agencies. The PFRs for all these projects (with the first year tariff less than INR 2.50/kWh) were identified for preparation of Detailed Project Report (DPR). The governments in the centre and states aimed to realize 100% hydropower potential of the country by 2025-26 with the new liberal measures spelt out in the policy.

The objectives were to be able to surmount some of the identified engineering, geological, geotechnical, hydrological, economical as well as financial and other social/environmental constraints.

Despite the above, hydro-development is lagging behind and investments, both public and private sectors, could not provide the desired impetus. A review of difficulties of the private sector needs better appreciation.

A few reasons for hesitation by independent power producers and planners to participate in hydro-development were the following:

(a) Long gestation period

- Time-consuming process for project clearances
- Until recently, the national focus has been on thermal generation.

⁵Please see reference 4

- Highly capital intensive and absence of committed funds
- Technical, including difficult investigation, inadequacies in tunnelling methods
- (b) Inaccessibility of the area
- (c) Geological surprises (especially in the Himalayan region where underground tunnelling is required)
- (d) Technical constraints due to complex geological nature of the projects
- (e) Managerial weakness (poor contract management)
- (f) Problems due to delay in land acquisition and resettlement of project affected families
- (g) Law and order problem in militant-infested areas
- (h) Financial (deficiencies in providing long-term finance)
- (i) Tariff-related issues
 - Absence of long tenure loans makes it difficult for private investors
 - Advance against depreciation is disallowed
- (j) Return on equity (ROE) (around 14%) is not attractive enough for investors
- (k) Dearth of competent contracting agencies to construct the project in the remaining dams and hydro plant sites that are increasingly quite challenging where infrastructure such as roads, etc. are unavailable, in totality. In a few cases, security issues and internal disturbances are not uncommon.
- (l) Inter-state disputes as water is a state subject has however remained a bottleneck.
- (m) The poor financial health of State Electricity Boards (SEBs).
- (n) Environmental interests bringing additional new issues such as the hydro reservoirs impact “greenhouse gases”, etc.
- (o) The civil society’s activism, especially on other

sociocultural issues got triggered, in addition.

- (p) There were sacred shrines and temples along the rivers and at the confluence of rivers sites and though in all such cases, plans are dovetailed to relocate them in a socially best possible manner, these were questioned and status quo was demanded. They are roadblocks in a few cases.

● E Flows

Environmentalists urging rivers to be left as such, activists arguing for a higher stake for eco-flows for protecting aquatic ecosystem such as riverine fish, dolphins, etc., issues connected with species, flora and fauna and protection of archeological monuments and places of worship commonly found in the development sites results in extended dialogue and judicial interventions. In a recent case, projects that were being developed were halted due to such perceptions and litigation even after sizeable investment (Lohari Nagpala HEP of NTPC). The project is in an abandoned status now, with new threats for decommissioning the head race tunnel that was halfway through, after surmounting tunnelling problems with a tunnel boring machine (TBM), with certain unique site-specific solutions while problem shooting.

Thus, the old as well as new issues are, oftentimes, affecting the smooth progress of hydro projects, even after the policy announcements.

The bottlenecks that retard the progress in hydro could also be traced to the multiplicity of agencies involved in the hydro sector such as Ministry of Environment & Forests (for forest clearance and ecological flow assessments and provisions), the issues of affected families due to projects in the submergence areas and other affected ancillary structures.

The issue of resettlement and rehabilitation has been always by and large in the fore as a social problem and despite many efforts such as the national policy supplemented by state-level policies that are further liberalized substantially in many projects, the delays due to agitation from project affected people with some support from NGOs and civil societies continue to

impede the development of hydropower projects to the extent envisaged.

National Resettlement and Rehabilitation (R&R) Policy⁶

The National R&R Policy-2007 provides the basic minimum requirements, and all projects leading to involuntary displacement of people must address the rehabilitation and resettlement issues comprehensively. The state governments, public sector undertakings or agencies, and other required bodies are given in the policy further liberty to put in place liberalized benefit levels than those prescribed in the NRRP-2007. These have enabled several successful attempts to address the issues of concern so that the development could proceed as planned for the overall betterment of the nation and assure the targetted GDP.

The NRRP 2007 took on board the need to provide succor to the asset-less rural poor, support the rehabilitation efforts of the resource poor sections, namely small and marginal farmers, SCs/STs and women who have been displaced. Besides, it sought to provide a broad canvas for an effective dialogue between the project-affected families and the administration for resettlement & rehabilitation to enable timely completion of project with a sense of definiteness as regards costs and adequate attention to the needs of the displaced persons. The objectives of the policy are to minimize displacement, plan the R&R of PAFs including special needs of tribals and vulnerable sections to provide better standard of living to PAFs and to facilitate harmonious relationship between the Requiring Body and PAFs through mutual cooperation.

National Water Policy 2002 (and the Draft Revision in Consultation of NWP 2012)⁷

The National Water Policy 2002 explicitly brings out national-level preferences in water use. Hydropower ranks next to drinking water and irrigation in the water allocation priorities in the relevant Section 5. Other energies that consume water are apparently to be considered under “other industrial use” ranked

subsequently after “ecology” but prior to “navigation”. In the recent draft revision of National Water Policy, the need for storage finds a place in the increasing water scarcity scenario. Apart from other measures for water harvesting, large dams also have been explicitly mentioned; the importance of prudential water use and management on a basin level is an interesting addition. Setting up of basin level authorities with the cooperation of the basin states, new institutional mechanism etc., are welcome features as they can pave way for the holistic planning and operation of a system of basin water storage for multiple uses including hydro plants, for optimal basin water resources management. The earlier NWP 2002 had been explicit on issues concerning storage, R&R, etc. and in the light of other parallel national policies brought out by line ministries, the focus in the revised draft (2012) has been on efficiency and water savings.

Renovation, Modernization and Up-rating (RM&U)

In order to augment the hydropower generation and improve the availability of existing hydropower projects, the Government of India has laid emphasis on renovation, modernization and up-rating of various existing hydroelectric power projects in the country. RM&U of the existing/old hydroelectric power projects was considered the best option, being a cost-effective and quicker solution option to achieve than setting up of green field power projects. The cost per MW of a new hydropower project hovered around INR 4 to 5 Crores (2006-07); whereas the cost per MW of capacity addition through up-rating and life extension of old hydro power project worked out to just about 20%. It was opined that the RM&U of a hydro project can be completed in 1 to 3 years depending upon scope of works as compared to gestation period of 5 to 6 years for new hydro projects.

Under the hydro RM&U programme, 33 hydroelectric projects (13 up to the 8th Five Plan & 20 in the 9th Five Plan Plan) with an installed capacity of 6174.10 MW were completed by the end of the 9th Plan. During the 10th Plan (2002-07), 47 hydro power projects with an installed capacity of 7449.20 MW were selected. For the 11th Plan (2007-12), a

⁶Please see reference 8.

⁷Please see reference 10.

total of 59 hydroelectric power projects having an installed capacity of 10325.40 MW, were programmed for completion of RM&U works to yield a benefit of 5461.18 MW.

Capacity Addition Scenario 11th Five Year Plan (2007-12)⁸

The plans of the government to wipe out all energy shortage by the end of 2011-12, i.e. by end of 11th Plan and also to provide spinning reserve and ensure uninterrupted quality power at affordable cost did make some impact. With coal-based power plant as the backbone of the Indian power sector, during the 11th Five Year Plan, there was a capacity addition of about 47,000 MW coal-based plant with the introduction of super critical technology.

Table 2: Sector-wise plan of capacity addition in the 11th plan

Prime Movers	Hydro (MW)	Thermal (MW)	Nuclear (MW)	Total (MW)
State Sector	3957	15538	—	19495
Central Sector	11080	19880	3160	34120
Private Sector	3744	11145	—	14889
Total	18781	46563	3160	68504

Steps taken from time to time to accelerate hydropower projects in India

- Clearances of projects with a “Three-stage clearance system”⁹

A three-stage clearance system has been set up to enable relatively faster and hindrance-free clearance of suitable projects and includes survey, investigation and pre-construction activities. The three-stage clearance system works as follows:

Stage I: Survey and preparation of pre-feasibility reports

Stage II: Detailed investigation, preparation of Detailed Project Report (DPR) and pre-construction activity including land acquisition

Stage III: Execution of the project after investment decision through PIB/CCEA

(Small hydropower projects up to 25 MW can be set up in private sector without central government’s involvement. Techno-economic clearance needs to be obtained from CEA if the estimated cost of the project exceeds INR 2500 million and/or there are inter-state issues involved).

To expedite early execution of hydro projects, bankable DPR based on detailed survey should be prepared to avoid geological uncertainties. Survey & investigation and analysis of geological, geomorphological, hydrological data, etc. should be done at the time of preparation of a DPR itself in order to minimize the impact of risks. The survey and investigations should be expedited with the latest state-of-the-art technology. It is necessary to prepare a shelf of projects for execution. The quality of DPRs should be of high standard which should infuse confidence in the national/international developers to take up the execution of projects without losing time in rechecks, etc. at the same time, contract monitoring as distinct from project monitoring should be emphasized and land acquisition and infrastructure development be settled and completed before the start of the project.

Pumped Storage Hydropower

The pump storage potential was a new type of hydropower identified to be harnessed as it was considered quite helpful in optimizing energy generation from base load thermal stations and in meeting peak load and system contingencies. Only 2.45% of the total identified potential of 94,000 MW pump storage schemes was assessed to have been harnessed while another 2.5% were under construction stages. A new exclusive programme/action plan for pumped storage schemes was therefore encouraged to tap the vast potential.

⁸Central Board of Irrigation & Power 2012: a Publication on Hydropower

⁹Internal circulars

Standardization in Hydropower and the Status of Engineering of Indian Hydro Projects in Regard to the Global Hydro Projects Including Innovations

Hydropower development has a unique character that demands site-specific solution not only in articulating the layout of headworks (diversion or storage dam with other objectives embedded), but also in every bit of its several components such as desilting chambers for desanding to draw as much as possible, silt-free water to prolong turbine life, water conductor systems in long tunnels or surface channels, penstocks with surge chambers where needed, machine hall/transformer hall in case of underground structures with geological and geotechnical challenges, etc. Tail race arrangements for letting water back to the stream can be included in this list.

There is no universally accepted standard in hydropower. The International Congress on Large Dams (ICOLD) and recently the International Hydro Power Association are bringing out general bulletins (ICOLD bulletins are over 180 in number). Each aspect of hydropower project design is attempted to be influenced by Indian standards (leaning upon international bulletins or earlier CWC manuals), but each large or medium hydro project, being unique adopts its own distinct design as per compelling circumstances encountered at each site.

Hydro projects are site-specific. Tremendously sizeable hydro development in recent times has been witnessed globally. Examples such as the Chinese Three Gorges Project or Brazil's Itaipu Project display as to how hydro power could strengthen the nation's power potential in a big way; but as one could easily appreciate the geo, political, social and other environment matter a good deal in planning boldly very large structures in Indian settings, given the complex decision-making processes in democratic India involving many states and disciplines that cut across and spill beyond pure engineering sciences. India has experienced enough hiccups with respect to Sardar Sarovar Project or Tehri Hydro Development Project with the highest rock fill dam in the Himalayas. The resistance to hydro project development in any form, storage-based or the run-off plants continues unceasingly notwithstanding the proximity to green

power development that hydropower offers. Thus, a comparison of Indian hydro sector with that of global hydro development and their particular features is difficult.

The National Electricity Policy 1998 adequately attempts to address the aspirations of hydro sector as well as the challenges that one confronts in hydro development. Elsewhere in the article, this aspect has been elaborated. The elaboration of each one of these challenges, particularly when it transcends the engineering disciplinary features (social, socio economic, political, geographic/administrative state boundaries and water sharing issues, legal and others of similar nature) is beyond the scope of this chapter.

Infrastructural Issues, Viewed from Private Participation in Hydro Sector

The independent power producers (IPPs) feel a strong a need to set up a single window clearance for hydro projects. Various authorities such as CEA, the Ministry of Finance, Ministry of Environment and Forests, etc. who are involved in the appraisal of a hydro power project before it is certified for development. It is being increasingly felt should get their actions together by a time-bound manner. A single window dispensation/authority is advocated so that a project can be cleared without many hassles. Any hydro project submitted for clearance should receive, as per their demand, all the statutory/non-statutory clearances/approvals within six months of submission of the proposal. The certification of commercial viability should be given within 15 days, especially to private developers. The Techno-Economic Clearance (TEC), MoEF and CCEA clearances should be given within 1, 2 and 2 months respectively, as voiced by these groups. The Ministry of Power should have a set of hydro projects cleared from all the angles to avoid hold-up after project commencement by private sector players.

Also unidentified are the long delays on account of land acquisition for the project. The process of land (both private and government) acquisition for a project differs from state to state as per the Land Acquisition Act. The government should amend the Land Acquisition Act and include hydropower projects

in the priority list and state governments should be persuaded to provide land to the project authority in the agreed time frame to facilitate shifting of project-affected persons (PAPs).

Hydro projects which involve lesser risk element and entail lesser capital investment can be considered for development in the private sector. Public sector entities could preferably take up all.

- (a) Multipurpose projects
- (b) Projects involving inter-state issues and in inter-state river systems
- (c) Projects involving cooperation with neighbouring countries
- (d) Projects for complementary peaking with regional benefits
- (e) Projects in the north-eastern region, etc.

Financial Issues Generic to the Hydro Sector

There is also a need to off-load indirect cost components on the hydro project. Many hydro projects are located in troubled areas infested by militancy and terrorist activities. There is an urgent need to amend the present policy of the government with regard to charging the entire security expenditure from concept and until commissioning on the project cost. However, the recurring expenditure incurred on security, once a project is started, could to be charged on the project developer.

The cost of access roads should not be included in the project cost as development of hydro projects triggers economic and commercial activities around the project site and results in economic benefit to the state. Inclusion of R&R, flood moderation costs, along with the provision of 12% free power to the state in the capital cost of the project needed reconsideration as the provision did not apply to thermal power projects.

Although the government planned to achieve 50,000 MW of additional power by the end of the 11th Plan, and brought in private players, it is argued that incentives such as benefits/concession in custom duties

and local levies/taxes on project components are being denied for projects even up to 250 MW resulting in low investments in new power schemes.

A premium as well as lease rent @10% is charged where forest land is diverted for a hydro power project. This is also a point of dialogue between the state governments and developers, as land is a state subject matter as per the Constitution.

The Way Forward

Notwithstanding the apparent efforts of the Government of India by enabling provisions for promoting large-scale development of hydropower in India including a few that brought in a new set of greater private entrepreneurs, problems persist unfortunately due to certain inherent conflicting policies and issues. There is no doubt that several major issues plaguing the hydropower sector have been identified but mending the barriers requires working together at various levels of the ministries in the Centre, and states with the Centre.

Some of these issues have been discussed earlier in this chapter. A few aspects may merit greater attention in the days ahead and the way forward is as follows:

- Recommendations by the Standing Committee for hydropower development are crucial and should be enforced for maximum benefit to the Indian hydropower sector.
- Consistent policies and regulations should be made through the states. Any variation in policies and benefits offered by different states will cause problems in development of many project sites in different states.
- Large-scale hydro projects which involve greater risks due to geological uncertainties, etc. should be implemented by the state agencies, while the relatively safer projects with reduced risks and smaller capital investments should be offered to private entrepreneurs.
- A single window clearance set up for hydro projects will solve most problems related to clearances, etc.

- The hydro sector needs to develop a set of competent civil engineers/contracting agencies that have the technical and management expertise to conceptualize and develop a project of the required scale.
- Contract management practices with a transparent system of selection of contractors could resolve any disputes that may arise in the course of execution of various works of complexities in underground works such as long tunnels that can pose several risks such as geological and geotechnical besides being hydrogeological in nature. This also applies to underground power houses as well surface power houses with many hill slope instability problems and surge shafts and other cavities such as de-silting chambers underground and other chambers for locating valves and expansion chambers.
- Development of each of the hydro projects is unique and may require special provision that could help obviate difficulties, be it of technical, social or environmental nature. Once the project stands launched, revisiting the very scope of the project such as those happening in Ganga Valley or elsewhere, are detrimental to the country's larger interest in protecting the energy needs by diversifying the generation to assure a stable grid in a sustainable manner.
- More and more of the pumped storage schemes, involving unique solutions depending on site possibilities shall add more capacity to hydropower generation.

Conclusion

Hydroelectricity is currently the largest renewable source for power generation in the world, meeting 16% of the global electricity needs in 2010 (IEA, 2012). Globally, over the last decade, the growth in electricity generation from additional hydro capacities has been similar to the combined growth of all other renewables. It has also been recognized the world over that hydropower when associated with water storage in

reservoirs, can store energy over weeks, months, seasons or even years. As spinning turbines can be ramped up more rapidly than any other generation source, hydropower and pumped storage contribute to the stability of the electrical system by providing flexibility and grid services; therefore, providing the full range of ancillary services required for the high penetration of variable renewable energy sources such as wind and solar.

India needs to catch up on its hydropower generation with the rest of the world. There has always been an anticipation that the share of hydropower would reach around 40% for which ample scope exists in India. However, the steady decline in hydropower share and the looming further decline from its 19% of grid share should be reversed for the overall welfare of energy mix.

The share cost of hydropower generation in a multipurpose reservoir scheme is far less than the one projected; and, it will continue to be the least cost, sustainable development solution in energy generation. In the ever changing dynamism that the globe faces with climate change, economic swings and downturns with fuel policies and global compulsions to contribute to greenhouse gases, at the least, hydropower would always remain the best sustainable energy option.

It is hoped that with the all-round efforts and technological advancements, the most intricate Himalayan projects could also come up with regional cooperation and strength. India should show the way to lead the South Asian power stability by utilizing the enormous untapped hydropower potential in the Himalayas in the decades to come.

The engineering community would be ready to meet any challenges, having demonstrated their immense capabilities in accomplishing very challenging projects such as the high dam in Tehri in a highly seismic environment, the longest tunnel and underground works in Nathpa Jhakri, impressive Tala Project in Bhutan etc., to quote a few recent engineering marvels.

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Review Article

Science-based Technologies for Sustainable and Adequate Energy for India: Wind and Tidal Energy Sector

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Wind power in India accounts for about 8% of the total installed energy capacity in the country and is projected to grow at a fast pace. India today stands at 5th place in the world with regard to wind power utilization. The main technological barrier to exploitation of wind energy in India is that the country lies in low wind regimes, which calls for considerable changes in the design of turbine components and in the generator configuration itself to make them optimum for use in the Indian conditions. Most of the wind turbines operative in India are of foreign design or origin which may not be most suited for this purpose. A US-based study presents technology improvement opportunities for low wind speed turbines and associated cost and performance benefits, and hence is highly relevant to India. Further, India has a long coast line which presents tremendous opportunities for offshore wind energy harvesting. Some indigenous efforts have indeed been made towards wind mapping and suitable wind turbine design and development, but there are gaps in domestic capability that need to be plugged for better utilization of wind power. This article presents the current status of the wind power sector and discusses some of the concerned issues. Possible avenues for increased utilization of wind power in the country are also presented.

Tidal power has the potential to generate significant amounts of electricity at certain sites around the world. It is a valuable source of clean, renewable energy to an electricity supply system. The negative environmental impacts of tidal energy harvesting are probably much smaller than those of other sources of electricity, but are not well-understood at this time. The technology required for tidal power is well-developed, and the main barrier to increased use of tides is that of construction costs. The future costs of other sources of electricity, and concern over their environmental impacts, will ultimately determine whether humankind would extensively harness tidal energy. Tidal power in the Indian context is addressed taking into account the status, issues, concerns and challenges in the two sites at Sunderbans, West Bengal and Gulf of Kachchh, Gujarat. While tidal energy is a viable resource, it may prove to be expensive at first, but economical in the long run if the technology improves.

Keywords: Wind Energy; Tidal Energy; Turbine; Rotor; Drive Train; Barrage; Cost of Energy; Offshore

1. Wind Energy Sector

1.1 Introduction

It is reported that at the end of 2012, India was in the fifth position in the world with a total installed wind power capacity of 18,424 MW (megawatt), behind China, USA, Germany and Spain (GWEC, 2013). The Ministry of New and Renewable Energy (MNRE),

Government of India (GoI) gives a figure of 19,779 MW of total installed capacity for India as on 31 August 2013 (<http://mnre.gov.in/mission-and-vision-2/achievements>). By the end of 2012, wind power was about 69% of the total installed renewable energy and 8% of total installed energy capacity in the country (GWEC, 2013). The Centre for Wind Energy Technology (C-WET), Chennai estimates the

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installable wind energy potential in India at 80 m level to be 102.778 GW (gigawatt) (<http://www.cwet.tn.nic.in/>). However, a study conducted by the Lawrence Berkeley National Laboratory (LBNL), USA estimated the same to be in excess of 2000 GW (Phadke *et al.*, 2012).

Though India has significant wind power potential, there are several factors which constrain its optimum exploitation such as (i) its geographical and meteorological diversity, (ii) low wind speed regimes, (iii) dusty environment, (iv) non-availability of accurate data on wind and land use, (v) lack of adequate road infrastructure, (vi) lack of adequate indigenous effort in design and development, etc.

Most parts of India except parts of Tamil Nadu have low wind regimes (Class II (8.5 m/s)/III (7.5 m/s) wind speeds), which calls for considerable changes in the design of wind turbine systems for maximum exploitation of the available wind energy (GWEC, 2012). So, the success of an 'India-specific' wind turbine design will be judged on how effectively on a combined techno-economic basis, it can suit the relatively low wind speeds and a dusty/insect-laden environment with acceptable life cycle costs. Also, from an energy security angle, it is desirable that the design employs indigenous materials and technology. It may also be noted that India is also emerging as a major wind turbine manufacturing hub due to increased domestic demand, lower manufacturing costs and expansion of in-house manufacturing capacity with an annual production capacity of over 9500 MW as of 2012 (GWEC, 2012). However, almost all the wind turbines installed so far in the country are of foreign origin, design or technology (<http://www.cwet.tn.nic.in/>; GWEC, 2012).

The following sections present different aspects with regard to the wind energy sector. In Sections 1.2 and 1.3, general aspects of wind turbine technology and components and cost breakdown of a typical wind turbine, respectively are highlighted. Section 1.4 presents the status of technologies used in wind turbines currently operative in India. In Section 1.5, technology trends towards reduction in cost of energy with reference to the important components of a wind turbine system and their manufacturing, based

primarily on a report of a study carried out at the National Renewable Energy Laboratory, USA are presented (Cohen *et al.*, 2008). Technologies relevant to offshore systems are presented in Section 1.6. In Section 1.7, indigenous wind turbine development programmes and the lessons learnt are discussed. The status of wind mapping in the country is presented in Section 1.8. The gaps in domestic capability and possible action plans to bridge the same are elaborated in Section 1.9, and Section 1.10 summarizes the conclusions of the study with regard to wind power.

1.2 General Aspects of Wind Turbine Technology

In a typical horizontal-axis wind turbine, the power extracted from the flowing wind by the rotor is transmitted through a step-up gear box to the generator for conversion to electric power. The power, P extracted by a wind turbine is proportional to the rotor swept area, A and the cubic power of wind speed, V (Grogg, 2005). Typically, the wind power density (WPD), which is the maximum wind power available per unit area, lies in the range of around 0-400 W/m², and a value of 200 W/m² is considered to be the threshold for harnessing. The sizing and costs of the wind power generation system are essentially determined by the size of the energy collector represented by the rotor swept area, A for a given wind speed. It also indicates that for a given wind turbine, the power generated varies drastically with wind speed. It is thus important that the design wind speed is chosen carefully to ensure optimum performance of the wind turbine.

The cost effectiveness of a wind turbine generator, defined by the specific cost per kW (kilowatt) of energy generated, varies linearly with the diameter. Further, the gravity load on the blades and the turbine varies as the cube of the rotor diameter. Hence, while there is a trend towards larger rotor diameters permitting greater power capture for a given site (and corresponding wind speed), it must be noted that the weight and cost will also increase and there would be increasing complexities due to larger rotor deformations under load and difficulties in handling larger sized systems, all of which must be addressed through appropriate technologies and

designs. On the other hand, higher hub heights (calling for taller towers) will allow taking advantage of higher wind speeds and less turbulence and also of sites with high wind shears.

1.3 Components and Cost Breakdown of a Typical Wind Turbine

Conventional horizontal axis wind turbines (Fig. 1) consist of the following three components with corresponding cost breakdowns as percentage of total wind turbine cost (Grogg, 2005); (i) the rotor assembly which includes the blades and the hub, converting wind energy to mechanical energy (low speed rotation), the corresponding cost being about 20%, (ii) drive train and nacelle, consisting of low-speed and high-speed shafts, electrical generator, gear box, braking system and control electronics, all inside a nacelle, converting mechanical energy to electrical energy and

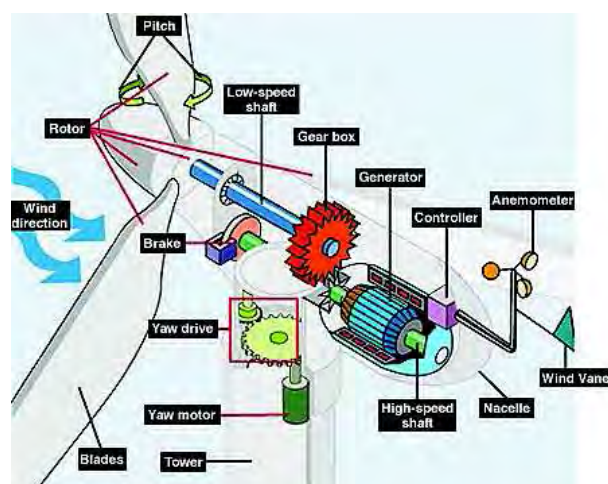


Fig. 1: Components of a wind turbine. Source: <http://en.wikipedia.org/wiki/wind/Wind-turbine>

contributing to about 34% of the cost, and (iii) the tower and the rotor yaw mechanism, which support the wind turbine and keep the rotor facing the wind, contributing to about 15% of the cost. It is thus seen that the wind turbine generator cost ((i) and (ii) above) is about 54% of the initial capital cost (ICC) and the turbine capital cost (TCC) is about 69% of the ICC.

1.4 Status of Technologies Used in Wind Turbines Currently Operative in India

The most common features among the machines

currently operative in India are as follows (<http://www.cwet.tn.nic.in/>; GWEC, 2012): (i) wind turbines of 1 MW class in the upwind, variable speed configuration, (ii) most of the machines are tuned to lower wind speed (Class II/Class III winds), (iii) blade diameter: mostly in the range 75-90 m, wind speed: 12-14 m/s, RPM (rotations per minute): 10-20, Hub height: 55-85 m, (iv) rotors have three blades, largely made of GFRP (glass fibre reinforced plastics) and use pitch control for speed/load control, (v) yaw control is employed to keep the rotors facing the wind, (vi) all use fixed towers, (vii) use both step-up geared (majority) as well as gearless drive train technologies, and (viii) variable rotor speed and a mixture of synchronous, asynchronous and double fed induction generators.

1.5 Technology Trends Towards Reduction in Cost of Energy

On the advanced technology front, many technologies are being investigated abroad for their potential to provide an acceptable trade-off between lower costs, greater energy productivity, increased lifetime and durability and lower maintenance costs. The study presented by the National Renewable Energy Laboratory (NREL), USA (Cohen *et al.*, 2008) is highly relevant to the Indian conditions as it deals with technology improvement opportunities (TIOs) for low wind speed turbines and associated performance and cost benefits, particularly from the point of view of minimizing the cost of energy (COE). Some of these considerations that are relevant to the Indian scenario are listed here with a view to draw maximum benefit while procuring off-the-shelf wind turbines or indigenously designing them. Inputs are also taken from Dayton *et al.* (2003) and Brian *et al.* (2008), particularly with regard to rotor design and manufacturing.

1.5.1 Advanced Rotor Designs

The approach here is to enlarge the rotor to increase its energy capture area without increasing structural loads. This is achieved through technology improvements in materials, structural-aerodynamic design, use of active and passive controls and higher tip speed ratios. Current rotor designs primarily use

glass fibre reinforced plastics in their design with both laminate and sandwich (mostly with foam core) structural concepts. New material and material forms increasingly being considered are carbon fibres in large tows, new fabrics including 3D (3-dimensional) weaves, new toughened resins, thermoplastic resins, pultruded parts for spars, preforms (for resin infusion moulding), and integrated glass/carbon hybrids in thick sections with proper inter-lapping and ply-drop. In the Indian context, natural fibre composites may also be considered from eco-friendliness and cost point of view.

With regard to structural design, the conventional design uses either an I-beam or a box beam spar made of fibre-reinforced plastics to provide the required bending and shear strength and stiffness and a sandwich structure for the rest of the outer shell giving the aerodynamic shape. The TIOs include integrated design processes to optimize blades for (i) load capability, (ii) manufacturing ease and (iii) aerodynamic performance with design concepts such as simple internal structure, constant spar cap thickness and width, and high thickness flat back airfoils in the inboard half of the blade, and high lift airfoils with least complex and low cost internal structure for the outboard region.

Active and passive controls aim to reduce rotor loads to permit rotor diameter growth without overall system cost increase, but significantly decreasing turbine costs. These include active rotor collective and independent blade pitch control, use of adaptive control algorithms and active load mitigation techniques, and passive techniques such as building advantageous bend-twist coupling in the blades through proper aligning of carbon fibres.

Increasing rotor tip speed by increasing rotor rotation rate and simultaneously decreasing blade solidity by reducing blade chord (to reduce blade airloads and low speed shaft torque) will also contribute to reducing COE.

1.5.2 Advanced, Cost-effective Manufacturing

The open mould, wet lay-up processes are still used by several blade manufacturers. However, increasing

environmental concerns with regard to processes with high emissions of volatile gases is driving the industry towards alternative processes such as resin infusion or use of pre-impregnated materials. Advancements in manufacturing will aim at reducing labour and material use and improved part quality. In the case of blades, automation of manufacturing processes will become necessary for larger blades. With regard to towers, onsite forming techniques for tower sections will reduce fabrication and transportation costs. Further, more consistent and reliable manufacturing processes will permit use of reduced safety margins in design due to reduced uncertainties.

1.5.3 Reduction in Energy Losses and Improved Availability

Energy losses occur due to complete shut down or operation at less than the design output due to blade soiling caused by dusty environment, damaged sensors or control errors. Remedial measures are use of soiling tolerant airfoils, blade coatings that shed dirt, building-in quality control and fault tolerance in design, effective control systems that are capable of sensing off-optimal operation and adaptive adjustment, and incorporation of health monitoring systems (based on acoustic emission, optical fibres and advanced sensor technology) for continuous monitoring of the state of degradation of blades, drive train, generator and support structures.

1.5.4 Advanced Tower Concepts

The wind power industry is moving towards designs with taller towers (100 m or above) to be erected in more difficult locations without high lift capacity cranes and with possibility of fabrication/assembly/maintenance on site. These advanced towers will require new materials such as carbon fibre or E-glass, innovative structural concepts such as space frame designs, fluted towers or hybrid towers with combination of tubular and lattice configuration, new installation methods such as self-erection/de-installation without high lift capacity cranes and advanced foundations such as tension anchors.

1.5.5 New Drive Train Concepts

Possible approaches for significantly advancing the state of drive train technology resulting in use of less material/reduced size and lower weight of support structure/less complexity, are using advanced gear profiles, integrated gear/generator systems, medium speed generators with permanent magnets (PMGs) in place of copper wound rotors (spinning at much lower speed compared to standard induction generators) coupled with a single stage gear box/single compound planetary stage gear box (delivering higher ratios that would normally require two stages) or alternative concepts such as multiple generators (having multiple drive paths with reduced design torque for each drive path) or direct drive generators (DDGs) which altogether eliminate the need for a gear box (with new high flux density, low cost permanent magnet design to reduce size and weight, power output conditioned by power electronics (PE), and segmented design for larger capacity machines).

Suggested TIOs to overcome bearing failure and lubrication depletion in gearbox are use of journal bearings, improved surface finishes and improved analytical methods, lubricant additives to resist depletion, and lubricant quality sensors for early detection of gear/drive train failure. Other future considerations in generator design/selection are higher generator efficiency at lower than design power levels, high voltage designs, use of generators with axial flux paths, active cooling systems with water or hydrogen, air cooling, use of superconducting generators, and high flux density magnets.

1.5.6 Advanced Power Electronics

Power Electronics is becoming an increasingly important part of modern wind turbine designs. As more single-stage, direct drive permanent magnet generators are developed, PE will be used to process and condition turbine power. Also, PE will permit control of factors such as low voltage ride through, reactive power, voltage, and ramp rate needed for greater range of grid compatibility. Further, PE can also be used to integrate energy storage and hydrogen production into the wind turbine or wind farm. Advanced PE can incorporate technologies such as

new circuit topology/design, new semiconductor devices, new materials (GaAs, SiC, diamond, etc.) and new ways of connecting thousands of switching devices leading to higher utilization efficiency and larger voltage/current handling ability.

1.5.7 Overall Assessment

The overall assessment was that primary contributions to potential COE reduction come from advanced rotors and site specific design/reduced design margins, the latter due to taking maximum advantage of local wind conditions at the site. It was projected by Cohen *et al.* (2008) that in the reported study, with reference to the reference turbine, TIOs described here could result in overall 23% reduction in COE with 95% confidence level and 37.5 reductions in COE (original goal) with 46% confidence level. Such considerations must be kept in mind while importing off-the-shelf machines from abroad or indigenously designing and developing wind turbines in the country for future use.

1.6 Technologies Relevant to Offshore Systems

India has a coastline of over 7500 km which presents prospects of significant offshore wind power development. MNRE, Government of India has prepared a 'National Offshore Wind Energy Policy - 2013' to enable optimum exploitation of offshore wind energy with a time-bound action plan. While the majority of the design features and technologies used in the on-land wind turbines are also applicable to offshore systems, there are distinctive features of the offshore scenario that will have an impact on the design of offshore systems. These are (Grogg 2005; Transport Research Board, 2011; Kothari and Umashankar, 2012): (i) Higher and more consistent wind speeds and larger site availability leading to higher capacity wind turbines (3-5 MW at present but expected to go up to 8-10 MW) with larger rotor diameters (in the range of 90-130 m at present, but greater than 150 m in future) and higher efficiency. In this context, it may be noted that current offshore WPDs are around 400 W/m². (ii) Higher tip speeds are possible as there is less constraint on acoustics emission levels, but adequate tower clearance of blade tips may be a problem as blades become longer and more flexible. (iii) Relatively large distances to the

coast make grid connections more complex and expensive and the deep water makes expensive foundations necessary. The result is that one must get the highest possible yield out of every single turbine to keep the COE low (currently 1.5-3 times that of land-based systems). (iv) Special attention is required to develop the pile foundation technologies (monopile for shallow waters and multiple driven piles such as tripods and jackets for transition depths of 30-60 m) and several such innovative concepts (reinforced concrete gravity-base foundations, suction caissons, etc.) to withstand the severe axial and lateral loading in the ocean environment. Floating type foundations (semi-submerge/spar buoy) are an alternative to fixed foundations. (v) Greater emphasis on reliability (including environmental controls to protect critical drive train and electrical components, upgrades to electrical systems) and access (personnel access platforms for maintenance/emergency shelter) is needed. (vi) Strengthening of the tower to handle added loading (including fatigue loading) from the waves, pressurization of the nacelles, etc. Remote sensing and condition monitoring assume greater importance in this context to reduce operational costs and yield better maintenance diagnostic information. (vii) Corrosion resistant materials and preventive coatings are necessary to counter corrosive effects of the saline atmosphere. (viii) Importance of surface wave patterns – technologies to examine and assess the generation and development of waves, and the nature and mathematical description of the sea states. (ix) Experiences gained from oil and gas industry may be translated including methods of installation and monitoring.

1.7 Indigenous Wind Turbine Development Programmes and the Lessons Learnt

The only major indigenous effort at design and development of wind turbines to suit the Indian conditions was at the CSIR (Council of Scientific and Industrial Research) - National Aerospace Laboratories (CSIR-NAL), Bangalore in partnership with CSIR- Structural Engineering Research Centre (CSIR-SERC), Chennai and an industrial partner, the Sangeeth Group, Coimbatore (Dayanand, 2013). The group embarked on the design and development of a

500 kW class horizontal axis, grid-connected wind turbine under a CSIR-NMITLI (New Millennium Indian Technology Leadership Initiative) programme during the 11th Five Year Plan. The wind turbine was a 2-bladed, stall-regulated, teetered, downwind machine on a guyed tilt-tower to allow for easy access to the blades for maintenance and R&D studies. It had a design wind speed of 12 m/s, rotors of diameter of 45 m at a hub height of 60 m, rotating at 23 rpm. The GFRP blades had advanced airfoils specially developed by CSIR-NAL. The turbine speed was regulated by aerodynamic tip brakes made of Carbon Fibre Composite (CFC) and mechanical disk brakes working on the high speed shaft. The drive train consisted of a two-stage planetary gear box and an asynchronous induction generator with 1500 rpm. It was successfully installed in a wind farm in Kethanur in Tamil Nadu and operated in the windy months during 2009-12 and was connected to Tamil Nadu Electricity Board Grid. This was India's first fully indigenous medium-scale wind turbine and its limited trials indicated success of the approach. The size of the turbine made it easier to transport and install and the fact that it was two-bladed and on a tilt tower made it easier to install and uninstall as required for testing/maintenance. This wind turbine could serve as a model for possible future variants to meet India's specific needs.

Besides, CSIR-NAL has an ongoing developmental programme, supported by an industrial partner, of a 0.5 kW class micro wind turbine (<http://www.nal.res.in/pages/ipjul12.htm>; <http://nal-ir.nal.res.in/10074/>). The in-house developed small wind turbine with four CFC blades is integrated with solar panels to realize a wind-solar hybrid system. According to CSIR-NAL, field trials have shown excellent sustained performance including improved performance at low wind speeds (2-10 m/s) compared to a commercial turbine of equivalent class.

The CSIR-NAL model for indigenization of wind turbine systems and technologies, involved a conscious decision to closely collaborate with MSMEs (micro, small and medium enterprises) in the private sectors across the country for the supply of component systems and services with required quality, ruggedness and reliability.

1.8 Wind Mapping

Wind mapping over different regions of the country will establish the national wind resources potential and help in identifying suitable sites for efficient and economically sustainable wind energy harnessing. The Indian Wind Atlas (C-WET and Riso DTU, 2010) presents such a data, including both regional assessment over large regions and wind siting at specific locations. Maps in the atlas show mean simulated wind speed and mean simulated WPD at 80 m a.g.l (above ground level) over the country including offshore regions up to a distance of 100 km from the coast.

By the end of 2013, a total of 777 dedicated wind monitoring stations had been commissioned in 28 states and 3 union territories in the country (http://cwet.tn.nic.in/Docu/list_of_WMS_on_31_12_2013.pdf). Overall, 236 stations showed MAWPD (mean annual WPD) in excess of 200 W/m² which makes them suitable for wind farming as per the existing criteria in the country.

1.9 Gaps in Domestic Capability and Proposals to Bridge the Gaps

Although considerable progress has been achieved in harnessing wind energy in the country, certain critical gaps still exist in the domestic capability as explained here, which need to be plugged to exploit the wind energy potential to its fullest extent (INAE and The IIM, 2014; CSTEP 2013; GWEC, 2012):

- (i) The *Indian Wind Atlas*, though a comprehensive guide for wind resources in the country, has certain limitations on its full applicability to the Indian conditions due to (a) the relevance to the Indian conditions of the assumptions made, particularly with regard to terrain roughness, orography and shelter effect, surface fluxes, land availability, etc., and (b) the approaches used, particularly with respect to calibration of numerical models with actual measurements which may be inadequate. These limitations need to be overcome with India-specific data and approach.

- (ii) Wind as a resource is characterized by both variability and unpredictability leading to substantial diurnal variations in power output which can create problems for the traditional grids in maintaining a supply and demand balance. Hence, the grid should have the capability to absorb this variation by backing down/ramping up other quick ramping generating sources as required. Also, excess of wind power can be efficiently handled by diverting to appropriate storage devices such as advanced batteries and compressed air storage systems which need to be developed. Further, the above mentioned operations for maintaining smooth grid operation and stability call for establishing an indigenous capability for now-casting (i.e., forecasting features of wind power patterns with reasonable accuracy within the next three to six hours). Now-casting will enable a “smart” electrical grid to optimally manage the different sources of energy viz., thermal, solar, wind, hydro and nuclear power.

There is thus great scope for using weather and climate informatics for efficient and commercially sustainable wind energy generation, though there are many difficulties and challenges in effective planning for utilization of wind energy because of the large diversity of climate and geography over the Indian peninsula and associated regional variations. The challenges are (a) establishing a network of monitoring stations of reasonable density and (b) evolving tools of simulation, assimilation and analysis appropriate to Indian tropical climate conditions and geography and local orographic and surface conditions with desired spatial resolution. Meeting these challenges effectively will help develop a high-resolution wind energy atlas over India. Capability must also be established to model the flows (atmospheric boundary layer, etc.) with a cluster of wind turbines in a wind farm at desired horizontal and vertical resolutions for optimum design/selection of turbines and their stacking leading to increased stacking density using different hub heights and inter-cropping.

- (iii) There is a need for enhancing indigenous design and development capability for wind turbine systems optimally designed for the low speed wind Indian conditions. At present, the wind turbine generators installed in India with imported design/technology would operate at 1/3 to 1/2 of their rated capacities for the maximum duration of any year, pushing the capacity utilization factor (CF) to a low level (<http://www.cwet.tn.nic.in>). The CF of wind turbine generators in India is in the range of 17-24% and the electricity generation from wind is about 3-4% of the net electricity generation from all sources as compared to 7% in Europe, 5.5% in UK and 3.5% in USA.
- (iv) On the whole, there is an acute lack of adequate design capability and human resources in all the segments of this area in the country. R&D programmes for technology improvement specific to the industry needs are lacking. There is an urgent need to include wind turbine design and technologies in the post-graduate curriculum and to support R&D efforts of the kind initiated at CSIR-NAL in more R&D laboratories with active participation from the industry.
- (v) On the materials and manufacturing side, although many manufacturers have set up their manufacturing and assembly facilities in India, in critical components such as blades, gears, generators and controls, about 60% import content is still present. Use of materials such as high nitrogen steels, high strength steels in the construction of wind turbine systems must be explored. Indigenous capability in rare earth materials for use in generators, high strength glass and carbon fibres and their hybrid composites for turbine blades, nano technology for improving blade fatigue strength, use of low cost, eco-friendly and locally available materials such as natural fibres and resins, materials and processes for improving corrosion resistance, etc. need to be developed. Materials and component manufacturers and suppliers in the country are capable of meeting the requirements

but need to be enabled with encouragement and support to bring in quality and reliability.

- (vi) India still needs to establish an interlinked and unified grid through integration of its local, regional and national grids (GWEC, 2012). Often inadequate and weak grids act as a barrier to smoother integration of power generation from renewables. Lack of adequate evacuation capacity in the state grids is a major concern in transmission planning which makes state distribution utilities reluctant to accept more wind power generation.

1.10 Conclusions: Wind Power

India has significant wind power potential and presently occupies the fifth position in the world in its harvesting. One of the factors limiting its exploitation is the fact that most regions of India lie in low speed wind regimes. This calls for wind turbine systems specially designed for Indian conditions for optimum exploitation of available wind power. Most of the wind turbines operative in India are of foreign design or origin which may not be most suited for this purpose. A study by NREL, USA presents technology improvement opportunities for low wind speed turbines and associated cost and performance benefits, and hence is highly relevant to India. Relevant aspects of this study dealing with advanced rotor designs, manufacturing, tower concepts, drive train and power electronics are required to be adopted here. Further, India has a long coast line, which presents tremendous opportunities for offshore wind energy harvesting. Hence, technologies relevant to offshore systems need to be pursued and the vast offshore potential needs to be exploited with a focused and concerted national action plan. Lastly, there is a need to scale up and also accelerate the indigenous design and development efforts taking note of the lessons learnt from the earlier efforts and of the gaps in technology in the various segments of the industry. It is, however, clear that enough knowledge, expertise and experience is available in the country in this important area and with encouragement and support, desired progress can be achieved within a short period of time.

2. Tidal Energy Sector

2.1 Introduction

Ocean produces two types of energy: thermal energy from the sun's heat, and mechanical energy from the tides and waves. The fact that the marine renewable sector is less developed than other energy industries presents both opportunities and challenges. The lack of an established industry structure can make entry into the market uncertain for newcomers. However, this lack of structure also means that potentially there are more opportunities than in other segments of the energy industry that are already developed and more mature (<http://mnes.nic.in>). A wide range of companies are involved in the marine renewable sector.

Tides are generated through a combination of forces exerted by the gravitational pull of the sun and the moon and the rotation of the earth. The relative motion of the three bodies produces different tidal cycles which affect the range of the tides. In addition, the tidal range is increased substantially by local effects such as shelving, funneling, reflection and resonance. Energy can be extracted from tides by creating a reservoir or basin behind a barrage and then passing tidal waters through turbines in the barrage to generate electricity. Tidal energy is extremely site-specific and requires mean tidal differences greater than 4 metres and also favourable topographical conditions such as estuaries or certain types of bays in order to reduce the cost of dams etc., (<http://www.cii.in>). Since India is surrounded by sea on three sides, its potential to harness tidal energy has been recognized by the Government of India.

2.2 Types of Tidal Plants

2.2.1 Barrage Tidal Plants: Barrage tidal plants are the most common type of tidal plants. A dam or barrage is installed (Fig. 2), usually where there is a narrow water channel, with gates and turbines at certain points. As the water flows through the turbines, it turns a generator that produces electricity.

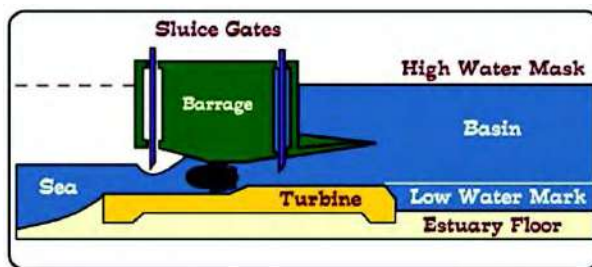


Fig. 2: Schematic of a tidal barrage. (http://www.esru.strath.ac.uk/EandE/Web_sites/01-02/RE_info/Tidal%20power%20files/image004.jpg)

With a barrage, water can spill over the top or through turbines in the dam because the dam is low. Barrages can be constructed across tidal rivers, bays, and estuaries (Khan *et al.*, 2008). Turbines inside the barrage harness the power of tides in the same way as a river dam harnesses the power of a river. The barrage gates are open as the tide rises. At high tide, the barrage gates close, creating a pool, or tidal lagoon. The water is then released through the barrage's turbines, creating energy at a rate that can be controlled by engineers through appropriate control systems.

The Energy E , stored in a tidal barrage is given by $E = (1/2)gA\rho h^2$, where ' g ' is the acceleration due to gravity, ' A ' is the horizontal area of the barrage basin, ' ρ ' is the density of water and ' h ' is the vertical tide range. The environmental impact of a barrage system can be quite significant. The landscape in the tidal range is completely disrupted. The change in water level in the tidal lagoon might harm plant and animal life. The salinity inside the tidal lagoon lowers, which changes the organisms that are able to live there. As with dams across rivers, fish are blocked into or out of the tidal lagoons. Turbines move quickly in barrages, and marine animals can be caught in the blades (<http://www.geni.org>). With their food source limited, birds might migrate to different places.

A barrage is also a much more expensive tidal energy generator compared to a single turbine. Although there are no fuel costs, barrages involve more construction and more machines. Unlike single turbines, barrages also require constant supervision to adjust power output.

2.2.2 Tidal Fences: Tidal fences block a channel, forcing water to go through it and turning its turbines to generate electricity.

2.2.3 Tidal Turbines: Tidal turbines work similar to an underwater wind turbine, using the tides to turn blades and generate electricity.

2.3 Working of a Barrage Tidal Plant

There are three main parts in a barrage tidal plant (Fig. 3A&B). These are:

- Barrage, which acts much similar to a dam, holding back water to be released later
- Sluice gates, which allow water to flow through the turbine
- Turbine, which spins as the water flows through it, rotating an electricity-producing generator.

When the tide rises, it will be first held back in the barrage and then released into the estuary; flowing through a turbine and causing it turn a generator, producing electricity. Later, when the tide falls, water behind the barrage is held in the estuary. The water is then released, flowing seaward and turning another turbine and generator, allowing the electricity-producing process to be repeated.

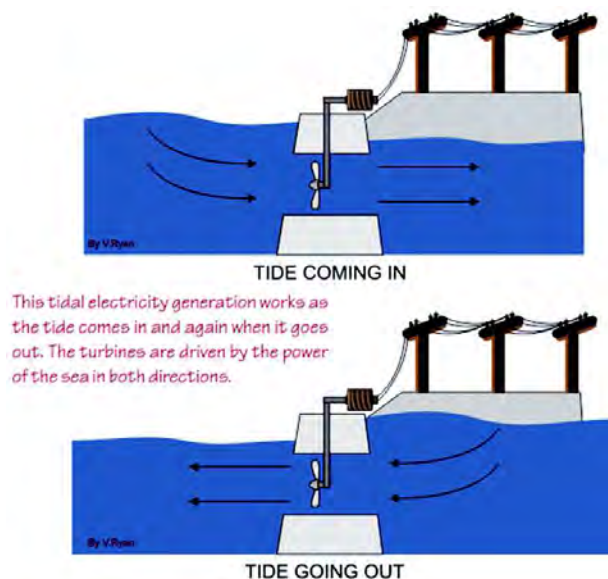


Fig. 3: (A&B) Barrage tidal plants. Source: Ryan, 2008; (http://2.bp.blogspot.com/_b5hcKABPIGI/TI2II1-juVI/AAAAAAAAAidc/xd1ZfJCJU7I/s1600/9-1310e.png)

A tidal turbine functions similar to a wind turbine under water (Fig. 4). The ocean's currents rotate the turbine blades turning a generator that converts the energy into electricity which is transmitted onshore by underwater cables. The turbines are mounted on pylons affixed to the sea floor or river bottom. The pylons contain bearings that allow the turbines to pivot so that they can catch the tide in both the directions.



Source: Devine Tarbell & Associates, Verdant Power, images courtesy of Verdant Power

Fig. 4: Tidal turbine configuration. Source: <http://www.verdantpower.com>

2.4 Tidal Power: Advantages and Disadvantages

Advantages	Disadvantages
Does not generate emissions or wastes	Expensive to construct
Uses an abundant, inexpensive fuel source (water) to generate power	Power is often generated when there is little demand for electricity
Electricity is reliably generated (tides are predictable)	Limited construction locations
May protect coastline against damage from high storm tides and provide a ready-made road bridge	Barrages may block outlets to open water. Although locks can be installed, this is often a slow and expensive process.
	Barrages affect fish migration and other wildlife – many fish such as salmon swim up to the barrages and are killed by the spinning turbines. Fish ladders may be used to allow passage for the fish, but these are never 100% effective. Barrages may also destroy the habitat of the wildlife living near it.
	Barrages may affect the tidal level – the change in tidal level may affect navigation, recreation, cause flooding of the shoreline and affect local marine life

Source: <http://www.virtualsciencefair.org/2006/wong6j2/tidal.html>

2.5 Technology of Tidal Power Generation

A tidal barrage is a way of converting the energy of tides into electric power. It works in a way similar to that of a hydroelectric scheme, except that in the latter case, the dam is much bigger and spans a river estuary. As stated earlier, when the tide goes in and out, the water flows through tunnels in the barrage (Arvizu, 2007). The ebb and flow of the tides can be used to turn a turbine, or it can be used to push air through a pipe, which then turns a turbine.

2.5.1 Global Scenario

Advances in materials science to develop high strength, lightweight materials for turbine blades and towers are required in order to facilitate the construction and continued operation of large tidal power turbines. Long lasting protective coatings will also be required to reduce maintenance costs and prolong the operating life of tidal energy devices. Globally, tidal energy production is still in its infancy and the amount of power produced so far has been rather small.

2.5.2 Tidal Energy Generators

There are currently three different ways of producing energy from the tides: tidal streams, barrages, and tidal lagoons. Tidal barrages is already described here.

(a) *Tidal Streams*: In most tidal energy generators, turbines are placed in tidal streams. A tidal stream is a fast-flowing body of water created by tides. As water is more denser than air, tidal energy is more powerful than wind energy. Unlike wind, tides are predictable and stable. Where tidal generators are used, they produce a steady, reliable stream of electricity.

The power P , generated in a tidal stream generator is given by $P = (1/2)\zeta A \tilde{\rho} V^3$, where ' ζ ' is the turbine efficiency, ' A ' is the turbine swept area, ' $\tilde{\rho}$ ' is the density of water and ' V ' is the flow velocity.

Placing turbines in tidal streams is complex, because the machines are large and disrupt the tide they are trying to harness. The environmental impact could be severe, depending on the size of the turbine

and the site of the tidal stream (Bedard, 2008). Turbines are most effective in shallow waters. This produces more energy and also allows ships to navigate around the turbines. A tidal generator's turbine blades also turn slowly, which helps marine life avoid getting caught in the system. The world's first tidal power station was constructed in 2007 at Strangford Lough in Northern Ireland, with the turbines being placed in a narrow strait between the Strangford Lough inlet and the Irish Sea. The tide could move at 4 metres (13 feet) per second across the strait.

(b) *Tidal Lagoon* : This type of tidal energy generator involves the construction of tidal lagoons. A tidal lagoon is a body of ocean water that is partly enclosed by a natural or manmade barrier. Tidal lagoons might also be estuaries and have freshwater emptying into them. A tidal energy generator using tidal lagoons would function much similar to a barrage. Unlike barrages however, tidal lagoons can be constructed along a natural coastline. A tidal lagoon power plant could also generate continuous power. The turbines work both as the lagoon is filling and as it is emptying.

The environmental impact of tidal lagoons is minimal. The lagoons can be constructed with natural materials such as rock. They would appear as a low breakwater (sea wall) at low tide, and be submerged at high tide (Bedard, 2007). Animals could swim around the structure, and smaller organisms could swim inside it. Large predators such as sharks would not be able to penetrate the lagoon, so smaller fish would probably thrive. Birds would likely flock to the area.

However, the energy output from generators using tidal lagoons is likely to be low. There are no functioning examples yet. China is constructing a tidal lagoon power plant at the Yalu River, near its border with North Korea. A private company is also planning a small tidal lagoon power plant in the Swansea Bay in Wales.

2.5.3 The Next Generation Marine Turbine

The next generation marine turbine, the transverse

horizontal axis water turbine (THAWT) developed by the Oxford University Engineering Department is shown in Fig. 5 (Bedard, 2008; 2007). While the conventional turbines operate similar to windmills and must be turned with the tides, the THAWT configuration works equally well with flow from either direction and hence requires no adjustments as the tide changes direction (Guy, 2011). It can also be easily scaled and requires fewer foundations, bearings, seals and generators than a more conventional axial-flow device. It is also more robust and so can be larger in size, harnessing more of the energy of flow with outputs more than 50% higher than those achievable by propeller-type turbines placed in the same site. A full-scale device might have a diameter of 10-20 m, length of about 60 m and would operate in a flow depth of 20-50 m. Further, multiple THAWT rotors can be chained together across the width of a channel (McAdam, 2009).

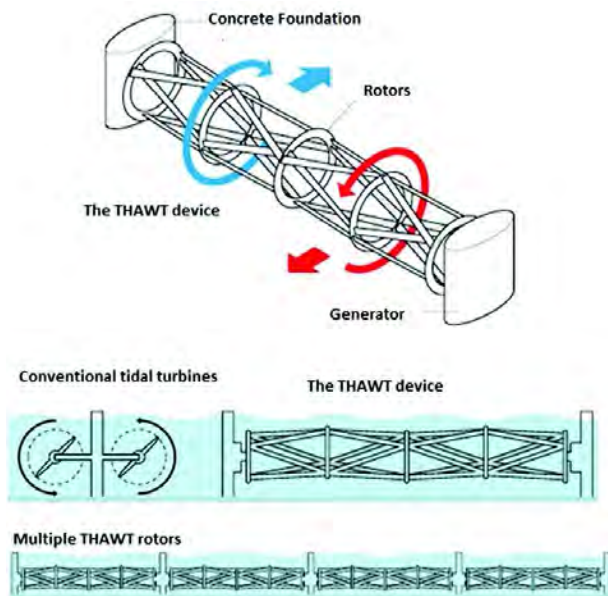


Fig. 5: Transverse horizontal axis water turbine (THAWT).
Source: <http://www.inhabitat.com/wp-content/uploads/turbine1.jpg>; McAdam (2009)

2.6 Potential of Tidal Energy in India

The most attractive locations for tidal energy in India are the Gulf of Cambay and the Gulf of Kachchh on the west coast where the maximum tidal range is 11 m and 8 m, with average tidal range of 6.77 m and

5.23 m, respectively. The Ganges Delta in the Sunderbans in West Bengal also has good locations for small-scale tidal power development. The maximum tidal range in Sunderbans is approximately 5 m with an average tidal range of 2.97 m.

The identified economic tidal power potential in India is of the order of 8000-9000 MW with about 7000 MW in the Gulf of Cambay, about 1200 MW in the Gulf of Kachchh and less than 100 MW in Sunderbans.

2.6.1 Proposed Tidal Power Projects in India

The Ministry of New and Renewable Energy announced in February 2011 that it may provide financial incentives as much as 50% of the cost for projects seeking to demonstrate tidal power (<http://www.teriin.org>).

(a) *Kachchh Tidal Power Project* : In 1970, the CEA had identified this tidal project in the Gulf of Kachchh in Gujarat. The investigations were formally launched in 1982. Sea bed analysis and studies for preparation of feasibility report were of highly specialized and complex nature without precedence in the country. More than 12 specialized organizations of the Government of India and Government of Gujarat were involved in the field investigations. The techno-economic feasibility study was completed in a very scientific and systematic manner and the feasibility report submitted in 1988.

The proposed tidal power scheme envisaged a 900 MW project, biggest in the world, located in the Hansthal Creek, 25 km from Kandla Port in District Kachchh of Gujarat. Its main features were as follows:

The main tidal rockfill barrage of 3.25 km length was proposed to be constructed across the Hansthal Creek which will accommodate the power house, sluice gates and navigational lock. It envisaged installation of 900 MW capacity, comprising 36 geared bulb type turbo-generator units of 25 MW each, and 48 sluice gates, each of 10 M × 12 M. size, generating 1690 GW of energy annually (<http://www.powertoday.co.in/fut4.html>). Unfortunately, execution of this project has not been taken up so far because

of unknown reasons.

In January 2011, Gujarat announced plans to install Asia's first commercial-scale tidal current power plant; the state government approved the construction of a 50 MW project in the Gulf of Kutch.

(b) *Durgaduani Creek* : The country's first tidal power generation project is coming up at Durgaduani Creek of the Sundarbans. The 3.75 MW capacity project is a technology demonstration project and will span over an area of 4.5 sq. km (2008 data).

2.7 Economics of Tidal Power

Tidal power is characterized by high capital cost per MW of installed capacity, long construction times, no fuel cost, low running cost, and long lifetime with little maintenance, where annual operation and maintenance costs are typically less than 0.5% of initial capital cost of the scheme (http://geda.org.in/other_sources/other_re_sources.html). Operation, however, is intermittent with a consequent low load factor of about 35%. There does not appear to be any significant economy of scale. Tidal barrage studies in UK with capacities from 30 MW to 8.64 GW yield similar energy costs. Possible consumption of power locally and shorter construction times for small schemes may make them more economic than the larger schemes. The high capital costs and long construction times of large tidal barrages make tidal energy particularly sensitive to the discount rate on the capital employed. Studies on the Severn Barrage

show an almost linear relationship between the discount rate and cost of electricity generation in the scheme.

No energy benefits should be identified and taken into account in assessing viability of potential schemes.

2.8 Conclusions: Tidal Power

Tidal power generators are significant in their scale of engineering and are feasible for barrages in water depths up to 35 m. The Caisson method of construction is generally favoured, and suitable axial flow turbines of bulb or rim-generator type are proven and are commercially available. In operation, ebb generation is generally preferred while flood pumping can be used in addition, to increase and retime output. Output can generally be injected into strong transmission networks without retiming by use of pumped storage.

Regarding economics, there is no clear economy of scale; promising schemes which vary from 10 MW to 50 GW have been identified, but cost of electricity is sensitive to the discount rate on account of the technology being capital intensive. Positive environmental benefits include savings in emissions from fossil fired generation, but specific site environmental assessment is recommended for each barrage to clarify effects and establish acceptability. No insurmountable barriers to the technology have been identified to date.

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Review Article

Ocean Energy

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Ocean energy is an important and promising renewable energy for the future. Even though extensive technology development and demonstrations have occurred in the areas of ocean thermal energy, wave energy and tidal energy over the last 40 years, commercial plants based on these technologies are very slow in coming up because of the high capital costs. In recent years, due to increase in the fossil fuel costs, renewable energies such as solar photo voltaic systems and wind energy systems have become cost competitive. Ocean energy systems are likely to become cost competitive in a decade or so, especially for remote islands and coastal areas. This chapter presents the highlights of developments in the areas of ocean thermal energy, wave energy and tidal energy.

Keywords: Ocean Energy; Ocean Thermal Energy; OTEC; Open Cycle and Closed Cycles for OTEC; Wave Energy; Oscillating Water Column; Tidal Energy

Ocean Energy

Ocean energy, which is an indirect form of solar energy, is a very large resource. The development and demonstration of ocean energy technology has been suffering all along because of high cost of plant structures and offshore infrastructure. The sharp increase in the oil prices has highlighted, once again, the need to develop large-scale renewable energies including ocean energy.

The three forms of ocean energy conversion systems which have reached already a “technology demonstration” or “pre-commercial” phase are:

- i. Ocean thermal energy conversion (OTEC)
- ii. Wave energy conversion (WEC)
- iii. Tidal energy conversion (TEC)

The highest priority of ocean technologists today is to reassess the techno-economic viability of ocean energy plants vs fossil fuel plants, in the context of high oil price and the available carbon credit.

The potential of ocean energy in different regions depends on their geographical location with respect to the equator. Countries closer to the equator having tropical seas around them have good potential for OTEC and countries in northern and southern latitudes have a good potential for wave energy. Tidal energy, caused by gravitational pull of moon and sun on the ocean mass of water, is high only in estuaries and bays where the tidal oscillations are amplified.

Ocean Thermal Energy Conversion

Regional Availability and Current Status

OTEC utilizes the temperature-difference between warm surface sea water of around 27-29°C in tropical waters and the cold deep sea water of around 5-7°C, which is available at a depth of 800 to 1000 m, to run a heat engine under Rankine cycle. This temperature differential worldwide and typical temperature depth profiles are shown in Fig. 1 (Ravindran, 2010).

The warm surface water exchanges energy with low temperature boiling fluids such as ammonia and

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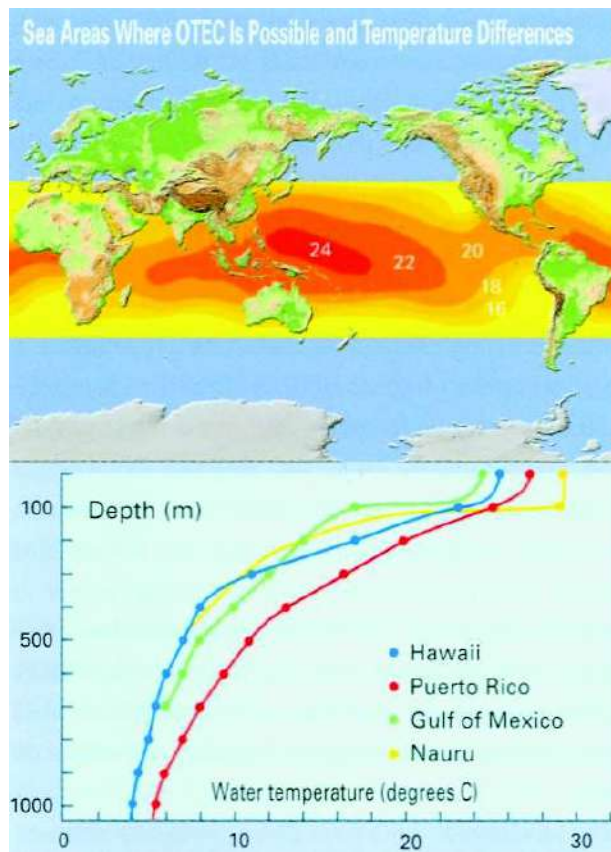


Fig. 1: Temperature variation with depth of the sea. (Source: Ravindran 2010)

the vapour generated is passed through a turbine to produce work. The vapour, after expansion in the turbine, is condensed using deep sea cold water and re-circulated. This is how a closed cycle OTEC plant, which can easily be scaled to MW range, operates. In the Asia and Pacific Region, Japan and India are

the only countries actively involved in OTEC research and there are a large number of islands which are ideally suited for OTEC plants. In these islands, the deepwater is close to the shore and facilitates the installation of shore-based OTEC plants. India started research in the Lakshadweep and Andaman Nicobar region (Ravindran, 1999).

In an open cycle system, warm surface sea water at 28°C is flash evaporated in a vacuum chamber. The ensuing low pressure steam drives a fairly large diameter turbine and is condensed by circulating the cold deep sea water. The condensate is potable water which is also valuable. However, the closed cycle OTEC plant is more compact.

A number of OTEC technology demonstration plants have been tested across the world from the late 1970s (Avery, 2002), as listed in Table 1.

India with its vast potential of OTEC resource started feasibility studies of 1MW land-based OTEC plants in 1982. Later in the mid-90s, the National Institute of Ocean Technology, Chennai, India, (NIOT) started the design and construction of a 1MW floating plant with a closed cycle ammonia system. Even though the barge and onboard systems were tested, (Manivannan *et al.*, 2003), the whole plant could not be commissioned due to the failure of the flexible joint between the barge and the 1000m long cold water pipe. Subsequently, NIOT applies the open cycle OTEC principle for the desalination purpose using cold water drawn from 600m depth and warm surface water at 29°C. A desalination plant of 0.1 million litre

Table 1: Summary of OTEC demonstration plants

S.No.	Agency/Name	Year, location	Power rating (kW)		Cycle	Type of plant
			Gross	Net		
2.	Mini OTEC (US)	1979, Hawaii	53	18	Closed (Rankine)	Floating
3.	OTEC-1 (US)	1980, Hawaii	1000	-	Closed (Rankine)	Floating
4.	Toshiba & TEPC (Japan)	1981, Nauru	120	31.5	Closed (Rankine)	Shore-based
5.	Japanese Mini OTEC	1979, Japan	100 kW	-	Closed	Floating
6.	NELHA (US)	1992, Hawaii	210	40	Open	Shore-based
7.	Saga University (Japan)	1984, Saga	75 W	-	Closed (Rankine)	Lab model

capacity daily is successfully operating at Kavaratti, in the Lakshadweep islands for the last 3 years. Later, in 2007, a floating desalination plant with a capacity of 1 million litres of fresh water daily was demonstrated at 1000m depth off Chennai (Ravindran *et al.*, 2007). The climatic conditions required for the operation of an OTEC plant are satisfied in about 100 countries.

Current Technologies

There is a need to reduce the cost of OTEC plants, with a medium output of 10–40 MW. The major cost of a closed cycle OTEC plant comes from the cost of heat exchangers, the floating barge and the 1000m deep cold water pipe system. Compact titanium plate heat exchangers plates used in the Indian plants have been coated with stainless powder to enhance the heat transfer coefficients. Almost all the OTEC demonstration plants have used cold water pipes made of HDPE. The new experience in offshore oil has introduced the concept of flexible steel riser pipes which are likely to reduce the cost of deployment.

Merits and Demerits of Open Cycle for OTEC

Merits : Open cycle does not deal with any fluids (such as ammonia or freon), which are not environment-friendly. Water is the working fluid and the condensate exiting from the system is potable water.

Demerits : Since the turbine handles very low pressure steam (.02 bar), the size of the turbine is very large. Hence, open cycle is useful only for low ratings.

Merits of Closed Cycle OTEC

Since working fluids such as ammonia/freon are enclosed in a sealed system under pressure (approx. 6 to 8 bar), the size of the turbine is compact. Closed cycle OTEC is suitable for large commercial plants.

Wave Energy

Regional Availability and Current Status

The potential of wave power in wind generated waves is

$$P = 0.55 H_s^2 T_z \text{ (kW per metre of wave crest length),}$$

where H_s = Significant wave height of random waves in metres.

T_z = Zero crossing period in seconds.

Normally, this potential is 10 to 15 kW/m in countries lying between N and S 10° latitudes. For regions in higher latitudes, the potential varies from 20 to 70 kW/m (Thorpe, 1999). Most of the countries including island nations possess this potential. Even though energy from waves has less variability compared to wind energy, the actual wave power varies from time to time and from season to season. The offshore devices have higher potential because deep water waves possess higher energy.

Japan was the first nation to use wave power, almost 50 years back, for application in navigational buoys (Masuda and Miyazaki, 1978). The UK started serious research on a variety of devices during the mid-70s. During the early 1980s, Japan, other countries in Europe such as Norway, Sweden and Portugal started testing a variety of devices.

India, China, Korea, Australia and USA joined the group during the mid-80s. Thorpe (1999), Muetze *et al.*, (9)* and Brooke, (2003) have provided a review of all these devices and technology demonstration studies.

Among all devices, the oscillating water column (OWC) device was the most often studied and tested by many countries in Europe and Asia (see Fig. 2).

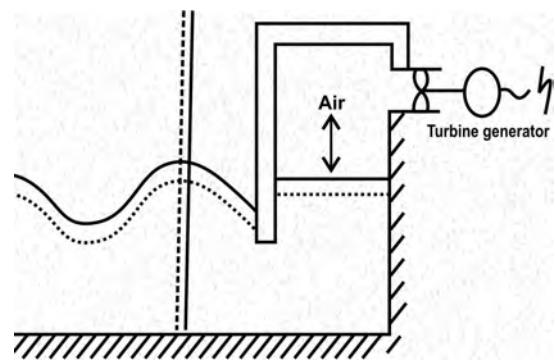


Fig. 2: Oscillating water column

*The number refers to the website reports given under references

The OWC device has a submerged opening through which waves enter a chamber, the wave oscillates the water level inside the chamber and causes bidirectional airflow in and out of the chamber. The power take-off system consists of an air turbine and generator. There has been a variety of turbines developed with flow rectifying valves and without valves. The turbine types varied from the Wells type (Raghunathan, 1985) to impulse turbines (Setoguchi, 2001, Santha Kumar *et al.*, 1998). Similarly, different types of generators/controls were also developed (Ravindran *et al.*, 1997). The OWC-based plants built in Japan, Norway, UK, Portugal and India have demonstrated the technical feasibility of generating electricity from waves, but with output power in the range of few hundred kilowatts only. The plant erection and operational costs were high. However, if scaled up to multiple megawatts, the cost is expected to be around 8 cents (U.S)/kWh (Thorpe, 1999).

Current Technologies

The most promising device with large capacities for shoreline applications is the bottom-standing OWC device. Field experiments have been conducted on systems of varying capacities, namely, 30 kW unit at Kujukuri, China, a 60 kW unit at Sakata port in Japan; 75 kW unit at the island of Islay, Scotland, a 150 kW unit at Trivandrum, India, 500 kW unit at Toftes fallen, Norway and at the island of Pico, in Azores in Atlantic Ocean.

Thorpe (1999) has listed the following four promising wave energy devices for use as offshore devices in water depths of more than 40m (Figs. 3-5). The offshore devices mainly consist of vertically heaving submerged buoys or multiple floating bodies hinged together.

Emerging Technologies

The coastal regions and islands mostly need to augment drinking water supplies. Hence, the wave energy devices are also being used to desalinate sea water. The Indian OWC plant with its installed capacity of 50 kW was used to run an R.O. plant supplying 10,000 litres of fresh water to a nearby fishing village (Sharmila *et al.*, 2004). Carnegie Corporation, Perth, Australia is planning to install an array of submerged heaving buoys to pump sea water to a Pelton wheel for power generation up to 300 MW in addition to a R.O.-based desalination plant (7). Three units of Pelamis device have been tested in a wave farm in Portugal during 2007 with a total capacity of 3×0.75 MW and the technology is being offered for worldwide use. Pelamis has received a venture capital US \$ 68 million for this development (8).

Potential Regional Applications

In the Asia Pacific region, the south western Australian coast has the highest wave energy potential of 40-70 kW/m. Japan and other island nations in the region with a wave power potential of 15-40 kW/m can choose between shoreline devices or offshore devices depending on the sites. In India, the achievable

Table 2: Promising offshore wave energy devices

Device	Concept	Unit rating
McCabe Wave Pump	Three pontoons hinged across their beam. Relative movement at hinges pressurizes a liquid which drives a hydraulic motor – generator	40 m long device - power 400 kW - tested off Ireland
Ocean Power Technology WEC	Heaving motion of a buoy converted into mechanical power	400 kW - tested off Ireland
Pelamis Device	Cylindrical sections linked by hinged joints. Relative movement at these joints develops high pressure liquid driving a hydraulic motor – generator system	A 130 m buoy device has a 375 kW rating
Archimedes Wave Swing	A cylindrical air filled chamber is moving up and down due to action of waves – this movement is used for power generation	Typical diameter of chamber 10-20 m

Source: Thorpe (1999)

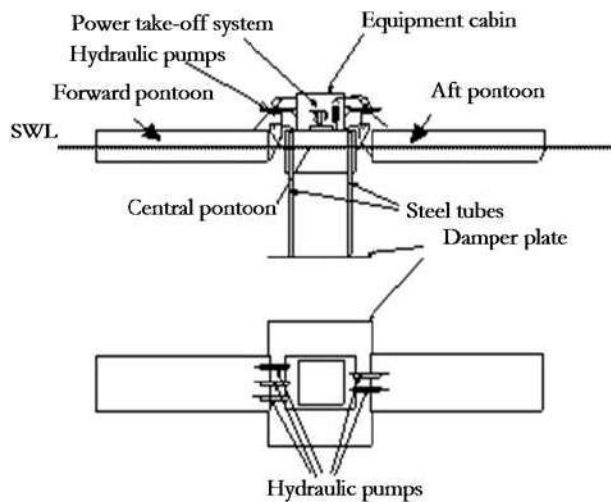


Fig. 3: McCabe wave pump

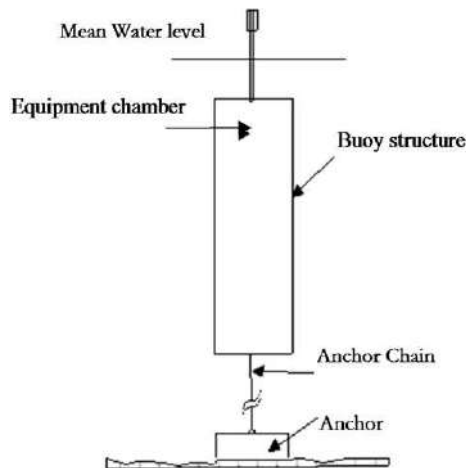


Fig. 4: The OPT WEC

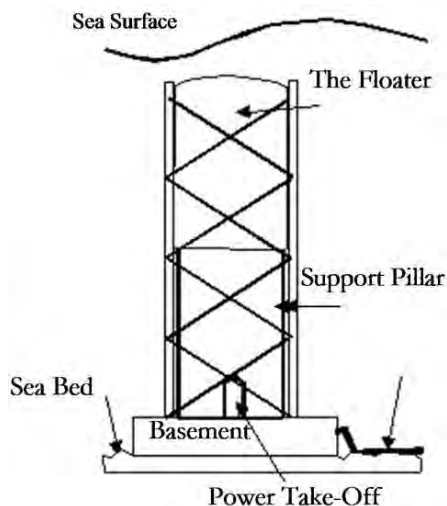


Fig. 5: The Archimedes wave swing

resource from wave energy is estimated to be 20,000 MW (Ravindran *et al.*, 2007).

Tidal Energy Conversion

Regional Availability and Current Status

Tidal power plants use the gravitational pull of the moon on the ocean mass of water. The mass of water within the boundary of estuary goes through higher oscillations on being excited by the tidal waves in the open ocean. Wilson (1973) studied the tidal power potential at many locations in Europe and Asia and highlighted its promise.

The water level difference between the open ocean and bay/estuary causes tidal flows with higher velocities. Tidal power can be generated by allowing the water to flow through turbines located in the barrage separating the estuary from the sea or by allowing the tidal current to directly drive the freely located turbines in the creeks or the channels. If the turbines are provided with casings/shrouds, then power developed could be 3 to 4 times the power from an open flow or free stream turbine.

Locations suitable for tidal power are few in each country.

Among all the forms of ocean energy, tidal energy was the first to be exploited on a large scale. The Rance tidal plant, commissioned in 1966, with a barrage across the Rance river estuary in France, has an installed capacity of 240 MW with 24 bulb turbines of capacity 10 MW each. The plant is working efficiently even today. There were smaller tidal power plants built at Kislaya Guba in Russia and at Bay of Fundy in Canada. China has built 10 mini tidal plants with a total capacity of 20 MW. Many tidal current turbines have been installed and are operating successfully at many locations in the world.

Current Technologies

The barrage of the Rance power plant is similar to a barrage in a low head hydropower plant. However, the cost of construction was very high, since the barrage had to be built in the ocean. Subsequent tidal power plants prefer using pre-fabricated concrete

caisson technologies to reduce the cost of construction in the sea (Sharma, 1983). In smaller power plants, free stream turbines are preferred.

Emerging Technologies

The main aim of future tidal power plants is to reduce installation cost and to maximize power output. Shrouded turbines or free-standing turbines located in a duct are most promising in this direction (2).

Potential Regional Applications

India has tidal power potential of around 20,000 MW mainly from the two states of Gujarat and West Bengal. The Gulfs of Cambay and Kutch in Gujarat have a peak tidal range of 11 m and the current velocities reach about 5 m/s. A number of feasibility studies have been conducted. The Sundarban region in west Bengal has a tidal range of around 5m. In December 2007, the Government of India has announced the approval to build a tidal power plant of 3.65 MW capacity in the Durgaduani creek of Sundarban area at a cost of US \$ 12 million (3).

South Korea is building a small tidal power plant of 1 MW capacity at the Myeongnyang channel, South Jeolla province. Also planned are a 252 MW plant at Gari Island (4), and a 812 MW plant in Ganghwa region (5). China is designing a plant of 300 MW. New Zealand is planning a tidal current power plant at Kaipura Harbour with 200 free stream turbines with a capacity of 60 MW (6). North West Australia has high tidal power potential. The resource in Derby region alone is 3000 MW. A 50 MW tidal power plant is being planned there (1).

Closure

Tidal energy has large potential and the technologies are proven. We are likely to see commercial tidal power plants soon. There is a need for innovations to reduce the cost of civil works. Increase in energy costs of conventional sources and concerns related to greenhouse gases would give an impetus to tidal power plants.

Areas for Research

Ocean Thermal Energy Conversion

The main requirements are to reduce cost of installation per MW output and to increase income by providing additional byproducts. The following research areas are suggested:

- Develop cheaper and lighter materials such as aluminium alloy to replace costly titanium plates. Heat exchangers contribute to about 30% of the total plant cost.
- One of the critical technology challenges is the interface between the floating barge and the 1000 m long cold water pipe. Studies on flexible steel risers and inflatable risers with deep water submersible pumps mounted at the bottom end of the inflatable cold water pipe will help to reduce the cost of cold water pipes.
- Innovative designs for the floating platform and their mooring devices by adapting the recent designs from offshore oil platforms to reduce the capital costs.
- By providing valuable byproducts such as fresh water, hydrogen and exotic species from aquaculture using cold deep sea water effluent will enormously improve the economics of the plant. Studies on nutrients in deep sea water and their impact on aqua culture will enhance the total income from OTEC plants.
- The cable for transmitting power from floating OTEC plants to shore is also an expensive component of the plant. Efforts are needed to develop cheaper and reliable cables for large-scale power transmission in deep water applications.

Wave Energy Conversion

Major challenges in WEC system are the cost reduction of the supporting structures. To address these issues, the following research areas are suggested: study of breaking wave forces on shoreline devices and optimizing the structural design with innovative construction techniques; and fatigue

analysis, corrosion and wear analysis of all mechanical parts exposed to wave action. A variety of materials have to be studied so that long-term reliability could be ensured at a reasonable cost.

Tidal Energy Conversion

A major cost component of a tidal power plant is the civil engineering construction cost of the barrage-based plants. In free stream tidal current plants, the operating efficiency of turbines without shrouds/casing ducts need to be enhanced. To address these points, the following research areas are suggested:

- Studies on cheaper designs and their deployment procedures for prefabricated caissons to be used in the barrage construction.
- Performance studies on variety of turbine designs/blade profiles to ensure high efficiency.

Apart from the three areas suggested for energy conversion, two more important areas common to all the three energy systems are:

- Conduct updated techno-economic analysis of the ocean energy plants to compare them with other fossil fuel plants using the current cost of fossil fuels.
- Conduct surveys for assessing the potential from the three ocean energy sources and create awareness among policy makers, for funding technology demonstration and later commercialization of ocean energy in countries of the Asia-Pacific region.

Indian Contributions

The main Indian contributions are in the areas of wave energy, OTEC and its spin-off desalination.

Wave Energy

Sponsored by Department of Ocean Development, a 150 KW wave energy pilot plant, 3500 ton concrete structure, a first of its kind in the world, was built at Vizhinjam by IIT Madras. The National Institute of Ocean Technology (NIOT) took over the plant in 1996. Several power modules were tested. A fixed blade impulse turbine connected to a variable speed

alternator gave the best efficiency. The generated power was also used to run a RO-based desalination plant of capacity 10,000 litres per day. The capability for the construction, operation and maintenance of the plant was demonstrated. What was not assessed correctly was the matching of the turbine characteristics with that of the OWC. Hence, while power was generated successfully, efficiencies were poor. Breakwater-integrated OWC modules may still prove to be economical in the context of modern day construction.

Ocean Thermal Energy Conversion

In 1998, NIOT embarked on setting up a 1 MW floating OTEC plant in 1000 m water depth about 40 km off Tuticorin in South India. The major challenge was the design of the platform and cold water pipe. A non-self-propelled barge was designed with special features such as three moon pools and a retractable cold water sump to suit the requirements of the pumps. The barge was built in a shipyard on the west coast of India and named “Sagar Shakthi”. A cold water pipe of length 1 km and diameter 1m was joined by thermal fusion at the Tuticorin port and towed 40 km offshore where 1000 m water depth was available.

Sufficient offshore handling facilities were not available; hence, the deployment had to be carried



Fig. 6: Wave energy power plant at Vizhinjam.
Source: Ravindran (1997)

out with serious limitations. Twice with two different pipes/mooring systems, lack of infrastructure and rough weather conditions, loss of the pipeline occurred. Hence, the project could not be completed. Later the same barge was used for mounting the desalination equipment and fresh water was first generated in shallow water.

The OTEC project led to extensive capacity building, as everything was designed in-house and attempted with mostly indigenous equipment. The experience led to success in desalination.



Fig. 7: One lakh litre per day LTTD plant at Kavaratti, Lakshadweep Islands

Desalination

Low temperature thermal desalination is actually a spin-off from the OTEC cycle. Whenever two bodies of water at different temperatures are available such as the surface and deep ocean waters, the temperature gradient can be utilized to generate fresh water.

NIOT carried out extensive laboratory studies and set up the first land-based demonstrative plant at Kavaratti in Lakshadweep with a capacity of 1 lakh litres per day. A long HDPE pipe was deployed in a special configuration successfully. The plant has been running continuously since 2005 fulfilling the needs of the 10,000 strong local communities. On seeing the success of this plant, NIOT was asked to setup more similar plants. Accordingly, the plants at Agatti & Minicoy were also commissioned and are running successfully.

Implementation of the low temperature thermal desalination is a true case of translating complex engineering into a societal benefit. This has been a pioneering effort in the fresh water generation scene in any part of the world. Subsequently, NIOT has also demonstrated the technology on the same OTEC barge offshore in deep waters.

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Review Article

Geothermal Energy

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Geothermal energy as a source of heat and power generation has unique attractive features of environmental consideration and is economically viable as well. The general nature and distribution of geothermal sources along with exploration and conceptual aspects of power generation and the economics are discussed here. The global as well as Indian scene is discussed briefly. The novel aspects which would lead to expansion of geothermal energy utilization beyond restricted favorable sites are briefly reviewed.

Keywords: Geothermal Energy; Renewable Power; CHP; EGS-Engineered Geothermal System; Binary Cycle Power Plant

Introduction

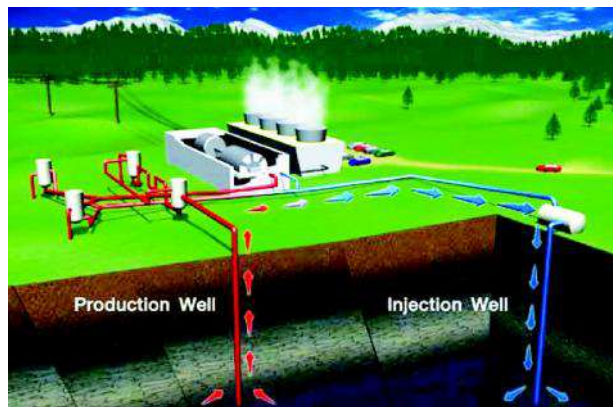


Fig. 1: A production well setup in a geothermal power plant

Sources of Heat

The Earth is the only planet which has a hot interior among all planets in the solar system; and in that sense is “alive” with volcanoes and is far from thermal equilibrium. The temperature at the centre of the Earth is around 6000°C. About 20% of the heat is from the gravitational accretion of the matters which coalesced and crashed to the centre. The remaining 80% of the

heat is of radioactive origin. The long half-life radioactive elements namely thorium, uranium 238, potassium and uranium 235 decay and contribute radioactive heat in that order. The half-life of these elements are 14, 4.5, 1.25 and 0.7 billion years, respectively. This fact ensures that the source of heat is *perennial* on human scale and the source is certainly *sustainable* in a general sense.

Thermal Gradients

There is a thermal gradient from the centre to the surface. The internal architect of the Earth is shown in Fig. 2. In the crustal part, the average temperature gradient is 22°C/km. The heat flux on the average near the surface is 55 mW/m². Thus, there is a kind of dynamic equilibrium. The heat generated by the radioactive decay is conducted out and dissipated.

Two properties of rocks are important in the production of geothermal energy. They are specific heat and thermal conductivity. The specific heat for the rocks is in the range of 700 to 1000 Joules/kg/°C. For comparison, the specific heat of water is 4800 Joules/kg/°C. For rough and ready calculations,

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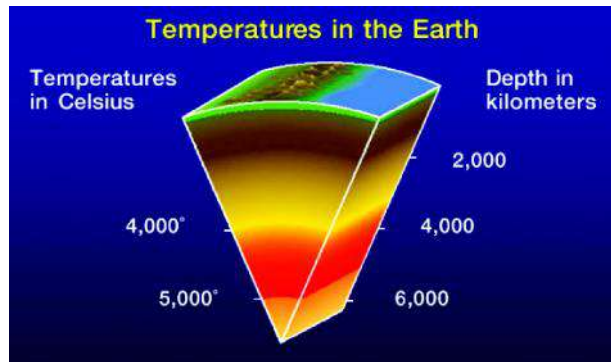


Fig. 2: Earth's interior

specific heat of a typical rock is 1000 Joules/kg/°C, which is a good number and easy to remember and use. The other property is thermal conductivity. The range for thermal conductivities of the rocks is 1.7 to 7W/m/°C, the measure of heat flux across a rock sample with 1m² cross-sectional area, with 1°C/m temperature gradient; 2.5 W/m/°C is a good working value for the rock. For comparison, the thermal conductivity of copper is 400W/m/°C, steel is 15W/m/°C, while that of wood, is of the order 1W/m/°C.

Theoretical Geothermal Energy Available

We are now already equipped to obtain the good overall picture of the heat content and fluxes. The heat flux on the continents is $K \cdot A \cdot (dT/dZ)$, where K is thermal conductivity, A is the area and dT/dZ the temperature gradient. With area of the land as 148 million km², we obtain 9 TW as the total heat flux through land. The world today consumes electric energy at the rate of 2.4 terra Watts (TW) and India consumes 0.12 TW. The total energy consumption rate of the world is 18 TW (heat) and that of India 0.7 TW (heat). If we restrict ourselves to land area, then around 9 TW is the heat flux of geothermal origin. Due to ever increasing population and exploding per capita consumption, the energy requirement already exceeds the heat flux from the ground. So, even if we can utilize all the energy by geothermal source on the land; we cannot meet the present day energy demand.

The energy is available as heat and in final analysis running some kind of heat engine to extract useful work is the way to exploit it. This limits the

efficiencies to Carnot engine efficiency. We know that in practice at the most 50% of this efficiency is realized. Thus, to have actual efficiency of say 15%, we must aim at temperature of 150°C plus. With the temperature gradient of even 35°C, /km, the desired temperature is present at a depth of 3500 m. For a plant delivering 1 MW power, we need to capture 5MW flux for conversion with 20% efficiency. With flux of the order of 0.06W/m², that will require an area of around 100km². Thus, the geothermal energy cannot be practically exploited at any random place on the Earth.

Geological Prerequisites for Geothermal Site

On the geological time scale, the continents move around as plates. The plate tectonics is driven by the convection caused by temperature gradients and leads to movement of continents. In addition, the magma now and then pierces through the thinner sections of the crust as volcanoes. Further, there are ridges along which the plates are pulled apart and fresh hot magma erupts along these mid-continental ridges. There are certain hot spots in the mantle where temperature is very high. When the wandering plate moves over the hot spot, it gives rise to lava flows forming a trap. The Deccan Trap is an example from India. Around 65 million years ago, the Indian plate moved over a hot spot situated in the Indian Ocean leading to eruption of Deccan Trap as hot lava flows. These geological realities give rise to heterogeneities in the temperatures and temperature gradients.

Mid-continental ridges, active volcano belts and hot spots are suggested as the natural places to look for favourable conditions to exploit the geothermal energy as energy source. The crust of the Earth does not consist of monolithic blocks. There are layered sedimentary formations, intrusions of igneous rocks and so on. The rocks on the large length scales are plastic and undergo deformations under stress. They are also fragile and are faulted and fractured. Once we cover them with surface water and ice flows of rivers and glaciers, the picture is more or less complete.

The geysers, which are periodic eruptions of steam and hot water in the form of natural fountains, have all the elements required for the ideal geothermal

site:(1) Very hot environment at relatively shallow level (around 2000 m) provided by the magma, (2) Seepage of telluric water through fractures and faults to that level, reservoir of porous rock and or fractures and vugs and finally (3). A system of faults and fractures providing a path up to the surface through which the hot fluids flow up to the surface.

Here, the water flowing from the surface flows down and comes in contact with the hot rock and exchanges heat and converts into steam. The steam then builds up pressure in the reservoir and once the pressure crosses the threshold, the fluids erupt as a jet on the surface carrying heat with it. That results in pressure drop in the reservoir and the jet cannot be sustained any further. The cycle repeats.

Thus, for a geothermal site, in addition to hot magma as a heat source relatively near the surface, an aquifer with very good support of water from the surface is required. By drilling a well, a controlled system for bringing out the hot fluids is provided. Depending on the temperature, pressure and quality of the produced steam, different methods are adopted for generating electricity. A typical geological setting is depicted in Fig. 3.

Geothermal Project: Surface/subsurface Installations

Having located a geothermal site, a well is drilled up to the reservoir and the reservoir fluid is produced on the surface. If the produced fluid is dry steam, then a steam turbine is run to produce electricity. If the reservoir does not have prolific water support, then the condensed water is injected back into reservoir through an injection well. The schematic is depicted in Fig. 4.

If the produced fluid is hot with temperature above 180°C and at a high pressure, then the fluid can be flashed at lower pressure causing the liquid to evaporate fast. The produced steam is then fed to run the turbine to produce electricity. The condensed water then is injected into the reservoir through an injector. The schematic is depicted in Fig. 5.

When the produced fluid is moderately hot (below 180°C), then a different scheme is adopted,

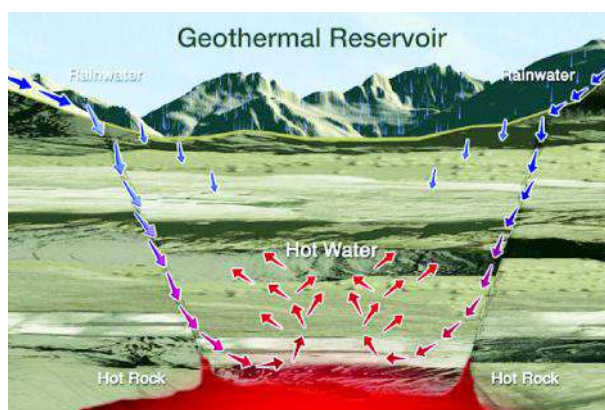


Fig. 3: Geothermal reservoir

Dry Steam plants

Steam directly from geothermal reservoir is used for running the turbines

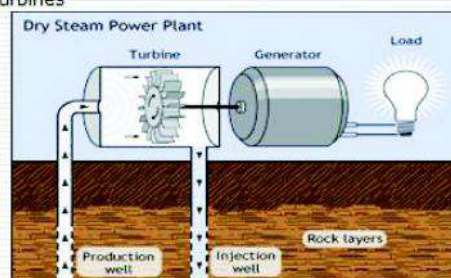


Fig. 4: Dry steam geothermal plant

Flash Steam Power plants

Fluids above 182°C can be used in flash plants to make electricity. Fluid is sprayed into a tank at lower pressures causing some of the fluid to rapidly vaporize/flash which in turn drives a

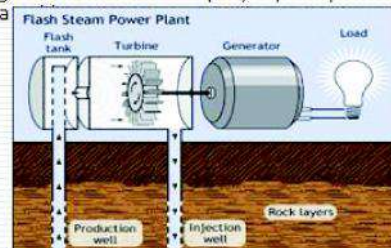


Fig. 5: Flash steam geothermal power plant

called as the binary cycle power plant. The heat is exchanged with an organic fluid with lower boiling point. Thus, with exchanged heat the organic fluid vaporized, a turbine is run on this vapour to produce electricity. The condensed organic fluid is then again fed to the heat exchanger. The water produced from

Binary Cycle Power plants

Energy is extracted from moderate-temperature water (below 400°F) by a secondary (binary) fluid with lower boiling point than water. Heat from geothermal fluid causes the secondary fluid to flash to vapor, which drives the turbine

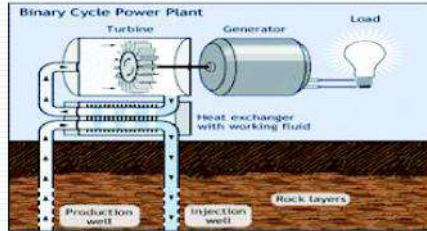


Fig. 6: Binary cycle geothermal power plant

the reservoir after exchanging the heat is then injected back into the reservoir. The schematic is depicted in Fig. 6.

There are situations where it is possible to dovetail the binary cycle with dry steam or the flash steam power plant to extract more work out of the condensed water if it is hot enough to run the binary cycle plant. This is an example of a hybrid plant.

In any case, if it is possible to utilize the low quality heat for space heating or crop drying or any other agricultural or industrial applications, the overall efficiency of the geothermal heat utilization is very high. Such opportunity if available, then it is a combined heat and power plant (CHP plant).

It is also possible that temperature of the produced water is around 100°C or less. In that case, there is no possibility of power generation. It is still possible depending on the location to find an application for utilizing heat as space heating or some other agricultural or industrial application.

Global Scene

Currently, 24 countries have exploited geothermal energy for power generation and 72 countries use the geothermal heat directly for other applications. Historically, hot water springs have been always used as a source of heat energy for space heating, bathing, and cooking. The world has an installed capacity of around 11,000 MW. This is about 0.5% of the total installed capacity. In addition, 28,000 MW of geothermal energy is exploited for direct heat

application. Iceland is a leader in direct heat applications. The space heating is a necessity in Iceland all round the year; 93% of space heating is from geothermal energy. Reykjavik, the capital of Iceland has the world's biggest district heating system in the world based on geothermal energy. Earlier, Reykjavik was known as the most polluted city in the world since coal was used for space heating. However, today with changeover to geothermal heating, it is the world's cleanest city!

So far, the utilization of geothermal energy is mainly restricted to areas along the circum-Pacific "Ring of Fire," spreading centres, continental rift zones and other hot spots. Fig. 7 shows the "Ring of Fire" and other known hot zones.

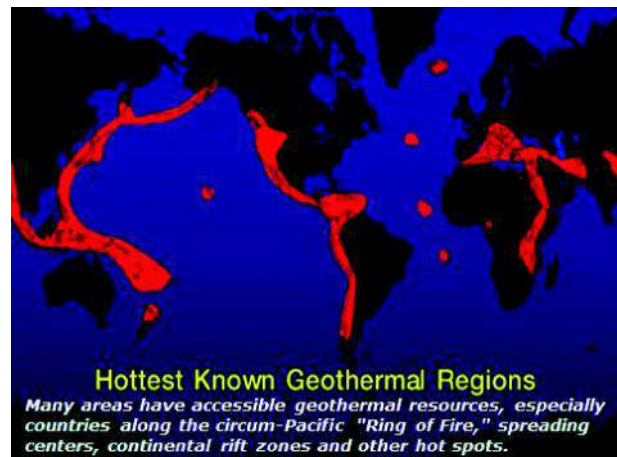


Fig. 7: Ring of Fire

Fig. 8, shows the location of existing geothermal power plants in the world.

As expected, we see a total overlap in the ring of fire and the locations of geothermal power plants. Thus, it is a location-specific niche energy source. We also note that a reservoir with sufficient capacity and sustaining high production rate is also a necessary condition. In fact, it is the productivity of the well which determines and limits the power generation potential, given the geothermal reservoir. Depending on ambient temperature and fluid temperature (say, about 150°C) for a closed loop binary cycle, geothermal power plant water production capacity is required to be in the range of 100 to 140 m³/h or 2400

to 3500 m³/day for 1 MW electricity generation. These are very high capacities requiring thick and very permeable water-bearing zone. For water temperature of 100°C, the required production rates are in the range of 300 to 400 m³/h.

Exploration for Geothermal Field

The exploration for geothermal site starts from satellite pictures and field geological surveys to isolate the promising areas. Geysers, hot water streams, leakage of steam along fractures, active volcanoes and craters of extinguished volcanoes are the preliminary signs of a possible site. After identifying the area of interest, the geology of the region is studied. Seismic, electromagnetic and geochemical surveys are conducted. Based on these studies, shallow and deep exploration drilling is undertaken mainly to collect the cores of the subsurface rocks and to measure the subsurface temperatures. Based on these studies, if a good prospect is located, an exploratory testing well is drilled targeting the reservoir. The reservoir is then tested for fluid production extensively to determine the extent of the reservoir laterally and thickness as well as the productivity of the well. With the help of these data, the size of the plant is decided and the power plant is designed and installed. The injection well is then drilled to inject back the fluids.

Economic Considerations

About 50% of the cost of the plant is incurred in drilling. Exploration is very expensive. Even in known areas with high temperature gradients over extensive zones, exploration risk is high. In contrast to hydrocarbon exploration, the rewards are not very high. One MW electric power plant is just equivalent to 40 barrels of oil per day. The evacuation of power is also an issue. Unless the site is situated near the market for low quality heat and an electric grid in which power can be fed, the economics may not be favourable. The project with additional financial burden of a transmission line may not be viable. Comparatively, direct heat applications require shallower drilling because the required temperatures are not very high.

A pair of wells, depending on the quality of the

heat source, can produce around 5 MW power. In extremely favourable circumstances, even a single well dry steam producer can yield 8MW capacity.

Novel Approaches and Concepts

The known areas of geothermal potential in many cases are getting saturated. Therefore, efforts are in progress to expand geothermal potentials in two different directions. The first approach has led to rapid expansion in the relatively low temperature applications through a binary cycle power plant. The other direction is to eliminate the need for high temperature gradients and water reservoir altogether. This would enable the exploitation of geothermal energy practically all over the world at any location!

On drilling deep enough, one is guaranteed to come across high exploitable temperatures. The rock is likely to be a igneous rock such as basalt or granite; or metamorphic. If two wells are drilled and fractured over a long horizontal section, then we can use this pair as injector and producer. The fracture complex connecting the two wells can act as a conduit for fluid as well as a heat exchanger between the rock and fluid. Thus, in a closed loop, this arrangement will fulfill the requirement of a geothermal prospect. The concept is depicted schematically in Fig. 9.

Another variation of this concept is possible in the sedimentary basin. In sedimentary basin, aquifers are very common occurrences. If deeper aquifers are known to occur based on the drilled data of oil

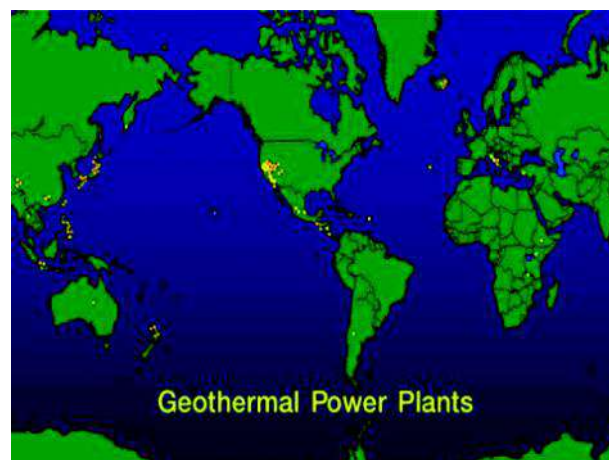


Fig. 8: Locations of geothermal power plants

and gas exploration and production, then utilizing the aquifer as a reservoir and heat exchanger and developing a geothermal prospect in such a location is feasible. The otherwise expensive exploration studies and data are already available with the oil companies. Thus, the first very expensive phase is already accomplished in the oil and gas province. Such concept is under development. It may eliminate the difficult, uncertain and expensive fracturing step from engineered geothermal system (EGS).

Unique Features as Energy Source

Geothermal energy consists of many attractive features. First and foremost, it is a “green” environmentally benign and clean energy source renewable on the human time scale; but unlike other renewable sources such as solar or wind, it is not intermittent and is available round the clock. The land requirement is also minimal. For production of 1000 MW, a geothermal plant has footprint of only 3.5 km² versus 32 km² and 12 km² required for coal-based plant and wind farm, respectively.

Along with land, fresh water is another resource which is getting scarce and has multiple competing demands. Geothermal plant requires just 20 litres of freshwater for 1MWh compared to 1000 litres per MWh required for coal, oil or nuclear plants.

Dissolved greenhouse gases are present in varying proportion in the produced fluid. Greenhouse gases are emitted by the source of auxiliary power for pumps. Existing geothermal plants emit 122kg of CO₂ per 1MWh, which is just a fraction of the emission intensity of fossil fuel-based plant.

Finally, if an appropriate site is available, then geothermal energy is affordable and does not require any subsidy. The major cost is incurred in drilling of two wells. Electric plant construction and drilling of the wells may cost about (€ 2 to 5 million) Rs. 14 to 35 crores per MW. Electricity and breakeven tariff costs (4 to 10 eurocents) Rs. 3 to 7 per unit. The plant load factor is very high. Only normal maintenance of the plant is required. There is no fuel cost and the plant is immune to rising fuel costs. The wells can last for several decades.

The expertise required for exploration and drilling operation is very similar to the upstream oil and gas industry. Hence, it is not a surprise that Chevron, the well-known oil company, is the biggest private producer of geothermal energy.

The Indian Scene

In India, there are several geothermal provinces where hot water streams are present. The provinces are: Tattapani in Chhatisgarh, Puga Valley in Jammu and Kashmir (J&K), Cambay graben in Gujarat, Manikaran in Himachal Pradesh, Surajkund in Jharkhand and Chhumathang in J&K. In India, geothermal energy is a state subject. Various states have floated tenders or called for ‘Expression of Interest’. However, lack of background knowledge is the main hurdle. Secondly, though there is no doubt of temperature anomalies, the quality, depth and areal extent are not known. In places such as Puga Valley, the terrain is tough and there may be evacuation problem. As a result, no serious deep exploratory drilling has been undertaken so far at any of the sites. Unless there is more clarity on geology and nature of the prospect, private parties may not come forward. The state governments need to work in partnership with companies coming forward rather than treat it as a proven geothermal field and expect an income out of it.

Apart from these provinces, there is the Himalayan Geothermal belt passing through India, Tibet, China, Myanmar and Thailand replete with more around 1000 hot water springs. Thailand has a 300

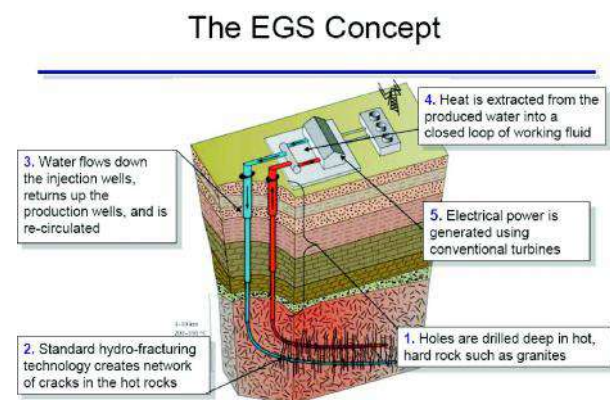


Fig. 9: Engineered geothermal system

kWe plant in tandem with utilization of exhaust heat for crop drying, cold storage and recreational park with bathing pools. Yangbajang in Tibet generates 25 MWe supplying 40% electricity requirement of the city of Lhasa. There are seven more plants near this area producing 1 MWe each.

Inaccessible areas, rough and tough terrain, away from the major metropolitan or industrial centres are some of the reasons why this promising but limited source has not received focused attention so far.

Conclusions

We note that geothermal is a clean and sustainable source of energy. In CHP (combined heat and power) mode, the efficiency is very high. Therefore, countries which require space heating have an added advantage. However, the present day technology allows exploitation of geothermal energy only in geologically suitable zones. Unless new technologies such as EGS succeed in the sedimentary basin, there will be limits to the development of the geothermal energy sector. Globally, renewable energy (excluding conventional hydroelectric power generation)

accounts for less than 1% of the total energy consumption and within that geothermal contributes 10%.

For India, exploration in the prospective area is a high-risk venture; yet the rewards are not very high. Hence, concentrating on geothermal energy in the sedimentary basin and keeping track of development elsewhere in EGS is the best strategy.

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Review Article

Solar Photovoltaic Energy Harnessing

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There is an urgent need for clean and sustainable methods of power generation to meet the ever increasing demand of energy for human activities. Photovoltaic (PV) technologies are some of the most attractive forms of clean and sustainable power generation. This study introduces the basic PV process and goes on to describe the different solar PV technologies extant today. The strengths and challenges in the deployment of each of the prominent technologies are described. The study concludes by highlighting the government plans for promoting PV and the short, medium and long term initiatives that need to be undertaken in the Indian context for the success of solar PV to harness the sun's energy effectively.

Keywords: Photovoltaic Technologies; Solar Cell; Renewable Energy Generation; Sustainable Energy Generation

Introduction

It is well-established that the quality of life (QoL) – often defined or estimated with the help of parameters that are indicative of the general well-being of a population group or country such as employment opportunity, access to health, education level, socio-political and economic equality and empowerment, etc. – is strongly dependent on the per capita energy availability. This is especially borne out when the energy availability in a particular country or society is low. Beyond a certain threshold of energy availability, the QoL appears to saturate. This optimal per capita electrical energy availability in industrial and democratic countries for good QoL appears to be around 15-18 kWh of electrical energy per person per day as shown in Fig. 1 (based on data from <http://www.eia.gov/> and http://www.economist.com/media/pdf/QUALITY_OF_LIFE.pdf). The electrical energy available per person per day in India in the beginning of the first decade of the twenty-first century was around 1.5 to 2 kWh per day. It should also be noted that the energy availability is skewed significantly towards the residents in and around urban centres.

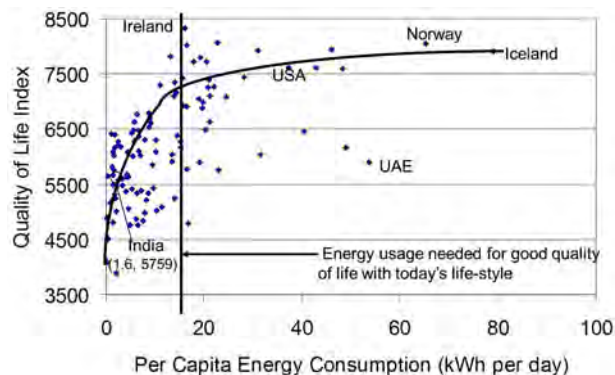


Fig. 1: QoL today has a strong link with the per capita electrical energy available for small values of energy availability. (Plotted with data taken from <http://www.eia.gov/> and http://www.economist.com/media/pdf/QUALITY_OF_LIFE.pdf)

Thus, to raise the QoL in India for all its citizens, we will need exponential increase in electricity production. As of 2011, India generated 985 billion kWh of electricity (<http://www.eia.gov/>) and by the yardstick of maximizing QoL for all citizens, 6000 billion kWh needs to be generated – an almost six-fold increase in power generation. Relying purely on fossil fuels

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might be counter-productive economically and environmentally and one needs to explore renewable sources. Among the various renewable sources of energy, tapping solar energy directly with photovoltaic (PV) technology is an attractive and practical option, especially for a country such as India which received abundant sunshine for most of the year.

Approximately 170 PW ($P \equiv \text{peta} \equiv 10^{15}$) is incident on the face of the earth at any point of time, which is 6000 times more than the current world demand of 17 TW of energy used – out of which electricity generation is around 2.3 TW. The total energy demand is expected to increase to 30 TW by the middle of this century (Hoffert *et al.*, 1998).

The electricity production in India as of 2011 was 112 GW (985 billion kWh per year), which is about 5% of the total world energy production (<http://www.eia.gov/>). As seen in the solar insolation map of the Ministry of New and Renewable Energy (MNRE), Government of India (Fig. 2) (<http://www.mnre.gov.in/sec/solar-assmnt.htm>), most parts

of India receive more than $5 \text{ kW} \times \text{m}^{-2} \times \text{day}$. Even with 10% efficient PV power generation, India's current electricity requirement can be generated in an area less than $75 \text{ km} \times 75 \text{ km}$ which is less than 1% of its land area. This deployment should, of course, be distributed to take advantages of its inherent strength and also to minimize transmission losses. The capital involved in the deployment of so many PV panels and their availability will be a bottle neck – besides the challenge of storage of energy for use at night when PV panels cannot generate power. However simplistic this calculation might appear, it helps us realize that with availability of the right technology and policies, India is well-placed to generate a significant fraction of its energy requirement directly from incident solar radiation.

While the solar power may be tapped by various means such as solar thermal and photochemical approaches, PV allows for direction conversion to electricity which has evolved to be the most convenient form of energy for human use. The other approaches too have their advantages (as discussed in the other contributions in this volume), and one should evolve methods of combining the different approaches for effectively harnessing solar power for human use. We will focus on the current status of PV technologies, the challenges and opportunities these provide in tapping solar power and finally discuss possible approaches of deploying them effectively, especially in the Indian context.

Brief History and Status of PV Deployment

While the photovoltaic process was described and some of its aspects were understood in the 19th century, especially by Alexandre-Edmond Becquerel, it was in 1952 that the first solar cell with more than 1% efficiency was demonstrated in Bell Labs by Chapin, Fuller and Pearson (Chapin *et al.*, 1954). Their cell fabricated with a *p-n* junction on Czochralski process grown monocrystalline silicon had an efficiency of 6%. The news of its fabrication was received with much enthusiasm by the press and the scientific community. Within a couple of decades, PV established itself as an important and mature

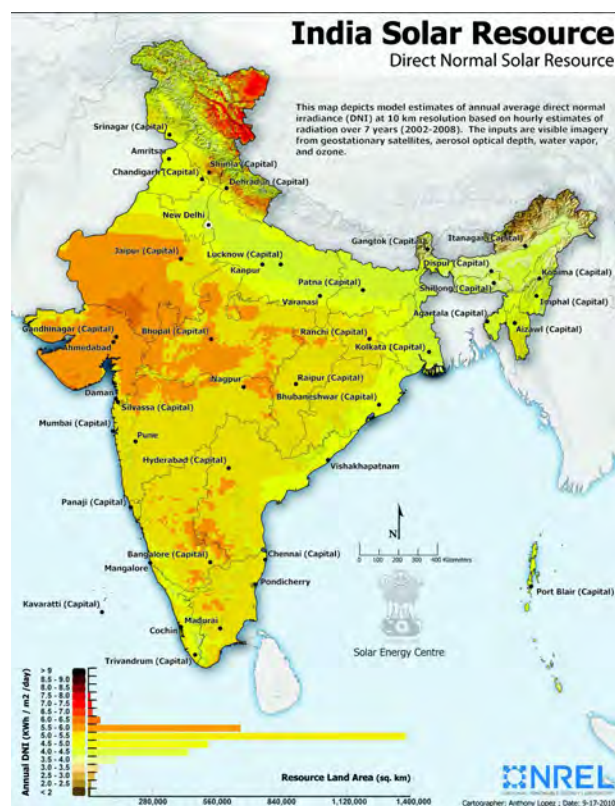


Fig. 2: Annual average energy that can be generated per m^2 per day for India. (<http://www.mnre.gov.in/sec/solar-assmnt.htm>)

technology for power generation, especially in niche applications such as power generation in space, remote locations and in consumer electronics. However, its use for large-scale power generation replacing the use of fossil fuels did not happen due to the higher cost in the fabrication of the solar cells as well as the huge energy payback time for the solar cells fabricated with the existing technologies.

There was a big push to promote renewable power including PV in the decade of the 1970s, especially in USA and other western countries due to the unavailability of petroleum. In India too, in that decade, the existing research institutes of the time were involved in PV research and development. However, with the political and economic resolution of the issues with oil producing nations and the supply of petroleum becoming more abundant, the emphasis on PV research was reduced – although it did not stop but continued only in low key. It was only in the first decade of the 21st century that the emphasis on PV research has come back, especially in the context of growing awareness of global warming due to continued use of fossil fuels. Owing to government incentives in countries such as Germany, PV manufacturing has taken off rapidly in the last decade and the cost of solar PV power is quickly moving towards grid parity making it more and more competitive.

Components in the Deployment of PV Technology

The components that need to be handled for the deployment of solar PV power generation technology consists of the following: (i) power generation; (ii) power electronic system and (iii) a load or a storage where the generated power may be used up immediately or stored as energy for future use.

Power Generation

Electrical power is generated from solar insolation with the help of solar modules which are implemented by a range of technologies. These technologies are at various stages of maturity and development, which offer various trade-off in cost, efficiency, stability, weight and aesthetics. The most popular technology

is based on silicon – both single crystalline and multi-crystalline. However, due to the high cost per watt of energy with these PV cells, various thin film silicon have emerged. Some of the more popular technologies in this category are cadmium telluride (CdTe) and copper indium gallium diselenide/sulphide (CIGS). Another promising technology, especially in the Indian context is amorphous silicon solar cells and their variations. In recent years, a variety of promising technologies have emerged including dye-sensitized solar cells, organic solar cells and quantum dot solar cells. The high efficiency compound semiconductor-based cells and multi-junction solar cells have also made rapid strides in recent years. Often the costly, but high efficiency solar cells are used with concentrators, where the mirrors which are cheaper than the high efficiency cells collect sunlight from a wider area and concentrate on to a small area.

The choice of the technology to be deployed will depend on the specific application, availability of land and the capital cost restrictions. The current status of many of these technologies and the challenges they face will be discussed in more detail in section - *PV Technologies for PV Power Generation*.

Power Electronic System

Once the charges have been separated and the PV process is complete in the PV cell/module, the power needs to be extracted to the outside world efficiently for practical use. The power extracted will be a maximum only for a particular load value as seen by the photovoltaic cell/module. It is possible to build electronic circuits that can track the *I-V* characteristics of the PV cell/module and help extract maximum power from the module. Such circuits are called maximum power point tracking (MPPT) circuits and are to be designed for the specific solar module technology and system as well as the load to which the power is to be actually delivered. Besides the power extraction from the power generating cell/module, the power electronic system also balances the variations in power from the different modules as well as the specific requirements of the load which might be a battery bank where energy is stored or a grid to which the generated power is immediately evacuated. The power system has to be custom built

according to the specific location and purpose of the PV system. The Indian grid system's features are distinct from those in developed countries. The weather and maintenance conditions possible in the places where the PV deployment is taking place may also vary. These have to be also factored in when putting together a power electronic system. In the Indian context, location-specific power electronic system design and deployment is a critical factor in the successful deployment of PV technology.

Energy Storage

The power harnessed by a solar PV system and provided as electrical power could be immediately used up by supplying to the grid or it has to be stored as energy, possibly with the help of batteries. This is unlike the solar thermal and solar chemical routes for harnessing solar power where the harnessed energy is automatically stored in the steam generated or as chemical energy which could be used after a gap in time.

For solar PV, directly supplying the power generated to the grid is increasingly popular. This is particularly attractive if the peak power demands coincide with the power generation periods during the day. This solution may be acceptable today when power generated and fed to the grid is a small fraction of the fossil-dominated power generation. When the main source of power in a grid is from PV, stability of the grid can be captive to the vagaries of the power generation due to the availability of sunshine and its variation during the day. In systems and situations where the generated power from PV needs to be used later (e.g. at night when sunlight is not available), it is important to evolve low-cost, economically viable and environment-friendly methods of energy storage. This could take the form of storing water in elevated reservoirs, or electro-chemical methods such as batteries or with hydrogen fuel cells.

The storage duration required may be: *short term* to ease of transfer of power to the grid and to protect output power from momentary fluctuations, possibly due to a bird flying over the panel or cloud momentary covering the sun or other causes; *medium term* to take care of hourly variations in solar PV power

generation as the sun moves across the sky or a few hours of cloudy weather; or *long term* to manage seasonal variations in PV power generation and longer periods of lack of sun as during monsoons or foggy winter months. For the success of large-scale PV technology deployment and to effectively use the technology, it is critical to address storage methods that are economical and compatible to PV technologies.

While all three aspects – power generation, power electronic system and energy storage – discussed in the above three sub-sections - *Power Generation* to *Energy Storage* are important for deployment of PV power generation technology, we will focus on power generation with PV. The other aspects are discussed elsewhere in this volume.

Photovoltaic Action and Power Generation Efficiency

Photovoltaic action may be divided into three steps: (i) absorption of incident photon; (ii) creation of an electron-hole pair that can conduct current; and finally (iii) separation of this electron and hole to separate electrodes to create the electro-motive force (emf) of the PV cell as a power source.

Absorption of Incident Light

The intensity of incident light drops exponentially in a material as it goes through it. This is modelled by the Beer-Lambert's law (Swinehart, 1962):

$$I(x, \lambda) = I_0(\lambda) \cdot \exp[-\alpha(\lambda) \cdot x],$$

where $I_0(\lambda)$ is the intensity of the incident optical beam of wavelength λ and $I(x, \lambda)$ is the intensity of beam after it travels a distance x from the surface within the material. Here, $\alpha(\lambda)$ is the absorption coefficient in the material for light of wavelength λ . For photovoltaic material, we would want $\alpha(\lambda)$ to be large for the λ s present in the solar spectrum. Thus, less material will be sufficient to absorb the photons coming in from the sunlight to contribute to the PV process.

Creation of Electron Hole Pairs

An incident photon in a material can be absorbed provided an electron can absorb its energy and is able

to find an energy state in the electronic band structure that can accommodate the excited electron. For example, in the schematic shown in Fig. 3, any electron in the filled valance band can absorb energy in the range of $E_m < E < E_g$. Thus, the absorption coefficient $\alpha(l)$ depends on the band-gap, besides the electronic band structure of the material. For indirect band-gap semiconductors such as silicon, the non-zero change in momentum has to be accommodated with the involvement of phonons which makes the absorption less probable. This is why for indirect band-gap semiconductors, the absorption coefficient is small.

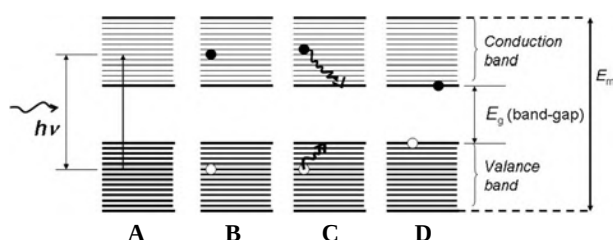


Fig. 3: Incident photon of energy $h\nu > E_g$ (band-gap) A: Excites an electron from the valance band to conduction band, which results in, B: An excited electron and an excited hole. C: The excited charges thermalize in a short time to come to the bottom of conduction band and top of the valance band, respectively. D: The free electron and hole now need to be separated physically which is usually accomplished with the help of a built-in electric field to create an emf in the solar cell

Once the photon energy is absorbed by the electron to form the electron–hole pair, they thermalize rapidly. The electron comes to the lowest possible state in the conduction band and the hole to the highest possible state in the valance band. This change in energy in the electron and hole is dissipated as heat.

Physical Separation of Electrons and Holes

The thermalized electron and hole now need to be physically separated. This is usually achieved by a built-in field present in the device at the location of the formation of the electron–hole pair. The most popular way of achieving the built-in field is by creating a p - n junction in a semiconductor. The electron gets swept towards the cathode and the hole gets swept towards the anode. This separation of charge creates

an emf in the solar cell which can do useful work on an external load connected across the PV cell terminals.

Efficiency of a PV Cell

The power conversion efficiency of a PV cell for comparative purposes is determined by exposing the cell/module to a known intensity of optical radiation of a given spectrum. The maximum electrical power that can be extracted from the cell by choosing the appropriate load, is then determined and this is taken to be the useful electrical power generated. This latter quantity may be expressed as the product of V_{oc} , the open circuit voltage obtained in the PV cell, I_{sc} , the short circuit current for the PV cells and the fill factor (FF). The FF is a fraction of the maximum power that can be extracted by an optimum external load from the solar cell to the product of V_{oc} and I_{sc} . (For more information on FF, please refer to the article by Saha *et al.* in this Special Issue of INSA on Energy.) Thus, the power conversion efficiency (η) in the solar cell for an incident power of P_{in} is given by

$$\eta = (V_{OC} \times I_{SC} \times FF) / P_{in},$$

where η may often be expressed as a percentage.

Sun's Spectrum and Units Specific to Solar Cells and Modules

When a photovoltaic cell is used for generation of power from solar irradiation, it is often referred to as a solar cell and the module built with it is called a solar module. Thus, solar cells and modules for terrestrial applications need to be calibrated to the sun's spectrum on the earth's surface. The rating of the solar cells and modules are also made with distinct units which are described here.

The Solar Spectrum

The energy from the sun reaches the earth in the form of solar irradiation. The incident power is distributed over different wavelengths. The spectrum observed corresponds to a black-body radiation at 6000°C, which is the temperature of the sun on its surface. The radiation from the sun reaches earth located approximately 8.32 light minutes away. Just

outside the earth's atmosphere, the total intensity of light is 1353 W m^{-2} (Sze, 1991). When the light reaches the earth's surface, not only does its intensity get attenuated, but its spectrum also gets altered. This is due to the absorption of sunlight as it passes through the atmosphere to reach the earth's surface. Thus, depending on the distance in the atmosphere that the light travels, which in turn depends on the sun's position with respect to the zenith, the spectrum and intensity of light reaching that location on the earth's surface varies.

When the sun is overhead, solar irradiation travels through one atmosphere length before reaching earth's surface. The spectrum corresponding to this is called AM1.0. When the sun is about midway to the zenith from the horizon (more accurately at 48.19°), the sun's radiation traverses 1.5 times the thickness of the atmosphere and the spectrum is called AM1.5 (Fig. 4). This spectrum is considered as the average of the sun's radiation during the day as it moves from the horizon at sunrise (90°) to the zenith position during midday (0°) and finally again at the horizon at sunset (90°). Moreover, solar spectrum gets modified depending on whether direct sunlight is considered or scattered light is also taken into consideration. This modification in spectrum is indicated with a G for "global" or D for "direct".

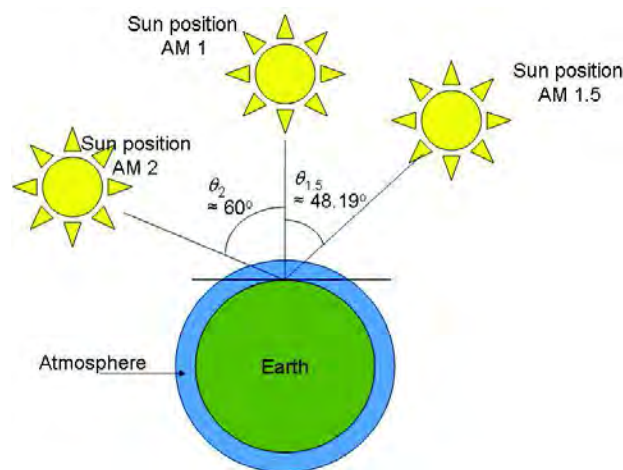


Fig. 4: Spectrum of the sunlight reaching the earth's surface is modified by the distance the sunlight has to travel through the atmosphere depending on the sun's position with respect to the zenith. AM1.5 G is taken as the spectrum to calibrate solar cells and modules

Rating and Output of a Solar Cell/panel

For terrestrial applications, the internationally accepted standard is to calibrate all solar cells and panels at 25°C for a spectrum of AM1.5 G with a light intensity (integration of the intensity of light for all the wavelengths) of $1000 \text{ W}\times\text{m}^{-2}$ ($100 \text{ mW}\times\text{cm}^{-2}$) as shown in Fig. 5. This intensity of light is also often referred to as 1 sun intensity. The maximum electrical power that can be garnered from the solar panel for this standard illumination (AM1.5G spectrum with 1 sun intensity) is referred to as the watt peak (Wp) rating of the solar panel.

There are, however, variations in the intensity and spectrum of light that reaches different locations on earth depending on the latitude, altitude, local weather and atmospheric conditions and the immediate surroundings of the solar panel. For example, a 1 Wp (watt peak) in the higher latitude might be able to generate less than 3 Wh in a period of one day in winter, while the same panel in a desert region located near the Tropic of Cancer might generate more than 6 Wp during a long summer day. Thus, the size of the solar panels in terms of Wp that will need to be installed for generating the required energy will depend on the exact location of their deployment.

India, by virtue of its location is blessed with sunlight for most of the year. On average, over the year, most parts of the country can generate 5 to 6 Wh of energy from a 1Wp solar panel (Fig. 2). During rainy season and in foggy winter months in some parts of the country, the energy that can be harnessed might decrease to much lower values. More details for specific locations in India can be obtained from the MNRE, Government of India website (<http://www.mnre.gov.in/sec/solar-assmnt.htm>).

Shockley-Queisser Limit for Solar Cell Materials

As seen earlier in section - Creation of Electron Hole Pair a material with a band-gap E_g will absorb only the part of the spectrum with energy greater than E_g . Moreover, energy more than E_g that is absorbed from the photon is lost as heat during thermalization. Thus, only a limited part of the spectrum of the sun's radiation

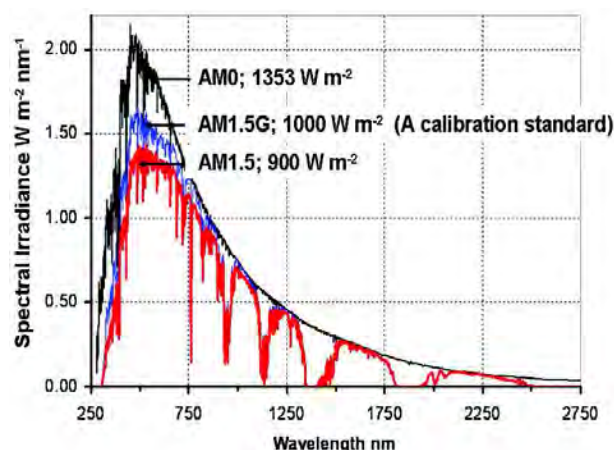


Fig. 5: Solar spectrum and intensity for AM0 (just outside the atmosphere) and for AM1.5 when the sun is at 48.19° to the zenith (<http://rredc.nrel.gov/solar/spectra/>)

and only a part of the absorbed energy will be useful during the photovoltaic process to generate the emf in the solar cell. Based on a detailed thermodynamic argument by Shockley and Queisser, the upper bound of efficiency for solar cells built with materials of a given band-gap can be estimated (Shockley and Queisser, 1961). This efficiency bound is known as the Shockley-Queisser limit (Fig. 6). The fundamental losses are due to inability of semiconductor to capture photons with energy less than the band-gap; thermalization loss in the electron-hole created with energy larger than the band-gap; Boltzmann loss; and Carnot loss (Hirst and Ekins-Daukes, 2011).

However, this upper bound may be extended beyond the Shockley-Queisser limit by building multi-

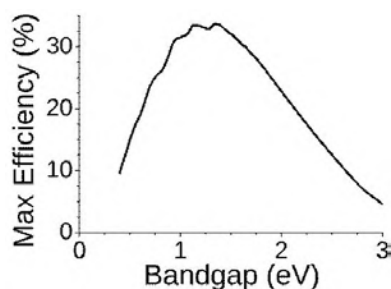


Fig. 6: Upper bound of efficiency of a single junction solar cell with a material of a given band-gap is called the Shockley-Queisser limit after the scientists who proposed it (Shockley and Queisser, 1961)

junction or tandem cells, i.e., solar cells built one above the other so that the lower cells absorb the spectrum of light not collected by the cells above. Efficiency may increase in a well-designed system due to the lowering of thermalization loss in the individual solar cells. The theoretical limit of upper bound of efficiency has been determined by Alexis De Vos (De Vos, 1980). When two or more cells with varying band-gap materials are used, the upper bound efficiency can be increased significantly. For unconcentrated incident sunlight with a large (infinite in theory) number of cells stacked in series on top of each other, the upper bound of efficiency is 68% and for concentrated sunlight, the upper bound is as high as 86%. Concentration of light helps increasing the open circuit voltage as well as the short circuit current which can result in generation of more electrical power to increase incident photons, provided the gain is not offset by too much rise in temperature or recombination of excess carrier within the cell.

From a practical point of view, however, it is to be noted that building tandem cells can be costly and a design ensuring the same current through all the tandem cells connected in series can be difficult and will be valid only for a particular relative position of the sun with respect to the zenith as the spectrum of sunlight changes with the sun's location in the sky. Similarly, using concentrators will require extra care in tracking the sun and ensuring that the cell temperature does not become unacceptably high. All the same, these calculations are useful as they give the upper bound of efficiency for solar cell designers and fabricators. They may be pursued in situations where cost consideration is not a limiting factor for generating power, for example, in the context of space exploration.

PV Technologies for PV Power Generation

A snapshot of the various technologies is provided in Fig. 7 which shows the “Best Research-Cell Efficiencies” being compiled and updated by the National Renewable Energy Laboratories in Golden Colorado (http://www.nrel.gov/ncpv/images/efficiency_chart.jpg). The solar PV technologies available today may be broadly classified in the

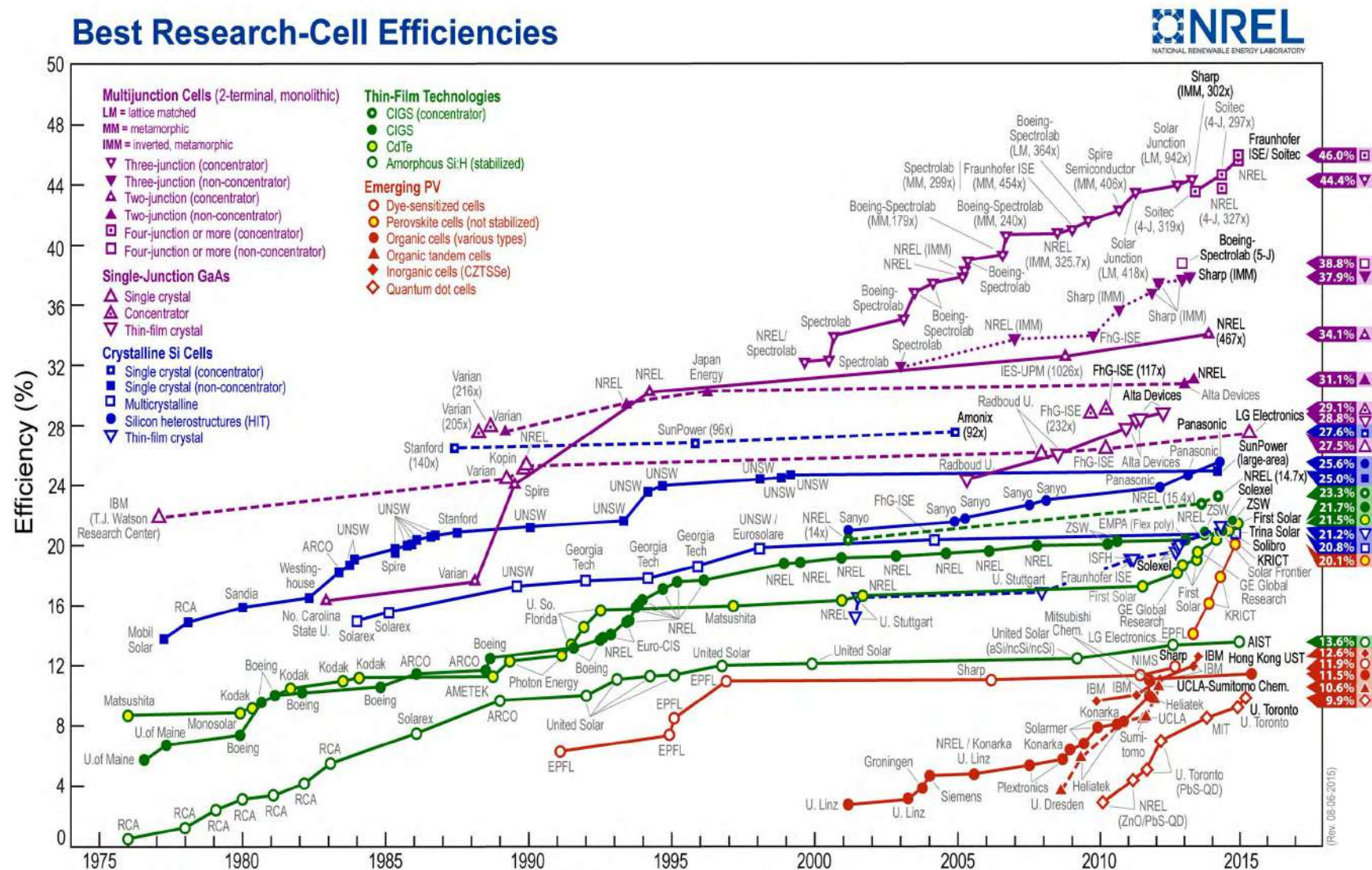


Fig. 7: Plot of compiled values of highest confirmed conversion efficiencies for research cells, from 1976 to August 2015. This plot is obtained by courtesy of the National Renewable Energy Laboratory, Golden, Colorado, USA (http://www.nrel.gov/ncpv/images/efficiency_chart.jpg)

following categories: (i) silicon-based solar cells (first generation); (ii) thin film inorganic semiconductor including amorphous Si, CIGS and CdTe solar cells (second generation); (iii) higher efficiency compound semiconductor solar cells such as GaAs and multi-junction solar cells (third generation) and (iv) newer and futuristic technologies in solar cells such as organic, dye-sensitized solar cell (DSSC) and quantum dot solar cells (also classified as third generation). The advantages and challenges of popular solar cell technologies are presented here.

Silicon-single Crystalline and Multi/polycrystalline

Silicon is one of the best understood materials, owing to the immense research and development in the very large-scale integration (VLSI) industry where silicon technology is the mainstay. Moreover, the abundance of silicon on earth's crust makes it attractive when one envisions building solar cells in large volumes that can produce terawatts of power needed in the future.

The mainstay of solar cells till date has been silicon solar technology. In this technology, scientists have managed to prepare solar cells on silicon substrates with efficiency close to the maximum possible 25% for single junction cells on Si, as predicted by the Shockley-Queisser limit and assuming the best attainable values of material properties with today's technologies (Zhao *et al.*, 1998).

The cost of manufacturing a silicon solar module consists of broadly three components – the material cost which is primarily the silicon wafer cost, the cost of processing the wafer and the cost of building the module with the wafers. There has been a constant effort in the industry to reduce all these components of cost, while not adversely affecting the efficiency of the solar module. One of the approaches to reduce the material cost is to simply reduce the amount of silicon used to build the solar cells (thin-film silicon solar cells). This may take the form of poly or multi-crystalline solar cells that are formed by lower cost process compared to the costly Czochralski process. Another approach is to use amorphous silicon to build solar cells as discussed in the next sub-section. The lower cost material, often result in lowering of the overall efficiency of the solar module built. Fig. 8

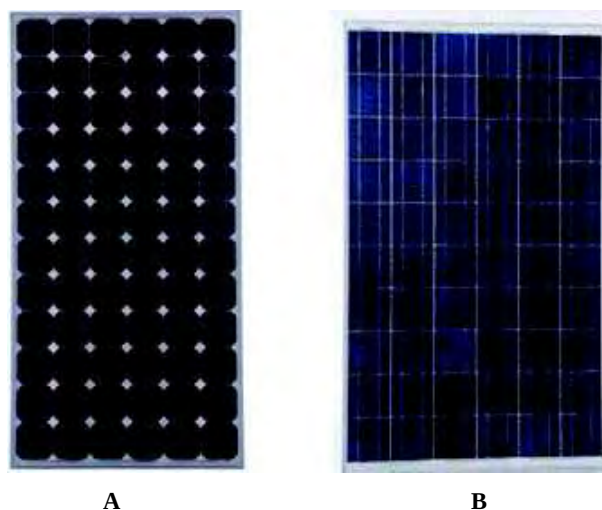


Fig. 8: A: Module built with single crystalline solar cells; and B: A module built with multi-crystalline solar cells. (<http://solarmaxdirect.com/>)

shows examples of single crystalline and multi-crystalline modules. The former modules are often immediately identifiable by the gaps between the cells in the module – the single crystalline cells being made with circular wafers which are often optimally chamfered to increase the packing density while minimizing the wastage of high quality single crystalline substrate.

Yet another approach to reduce cost of material used in the solar cell is to use ‘solar grade’ silicon rather than the “electronic grade” silicon (Solanki, 2011). In the past, the lower grade silicon that was left over after supplying to the VLSI industry was sufficient to supply manufacturers of silicon PV modules. The VLSI industry has stringent requirements about impurity contents such as Fe, Al and other metals. Electronic grade silicon would need impurity levels of less than parts per billion. On the other hand, wafers with lesser purity might be agreeable for solar cell fabrication with acceptable performance. These ‘parts per million’ purity solar grade wafers incur significantly lower costs. In recent years, since the boom in PV production, the volume of silicon used to build solar cells is exceeding that used for VLSI chip production. Many plants for solar grade silicon have been set up, especially in China, which have flooded the market and have brought down

prices of silicon wafers to unprecedented levels.

Even with solar grade wafers, prices can be brought down further if the wastage during the sawing of ingots could be minimized (Goetzberger *et al.*, 2003). Typically, almost 50% of the ingot may be lost due to “kerf” losses. Some have tried to remedy this by preparing kerfless silicon wafers. Two of the popular methods used are edge-defined film-fed growth (EFG) and string ribbon silicon technologies. In the case of EFG, Si-wafers are pulled out from the melt by using graphite die with capillary action. ASE Americas are primarily responsible for this technology. One may also pull out the wafers with a pair of high temperature wires from a silicon melt. This process was championed by Evergreen Solar (<http://www.evergreensolar.com/en/about/>).

To reduce the cost even further, ultrathin silicon technology is being pursued where 5 to 50 mm thick wafers are fabricated. Simulation results from Martin Green show that you can obtain 19.8% efficiency solar cells with 1 mm thick silicon solar cells although some touch up processing will be needed on these thinner wafers (Green, 1999). The traditional assumption was that you need more than 100 mm silicon wafers to be able to absorb sufficient light due to the indirect band-gap in the material – but the fractional higher efficiency one gets will come at a cost. So, these ultrathin silicon wafers, if successfully made and handled during fabrication, can bring down the cost of material by an order of magnitude. One of the interesting ways of preparing ultra-thin wafers is by cleaving the wafers at the edge, a process pioneered by Silicon Genesis and called as the PolyMax™ process. This is a kerfless technology which makes it competitive with much potential.

Besides reducing material cost, novel modifications are continuously attempted by silicon manufactures such as printing of the contacts (Hilali *et al.*, 2004) or ion implantation (Rohatgi *et al.*, 2012) in order to reduce the processing cost and time. Use of backside contact by SunPower to avoid shadowing effects (Mulligan and Swanson, 2003), anti-reflection coating (Rowlette and Wolden, 2009) and plasmonic techniques (Atwater and Polman, 2010), especially in thin silicon wafers (also common to other PV

technologies), are some of the processing tricks used by various manufacturers to increase the efficiency of solar cells. A good reference on issues related to silicon PV can be found in Goetzberger *et al.* (2003).

Internationally, the whole manufacturing of silicon solar cells has shifted to China due to the ability of the industries to produce cells and modules at low cost. In spite of tariffs imposed on Chinese solar products by other countries, they remain competitive to the products manufactured in the USA and Europe. In India, there are a few companies such as Lanco Solar in Rajnandgaon, Chhattisgarh and Moser Baer in Greater Noida in Uttar Pradesh that engage in panel assembly. However, there is no wafer to module type integration or manufacture today in India. Some research activities are being carried out in IIT Bombay in the Microelectronics Centre and the National Centre for Photovoltaic Research in crystalline silicon PV technology. National Physical Laboratories, New Delhi is also researching various methods to improve silicon PV efficiencies. Central Glass and Ceramics Research Institute, Calcutta and other CSIR labs are also looking into developing materials for improved light harvesting for silicon (and other) PV technologies.

Silicon-amorphous and Nano-crystalline

Amorphous silicon solar cells are simpler to fabricate since the solar module is directly fabricated on the substrate with amorphous silicon deposition being one of the intermediate steps. The maximum temperature of processing is typically 450°C and often lower making it especially attractive for solar cells implementation on flexible substrates and for light weight building integrated PV (BIPV). The deposition is carried out using hydrogen (H₂) and silane (SiH₄) gases by the plasma enhanced chemical vapour deposition (PECVD) process – which is the most popular method in commercial use. Since the doping of the amorphous silicon causes decrease in lifetime of carriers, usually, *p-i-n* structure is used in this technology with the absorption of light taking place in the lightly doped intrinsic region. Since the first demonstration of this technology in 1976 (Carlson and Wronski, 1976), buoyed by prevalence of the deposition process in the VLSI industry, it made rapid progress;

and by 1980, more than 10% of the efficient cells found commercial application. However, this technology was soon plagued by instability in the efficiency – known as the Staebler–Wronski effect (Staebler and Wronski, 1977). The passivating hydrogen moves with time resulting in drops in efficiency which stabilizes around 6–7%. Due to its lower efficiencies, amorphous silicon modules are usually popular for portable and distributed power generation (Fig. 9).



Fig. 9: An example of an amorphous silicon module along with a solar lantern (<http://www.solar-global.cn>)

One way to avoid this drop in efficiency due to Staebler–Wronski effect is to build amorphous silicon – nanocrystalline silicon (aSi-ncSi) multi-junction stacks. The nc-Si is more stable and can be achieved by increasing hydrogen concentration during the PECVD deposition. However, the deposition process is significantly slowed due to this (Roschek *et al.*, 2002).

Internationally, this technology seems to have peaked and is on the wane, at least temporarily. However, in the Indian context, the low cost of fabrication of these cells might still make it attractive for many applications, such as portable PV and for BIPV. Also, the use of plasmonics and other photon management techniques might help extract better efficiencies and lower costs for the power produced.

In India, Bharat Heavy Electrical Limited (BHEL) has set up an Amorphous Silicon Solar Cell Plant (ASSCP) at Gwal Pahari, Gurgaon. Research and development in amorphous silicon is being carried out by Indian Institute of Engineering Science and Technology at Shibpur, Jadavpur University and Hind Hivac Ltd. Many private research institutes such as SSN Research Centre located in south Madras are also working to develop amorphous silicon solar cells.

HIT Cells – Amorphous and Single Crystalline

The combination of crystalline silicon with amorphous Si – popularly referred to as heterojunction with intrinsic thin layer (HIT) cells – is increasing attractive to supplement the efficiency of single crystalline silicon PV cells with marginally increased processing cost. The aSi/cSi heterojunction cells with intrinsic layer, have achieved record efficiencies of more than 21%. There are many variations of the HIT cells with *n*-type or *p*-type a-Si, for example, those developed at Sanyo (Taguchi *et al.*, 2005) and EPFL, Neuchatel (Hänni *et al.*, 2013). In India, BHEL in Gurgaon has also managed to demonstrate structures similar to HIT cells successfully.

Copper Indium Gallium Diselenide/sulphide

In its earlier version, the thin film solar cells with efficiencies of around 6% to 7% were demonstrated with CuInSe₂ by Kazmerski *et al.* (1976). This material combination had a band-gap of around 1 eV. It was found that the band-gap could be tuned by substituting Ga in place of In and S in place of Se from 1 eV to 2.5 eV – giving rise to CIGS. Depending on the process and the group fabricating it, the actual absorption layer may contain four or five elements. There was rapid progress in 1990s in this technology and best cells with efficiencies of 16% were demonstrated. Unlike many other technologies, CIGS efficiencies have shown a steady climb over the years in performance and devices with efficiencies of more than 20% efficiencies have been demonstrated recently. The potential for further improvement makes this technology very promising. Since 2007, production capacities of many tens of MW of solar panels with this technology have been installed. They are particularly popular as they can be deployed on flexible

substrate (Fig. 10) such as stainless steel and titanium sheets. They can also be fabricated on polyimide, but the low temperature of processing ($<450^{\circ}\text{C}$) results in lower efficiencies.

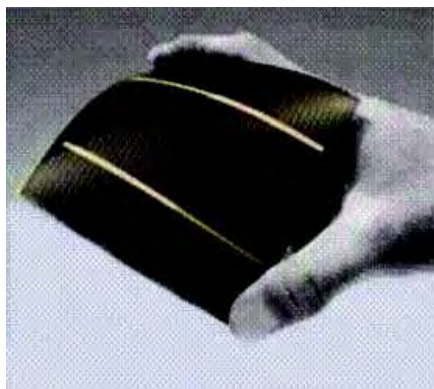


Fig. 10: CIGS is a thin film solar cell that may be fabricated on flexible substrates making it ideal for building integrated PV. Here, a CIGS solar cell from Day Star Technologies, Inc. (01/11/2006) is shown (http://www.solarserver.com/solarmagazin/news2006_01_e.html)

Typical CIGS cells consist of Mo back contact, a *p*-type CIGS absorption layer and doped ZnO as the transparent conducting oxide (TCO). However, the methods of manufacturing followed by different groups are varied. Broadly, there are three methods of fabrication of the absorption layer. One method is co-evaporation of the elements on heated glass substrate at 600°C (usually held below the sources). Modern in-line diagnostics help in getting the right stoichiometry. Another method is to form the metal films and then subject them to selenidization/sulphurization. The latter may be carried out with hydride gasses ($\text{H}_2\text{Se}/\text{H}_2\text{S}$) for better control, although toxicity can be an issue. The third method is to deposit the films by wet processes such as electrodeposition/particulate deposition/solution processing. However, this method does not form as dense a film and efficiencies are usually lower. Usually the first and second methods result in higher efficiencies, but with a larger cost and challenges for large-scale production (Hibberd *et al.*, 2010).

CIGS involving five elements can have many stable phases which are not useful for solar cell

purposes. Thus, the process window is small and is a challenge for manufacturing. Moreover, there are limitations on the window layer where CdS (Cd toxicity is an issue), ZnS and InS are explored. Similarly, the doped ZnO as TCO raises concerns about stability. A few extensive studies on CIGS solar cell technology are Tiwari *et al.*, (2010) and Kodigala (2010), which also highlight the different international groups involved in research, development and production. Moser Baer India Ltd. has undertaken an MNRE-supported project to come up with a manufacturing technology for CIGS solar cells.

One of the biggest challenges posed by CIGS towards terawatt power production is the limited supply of In in earth's crust. There have been attempts to recycle the In from old modules, but more research and development is needed to make this efficient and cost-effective. This has prompted researchers to look for earth-abundant element-based solar cells.

Copper Zinc Tin Selenide/sulphide

Copper zinc tin selenide/sulphide (CZTS) has evolved as a possible alternative to CIGS solar cells using earth-abundant elements. The first solar cells of this type were reported in 1988 (Ito and Nakazawa, 1988). There has been rapid increase in the efficiencies in the last one and half decades. In 1997, 2.3% efficiency was reported and by 2010, the efficiency had crossed 10%. In August 2012, IBM, partnering with Solar Frontier, Tokyo Ohka Kogyo (TOK) and DelSolar, announced CZTS solar cell of efficiency up to 11.1% (<http://phys.org/news/2012-08-ibm-efficiency-abundant-material-solar.html>). Much of the rapid improvement in these solar cells is due to cross-learning from CIGS. Thus, there is much promise in this technology. Within India, the thin-film solar cell group at NPL has been working on CZTS solar cells along with research activities on CIGS.

Cadmium Telluride

The first Cadmium telluride (CdTe) solar cells were reported in 1963 (Cusano, 1963), but it was in the 1990s that interest in the technology picked up. Due to some good technological improvements, in the

middle of the first decade of the twenty-first century by companies such as First Solar, power generated for less than \$1 a watt from CdTe solar cells was reported. With significant lowering of cost of Si solar cells in the last couple of years, the excitement for CdTe technology in recent years has somewhat diminished.

There are many facets that make CdTe technology attractive. Its band-gap of 1.44 eV at 300 K is in the region where the Shockley-Queisser efficiency limit will be among the highest. Its absorption coefficient is high and a couple of microns of the material can absorb most of the incident light in the spectrum. As with other II-VI compounds, Cd and Te sublime congruently and the compound CdTe is thermodynamically stable. Thus, it is easy to form stoichiometric CdTe by simple thermal deposition process with high deposition rates of more than 20 microns per minute.

A typical CdTe solar cell is fabricated on a glass substrate (Meyers and Albright, 2000) with the TCO- $\text{SnO}_2\text{:F}$, followed by an *n*-type window layer of CdS and the absorption layer of *p*-type CdTe. Finally, the contact is made with ZnTe or Cu or C. One big advantage is that the temperature of deposition of the first three layers – TCO, CdS and CdTe of $\sim 600^\circ\text{C}$ is the temperature where the glass exits a float line. This advantage to manufacturing has been used to the fullest extent by First Solar and other companies to reduce the cost of production.

In spite of the above advantages, the highest efficiency of CdTe solar cells today are only around 50% of the Shockley-Queisser limit and the manufacturing efficiencies are around 11-12%. This can be alleviated only by increasing both the I_{sc} and the V_{oc} for these devices.

The I_{sc} can be improved by increasing absorption of more light in the CdTe absorption layer and not in other parts of the cell. The $\text{SnO}_2\text{:F}$ TCO layer and CdS window layer absorb much of the blue part of the solar spectrum. Attempts have been made to improve this by changing the TCO or by substituting of CdS with alternative TCOs such as indium tin oxide (ITO) and cadmium stannate. However, they are

either costly or too complex to handle. Sulphides of Zn and In or oxygenated CdS have been tried for window layers.

The V_{oc} observed for CdS is more than 200 mV and less than that for GaAs which has a comparable band-gap of 1.42 eV. This is primarily due to the low carrier lifetime of a few ns arising from defects as well as grain-boundaries in the polycrystalline CdTe layer. Crystalline CdTe on the other hand gives minority carrier lifetimes of about 1 ms. However, solar cells in crystalline CdTe are poorer in performance than in polycrystalline CdTe. This apparent paradox is due to the fact that the grain boundaries may be playing a critical role in the transport of charges and thus help in other aspects of the photovoltaic process. Although in the industry, some empirical solutions are being used and touted to solve the issue, there are no simple or reliable solutions as yet. One needs to understand the role of defects and carrier lifetime in CdTe and see how to increase the latter without compromising on the mobility of the charges (Wolden *et al.*, 2011). One potential solution is to build *p-i-n* structures, but the control of dopants in CdTe to obtain these structures needs to be mastered.

The toxicity of Cd is often raised as an issue when considering deployment of CdTe solar cells. However, tests indicate that contamination due to Cd even during fire hazards or cracked modules are negligible. In fact, it is argued that Cd, which is a by-product of mining Zn, can be safely sequestered in the solar panels between the glass plates. The manufacturers are also committed to taking back the panels for re-using Cd at the end of the solar panel lifetime. It will also be useful to re-use the Te which is a rare element of limited supply. On the whole, while CdTe is likely to play a role in the PV technology, much research needs to be carried out before it can take the centre stage. Moreover, the limited availability of Te can be a bottleneck for terawatts of power being generated by CdTe solar cells and this issue has to be addressed. A couple of useful review articles on CdTe technology by Wu (2004) and Morales-Acevedo (2006) are available.

High Efficiency Solar Cells: GaAs, Multi-junction and Solar Trackers

Some of the highest efficiencies are achieved by direct band-gap semiconductor solar cells such as GaAs solar cells. These solar cells routinely achieve efficiencies close to 30% (single junction – 28.8% by Alta Devices in 2012), while the practical maximum efficiency of Si solar cells is only 25%. Researchers such as Yablonovitch and Atwater have championed the use of these devices (<http://www.altadevices.com/technology-overview.php>). However, the GaAs solar cells could end up much more costly to produce.

Another option to increase the efficiency is the multi-junction solar cells, one cell stacked on the other with highest band-gap closer to the light source and smallest band-gap farthest from it (Fig. 11). With two cells, the theoretical Shockley-Queisser maximum efficiency achievable jumps to 42% and with three junctions, it increases to 49% (De Vos, 1980). With the highest possible light concentration, the theoretical maximum efficiencies for single, double and triple junction solar cells are 40%, 55%, and 63%, respectively. As seen from the chart in Fig. 7, researchers at Sharp with triple junction, inverted, metamorphic cells and 302 times concentration have managed to achieve 44.4% efficiency – the highest efficiency solar cells as of 2013).

Besides the higher efficiencies achieved with concentration of light, there is also economic advantage as the cell size can be small while much of the solar panel is covered by concentrating mirrors. Mirror cost per unit area is cheaper than the cost of cells. This approach has been found to be attractive, especially in large area deployment in desert areas with copious direct radiation. One additional requirement of the concentrators is to include trackers in these solar modules (Fig. 12) because the concentrators will not be effective in diffused radiation and are optimal when parallel rays of light fall on them. For the same reasons, these solar panels are not effective in cloudy and foggy conditions and are unlikely to find larger use in medium and small scale deployment – although in drier and predictably sunny weather conditions, they can be economically attractive. One also has to factor the mechanical

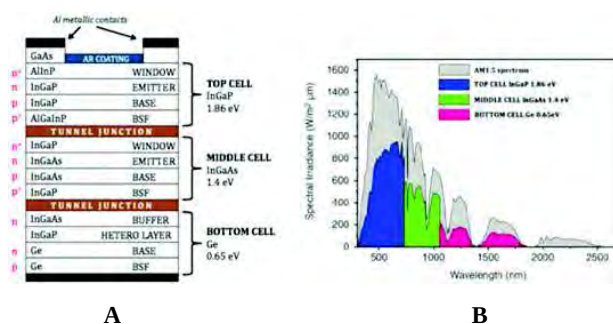


Fig. 11: A: An example of a triple-junction solar cell structure with cell junctions formed with Ge, InGaAs and InGaP stacked on top of each other. B: The cell absorbing the blue part of the solar spectrum (InGaP) is on the top facing the incoming radiation, the cell absorbing the green part (InGaAs) is in the middle and the cell absorbing the red part (Ge) is at the bottom of the stack (Yastrebova, 2007)



Fig. 12: A 1.2 kWp tracker set up by Moser Baer Photovoltaic Pvt. Ltd. Each of the parabolic mirrors has a high efficiency solar cell located at the focus. A similar tracker has been installed at IIT Kanpur by the company

functioning of the trackers and their maintenance requirement.

Excitonic Solar Cells

A third generation futuristic technology based solar cells which does not use the classic semiconductor

p-n junctions has emerged in the last two decades. These are often called “excitonic” solar cells because of the increased role of excitons in the photovoltaic process in these devices. Every electron when it absorbs energy from a photon forms an exciton – an excited electron. This may also be viewed as an electrically neutral packet of energy consisting of a bound electron and hole. In most inorganic semiconductors, at room temperature and above, these excitons almost immediately break up into free charge carrying electrons and holes. This is because their binding energies are typically less than 25 meV. In excitonic solar cells, however, the exciton binding energies are of the order of 100 meV and hence, they do not automatically break up into electrons and holes without facilitation. On the other hand, if the electron and hole pair is not formed, the exciton annihilates after some time, often dissipating the energy as heat. Two of the most popular excitonic solar cell technologies which have seen a surge of research activities in the last two decades are DSSC and organic solar cells or organic PV. In the last one year or so, Perovskite solar cells have caught the imagination of researchers and are making rapid progress in terms of the power conversion efficiencies that are achievable with this technology.

Organic Solar Cells (OSC)/organic PV

The fabrication of OSC devices with bi-layers by C.W. Tang of Eastman Kodak in 1986 (Tang, 1986) opened the floodgates of research activities on the subject. The devices are typically made of either soluble organic material such as polymers or by simple thermal evaporation of “small molecules” such as phthalocyanine of Cu, Zn and other metals, pentacene and fullerenes such as C_{60} , among others. The latter molecules are not exactly small, but are small in comparison to the gigantic polymers. The simplicity of the low temperature processes involved, amenability to high-throughput processes such as printing, and the abundance of the constituent elements present in organic compounds such as C, H, O, N, S, etc. make these attractive for large area, large volume and high throughput production – which will increasingly become a critical requirement for PV technologies.

Indeed in the last decade, the progress in this technology, especially in the research domain has been spectacular. The maximum efficiencies have been steadily climbing over the last decade from 3.6% in 2004 to more than 10% in 2013. Higher efficiencies have been pursued by various strategies including newer molecules and device structures. The most popular material for research is poly 3-hexyl thiophene (P3HT) and (6, 6)-phenyl C_{60} butyric acid methyl ester (PCBM) usually used in a blend form to yield bulk heterojunction solar cells. Many new organic molecules are being routinely synthesized and some have shown promising results. An important breakthrough in the stability of the OSCs has been the fabrication of devices with “inverted structures” (Li *et al.*, 2006). Unlike the regular structures, the inverted structure devices consist of ITO (which is the TCO) as the cathode terminal instead of an anode.

Several groups such as Helaitek in Germany and Yang Yang’s group in the University of California at Los Angeles have used small molecules to build the devices. One of the advantages of this approach is inherently the presence of more structured layers of the organic semiconductor and the ease of forming tandem solar cells by stacking cells which absorb different parts of the solar spectrum to achieve higher efficiencies.

While significant progress has been made in the efficiency and stability of OSCs, there is still much to be covered before this technology can be hoped to replace established technologies such as silicon PV. Efficiencies above 15% will make this technology competitive. More importantly, the stability of these devices has to improve. Some companies such as Konarka Technologies, Inc. have earlier demonstrated stability for three years (<http://www.swissphotonics.net/libraries.files/Brabec.pdf>, slide 25). This might be adequate for some applications, especially disposable electronics. However, for wider power generation application, stabilities of more than a decade will be necessary.

The promise of this technology, however, is the ease with which the OSCs can be fabricated from a wide variety of substrates such as glass, paper, cloth, steel, etc. (Fig. 13). These solar cells are also



Fig. 13: (A) OSC printed on paper at Chemnitz University of Technology, Germany (Hübler *et al.*, 2011); (B) OSC fabricated on flexible polyethylene terephthalate (PET) at IIT Kanpur (Dembla, 2009)

amenable to novel applications such as transparent solar cells that could be used on windows – it will allow visible light, but harness portions of the solar spectrum outside the visible region to generate power. While no commercial products are widely available with organic PV technologies – there exist some demonstration products – the strength of this technology will be its low cost, ease of use with a variety of substrates, abundance of the material needed to fabricate the main device and the potential for environment-friendly production and recycling after the product lifetime.

Owing to the promise and ease of fabrication, a large number of research groups around the world are working in the area of OSC. Indeed, the number of research-related publications for this technology is among the highest. In India too, there are a number of groups working in this area. IIT Kanpur, IIT Bombay, Indian Association for the Cultivation of Science in Calcutta, Jawaharlal Nehru Centre for Advanced Scientific Research in Bangalore, National Physical Laboratory in New Delhi, National Chemical Laboratory in Poona and many other institutions are conducting state-of-the-art research in this field. Many private institutions such as PSG Institute of Advanced Studies in Coimbatore are also pushing the frontiers of research by exploring OSC on flexible substrates. Due to the large strength of research activity in this area in India, with right coordination, this futuristic area of technology can be the one where Indian researchers and industries can excel.

Dye-sensitized Solar Cells

Dye-sensitized solar cells (DSSCs), which are based on the photo-electrochemical effect, were first reported in 1991 by O'Regan and Grätzel (O'Regan and Grätzel, 1991). These cells are also often referred to as Grätzel cells after the name of the inventor. Within a few years of DSSC invention, researchers in Prof. Grätzel's group managed to build solar cells with 11% efficiency.

DSSC uses metallo-organic dyes molecules adsorbed to a mesoporous titania nanoparticle films. Gaps between the particles are filled with an electrolyte and a plantinized electrode is provided. When light gets absorbed in the dye, an exciton is created. This exciton transfers its electron to the TiO_2 molecule at the dye-particle interface. The electron makes its way through the TiO_2 film to the photoelectrode. It then completes the circuit by doing external work and returning to the plantinized electrode to reduce a redox couple in the electrolyte. The reduced ion makes its way to the dye molecule with the positively charged hole and regenerates the molecule.

DSSC technology has found application as chargers for portable electronics. The various colours in which these cells are available as well as the possibility of semi-transparent cells make them attractive for BIPV. One of the main challenges faced by this technology is the inability to increase the power conversion efficiency beyond 11% in the last many years. The material system of Ru-based dye, photoanode and iodine-based redox couple in the electrolyte has not changed and there is little room for improvement. Typically, modules of less than 100 cm^2 are built as the series resistances can become too high, bringing down the efficiency. By far, the biggest challenge is in the encapsulation of these devices and their lifetimes. While properly encapsulated devices have shown promise of more than a decade of lifetime, devices made on plastic typically show lifetimes of a couple of years. Attempts to replace the liquid electrolyte with gels or solid electrolyte have not been very successful as the efficiencies drop.

This is a promising technology in the long term, but is awaiting research breakthroughs in dyes, photoanode and electrolyte. The simplicity of processing makes it amenable for large volume and high throughput production. A number of research groups within India are funded for research activities in this technology and have been contributing to the understanding and innovations in this technology, notably at National Chemical Laboratory in Poona, IIT Delhi, Cochin University of Science and Technology, Indian Association for the Cultivation of Science in Calcutta and many others.

Perovskite Solar Cells

Typically, the perovskite material used for solar cells is a methyl ammonium tin or lead halide. The perovskite-based meso-super-structured cells (MSSCs) which have evolved from DSSCs have in the last year made rapid progress in terms of the power conversion efficiency that they are able to achieve but new structures are continuously being explored (Green *et al.*, 2014). Building upon the experience of DSSC, efficiencies of more than 12% and V_{oc} of more than 1.1 V have been fabricated. A $CH_3NH_3PbI_{3-x}Cl_x$ -based solar cell with the maximum temperature during device fabrication no higher than 150°C and a power conversion efficiency of more than 15.6% has been reported by Wang *et al.* (2014) opening up the possibility of fabrication on flexible substrates and large volume production processes as in printing. However, issues of device stability and presence of lead in the device will have to be addressed in the coming years. Whether this technology will overshadow all other technologies is too early to tell, but the rapid progress and promise this technology is showing through published results in less than five years indicates that perovskite solar cells may have an important role to play in PV power generation in the coming years (Green *et al.*, 2014).

There are a number of other material systems and device structures that are being explored for solar cell application such as cuprous oxide, pyrite, quantum dot solar cells, etc. Unless some major breakthroughs are achieved in future, the above discussed technologies will be the pertinent players for power

generation and we have restricted the discussion to those.

Government Initiatives

Internationally, it is seen in the last one and half decades that government initiatives have helped propel PV power generation to centre stage – the prime example being that of Germany. Even with poor sunshine as compared to many other countries across the world, it has become the leading consumer of PV technology. This has been possible because of well-thought out government initiatives and subsidies to promote PV for power generation. Recent reports indicate that in July 2013, 5.1 TWh has been generated from PV which exceeds the energy generated from wind (5 TWh). Germany is well on its way to generate more than 80% of its power from renewable sources, including PV (<http://thinkprogress.org/climate/2013/08/22/2508191/germany-solar-generation-record/>).

Governments in most European countries and the Far East too have been promoting power generation from renewables, including PV. The Chinese government has provided immense push and subsidies to make the country the leader in PV manufacturing today. In the USA, in recent years, the federal government has been promoting research, development and production of renewable technologies including PV through the SunShot Initiative (<http://www1.eere.energy.gov/solar/sunshot/>). Various states in the USA such as California have already been in the forefront of promoting power generation with PV resulting in widespread adoption of the technology. Almost all developed and industrial countries are giving importance to using PV for power generation to varying degrees.

The Government of India too has implemented a clear “National Action Plan on Climate Change”. within this “National Action Plan”, eight “National Missions” have been identified. One of the national missions is the “National Solar Mission” which was formally launched on 11 January 2010. This mission clearly provides a quantitative and qualitative target that the nation needs to achieve (see Box 1). One of the goals is deployment of 20 GW of solar power by 2022. Another goal is to deploy 20 million solar lighting

Box 1. Mission targets as specified in the National Solar Mission

(Announced on 23/11/2009; Launched 11/1/2010)

- To create an enabling policy framework for the deployment of 20,000 MW of solar power by 2022.
- To ramp up capacity of grid-connected solar power generation to 1000 MW within three years – by 2013; an additional 3000 MW by 2017 through the mandatory use of the renewable purchase obligation by utilities backed with a preferential tariff. This capacity can be more than doubled – reaching 10,000 MW installed power by 2017 or more, based on the enhanced and enabled international finance and technology transfer. The ambitious target for 2022 of 20,000 MW or more, will be dependent on the “learning” of the first two phases, which if successful, could lead to conditions of grid-competitive solar power. The transition could be appropriately up-scaled, based on availability of international finance and technology.
- To create favourable conditions for solar manufacturing capability, particularly solar thermal for indigenous production and market coordinatorship.
- To promote programmes for off-grid applications, reaching 1000 MW by 2017 and 2000 MW by 2022.
 - To achieve 15 million sq. metres solar thermal collector area by 2017 and 20 million by 2022.
 - To deploy 20 million solar lighting systems for rural areas by 2022.

systems for rural areas by 2022. These goals and directions have given a shot in the arm to solar PV research, development, manufacturing and deployment. Much effort is required if the targets are to be reached and the country has to withstand, and if needed overcome, any adverse effects of international economic forces.

The MNRE mainly responsible for promoting PV in India has rolled out many programmes to promote PV activities in line with the National Solar Mission (<http://www.mnre.gov.in/solar-mission/jnnsn/introduction-2/>). Similarly, Department of Science and Technology (DST) has also given the research an impetus with its Solar Energy Research Initiative (SERI) under which many research programmes across the country as well as international collaborations are supported (<http://www.dst.gov.in/scientific-programme/t-d-solar-energy.htm>). Many other ministries and government departments including Ministry of Rural Development, Ministry of Power and Ministry of Communication Information

Technology (especially, DeitY – Department of Electronics and Information Technology) have also promoted PV activities through various existing projects where it is appropriate. The policies of the Indian government and intent of the various ministries have been conducive in the promotion of PV technology for power generation.

One major initiative in India is worth mentioning here. As announced by the Press Information Bureau of Government of India, Ministry of Science & Technology on 29 August 2013: “CSIR’s Solar Energy Initiative – Technologies and Products for Solar Energy Utilization through Networks (TAPSUN) has been conceptualized as a mega programme in partnership with Ministry of New and Renewable Energy. It is being implemented with a number of complementary approaches. The programme has created network of research institutes, academia and industry with an objective to integrate various components of technology development. The programme will play a transformational role in bringing

the benefits of solar energy to the people of India.” Promotion of PV for power generation is an integral part of the TAPSUN programme and has been shaping up as per plan in the last two and half years.

Implementation of Solar PV in India

The promotion of PV for power generation needs to be undertaken over short, medium and long terms. Ideas that emerged during various meetings and discussions with experts working in the field are compiled here.

Short-term (Three-year Time Frame) Goals

- (i) Emphasis should be given to the use and deployment of crystalline silicon solar modules which are time tested and reliable.
- (ii) Identify areas of chronic power shortage and deploy small and medium PV systems in those areas. The economy in many urban and sub-urban pockets is driven by the polluting diesel-powered generators and the power available is costly when compared to equivalent PV power cost – and hence, the effort should be economically viable as well. With the right economic packages, government has to undertake this on a war footing.
- (iii) The government should hasten to implement clearly defined policies and legal protection to promote BIPV. With proper incentives in place and smoother implementation, the building owner will ensure proper maintenance and running of the facility.
- (iv) Encourage and provide incentives to all industries to set up auxiliary PV systems to supplement power from the grid.
- (v) Encourage PV deployment on government buildings, roads, bus-stops, shelters and other such places already being used by humans. In some states such as Gujarat, canal carrying irrigation water are covered with PV panels, as a result of which the space is maximized, cells are kept cool and water loss due to evaporation is minimized.

- (vi) Encourage researchers and industry to develop a robust power electronic system specific to the Indian grid and local conditions.

Medium-term (Three to Eight Year Time Frame) Goals

- (i) Set up foundries for the manufacture of solar grade silicon wafers. Build fabrication plants for silicon solar cells. In the short run, there is bound to be competition and loss due to the efficient and well-established Chinese solar industry. However, as India's power needs soar, indigenous systems can play a critical role if they are ready ahead of time.
- (ii) Invest in batteries and thermal storage for medium-term storage and fuel cells and hydel storage for long-term storage. Some form of long-term storage is imperative to make solar power attractive for year-round operations and to withstand the vagaries of weather conditions. Hydel storage might be possible in regions near high mountainous locations. PV in conjunction with other renewables such as biofuels and solar thermal should be promoted.
- (iii) Build reliable database and models to be able to predict weather for shorter time intervals, but as far in advance as possible. This will be critical to be able to use PV for power generation, especially if the generated power is directly fed to the grid.
- (iv) Encourage with contests and other incentives, innovations and development of consumer products which have application unique to Indian conditions.
- (v) Train manpower through existing and new institutions. The National Centre for Photovoltaic Research and Education at IIT Bombay is a good example of such an effort. More such centres around the country should be established.

Long-term (Beyond Eight Years) Goals

- (i) Encourage initiatives with long-term and challenging research goals in silicon and other

areas of PV technologies that will encourage competitiveness in manufacture in the coming decades

- (ii) Use hybrid systems with renewable technologies – solar, thermal, wind, biomass, etc. – to ensure stable power supply, synergizing the strengths of the different technologies and mitigating their disadvantages.
- (iii) Actively promote research in futuristic technologies with good environmental benefits such as OSC, DSSC and Perovskite solar cells and make India a powerhouse of these technologies. These technologies might be able to mitigate any potential environmental harm arising out of large-scale manufacture and use of PV cells and modules. They will also help create production methods that are distributed leading to more sustainable economic development.

Conclusions

Energy needs are only going to increase in the coming decades. For countries such as India, the future

energy requirements in 50 years will be much more than the current requirement. Thus, sustainable energy harvesting with PV is not just attractive, but is inevitable. There are many PV technologies available today. In the short run, silicon-based technologies are the best bet. However, in the coming decades, more attractive eco-friendly technologies with the promise of shorter energy payback time such as OSC and DSSC need to be explored. The Indian government departments, government labs, academia and the industry need to come together and continue to propel PV as one of the main means of power generation.

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I thank my colleagues and mentors with whom I received a chance to learn about PV technologies in various forums in the last decade. Much of what I have described above is a result of that learning. I especially thank Collin Wolden for the discussions when he was in India. His review article (Wolden *et al.*, 2011) is an excellent supplement for those who want to learn more about the current status of PV technologies.

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Review Article**Materials Research and Opportunities in Solar (Photovoltaic) Cells**

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The progress of solar (photovoltaic) cells over the years is reported here. The selection and engineering of materials that have been used in the first to the fourth generation solar cells present salient features on why such newer materials were or would be introduced are discussed. Our perspectives to look beyond silicon as solar cell materials are presented. The issues of toxicity and earth-abundance of elements in forming active materials of solar cells are discussed. Measurement parameters, methods to improve performance, and mechanism of operation of different solar cells have also been discussed.

Keywords: Solar Cells; Photovoltaic Devices; New Materials for Solar Cells

Introduction: Use of Solar Energy

It is now well-documented that several factors such as increasing energy needs, rapid decrease in energy sources from fossil fuels, and urgent requirement to protect the environment for the future generations, prompted the search for green and renewable energy sources more than ever. At the moment, almost 80% of world's energy supplies come from burning of fossil fuels. Apart from their limited reserve that would last for another couple of decades, use of these resources has been a major cause behind degradation of the environment such as global warming, acid rains, increase in carbon dioxide content in the environment, smog, etc. that affect all kinds of habitats cutting across borders and boundaries of countries and continents. Green energy resources such as solar, wind and tidal, and hydropower offer a supplement to the fossil fuels so that the usage of conventional source of energy can be restricted. All these renewable, nonconventional, and green resources of energy produce little or no pollution or greenhouse gases and also, more importantly, have unlimited resources. With the urgency to use such green energy resource, it is important that researchers tap all possible sources of

renewable energy. While each form of energy source is relevant and applicable to a geographical location or so, every quantum of such green energy will be beneficial to cater energy requirement of the future.

Among the green energy resources, sunlight is the most abundant, renewable, and readily available source. Another primary advantage of this source of energy is that it can be exploited even in remote areas, where supply of electricity is limited for various reasons. While both thermal and photonic components of solar spectrum could in principle be converted to electricity, photovoltaic (PV) solar cells were considered for immediate use since they were being successfully used in spacecraft for many years that studied terrestrial science. At present, photovoltaic solar cells are of relevance due to their rapid growth amounting to a total global capacity of 67,400 megawatts (MW) at the end of 2011 that represents 0.5% of worldwide electricity supply (<http://www.epia.org/home/>). The foremost challenge for large-scale commercial applications of photovoltaic solar cells is their high manufacturing cost. The solar panels are based on mostly monocrystalline, polycrystalline, or amorphous silicon, cadmium

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telluride, and copper indium gallium selenide/sulphide. Processing of active materials in the solar cells requires expensive instruments leading to an increase in the manufacturing cost. The fast growth of the PV market is sustainable if the manufacturing cost could be reduced to compete with the cost per watt (or \$/W) that the conventional mode of power generation offers. It is hence appropriate to look for newer materials which may lower the manufacturing cost reducing the \$/W of the solar cells. Another route to reduce the \$/W has been to improve the power conversion efficiency (PCE), i.e., the percentage of light energy getting converted to electrical energy, of a photovoltaic device with a proper choice of material(s). Different technologies have been developed to achieve a balance between the manufacturing cost of PV solar cells and their efficiency to compete with the cost of electricity from fossil fuels.

Evolution of Solar (Photovoltaic) Cells

While the principle of solar cells in the form of photovoltaic effect was discovered by French physicist Becquerel in 1839, a practical photovoltaic cell was developed in 1954 at Bell Laboratories (Chapin *et al.*, 1954). They used a diffused silicon *pn*-junction as a solar cell that yielded an efficiency of 6%. Since then, the quest for new materials that would offer an improved efficiency continued. Most of the semiconductor materials that researchers targeted had a bandgap of 1.0 eV or more, so that visible range of solar spectrum is absorbed for conversion to electricity. Shockley and Queisser established that a single-junction solar cell could reach a maximum efficiency of 30% for an optimum band gap material (Shockley and Queisser, 1961). On the basis of the materials used, mechanism involved, fabrication method, and the manufacturing cost of solar cells, researchers have categorized the generation of solar cells.

First Generation Solar Cells

The first generation solar cells are based on single crystalline and multicrystalline silicon. Crystalline silicon solar cells derived their name from the way they were made. The monocrystalline silicon solar cells are made from thin wafers that were cut from a

singular continuous crystal specially grown for this purpose. Polycrystalline silicon solar cells are made by melting the silicon material and pouring it into a mould. Since the discovery at Bell Laboratories, the crystalline silicon solar cell efficiency has reached up to 24% (Green *et al.*, 2005). The efficiency of single *pn*-junction crystalline silicon solar cells could reach up to the theoretically predicted limit of 30% (Shockley and Queisser, 1961). In India, much research has been carried out in this direction with microcrystalline and polycrystalline silicon (Ray *et al.*, 1988; Sastry *et al.*, 1985). At present, silicon solar cells cover roughly 86% of the PV market due to their relatively high conversion efficiency. The efficiency of commercial products in modules typically reach about 15-20% (<http://www.solarplaza.com/top10-crystalline-module-efficiency/>, 2012). The manufacturing techniques that are used to produce first generation solar cells are inherently expensive, resulting in years to pay back their purchasing cost.

Second Generation Solar Cells

In second generation solar cells, thin film technology has been used. These solar cells are thinner, flexible to some extent, and less expensive as compared to the first generation solar cells. The solar cells have a light-absorbing thickness of 10 μm as compared to 200-300 μm used for crystalline silicon solar cells. Semiconductor materials for the second generation solar cells ranged from amorphous and micromorphous silicon (Carlson and Wronski, 1976; Song and Anderson, 2000) to binary or quaternary semiconductors, such as cadmium telluride (CdTe) (Britt and Ferekides, 1993), gallium arsenide (GaAs) (Olson *et al.*, 1990) and copper indium gallium selenide (CIGS) (Sites and Liu, 1996). The use of direct band gap semiconductors, in contrast to indirect band gap silicon, lowered the cost of photoabsorbing materials since thinner-films of such semiconductors were enough to absorb sufficient amount of solar light for photoconversion. Thin-film solar cells based on such materials have shown signs of dominance in photovoltaic market covering 18% of the global photovoltaic market. This type of solar cells is stable and has been commercialized with a module efficiency of ~20%. Though the power conversion

efficiency of these solar cells is less than that of crystalline silicon solar cells, the second generation solar cells are expected to be cost-effective as compared to the cost of electricity generation from fossil fuels. A comprehensive review on this type of solar cells can be found in the literature (Green *et al.*, 2005). Unfortunately, there are still some unresolved issues in commercializing these solar cells in terms of production in mass quantities at a competitive price and at a reasonable efficiency level.

Third Generation Solar Cells

Organic semiconductors and conjugated polymers, with its success in light-emitting diodes and flat panel displays, are being considered as advanced materials for the third generation solar cells. Such solar cells, still at the laboratory level, are based on thin-films of the materials. With the difference in operation mechanism, organic/polymeric solar cells can be sub-classified into organic photovoltaic devices (OPV) and plastic (polymer) solar cells (Wohrle and Meissner, 1991; Peumans *et al.*, 2003; Yang *et al.*, 2005; Li *et al.*, 2005; Brabec *et al.*, 2001; Park *et al.*, 2009), photoelectrochemical solar cells (Keis *et al.*, 2002; Gratzel, 2001), and organic dye-sensitized solar cells (DSSC) (Oregon and Gratzel, 1991; Law *et al.*, 2005). Overall, the power conversion efficiency of DSSCs has reached more than 12% in the lab-scale (Yella *et al.*, 2011). Commercial applications of DSSCs may however be limited due to the liquid electrolyte used in the cells. In organic or polymeric PV devices, bulk-heterojunctions based on regioregular poly(3-hexylthiophene) (P₃HT) as a hole-transporting material and a fullerene derivative, namely phenyl-C61-butyric acid methyl ester (commonly known as PCBM), as an electron-transporting material are one of the most-studied systems (Li *et al.*, 2005; Scharber *et al.*, 2006). Recently, some low band gap polymers are being used to harvest near-IR spectrum of solar energy (Albrecht *et al.*, 2012; Peet *et al.*, 2007). In organic or polymeric solar cells, device operation involves photogeneration of excitons, exciton dissociation or charge separation, and carrier transport to the opposite electrodes. Some of the advantages of organic or polymeric PV devices are (1) films are spun from solutions, (2) fabrication of large-area

devices is possible, (3) the requirement and hence the cost of the materials is low, and (4) devices can be fabricated on flexible electrode substrates. The major disadvantage of this class of semiconductor is that the carrier mobility in these materials is often low hindering efficient flow of holes and electrons to the opposite electrode. Nonetheless, third generation solar cells are expected to enter the market soon.

Fourth Generation Solar Cells

Materials engineering being one of the fastest and rapidly growing fields of research, newer materials offer themselves as supplements or complements in device fabrication. A bright example in this direction is the inclusion of (inorganic) semiconducting quantum dots in organic/polymeric photovoltaic devices and dye-sensitized solar cells. Such devices, often termed as nanophotovoltaics, are considered to be the fourth generation solar cells and have a high prospect as a future of solar cell technology. Here, the advantages of semiconducting quantum dots have been brought to supplement performance of organic and polymeric solar cells. Some of the proven examples in this direction are quantum dot-sensitized solar cells (QDSSC) (Kamat, 2008; Nozik, 2002; Sun *et al.*, 2008), quantum dot-based thin film solar cells (Panthani *et al.*, 2008; Ip *et al.*, 2012), and hybrid bulk-heterojunction solar cells (Huynh *et al.*, 2002). Xu *et al.* have reported QDSSCs based on CdSe nanoparticles with an efficiency of 4.54% (Xu *et al.*, 2012). Sargent's research group has reported an efficiency of 7% in solar cells based on inorganic quantum dots (Ip *et al.*, 2012). Researchers across the globe are focusing on a range of materials and methods to fabricate devices in order to improve this emerging technology to achieve a proper balance between the manufacturing cost and the efficiency of solar cells.

Recently, a new type of solar cells based on organometal halide perovskite materials has attracted much attention due to high efficiency and stability. The efficiency of methylammonium lead halide perovskite sensitized solar cells reached 16.2% within a very short period of research and development (Kim *et al.*, 2012; Lee *et al.*, 2012; Burschka *et al.*, 2013;

Liu *et al.*, 2013). In Fig. 1, we have shown a bar diagram representing efficiencies of different types of solar cells. Some commonly used active materials in each type of solar cells are also mentioned. Fig. 1 shows that the efficiencies of photovoltaic devices based on the new materials are yet to match that of silicon solar cells. Researchers across the globe are still optimistic due to the rapid progress in the parameters of these higher-generation solar cells, in addition to low material production cost of such solar cells.

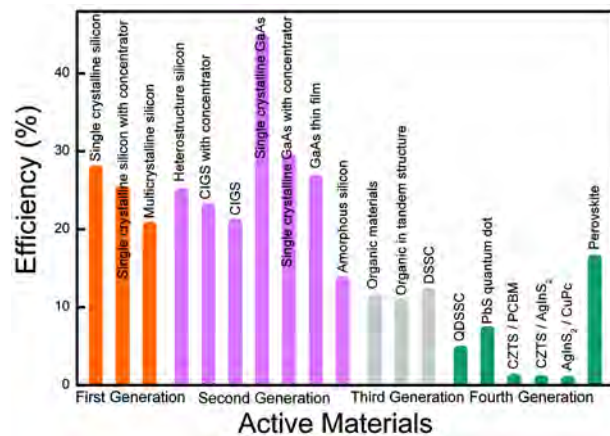


Fig. 1: Efficiency of different generations and types of solar cells along with some commonly used active materials in each type of solar cells. Data were obtained from Research Cell Efficiency Records, National Center for Photovoltaics (NCPV) at National Renewable Energy Laboratory (NREL), Golden, Colorado, USA (<http://www.nrel.gov/ncpv/>, 2014)

Parameters of Solar Cells

Open-circuit Voltage (V_{OC})

The photovoltage generated across the two terminals when the circuit remains open is known as the open-circuit voltage (V_{OC}). The difference in the quasi Fermi levels determines the V_{OC} of a solar cell. Generally, photoexcited electrons go through a thermalization process to lose their potential energy to the phonons until the electrons reach the lowest energy level of the conduction band (in case of inorganic semiconductors) or the lowest unoccupied molecular orbital (LUMO, in case of organic semiconductors). Thus, the band gap of the

semiconductor is often regarded as a measure of achievable photovoltage. A higher band gap could result in a higher photovoltage. In the same context, a higher band gap material cannot absorb sufficient light in the visible region. There should hence be an optimum band gap for an efficient performance of photovoltaic devices under a white light illumination. Shockley and Queisser calculated the optimum band gap for maximum power conversion efficiency assuming only radiative recombination under solar radiation (Shockley and Queisser, 1961). They obtained a power conversion efficiency of 30% for a semiconductor with a band gap of 1.12 eV. Interestingly, the value matches quite well with the band gap of silicon.

Short-circuit Current (J_{SC})

When the cell is short-circuited, the current which flows through the external circuit is known as the short-circuit current (I_{SC}). To achieve a high value of I_{SC} , we should have an active material of high optical absorption coefficient along with high carrier mobility. The I_{SC} of a solar cell also depends on the incident light intensity and the cell area. It is hence effective to calculate short-circuit current density (J_{SC}) under a given solar illumination to compare short-circuit current of different devices based on a range of materials.

Fill Factor (FF)

Since the I - V characteristics of a solar cell under illumination condition passes through the fourth quadrant, the power, which is a product of the voltage and the current, in this quadrant is negative implying that one would be able to draw power from the device. In Fig. 2, the current-voltage characteristics of a typical solar cell under dark and under certain illumination have been shown. In the I - V characteristics, we can obtain a point in the fourth quadrant that corresponds to maximum power achievable (P_{Max}), that is, product of the voltage and the current is highest at this point. The point is called as the maximum power point for which there are maximum voltage (V_{Max}) and maximum current (I_{Max}). The shape of the I - V curve in the fourth quadrant is very crucial to maximize the product at the maximum

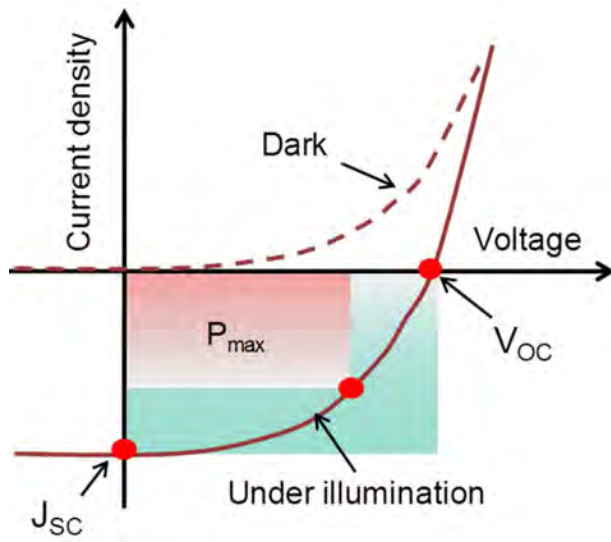


Fig. 2: Current density versus voltage (J - V) characteristics of a typical solar cell under dark (dashed line) and illumination (solid line) conditions. Parameters of solar cells such as the open-circuit voltage (V_{OC}), the short-circuit current density J_{SC} , and the maximum power point P_{Max} are shown on the J - V curve

power point. This maximum area is higher when the I - V curve resembles a rectangle with sides of V_{OC} and J_{SC} . The ratio between these two areas is known as the fill factor (FF) which represents a measure of the shape of I - V characteristics in the fourth quadrant, that is, the fill factor is defined as:

$$FF = \frac{I_{max} \times V_{max}}{I_{SC} \times V_{OC}} \quad (1)$$

Using this fill factor, power conversion efficiency (PCE) of a solar cell can be defined as :

$$\begin{aligned} PCE(\eta) &= \frac{P_{max}}{P_{in}} \times 100 = \frac{I_{max} \times V_{max}}{P_{in}} \times 100 \\ &= \frac{I_{SC} \times V_{OC} \times FF}{P_{in}} \times 100, \end{aligned} \quad (2)$$

where P_{in} is the incident light power. Since the power conversion efficiency (η) depends on the incident wavelength and intensity, η is measured under a simulated solar spectrum. In order to compare the

efficiencies of different solar cells, a standard solar irradiance is considered. The most common standard irradiance is AM1.5 (air mass 1.5 ~ 1 Sun) and this standard illumination ($\sim 100 \text{ mW/cm}^2$) can be achieved by most commercial solar simulators. The physical principles behind the operation of different types of solar cells are generally different. The current-voltage characteristics of well-performing cells are however similar and can be characterized and compared with each other in terms of FF , V_{OC} , and I_{SC} .

Power Conversion Efficiency

Power conversion efficiency (PCE) is the most important parameter of solar cells. It is defined as the percentage of maximum output of electrical power to the incident optical power. The generated output electrical power is the product of the generated photovoltage and the photocurrent. Therefore, in order to achieve a high PCE, one should have a high photovoltage as well as a high photocurrent under an illuminated condition.

Thin-film (Photovoltaic) Solar Cells: Device Architecture

The basic components of thin-film solar cells are an active layer and a pair of electrodes. The active layer may comprise one or several materials. The active layer absorbs sunlight; the two electrodes which have in general dissimilar work-functions collect carriers to yield photocurrent in the external circuit. The electrodes should form ohmic contacts with the active layer that is next to the electrode so that the interfaces do not impose barriers for the charge carriers to reach the electrodes. Depending on the materials used in the active layer and the electrodes, several device architectures can be formed:

- Metal₁/Semiconductor/Metal₂ (Schottky junction)
- Metal₁/ p -type semiconductor/ n -type semiconductor/metal₂-based on the same semiconductor material (Homojunction)
- Metal₁/ p -type semiconductor/ n -type semiconductor/metal₂-based on two different semiconductor materials (Heterojunction)

- Metal₁/p-type semiconductor/insulator/n-type semiconductor/metal₂ (*p-i-n* junction)
- Junction₁-Junction₂-Junction₃ (tandem solar cells)

When a *p*-type semiconductor and an *n*-type semiconductor are brought in contact, electrons from the *n*-type semiconductor diffuse to the *p*-type semiconductor due to a concentration gradient of the carriers. Similarly, holes from the *p*-type material diffuse to the *n*-type semiconductor. During diffusion process, the carriers leave behind uncompensated immobile charges at the regions from where they diffused. Electrons leave donor ions (+) at the *n*-type region and holes leave acceptor ions (−) at the *p*-type region of the *pn*-junction. These immobile charges create an electric field that forms a potential barrier which finally opposes the carriers to diffuse further. The region across the junction where the electric field appears is termed as the depletion region.

Under illumination, electron-hole pairs (excitons) form in both sides of the junction. These photo-generated electron-hole pairs if diffused to the junction become dissociated due to the electric field at the junction. (In case of a single layer structure based on a bulk semiconducting material, the excitons can be dissociated just after the photogeneration). Now, the holes flow through the *p*-type material and electrons flow through the *n*-type material to the opposite direction. These separated electrons and holes form quasi fermi levels at both sides of the junction and the difference between these two quasi fermi levels is the origin of open-circuit voltage (V_{OC}) of the solar cells. When contacts are made in the external circuit, a short-circuit current (I_{SC}) flows through the circuit without any applied voltage. In Fig. 3, a schematic representation of a *pn*-junction, depletion region, band-bending, and the origin of V_{OC} have been depicted.

The operation mechanism of organic photovoltaic devices differs from that of inorganic semiconductor solar cells. In organic PV devices, the built-in electric field due to the electrodes acts only near the interfaces. Since the active region of an organic device consists of two materials, the interface between the materials provides the required energy-offset to

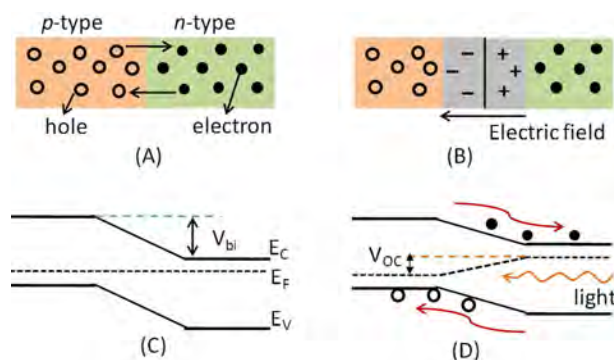


Fig. 3: Schematic representations of a *pn*-junction formation showing (A) diffusion of carriers under contact, (B) formation of a depletion region, (C) band-bending at the junction, and (D) movement of carriers under an illuminated condition and the origin of V_{OC}

dissociate excitons, that is, after photogeneration of excitons, they may diffuse to the donor-acceptor interface. If the difference in electron affinities or the difference in ionization potentials or the difference in both the levels of the donor and acceptor materials is higher than the exciton binding energy, the excitons in the organic PV devices become dissociated.

Thin-film (Photovoltaic) Solar Cells: Materials Engineering

As has been stated, device operation of organic or polymeric thin-film solar cells involves three steps, namely, (1) exciton generation due to illumination, (2) exciton dissociation or charge separation, and (3) carrier transport to the opposite electrodes. Since the three steps occur in a sequence, efforts have been made to enhance efficiency or output of each of the steps. Generation of excitons expectedly depends on matching of optical absorption spectrum of the active materials with the solar illumination. Active materials are hence chosen accordingly. Exciton dissociation or charge separation, which occurs at the interface between a donor and an acceptor layer, takes place due to the internal field that develops owing to the difference of energy levels at the interfaces. Carrier transport, the third step, is directed by the internal field generated by the difference in work-functions of the two electrodes. Apart from the electric-field, mobility of charge carriers plays a major role in determining the short-circuit current of photovoltaic

devices.

Considering the limitation of organic and polymeric materials in each of the steps of device operation, efforts have been made to incorporate quantum dots or nanostructures in photovoltaic devices. In other words, the fourth generation solar cells involving nanostructures in organic devices are meant to overcome the drawbacks of the third generation solar cells. In solar cells based on organic and inorganic semiconductors or hybrid materials, advantages of the both types of materials are clubbed together. Some of the advantages can be listed as follows:

- One of the major advantages of inorganic nanocrystals is their broad absorbance. Extinction coefficient of some nanocrystals is high ($\sim 10^4 \text{ cm}^{-1}$). Band gap of the nanocrystals can be tuned through quantum confinement to suit the need of photoabsorption in a wider spectral region.
- Wannier excitons in nanocrystals have a lower binding energy than Frenkel excitons that form inorganic molecules upon photoillumination. This is due to the fact that the electron and the hole of a Wannier exciton can reside in different molecules as opposed to Frenkel excitons, where the two carriers reside in the same molecule. Typical binding energy of excitons in inorganic quantum dots (diameter $\sim 2\text{-}4 \text{ nm}$) is in the range of 0.05 to 0.2 eV; whereas, Frenkel excitons in organic molecules have a binding energy of 0.1 to 1.0 eV.
- There is a possibility of formation of multiple excitons in nanocrystals from a single photon (Binks, 2011). The quantum mechanical origin of the process is still under debate.
- Mobility of both types of charges in inorganic nanocrystals is high.
- Most of the quantum dots are very stable under ambient condition.

Fabrication of organic solar cells with inorganic nanomaterials could leap the research on solar cells a

step forward. In general, some conjugated polymers are used as a hole-transporting material (*p*-type) and inorganic nanostructures are used as an electron-transporting material (*n*-type) or vice versa. The first hybrid solar with sufficient efficiency was reported by Huynh *et al.* (Huynh *et al.*, 2002). Since then several studies have been reported based on different inorganic nanocrystals such as CdS, CdSe, CdTe, ZnO, SnO₂, TiO₂, Si, PbS, PbSe, etc. (Cui *et al.*, 2006; Hines and Scholes, 2003; Holder *et al.*, 2008; Kuo *et al.*, 2008; Kuwabara *et al.*, 2009; Lutich *et al.*, 2009). Dayal *et al.* have reported a hybrid solar cell with an efficiency of 3.2% under AM 1.5 irradiation using a low band gap polymer and CdSe nanoparticles (Dayal *et al.*, 2009). One of the disadvantages that the inorganic nanocrystals imposes in photovoltaic devices is that the insulating capping ligands that are necessary to form dispersed solution or ink of the nanocrystals hinder inter-nanocrystal carrier transport.

International Status: Research to Technology

Country-wise, Taiwan, Germany, China, and USA are the market leaders of this technology. During 2013, with a most likely forecasting scenario, 25 different countries are projected to have >100 MW of PV demands. India seems to be catching up with a seventh rank (projected for 2013) worldwide.

The solar modules that are commercially available are generally based on crystalline Si, amorphous-Si, CdTe and CIGS materials. Some of the leading companies in this field are Yingli Green, First Solar, Suntech Power Co., SunPower, and so on. Konarka and Mitsubishi have been manufacturing solar modules based on organic photovoltaic devices. In the competing global solar markets, cost reduction and increasing cell efficiencies are the key factors to the module manufacturers to sustain their business or to drive the business to the next level.

Different companies have been trying to increase the ultimate output wattage by engineering the installation procedure of solar panels. Instead of simply collecting the solar light which is just shining the surface of a solar panel, a new technology has been developed with an addition of optical equipment such as lenses and mirrors to focus greater amounts

of solar energy onto highly efficient solar cells (concentrated solar power, CSP). Although this technique could hike the manufacturing cost slightly, the advantages of CSP over conventional solar panel setups offer a high throughput for further research and development technologies. There are also some upcoming technologies to develop new architectures for solar cell installation. The basic mechanism behind such a technology is that the solar panels keep moving with the sun to acquire extra solar light. Genie Lens Technologies has developed a new route to enhance light absorption of solar panels. A large polymeric transparent sticker is applied to the front of the panels. Microstructures on the polymer stickers are capable of bending and redirecting the sunlight which increases the power output by about 10% and more.

Manufacturers of other household products are also tapping solar energy in their product. To name a few, automobiles, roofs and facades of buildings, portable electronics, etc. will soon be decorated with solar cells not only to make the products attractive to consumers, but also contribute to renewable energy production in one's own household.

Research Directions Across the World

The basic aim behind the progressing technology is to make a balance between the manufacturing cost and the module efficiency. As we know, silicon solar cells require a surface coating that increases the cost of the modules. Tonio Buonassisi and his group at MIT developed an alternative in the form of a polymer layer on silicon solar cells that sustained more than 200 h of continuous operation without any degradation.

Stretchability, in addition to flexibility of polymers has brought a new dimension in the organic solar cell technology. Such a property of polymers would integrate them in textiles, moving parts of machinery, one-time bonding to curved surfaces such the exteriors of buildings, automobiles, and many others.

Scientists from the Swiss Federal Laboratories for Materials Science and Technology have developed thin film solar cells on flexible polymer foils with an efficiency of 20.4%. They used copper indium gallium (di)selenide (CIGS) semiconducting material for the

solar cell fabrication. It appears that CIGS has a large potential to provide cost-effective solar panels. The technology is currently awaiting scaling-up for commercial production.

These are more examples of new research directions to improve the efficiency of solar cell modules. Some of the techniques are almost ready for commercial production. In the laboratory scale, much research focuses on new materials and manufacturing processes. Recently, use of earth-abundant elements is gaining interest so that the cost of materials becomes low.

Major Contributions from Indian Researchers and Industries

Maharishi Solar Technology Pvt. Ltd., New Delhi, one of the oldest players in the market, has been manufacturing solar cells based on polycrystalline silicon material. Researchers at IIT Bombay, in National Centre for Photovoltaic Research and Education (NCPRE), have achieved 20-22% efficiency in single crystal silicon solar cells. The Solar Energy Centre (SEC), a unit of the Ministry of New and Renewable Energy, is providing technical assistance to industries for the development of solar energy products. Moser Baer, in collaboration with CSIR-NPL, New Delhi has developed CIGS-based solar cells with an efficiency of 12-15%. In the arena of dye-sensitized solar cells (DSSCs), IIT Kanpur, CSIR-IICT Hyderabad, and IIT Delhi are working to achieve 6-10% efficiency.

Thin-film (Photovoltaic) Solar Cells: Our Approach

Hybrid Core-shell Nanoparticles

Photoinduced electron transfer from a semiconducting quantum dot to another quantum dot (Tu and Kelley, 2006) or to certain organic molecules has been reported to be ultrafast (Boulesbaa *et al.*, 2007). We aimed to take the advantage of this ultrafast electron-transfer process in fabricating photovoltaic devices, that is, our target was to make use of the electron-transfer process so that exciton dissociation may occur at each and every quantum dot. To do so, we

introduced some hybrid core-shell nanocrystals with an inorganic nanocrystal in the core and a layer of organic molecules as a shell layer. Upon photo-illumination, a photoinduced electron-transfer process was expected to occur from the inorganic core to an organic molecule on the shell resulting in exciton dissociation. With the hybrid core-shell nanocrystals in a hole-transporting polymer matrix, it is expected to have movement of electrons and holes towards the opposite electrodes that have different work-functions. In this way, we aim to convert the ultrafast photoinduced electron-transfer process into short-circuit current in the external circuit for efficient hybrid photovoltaic solar cells. Here, we choose the shell molecules in such a way that they formed a homogeneous interface with the host polymer. Moreover, the organic molecules formed type-II band-alignment or a staggered gap with the quantum dots, so that electron-transfer process becomes efficient. In other words, the semiconducting quantum dots decorated with suitable organic molecules can be considered as novel hybrid materials for efficient solar energy harvester (Guchhait and Pal, 2010; Guchhait *et al.*, 2009). A schematic representation of hybrid core-shell formation has been shown in Fig. 4A. While formation of hybrid core-shell structures was studied through optical absorption spectroscopy (Fig. 4B), photoinduced electron-transfer from the core to the shell was manifested by quenching of photoluminescence emission of the nanocrystals (Fig. 4C). The electro-transfer process upon formation of the organic shell layer was further supported by a sharp decrease in photoluminescence lifetime measured through time-correlated single photon counting (TCSPC) measurements spectroscopy.

Fig. 5A depicts a schematic representation of the device structure. Fig. 5B shows the results from a device where only CdSe nanoparticles were used. Results from the device based on hybrid core-shell nanoparticles are shown in Fig. 5C. In both the cases, we have added *I-V* characteristics under dark condition that were rectifying in nature. From the results under white light illumination, we find that with the use of hybrid core-shell nanoparticles, the device performance improved to a large extent. The short-circuit current of the latter device increased by 10

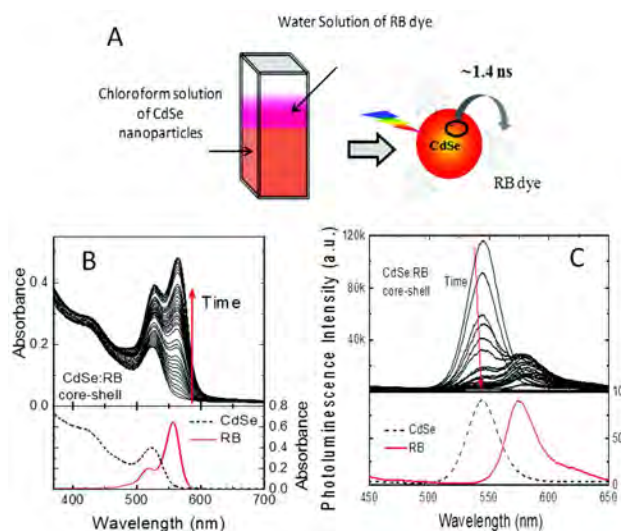


Fig. 4: A: Schematic presentation of hybrid core-shell formation, B: absorbance spectra of hybrid core-shell nanoparticles and C: photoluminescence spectra of the hybrid core-shell nanoparticles. In (B) and (C), red arrows indicate time evolution. Source: Guchhait *et al.* (2009)

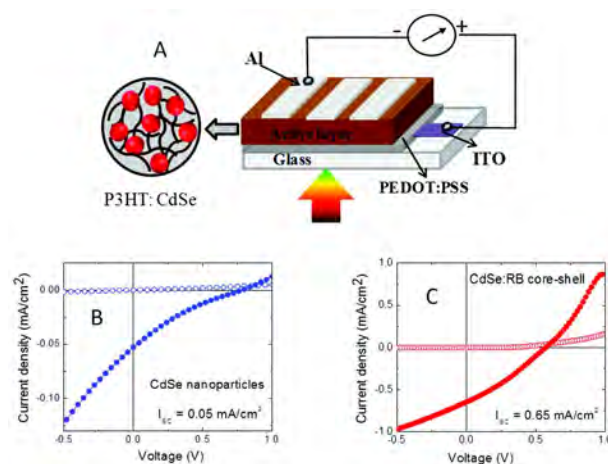


Fig. 5: A: Schematic presentation of a bulk heterojunction device. Current-voltage characteristics of a device based on B: only CdSe nanoparticles and C: CdSe-RB hybrid-core shell nanoparticles in P₃HT matrix under dark and white light illumination conditions. Source: Guchhait *et al.*, 2009

times as compared to that for the device with only CdSe nanoparticles.

We also observed that the rate of photoinduced electron-transfer process depends on the amount of dye present on the nanoparticle surface as well as on

the electron-accepting nature of the dye molecules. The rate of photoinduced electron-transfer process has been found to depend on the electron-accepting nature of the organic dye molecules in the shell layer. The device performance accordingly depended on the electron-transfer process. A one-to-one correspondence has been observed between the efficiency of the photovoltaic devices and the electron-accepting nature of the organic dye molecule (or decrease in lifetime of photoluminescence emission) of hybrid core-shell nanocrystals.

From the discussion, we could infer that introduction of hybrid core-shell nanoparticles in photovoltaic devices facilitates the use of inorganic nanoparticles in solar cell applications. Recently, researchers have introduced a range of hybrid nanocomposites in this direction. For example, Chang *et al.* have reported CdTe/SWNT nanostructures; photoinduced current in such nanostructures could be tuned by tailoring the nature of the semiconductor, morphology, and diameter of the CdTe nanostructures (Chang *et al.*, 2013). Mariani *et al.* have reported three-dimensional core-shell nanostructure for solar cell applications by using air-stable poly(3,4-ethylenedioxythiophene) (PEDOT) as a shell to periodic GaAs nanopillar arrays (Mariani *et al.*, 2012).

Organic/inorganic Hybrid *pn*-junctions

In the field of photovoltaic solar cells, researchers also search for environment-friendly or nontoxic elements with earth-abundance in fabricating high-efficient devices. The paths to achieve such a goal are not always unique, that is, a high-efficient device may often contain toxic elements, or green materials may not always return best solar cell parameters. Moreover, easiness of film-formation process should also be considered while choosing materials for fabricating solar cells. Finally, the mechanism of device-operation has remained worth-studying so that directions to improve device-performance can always be sought.

In such a complex scenario, new materials often bring fresh hopes. Earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) emerged as a promising absorber for thin-film solar cells (Shin *et al.*, 2013). CZTS is a quaternary kesterite

semiconductor with a direct band gap (~ 1.5 eV) and a large absorption coefficient ($\sim 10^4$ cm^{-1}). Thin-films of CZTS can be formed through various approaches. IBM Research (Yorktown, New York, USA) has already achieved the PCE of 11.1% in CZTS thin-film solar photovoltaic cells. The company also believes that these cells can be manufactured using ink-based techniques including printing or casting (<http://www.solarserver.com>, 2012). In the lab scale, thin films of *p*-type CZTS have generally been used in conjunction with a layer of *n*-type semiconductors such as CdS to fabricate *pn*-junction solar cells (Tanaka *et al.*, 2009). Recently, we have formed a *pn*-junction between a *p*-type CZTS layer and a fullerene derivative as the *n*-type material so that a solution-processed solar cell can be fabricated with materials based on earth-abundant and nontoxic elements that are more-importantly cadmium-free (Saha *et al.*, 2012). The junction can be termed as a hybrid *pn*-junction between layers of an inorganic semiconductor and an organic semiconductor. Here, we report characterization of CZTS/fullerene hybrid junctions under dark and illumination conditions evidencing solar cell applications to comment on the depletion region formed in *pn*-junction solar cells.

We have characterized the *pn*-junction devices based on CZTS nanoparticles and PCBM molecules. Schematic presentation of a *pn*-junction device structure and the equilibrium band-bending of the junction are shown in Fig. 6A&B, respectively. During the deposition of CZTS film, we have replaced the long-chain oleylamine ligands with short-chain pyridine by the layer-by-layer technique. This facilitated carrier transport through the CZTS nanoparticle film. In Fig. 6C&D, we have presented some results based on CZTS/PCBM junctions. In these ITO/CZTS/PCBM/Ca/Al devices under an illumination condition, excitons were photogenerated in both CZTS and PCBM layers. The excitons, which were generated within the depletion region at the CZTS/PCBM interface, would become easily dissociated into free carriers; the excitons, which are generated within the quasi-neutral region, might diffuse to the junction and become dissociated. Finally, the electrons move through the PCBM layer to the Ca/Al electrode and holes move through the CZTS layer to the ITO

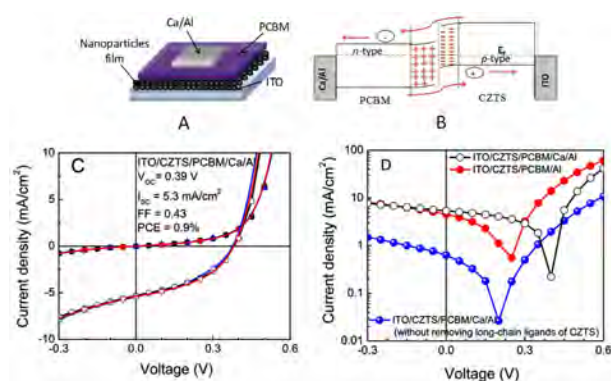


Fig. 6: A: Schematic presentation of a bilayer *pn*-junction device, B: energy band-bending of the junction under an equilibrium condition, C: current-voltage characteristics of the ITO/CZTS/PCBM/Ca/Al *pn*-junction device under dark and illumination conditions and D: characteristics under light of different devices as specified in the legend. Source: Saha *et al.* (2012)

electrode and yield photocurrent in the external circuit.

From C-V characteristics, we have determined the width of the depletion region and the density of carriers at the junction. A depleted and wider depletion-region has been observed in the CZTS/PCBM *pn*-junction as compared to those in Schottky devices. The results evidenced solar cell applications from nontoxic and earth-abundant materials forming hybrid *pn*-junctions.

pn-Junction Solar Cells Based on Inorganic Nanocrystals

Solar cells can also be fabricated on basis of only inorganic nanocrystals, so that issues related to degradation of organic semiconductors do not arise. In this direction, we grew solar cells based on a layer of *p*-type nanocrystals and another layer of *n*-type nanocrystals to form a *pn*-junction. In such a junction under an illumination condition, separation of charge carriers occurs due to a drift of minority carriers through the depletion region. We hence formed a fully-depleted *pn*-junctions so that additional materials near the electrodes (“dead zones”) could be eliminated that would otherwise have increased the internal resistance of the solar cells without contributing to any photovoltaic response (Dasgupta *et al.*, 2014). In Fig.

7, we show that a fully-depleted device yields an improved solar cell performance as compared to thicker *pn*-junction devices comprising “dead zones”. Schematic representations of equilibrium band-bending of CZTS/AgInS₂@Cu *pn*-junction device structure and the fully depleted *pn*-junction are also shown.

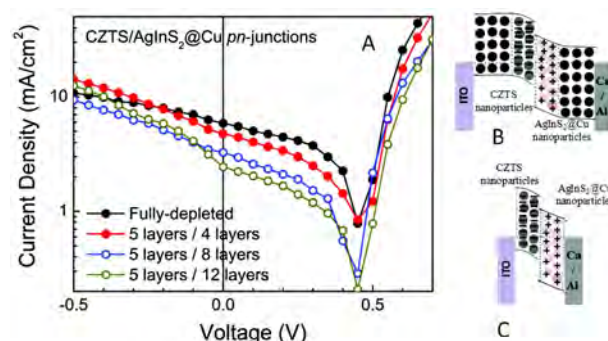


Fig. 7: Current-voltage characteristics of a fully-depleted and three other CZTS/AgInS₂@Cu *pn*-junctions under an illumination condition. Schematic representations of a conventional *pn*-junction and a fully-depleted *pn*-junction solar cell are also shown. Source: Dasgupta *et al.* (2014)

Future Avenues

As we must explore each and every form of renewable energy source, we must also continue to improve manufacturing/development of all types of solar cells. For the first generation solar cells, instead of aiming to improve efficiencies that may have reached saturation, reduction of the manufacturing-cost should be the goal. For the second generation solar cells, an improvement in efficiency would be beneficial to reduce the \$/W value so that supply to the grid becomes economical. For the third and fourth generation solar cells, selection of suitable materials through materials engineering and at the same time simplifying the fabrication process of large-area solar cells are the two major directions that researchers should work in tandem.

As in other devices, the missing link between the lab and the plant has to be bridged. When a critical mass of researchers starts to work in this fascinating field, we will be able to comply with the societal aspect of research by making the renewable source of electricity a reality.

Conclusions

In conclusion, we have reviewed the evolution of solar (photovoltaic) cells based on a series of materials over the years. Solar cell materials ranging from crystalline silicon to most-recent inorganic quantum dot vs. organic hybrid systems for nanophotovoltaics have been discussed. We have shown how newer materials and materials engineering have allowed researchers to look beyond silicon as material for the future of solar cell technology. The importance of using earth-

abundant elements in choosing active materials for solar cells has been discussed to reduce the cost/Watt of electricity. Also, the need for using non-toxic elements in the selection of the active materials has been discussed in order to achieve environment-friendly and industrially viable solar cells for the future.

Acknowledgements

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Review Article

Solar Thermal Power Sector

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Solar power will play a significant role in India's future energy mix. In addition to be able to provide process heat, concentrated solar power (CSP) plays a unique role in India's energy production because of its potential to use hybrid technologies with biomass or fossil fuels. Thermal energy storage is another aspect of solar thermal technology which helps provide dispatchable and base-load power. The low pressure steam available at the outlet of the power turbine can be utilized for other processes such as air-conditioning and thermal desalination. At high temperatures that can be brought about by concentrating solar thermal technology, hydrogen gas can be produced which serves as a clean fuel. Despite many advantages, much more needs to be done to scale-up CSP sustainably. Innovation and indigenization can address some of the barriers that pose challenges for the development of CSP market in India.

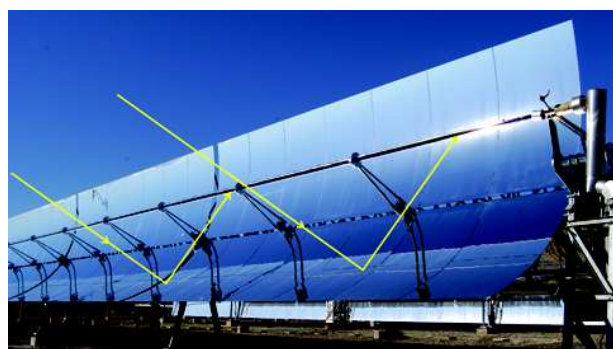
Keywords: Solar Thermal Power; CSP Performance; CSP Technology Improvements and Challenges; CSP Market in India; Solar Thermal Desalination

Introduction

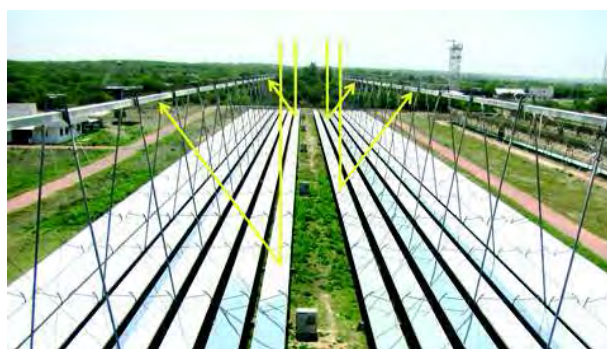
Concentrated solar thermal power (CSP) technologies have the potential to meet various forms of our energy needs on par with conventional fossil fuel and nuclear power technologies. By suitably selecting the concentration level, we can meet various process parameters required to carry out simple room heating/cooling, power generation, and high temperature material and chemical processing in an environment-friendly and sustainable manner. Owing to its wide range of applications, CSP technology offers a useful solution to global warming and steadily increasing demand for fossil fuels. Unlike solar photovoltaic (PV) technologies, CSP technology has an inherent capacity to store energy in the form of heat energy (International Energy Agency, 2010). CSP has the ability to provide transportable fuel and reliable electricity generation that can be dispatched to the grid even round the clock to meet the demand.

Generation of electricity using various CSP technologies employing conventional power cycle has significant potential in the global energy mix. Owing to the common power cycle, CSP technology can be easily integrated with conventional fossil fuel or biomass based power plants. At present, based on the type of concentration optics and temperature requirements, the four main CSP technologies shown in Fig. 1, are widely employed to generate power and process heat. The possibility of using CSP technologies to produce concentrating solar fuels (CSF) is an important area for further research and development. Solar-generated hydrogen can help to decarbonize the transport and other sectors by mixing hydrogen with natural gas, and by producing cleaner liquid fuels (Chu Yinghao, 2011). Collectively, these characteristics make CSP a promising technology to meet our future energy needs in a greener and cleaner manner.

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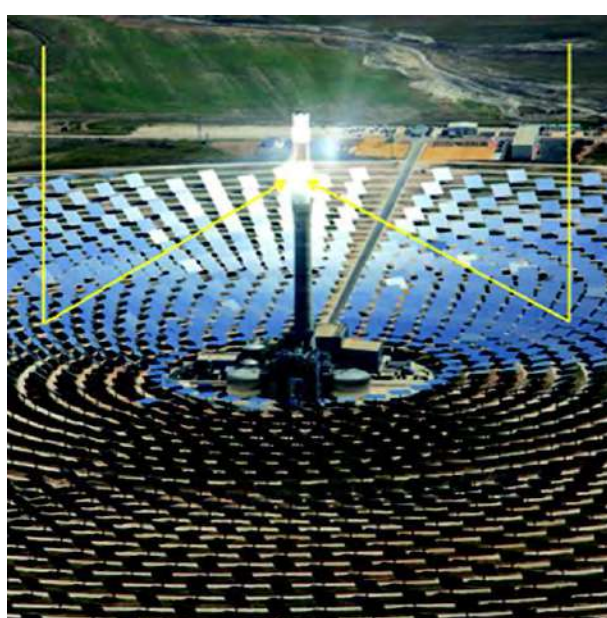
A : Parabolic trough, DLR, AG



B : Linear Fresnel, Empereal-KGDS Renewable Energy Pvt. Ltd.



C: Dish Stirling system. Maricopa Solar Plant, SunCatcher



D: Solar tower, Gemasolar, Spain

Fig. 1: Four main CSP technologies

Global Scenario of Solar Thermal Power Sector

At the end of 2010, there was 1,318 MW_e (MW electrical) of cumulative installed CSP capacity worldwide, with nearly 20 GWe of capacity in the pipeline (National Renewable Energy Laboratory, 2011). In 2010, Spain was the world leader in CSP installations, with 450 MW_e of added capacity and 55.4% of cumulative installed capacity worldwide. Meanwhile, USA added 78 MW_e of CSP capacity, for a total of 38.5% of cumulative installed CSP capacity worldwide. Iran (5.0%), Israel (0.5%), Australia (0.2%), and Germany (0.1%) have all recently entered the CSP market. Projects now in

development or under construction and in planning in more than a dozen countries (including China, India, Morocco, Spain and USA) are expected to total several GWe. Parabolic troughs account for the largest share of the current CSP market, but competing technologies are emerging. Some plants now incorporate thermal storage.

Spain, North Africa, Australia, and the Middle East are promising markets for CSP on account of the regions' high levels of insolation and land availability for solar deployment. The world insolation map in Fig. 2 depicts the most ideal areas for CSP development.

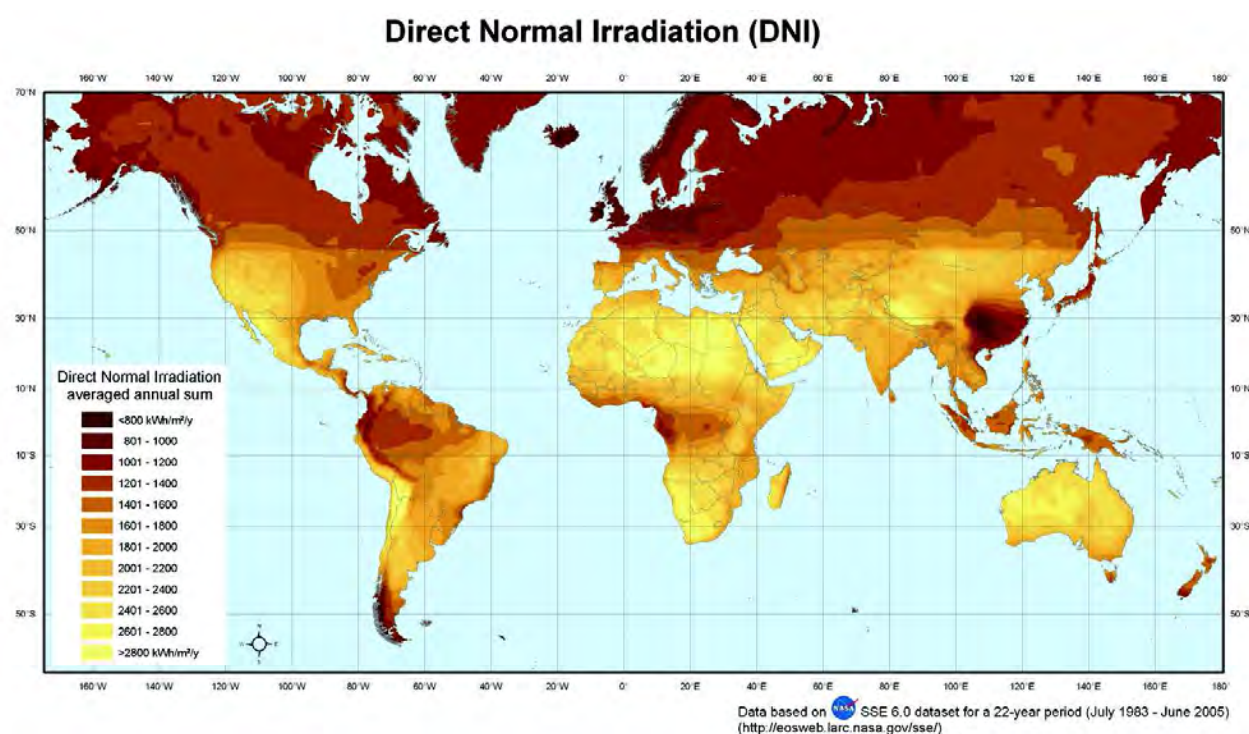


Fig. 2: World insolation map. Source: DLR (2008)

The first commercial CSP plant in Spain, the 11 MW tower system known as PS10 (Protermo Solar, 2010), was completed in 2006. With a high capacity factor, PS10 can generate 24 GWh/year, which is enough to supply about 5,500 households with electricity. Andasol 1, which came online in November 2008, has a maximum capacity of 50 MW and was the first trough system in Europe. Andasol 1 was also the first commercial CSP plant with an energy-storage capability designed specifically for electricity generation after sunset. This added feature enables the plant to provide electricity for approximately 7.5 h after sunset. Two additional plants, the Puertollano Plant and PS20, totalling 70 MW, were set up in Spain in 2009. In 2010, Spain added nine more CSP plants totalling 450 MW.

Just to the south of Spain, North Africa also has tremendous potential for CSP growth. Fig. 2 reveals the favourable solar irradiation in North African countries.

By late 2010, Morocco constructed a hybrid system with 20 MW of CSP that will be combined with a natural gas plant for a total generation of 472

MW_e. Similar plants were under construction in Algeria and Egypt. This type of design, known as an integrated solar combined cycle (ISCC), has gained some traction in these regions. The Tunisian Solar Plan aims to install a total capacity of 4.7 GW_e of renewables by 2030, which will represent 40% of the total installed capacity, with a budget of 2.3 billion euros.

Interest in CSP had also been growing in the Middle East for reasons similar to those in Africa such as high solar irradiation, available land and growing demand for clean energy. Abu Dhabi has launched a large CSP plant (SHAMS 1) of capacity 100 MW_e on March 2013. Shams 1 uses parabolic trough technology. Unlike photovoltaic solar panels, CSP concentrates heat from direct sunlight onto oil-filled pipes, produces steam, and drives a turbine and generates electricity. The solar project reportedly uses a natural gas-fired superheater to boost steam temperatures (from 380°C-540°C) before it enters the turbine to dramatically increase the cycle's efficiency. It also includes a dry-cooling system that significantly reduces water consumption which is a critical advantage in the arid desert of western Abu Dhabi.

Indian Scenario of Concentrated Solar Thermal Power Sector

India is endowed with abundant solar energy, which is capable of producing 5,000 trillion kilowatt-hours of clean thermal energy per year. India is blessed with around 300 sunny days in a year and solar insolation of 4-7 kWh per m² per day. If this energy is harnessed efficiently, it can easily reduce our energy

deficit scenario and that too with no carbon dioxide emission.

Many states in India have already recognized and identified the potential of solar energy and others are lined up to meet their growing energy needs with clean and everlasting solar energy. In the future, solar energy will have a huge role to play in meeting India's energy demand. Fig. 3 shows the direct normal irradiance in India.

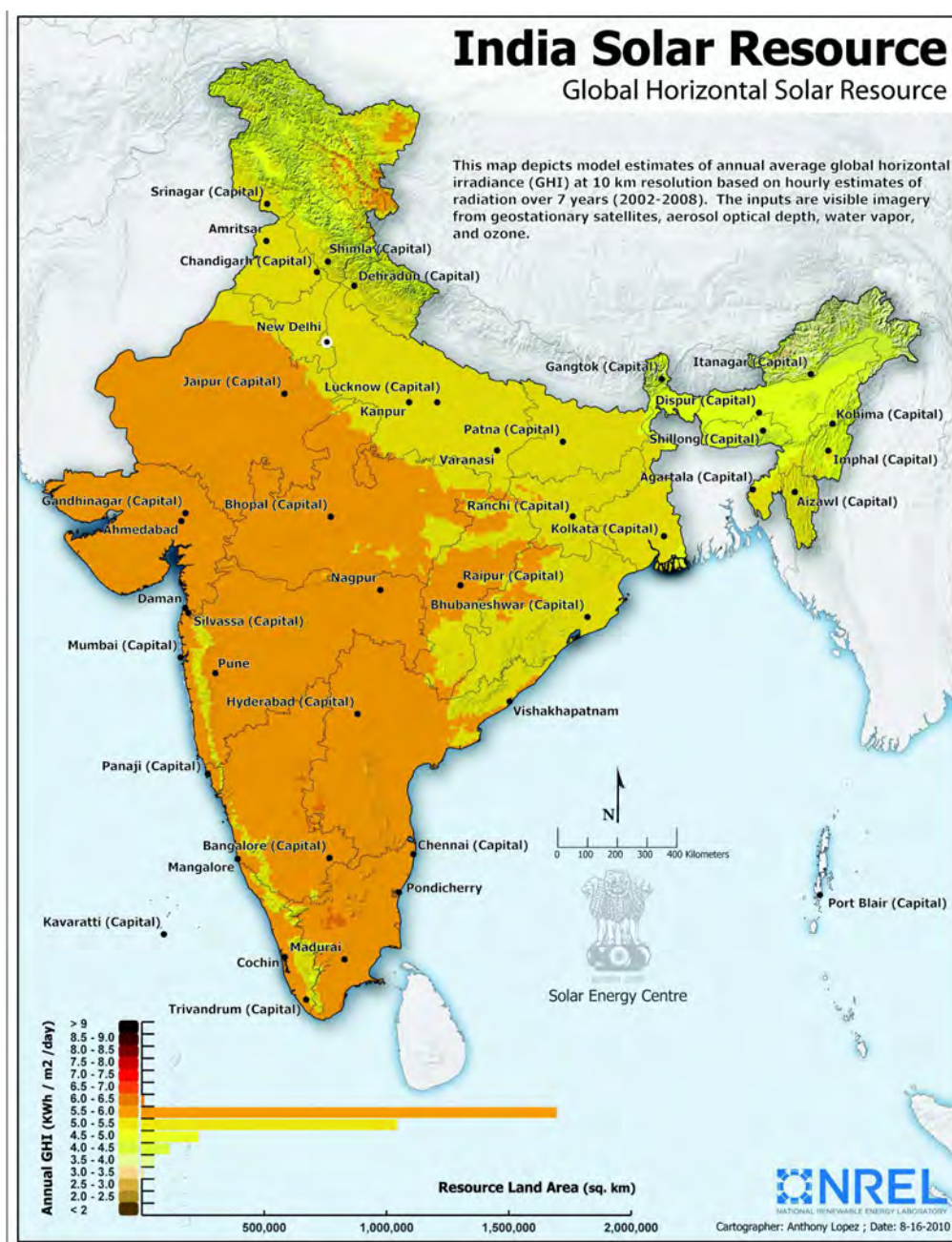


Fig. 3: Direct normal irradiance in India. Source: MNRE, Annual DNI (2010)

The main enabler for photovoltaic and CSP projects is the Jawaharlal Nehru National Solar Mission (JNNSM). The Solar Mission was launched by the Prime Minister, Manmohan Singh in January 2010. It focuses on a target of 20 GW_e of solar capacity by 2022. In the first phase, 1 GW_e of grid-connected solar was targeted for 2013 with an approximate 50:50 split between CSP and photovoltaic (PV) technologies. From 17.8 megawatts (MW) in early 2010, cumulative installed capacity reached 506.9 MW by the end of March 2012 out of which only 2.5 MW of CSP was in operation. However, there are seven projects of 470 MW aggregate capacity scheduled to be completed by May 2013 under the first phase of the JNNSM (report commissioned by the Australian government and prepared by IT Power, 2011).

India's first 2.5 MWe CSP plant (Fig. 4A) was commissioned in April 2011 at Bikaner, Rajasthan.



A: 2.5 MW_e Solar Tower, Rajasthan, (ACME, Rajasthan)



B: 125 MW solar thermal plant of Reliance (Areva, Dhursar)

Fig. 4: CSP plants in India based on tower and LFR

The plant, developed by ACME Group, employs eSolar power tower technology. During 2012-14, a 125 MW CSP was built by Areva for Reliance Power Ltd. in Dhursar, Rajasthan employing the linear Fresnel technology (Fig. 4B).

A total of 125 MW_e LFR-based solar thermal power plants and 350 MW_e of parabolic trough power plants are in various stages of development in Rajasthan and Gujarat.

Various R&D Activities

Two Types of Solar Steam Generating Systems :

One of the systems based on fixed receiver E-W automatically tracked concentrating technology (Scheffler Dish) and the other on fully tracked receiver using dish technology (Arun Dish), were developed under MNRE research projects. These systems are used for cooking, process heat, laundry, food and other processing industries. Fig. 5 A&B shows the pictures of Arun Dish and Scheffler Dish, respectively. Also a 1 MW_e Scheffler Dish power plant with 16 h of thermal storage is under construction at Mt. Abu (MNRE, Solar steam generating systems, 2011).

The 1 MW power generation facility is “an experimental project” being built collaboratively by the Solar Energy Centre (SEC) and the Indian Institute of Technology Bombay. The project is being implemented by IIT Bombay and a consortium of partners consisting of Empereal-KGDS Renewable Energy Pvt. Ltd., Coimbatore, Abengoa, Tata Power, Tata Consulting Engineers, Larsen & Toubro, Clique, KIE Solatherm. The linear Fresnel system of Empereal-KGDS produces dry saturated steam at 45 bar and 257°C with a 2 MW thermal power capacity. It is superheated to 370°C in a heat exchanger by the 390°C thermic fluid of the Abengoa parabolic trough system with 3 MW thermal power. The two superheated steam streams are combined to produce 5 MW thermal power at 370°C. This produces 1 MW_e electrical power from the steam turbine.

With funding from Department of Science and Technology (DST), Government of India, Empereal-KGDS Renewable Energy Pvt. Ltd. Coimbatore and National Institute of Ocean Technology (NIOT),



A



B

Fig. 5: A: Arun Dish at Ramakrishna Mission's Students' Home, Chennai and B: Scheffler Dish at JNV School, Leh-Ladakh

Ministry of Earth Sciences, in Chennai collaboratively developed a Solar-Biomass Multi-Effect Distillation System at Narippaiyur village in Ramanathapuram district of Tamil Nadu. The plant produces 6000 kg/h distilled water of less than 5 ppm total dissolved solids from the 32,000 ppm sea water drawn from the Bay of Bengal.



A



B

Fig. 6: A: LFR solar energy collector at Solar Energy Centre, Gwalpahari and B: Solar-biomass hybrid thermal desalination system at Ramanatha-puram district, Tamil Nadu

Performance Model of CSP Technologies

This chapter discusses the mathematical model that characterizes the performance of line focus and point focus CSP technologies. CSP technologies employ mirrors to concentrate sunlight onto a receiver where the energy is absorbed by heat transfer fluids (HTF) such as water, oil, molten salt and air. Suitable working fluid is employed to drive conventional power cycles such as Rankine cycle, Brayton cycle and Sterling engine to generate power. The three major components of CSP are solar collector/reflector field, receiver and the power block.

Here, general mathematical model of solar energy collector is discussed (Sukhatme and Nayak, 2008).

The efficiency of the system is calculated by

$$\eta_{th} = Q_{out} / (I \times A_C),$$

where Q_{out} is thermal power output of the system (kW); I is solar direct normal irradiance (kW/m²); A_C is solar collector area (m²); and Q_{out} is calculated from the total energy absorbed by the heat transfer fluid.

$$Q_{out} = \dot{m} \times C_p \times (T_{out} - T_{in}),$$

where $\dot{m}$ is mass flow rate of the heat transfer fluid (kg/s); C_p is specific heat capacity of heat transfer fluid (kJ/(kg K)) and T_{out} and T_{in} are outlet and inlet temperatures of heat transfer fluid (K).

However, if a phase change takes place, the thermal power output is the product of the mass flow rate and the enthalpy increases from inlet to outlet.

Theoretically, Q_{out} can also be calculated using the following formula.

$$Q_{out} = (I \times A_C \times \eta_{opt}) - Q_{loss}$$

The optical performance of the line focus is limited by

- Shading losses due to the adjacent reflectors shadowing the incident rays
- Cosine losses due to non-alignment of the reflector with respect to the direct beam radiation
- Intercept losses due to the spillage of reflected rays onto the receiver tube
- Line end losses when the reflection misses the absorber in the longitudinal direction due to the fact that the sun is not exactly overhead at solar noon. This effect is particularly visible in the winter months.
- Optical errors due to material, construction or tracking
- Reflectivity of the mirror, transmissivity of the glass envelope and absorptivity of the receiver tube.

- Heat losses from the receiver which depend upon the heat transfer coefficient of the fluid, emissivity of the absorber tube, geometry of the receiver, convective medium outside the receiver tubes and ambient conditions.

$\eta_{opt} = \text{Cosine factor} \times \text{Shading factor} \times \text{Intercept factor} \times \text{Reflectivity} \times \text{Transmissivity} \times \text{Absorptivity}$

The heat loss of the receiver is the heat loss from the outside surface of the absorber tube which is the sum of convective and radiative losses from the absorber tube to the surroundings.

$$Q_g = (h_g \times A_g \times (T_g - T_a)) + (F_{rad} \times \sigma \times \varepsilon_g \times A_g \times (T_g^4 - T_s^4)),$$

where h_g is convective heat loss coefficient at outside of the glass surface (W/ m².K); F_{rad} is radiation view factor; σ is Stefan–Boltzmann Constant; ε_g is emissivity of glass; T_a is ambient temperature (K); T_g is glass temperature (K); T_s is sky temperature (K) and A_g is surface area of glass (m²).

The performance of a CSP plant is measured by its annual solar-to-electric conversion efficiency. This metric includes all of the energy losses that affect the annual electricity produced by the plant, including optical, thermal, and electrical parasitic losses, as well as forced and planned outages for maintenance. Capacity factor is defined as the ratio of actual annual generation to the amount of generation had the plant operated at its name plate capacity for the entire year. Capacity factors vary greatly between different locations, technologies, and plant configurations. CSP plants with thermal energy storage (TES) are likely to be more cost-effective in the future than plants without TES, because, while the addition of low-cost TES does increase capital costs, it has the potential to reduce the levelized cost of energy (LCOE).

Current Research Areas for Technology Improvements in CSP

Development of More Advanced Reflectors, Receivers and Heat Transfer Fluids

Advanced Reflectors and Tracking System : To increase performance and reduce costs of CSP plants,

all components of CSP plants have to be improved, particularly the solar field elements (International Renewable Energy Agency, 2013). Effective but costly back-silvered, thick-glass curved mirrors could be replaced with troughs based on less expensive technologies such as acrylic substrates coated with silver, flexible aluminium sheets covered with silver or aluminium, or aluminium sheets glued to a glass fibre substrate.

Historically, Flabeg has been a primary manufacturer of bent glass reflectors, providing products with 95% or better reflectivity. PPG Industries and Rioglass also manufacture glass reflectors, and aim to lower capital costs of glass and increase durability. Emerging companies such as Reflec Tech, and 3M offer polymer films with comparable reflectivity. They are up to 60% lighter, and said to be more durable than glass. Alloy mirrors are also contending with glass reflectors. Patriot Solar Group introduced a clear, acrylic plastic surface with an aluminium or zinc backing, while Alanod-Solar manufactures nano-composite-coated, anodized alloy Miro-Sun mirrors. Glass manufacturers such as Rioglass suggest that polymer films suit only smaller installations with less serious durability requirements.

Development of self-cleaning coatings for reflector surface will greatly reduce the water consumption, one of the key problems in the arid regions where most of CSP plants are being built. Innovative compact reflector array configurations are required to improve land usage and other relevant material consumption. Wider troughs, with apertures close to 7 m (versus 5 to 6 m currently) and smaller capacity tower are under development, and offer the potential for incremental cost reductions. Development of new mirror supports and low power drives are very much needed to achieve overall cost reduction and auxiliary power consumption (International Renewable Energy Agency, 2012).

Tracking system scheme for small heliostat fields must be further improved. Current tracking system is based on the use of one drive per heliostat. However, small heliostat developers are developing a system based on a common row tracking with micro-robotic drives that couple at each heliostat individually.

Such a system can bring about a total tracking system cost reduction of 40% (Kearney and ESTELA, 2010).

Receivers and Coating

The current glass-to-metal seal of the evacuated tubes that collect solar energy could be replaced with a mechanical seal, if it proved capable of preserving the necessary vacuum for 20 years or more. Further improvements in the absorptance coating of the tubes, and reduction in emissivity at the operating temperatures could increase efficiency significantly.

The research team at University of California at San Diego is working to develop new high-temperature spectrally selective coatings (SSC) for receiver surfaces (National Renewable Energy Laboratory, 2012). The coating employs surface-protected semiconductor nano-particles to drastically reduce heat loss and allow for higher temperature receiver operation. The optical properties of the SSC directly determine the efficiency and maximum attainable temperature of solar receivers, which in turn influence the power-conversion efficiency and overall system cost. The proposed SSCs are aimed at achieving solar absorptance of >94% and infrared emittance of <7% at 750°C. These achievements can enable thermal receiver efficiencies of >90% and operation temperatures of heat-transfer fluids above 650°C.

Improvement in the power tower receivers with high temperature heat transfer fluid will raise efficiency up to 28%. High-temperature tower concepts also include atmospheric air as the heat transfer fluid (tested in Germany with the Jülich Solar Tower Project) with solid material storage. Solar-to-electricity efficiencies of up to about 25% can be delivered by such tower receivers.

Heat Transfer Fluid

Replacement of the costly heat transfer fluid currently used by trough plants should be considered because synthetic oil limits the steam temperature to about 380°C due to degradation at higher temperatures. Direct steam generation (DSG) in the collector fields would allow high working temperatures and reduced investment costs, as no heat transfer fluid and heat

exchangers would be necessary. DSG needs to be demonstrated in troughs on a large scale, but more research is needed to design specific options for storage with DSG, ensure the separation of water and steam, and handle the circulation of high-temperature, high-pressure working fluids, which is a challenge with mobile receivers.

Pressurized gas receiver is currently under testing at the Plataforma Solar de Almeria, Spain. Additional research is needed to improve heat transfers in the receiver tubes, and to ensure control of the solar field, which is more complex than the standard design. Molten salts used in the collector field simplify storage, as the heat transfer fluid becomes the storage medium. Salt mixtures usually solidify below 200°C, however. Hence, further research is necessary to reduce the pumping and heating expenses incurred to protect the field against freezing.

New liquids, in particular nanofluids are being investigated. Nano particles enhance the heat capacity of current HTF by introducing nanoscale phase change particles. Supercritical carbon dioxide (S-CO₂) operated in a closed-loop recompression Brayton cycle offers the potential of equivalent or higher cycle efficiency versus supercritical or superheated steam cycles at temperatures relevant for CSP applications.

Very High Temperature Solar Energy Collector for Material Processing, Solar Fuel Production and Advanced Power Cycles

In EU SOLASYS project, solar steam reforming of a methane-containing gas has been successfully demonstrated in a solar reformer at the Weizmann Institute of Science (WIS) in Rehovot, Israel. The necessary solar reformer was developed at DLR, then built and tested on a 400 kilowatt (thermal) scale. The novel pressure reformer is heated with concentrated solar radiation, which enters the reformer through a domed quartz glass window. In the reformer, the radiation then strikes a ceramic structure, which is highly porous and thus gas-permeable, and which is catalytically active. The radiation is absorbed in the bulk of this structure and

heats it to about 800°C or more. The methane-containing gas flowing through heats up and reacts on the surface of the catalyst to form synthesis gas (DLR, 2005).

Concentrating solar thermal technologies also allow the production of hydrogen (H₂), which forms the basis of fuels, or carriers, that can help store solar energy and distribute it to industry, households and transportation, substituting fossil-based fuels with low-emission solar energy. Solar towers and large dishes are capable of delivering the required amount of heat at appropriate temperatures.

The HYDROSOL-II project has developed a thermochemical technology that produces hydrogen solely from solar energy and water, up to the pilot plant scale. Aerosol & Particle Technology Laboratory (APTL, Greece), DLR (Germany, concentrating solar technologies), Johnson Matthey (U.K., automotive catalysis), Stobbe Tech Ceramics (Denmark, ceramic manufacturing), and the Centro de Investigaciones Energéticas, Medioambientales Tecnológicas (CIEMAT, Spain, solar tower facilities) are involved in HYDROSOL-II (Trommer *et al.*, 2005).

In order to produce solar gas by solar steam reforming, CSIRO has installed a 250 kW natural gas reforming pilot plant. CSIRO is also developing catalysts for carbon dioxide reforming (CDRM, known as dry reforming) and mixed reforming (SRM+CDRM). Research on similar projects such as SOLASYS and SOLREF is being carried out by DLR, Germany. Further research is being conducted in Japan and Israel.

Solar furnaces receive solar radiation by one or more heliostats such as solar towers. However, instead of a tower with central receiver, a parabolic mirror is used as a secondary optical component to concentrate the sunlight up to 20,000 times. The parabolic mirror may be faceted because single mirrors are restricted in their size. The largest solar furnaces in Odeillo, France, and Parkent, Uzbekistan, have thermal power of 1 MW and size equivalent to a 12-storey building.

Storage Technology and Hybrid Plant Configuration

Incorporating thermal energy storage enables CSP plants to provide power generation over a longer period (after sunset, for instance) or to shift power delivery to another time period. Therefore, it provides plant operators more flexibility, allowing them to accurately match electricity supply with demand as well as support grid reliability. However, thermal storage for 3-6 h will increase the capital cost due to storage equipment. Therefore, different power tariffs should be mandated for peak hour supply. Development of low-cost high-efficiency thermal storage technology is also essential to achieve cost reduction (NREL, 2003).

Selection of materials for storage (storage medium) plays an important role in the design of thermal storage system. Various materials have been addressed in the literature for both sensible and latent heat storage systems based on their thermo-physical properties (Bauer *et al.*, 2010; Hoshi *et al.*, 2005). CSP plant with more than 16 h of thermal storage using two-tank molten salt storage technology is operational in Spain (ANDASOL II). Thermocline-based storage technology having a single tank filled with low cost sand, rock and mineral oil is being developed (Pacheco *et al.*, 2001).

A few studies (Bayón *et al.*, 2010; Laing *et al.*, 2011 and Bahl, C. *et al.*, 2009) report different thermal storage systems for direct steam generation. Bahl *et al.* (2009) proposes a three-part storage system for a direct steam generation device using concrete and PCM. The concrete storage modules are used for preheating and superheating the steam and the PCM storage module is used to evaporate the heat transfer fluid. Integration of thermal storage system with power plant is considered favourable for the future market potential of such power plants (Feldhoff *et al.*, 2012). Steam accumulators integrated with suitable latent heat storage material is a promising option for most of the process heat applications.

Intermittency of solar energy and non-availability during night time makes hybridization an important aspect of CSP plants to achieve continuous operation

of the plant. So, suitable hybridization schemes such as solar-biomass and solar-fossil fuel must be developed and demonstrated (MNRE, 2012) for reliability, cost-effectiveness and durability.

Challenges for CSP Technology in India

CSP Technology and System Components

Import of key CSP technology and system components such as mirrors, absorber tubes, and other special balance of plant items lead to high cost of the CSP plants. Indigenous technology development and production of these components in the future will help deploy more CSP plants (National Solar Mission Interim Report, September 2012).

Solar Resource Data

India's solar programme hinges on the reliability of the solar resource data. In recent years, private developers have put in place ground measurements, predominantly in Gujarat and Rajasthan. The government has additionally tendered 50 stations to be distributed all over India, which will "significantly improve resource data" in the coming years. Solar thermal technology is successful in areas with high solar radiation.

Water Scarcity

Similar to other conventional power plants, concentrated solar power plants require water for condensing the steam used to power the electric turbine. In India, sun-rich areas such as Rajasthan or Gujarat (or cold desert of Ladakh) are already short of water resources. Air-cooled condensers can reduce the water requirement significantly, but the capital cost of air-cooling, and associated performance loss are significant. Non-availability of water can be solved by cogeneration of power and water in coastal areas. Solar thermal power plants can be coupled with desalination plants where sea water can be desalinated through multiple-effect distillation. Coastal areas of Gujarat, Tamil Nadu, etc., receive very good solar radiation, so implementation of solar desalination plants in such areas is a viable solution to power and water scarcities (DST Annual Report, 2013).

Financial and Policy Issues

Relatively high capital cost of Indian CSP plants due to lack of Indian supply chain must be properly addressed (National Solar Mission Interim Report, April 2012). Financial institutions and policy makers need to understand the technology, resource availability and the need for CSP technology emphasizing the ability of CSP technology to meet our future baseload requirements and production of transportable fuel. CSP is in a state of infancy but has vast potential to meet our future energy needs.

Concluding Remarks

CSP has excellent application in hot desert environments with high solar radiation and high

ambient temperatures. In order to realize the full potential of CSP, the industry should develop various building blocks with which the CSP technology can be assembled. For example, reflectors with low cost and high durability should be developed. Once large-scale production takes place, CSP capital cost will decrease promoting more demand for the CSP plants. Government policies should help develop large-scale production facilities. Solar thermal storage will make the plant dispatchable, and hybridization with other technologies will help to produce power after sunset. High temperature CSP plants can help produce renewable fuels. Funding for basic and applied research will promote vigorous development of the CSP technology which will result in good returns in the long run.

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*Review Article***Electrical Power Transmission and Energy Management System**SUBIR SEN^{1*} and S C SRIVASTAVA²¹Smart Grid Division, Power Grid Corporation of India Limited, Gurgaon, India²Department of Electrical Engineering, Indian Institute of Technology, Kanpur, India

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Electrical power transmission system forms an important part of the electricity network required to transfer bulk amount of power produced at remotely located generating stations to the load centres. In most of the countries, including India, the electricity sector has a vast interconnected system of generation, transmission and distribution network, which requires modern computer-aided operation and control system. Such a system is called 'Energy Management System (EMS)', conventionally based on Supervisory Control and Data Acquisition (SCADA) features. With the recent development of dielectric as well as conducting materials, power electronic devices, information technology and automation system, a new class of transmission and control equipment is being used and the energy management system is also being modernized. Recent blackouts in India and other countries have prompted the use of Wide Area Monitoring Control and Protection System (WAMCPS) based on synchrophasor technology for real time monitoring of dynamic states and security of the system. This paper describes the present status and future developments in the electrical power transmission, energy management system, and emerging technologies, specifically in the Indian context.

Keywords: Power Transmission; Energy Management System; Indian Scenario; New Technology

Role of Power Transmission in the Electricity Sector

Electric power has become the most essential commodity and vital input for the growth of any economy. It facilitates development across various sectors such as manufacturing, agriculture, commercial, education, railways, etc., to achieve economic growth. Accelerated economic growth of the country, along with globalization and liberalization, will result in high increase in power demand in future. To sustain the pace of growth, overall expansion of the electricity sector including generation, transmission and distribution, with adequate reliability, is required.

Indian power sector is one of the most diversified sectors, consisting of a variety of generation resources including conventional/non-conventional sources, to meet the demand. Utilizing the availability of these diverse resources, the country has been continuously

planning the generation capacity addition. As of March 2015, the total installed generation capacity in the country is about 267.6 GW (CEA Report, March 2015), consisting of 164.6 GW of coal-based, 23.0 GW of gas-based, 1.2 GW of diesel-based, 5.8 GW of nuclear, 41.3 GW of large hydro and 31.7 GW of renewable energy sources.

The generation mix of conventional sources is 87%, while the renewables contribute about 13% of the non-conventional sources. Coal still dominates (61%) as fuel resource in the overall electricity generation portfolio. The country's present peak power demand is about 148.2GW, whereas energy requirement is about 1067 billion units (BU). However, there is still a shortage of about 4.7% and 3.6% of the peak demand and energy requirement, respectively.

Electricity demand in the Indian power system is expected to increase to more than 300 GW by the

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end of the 12th five year plan (2016-17). Towards this demand, the Government of India has an ambitious plan to add about 88GW during the 12th plan through conventional resources. In addition, 30-40 GW capacity is also envisaged to be added through renewable/non-conventional sources during the 12th plan period.

The natural resources of electricity generation in India are unevenly dispersed and concentrated in a few pockets, while load centres are dispersed in all the regions. In this scenario, to cater to the bulk demand at the load centres, either natural fuel such as coal/gas needs to be transported over a long distance to run the power plants near the load centers or the electrical power has to be transmitted over a long distance through transmission lines. It has been found that the transmission of power from pithead coal-based power plants and remote located hydro plants to the load centres is economical and technically viable from the energy management perspective through High Voltage AC (HVAC) or High Voltage DC (HVDC) transmission networks.

Due to large demography, demand varies over the day/week/month as well as on seasonal/regional basis. To cater to such a variable demand pattern, the generation portfolio should have a mix of various fuel technologies. Therefore, the transmission system needs to be strengthened to transfer power from generating plants having a mix of fuels across regions and states as well as to cater to the demand under all operating conditions. In an open electricity market, wherein long-term, medium-term and short-term contracts are taking place, the price of electricity depends upon the supply-demand balance. The consumer aspires for affordable and reliable power while the supplier's concern is on maximizing the profit. The transmission network plays a key role in managing/wheeling electricity from one part to other part of the network to meet the transactions, while ensuring reliability and security of supply.

Thus, the transmission plays a vital role in the overall development of the power system. It is the central link in the entire electricity supply delivery chain interconnecting sources to the distantly located

load centres. A robust and reliable transmission network has to be planned to ensure supply in a secure manner at reasonable cost (Gonen, 2009). It also offers the sellers and buyers of electric power a choice and, thereby, facilitates development of an open electricity market.

Energy Management System

In the present day large interconnected power systems, the demand for power is always increasing, which requires expansion of the transmission networks. However, addition of new transmission lines is not always feasible due to economical, environmental and right of way constraints. This leads to the stressed operation of the system and calls for its continuous monitoring as well as assessment of security and stability. Increased vulnerability of the modern power systems to blackouts under contingencies, demands for the development of monitoring and assessment tools. Further, the operating conditions and the dynamics of the system change frequently with the changes in loading conditions. To understand and predict the operating conditions and to monitor the vital parameters of the system closely, automation, control and application software are required for quick response to the operating conditions as well as to perform the forecasting and postmortem analysis.

Since the last 4-5 decades, for the operation and control of the power system, a combination of computer and communication hardware along with software application suites, is being utilized by the power system utilities, which is commonly called as the 'Energy Management System' (EMS) (Talukdar and Wu, 1981). This system has been used in most of the power systems across the globe mainly at generation and transmission levels, which acquires measured quantities, such as Root Mean Square (RMS) values of the bus voltages, branch currents and power flows at a scan rate of 2-10 s. To scan the measured quantities, Remote Terminal Units (RTUs) are installed near the substations or generating stations to receive the analogue measurement and digital status signals from the field equipment, which are to be monitored remotely. The RTUs are equipped with

analogue/digital measurement devices, a suitable Analogue to Digital (A/D) converter, and communication channel to send and receive the data to control centres and also the control commands to the field equipment. Conventionally, telemetry links have been used for data communication, which are being replaced by fibre optic links.

In the past, the important application of the EMS has been the Supervisory Control and Data Acquisition (SCADA). The SCADA system spools the required power system measured quantities from the RTUs, filters and analyses it for various applications. The filtered data is further used by other software applications such as state estimator, security enhancement, contingency analysis, and short circuit analysis. A typical architecture of the EMS is shown in Fig. 1.

Important components of the EMS applications' suite includes SCADA application, communication and control applications, network management, state estimation, contingency analysis, economic load dispatch or optimal power flow, Automatic Generation Control (AGC), security assessment, fault detection, isolation and restoration, dispatcher training simulator, and various offline tools such as load flow, playback, historian, etc.

The dispatcher training simulator is the tool used to provide training on EMS applications to the operators responsible for the operation and control of the power system networks. In large electricity networks such as those in India, hierarchical architecture of EMS has evolved, having control

centres at national level, five at regional level and one in each of the states known as National Load Dispatch Centre (NLDC), Regional Load Dispatch Centre (RLDC) and State Load Dispatch Centre (SLDC). The required application software for functioning of electricity markets is also being embedded at the control centres, to be operated by the system operators (SOs). The EMS is continuously being modernized (Wu *et al.*, 2005) utilizing the new technologies of computing and communication. Of late, the distribution systems are also being provided with SCADA systems, commonly known as Distribution Management System (DMS) or Distribution Automation System (DAS), where application functions are different, such as load estimation and forecasting, Volt/Var management, network reconfiguration, automatic billing, equipment health monitoring, etc.

Present Status of Transmission Network

Existing Transmission Network in India

Electricity is a concurrent subject in India. Both the central and the state governments are responsible for the development of this sector. There are number of central generation utilities such as National Thermal Power Corporation (NTPC), National Hydro Power Corporation (NHPC), Tehri Hydro Dam Corporation (THDC), North Eastern Electric Power Corporation Ltd. (NEEPCO), Satluj Jal Vidyut Nigam Limited (SJVN), Neyveli Lignite Corporation Limited (NLC), etc. Power Grid Corporation of India Limited (POWERGRID) is the Central Transmission Utility

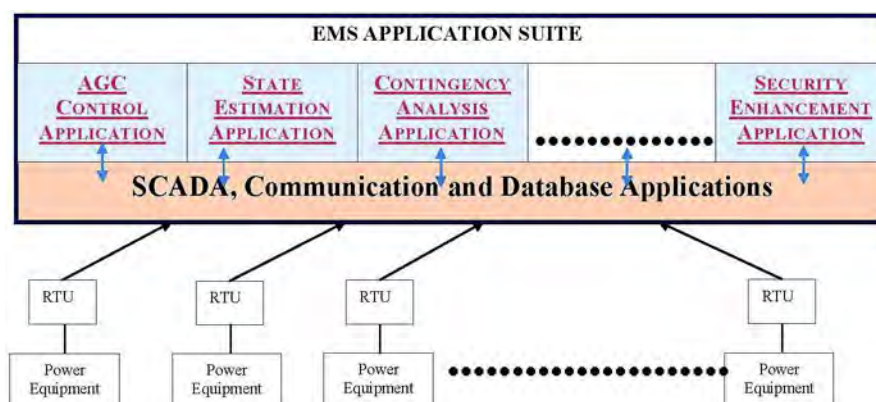


Fig. 1: Typical Energy Management System Architecture

(CTU). At the state level, separate Generation company (Genco) and Transmission company (Transco) have been formed. Distribution of power is under the purview of the respective state utilities. Central Electricity Regulatory Commission (CERC) is the regulatory authority at the central level with State Electricity Regulatory Commissions (SERCs) at the state level. For the sake of better coordination between the state utilities, the country has been demarcated into five electrical regions, namely Northern Region (NR), Southern Region (SR), Eastern Region (ER), Western Region (WR) and North Eastern Region (NER), as shown in Fig. 2.

Over decades, a robust inter-state/intra-state and inter-regional transmission system has been evolved in the country, which facilitates widespread reach of power over the vast areas. At the time of independence, maximum voltage level of transmission was at 132 kV, which was subsequently increased to 220 kV in 1960 and 400kV AC in 1977. To reduce the Right of Way (ROW) requirement for transmission lines along with large quantum of power transfer requirement and to overcome constraints on availability of land for substations, 765 kV AC transmission voltage and Gas Insulated Substations

(GIS) are now being increasingly used. In addition, the long distance ± 500 kV HVDC and back-to-back systems are also in place.

Both inter-state as well as intra-state transmission networks have seen rapid growth over the last two decades and have established a robust system mainly comprising 400kV/765kV AC and ± 500 kV HVDC as part of the national grid to facilitate widespread reach of power across the country. Till 2013, the Indian power system comprised two grids at national level viz., NEW grid (capacity 169 GW), which synchronously interconnected NR, ER, WR and NER grids, and Southern Grid (56 GW), with over 4000 MW asynchronous interconnection through HVDC lines between these two grids. In a recent major development, the 765 kV single circuit Solapur-Raichur transmission line was synchronized on 31 December 2013 midnight and it connected the NEW grid to the southern power grid. With the synchronization of the Solapur-Raichur line, the southern states are set to benefit by way of increased power import as it would obtain power from the power-surplus regions and states.

The backbone transmission system in India mainly occurs through 400 kV and 765kV AC network with approximately 1,54,593 circuit km (ckm) of line length and 3,13,922 MVA transformation capacity. These are supported by about 1,49,412 ckm of 220kV transmission network with 2,68,678 MVA transformation capacity. In addition, ± 500 kV, 1500/2500MW long distance HVDC (4 nos.) systems traverse about 9500 circuit km with 13,500 MW power transfer capacity including 4 nos. HVDC back-to-back interconnecting links. Details of existing transmission network (220kV & above) in circuit kilometers owned by state/private/central sectors are provided in Table1 (CEA Report, March 2015).

For the transmission infrastructure at the central level or Inter State Transmission System (ISTS), POWERGRID is responsible for its development as well as Operation and Maintenance (O&M). It owns and operates about 1,15,637ckm of transmission line at 400kV/765kV level, 192 nos. Extra High Voltage (EHV) substations and HVDC stations with about 2,31,709 MVA transformation capacity

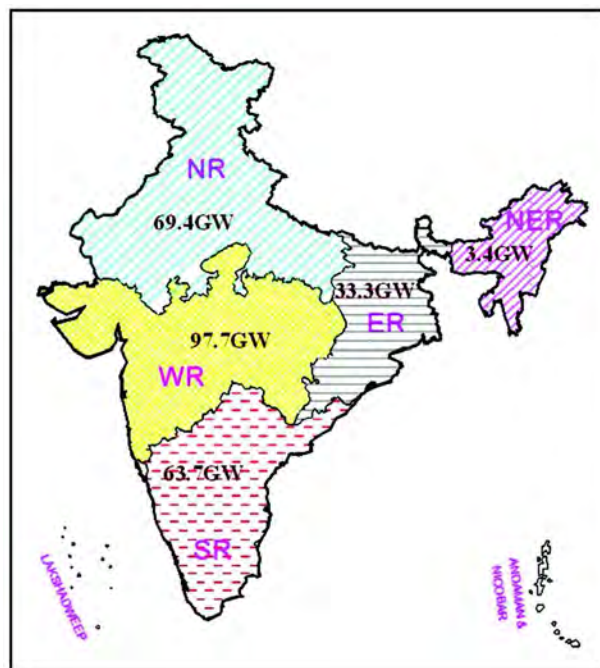


Fig. 2: Five Electrical Regions of India (CEA Report, March 2015)

Table 1: Present Status of 220 kV and above Voltage Transmission System in India (CEA Report, 2015) (as on March 2015)

S.No.	Line/station	Central sector	State sector	JV/Pvt	Total
Transmission line (ckm) Voltage Level					
1	765 kV	15810	840	1994	18644
2	400 kV	82786	40394	12769	135949
3	220 kV	10582	137932	898	149412
4	±500kV HVDC	5948	1504	1980	9432
Substation (MVA)					
1	765 kV	100500	9000	12000	121500
2	400 kV	99175	92617	630	192422
3	220 kV	8176	258935	1567	268678
4	±500 kV HVDC	9500	1500	2500	13500

(POWERGRID website). It has a plan to develop additional about 66,000 ckm transmission line mainly at 400 kV and 765 kV levels and more than 90 substations with about 1,50,000 MVA transformation capacity during 12th plan. (http://www.cea.nic.in/more_upload/conclave/23.pdf)

All the five regions are interconnected through the National Grid comprising the hybrid AC/HVDC system through the ISTS system. Recognizing the need for development of a strong National Grid, thrust was given to enhance the interregional capacity in a phased manner. The total inter-regional transmission capacity at present is about 46,450 MW.

Transmission Losses

Although the overall Transmission and Distribution (T&D) losses in India are quite high, about 26% (CEA report, March 2015), the transmission losses are in the range of 3.5% to 4%, which is comparable with other international utilities. The losses are mainly technical in nature, which are intrinsic to power transmission systems and depend on the type of conductors used, length of transmission lines, voltage profile, loading levels on the equipment, etc. Broadly, technical losses are categorized (Navani *et al.*, 2012)

as (a) resistive losses inherent in all conductors because of the finite electrical resistance of conductors, (b) dielectric losses resulting from the heating effect in the dielectric material used between conductors or conductor to ground, and (c) induction and radiation losses that are produced by the electromagnetic fields surrounding conductors.

In order to maintain transmission losses within limits, new transmission technologies have been introduced/under implementation in the country (CEA NEP report, 2012), including ±800 kV, 6000 MW HVDC system, 765 kV/1200 kV UHVAC, dynamic reactive compensation through the Flexible AC Transmission System (FACTS) in the grid.

Majority of the T&D loss occurs in the distribution sector, which contains both technical and commercial loss. Commercial loss occurs due to poor metering and return of revenue; whereas, higher technical losses are attributed to the unplanned growth of distribution sector, resulting in very long lines, lack of adequate reactive power support, lack of information about loading condition and poor health of equipment leading to their frequent failure. Certain measures to reduce the losses are re-conductoring of lines and reconfiguration of the distribution system, optimal capacitor installation, substation and feeder automation, with features of system and equipment health monitoring, load and demand side management, etc.

Future Requirement, Issues and Challenges in Transmission

Generation Capacity Addition Program

India has an installed capacity of 268 GW as of March 2015, the world's fifth largest, yet faces an energy deficit of 3.6% and a peak load deficit of about 4.7%. The average per capita consumption of electricity is a meager 957 kWh (2013-14), compared to the world average of about 2,500 kWh. The other comparable countries in the BRICS group (Brazil, Russia, China, and South African nations) have significantly higher per capita consumption than India. The average per-capita consumption in India has grown steadily at 4.7% CAGR annually over the last 10 years.

As per the estimates, peak demand in the country by 2021-22 and 2031-32 may increase to about 323 GW and 592 GW, respectively, and the corresponding installed capacity requirement shall be about 425 GW and 778 GW, respectively (IEP report, 2006). Progressively, the generation capacity requirement by 2031-32 is projected as shown in Fig. 3.



Fig. 3: Estimated Generation Capacity Addition (IEP Report, 2006)

Energy Resource Locations

The natural resources for electricity generation in India are unevenly dispersed and concentrated in a few pockets. Hydro resources are located in the Himalayan foothills and in the north-eastern region. Coal reserves are concentrated in Jharkhand, Orissa, West Bengal, Chhattisgarh, and parts of Madhya Pradesh; whereas, lignite is located in Tamil Nadu and Gujarat. North Eastern Region (NER) and Bhutan have vast untapped hydro potential estimated to be about 50,000 MW in NER and about 15,000 MW in Bhutan. India has some of the largest reserves of coal in the world (approx. 267 billion tonnes). Coal reserves are mainly located in Orissa, Chhattisgarh, Jharkhand, Maharashtra (Nagpur & Chandrapur), West Bengal (Ranijang), Andhra Pradesh (Khammam), and Tamil Nadu (Neyveli). Energy resource map of India is shown in Fig. 4.

The distribution of energy resources and load centres are extremely unbalanced. The load centres are scattered at far-off places away from resource-rich areas located in the northern part of India. Recent government initiatives for establishment of special economic zones have also given rise to new potential load centres. Projects are proposed to be located mostly at pit head/resource areas, with each location having capacities in the range of 5,000-10,000 MW.

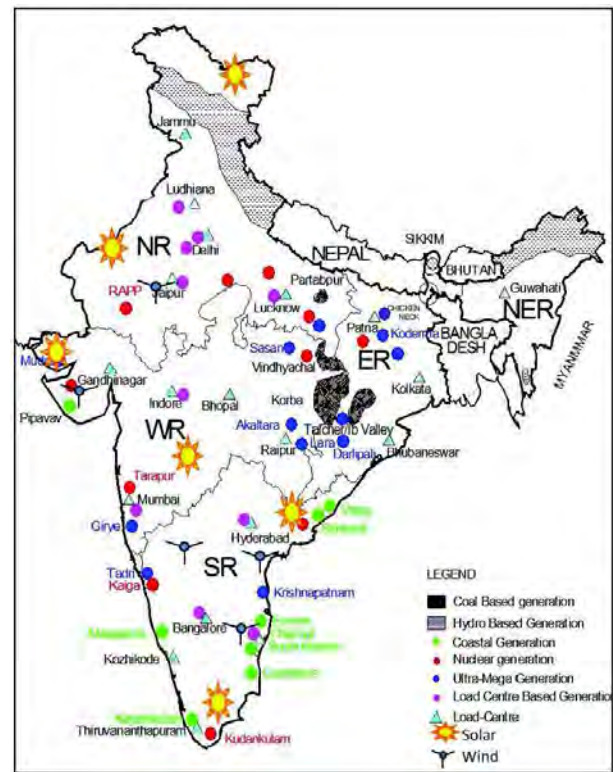


Fig. 4: Energy Resource Map of India (POWERGRID Website <http://www.powergridindia.com>)

Issues and Challenges in Transmission

Of late, transmission sector is facing new challenges which have arisen out of rapid growth of the electricity sector coupled with increased requirement of power transfer. Pocketed generation resources and wide spread load centers across the country, coupled with ROW problems, necessitate development of high capacity transmission corridors. However, major concerns towards planning of such corridors include right-of-way and protection of flora and fauna, Rehabilitation & Resettlement (R&R), flexibility to enhance the transfer capacity in view of uncertainty of generation projects, implementation in different phases, optimization of transmission cost and losses, non-discriminatory open access to facilitate electricity market, cable manufacturers' to research & develop cables with new type of insulating and conducting materials, integration of large scale renewable energy sources with the grid in an optimal manner, creation of reliable repairing facilities & development of indigenous manufacturing capacity, skilled manpower

for implementation of huge network, and new challenges in operation and maintenance.

In the current electricity supply regime, various uncertainties are associated with the transmission system development process. Some of the key uncertainties pushing a paradigm shift in transmission system planning include uncertainties in development of generation project, no firm beneficiaries at the development stage of generation project due to introduction of competitively bid generation tariff, and recovery of investment towards transmission development.

Transmission Plan

There has been a consistent increase in the transmission network and transformation capacity in India. This increase is in consonance with the increase in generation and demand of electricity in the country.

Considering the generation capacity addition plan for the 12th plan period and commensurate power transfer requirement, transmission line additions of about 1,00,000 ckm, HVDC terminal capacity of 13,000 MW and AC transformation capacity of 2,70,000 MVA has been planned for the 12th Plan.

Table 2: Projected Transmission Network Growth (12th Plan Report, 2012)

S.No.	Line/station Total	At the end of 11 th plan	Envisaged addition during 12 th plan	Expected by end of 12 th plan (cumulative)
Transmission line (ckm)		Voltage Level		
1	765kV	5730	27000	32730
2	400kV	113367	38000	151367
3	220kV	140164	35000	175164
4	HVDC	9432	7440	16872
Substation (MVA)				
1	765kV	25000	149000	174000
2	400kV	151027	45000	196027
3	220kV	223774	76000	299774
4	HVDC (MW)	11200	12750	22500

Table 2 shows the transmission infrastructure addition envisaged in the 12th plan.

The inter-regional transmission capacity of all-India grid level is about 46,450 MW which shall be enhanced to more than 66,000 MW by 2017 and 1,26,650 MW by 2021-22. Fig. 5 shows the growth in interregional capacity by 2021-22 (end of 13th plan). The generation projects are mainly concentrated in small pockets in areas such as pit-heads in Orissa, Chhattisgarh, Jharkhand or coastal sites with port facilities in Andhra Pradesh, Tamil Nadu or hydro sites in Sikkim, etc. To address the ROW issue as well as transfer of bulk power over long distances and keeping in view the long-term power transfer requirement, the development of High Capacity Transmission Corridors (HCTC) comprises 765 kV AC and ± 800 kV, 6000 MW HVDC multi-terminal line, which is being laid starting from NER to NR and other regions.

These transmission highways would facilitate transfer of power from remotely located bulk power generation projects to major load centres. A schematic diagram of 11 such planned HCTCs is shown in Fig. 6.

Based on the progress and development of generation projects and transmission systems during the 12th Plan, only a broad assessment of transmission capacity addition for the 13th plan can be made considering probable load growth and indicative generation capacity addition scenarios for the 13th plan.

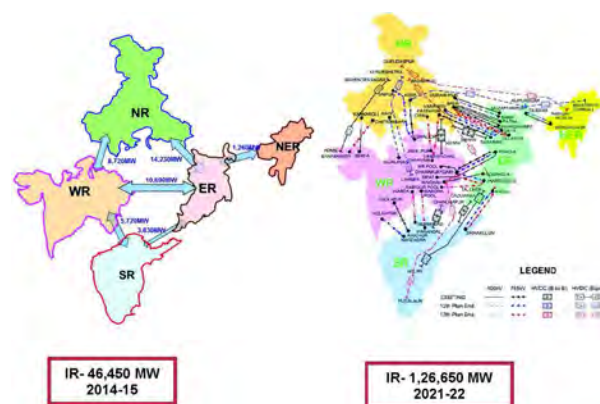


Fig. 5: Growth in Interregional Capacity (CEA Transmission Plan Report, 2014)



Fig. 6: High Capacity Transmission Corridor (NPTI Website, <http://www.npti.in>)

Accordingly, during the 13th plan period, transmission capacity addition of about 1,30,000 km and 3,00,000 MVA substation transformation capacity have been envisaged.

As part of the evolution of “Green Energy Corridors”, POWERGRID has identified transmission requirement both at inter-state and intra-state levels for grid integration of envisaged renewable capacity addition of the 12th plan (Green Energy Corridor Report, 2012). To address the intermittency and variability characteristics of renewable generation, other control infrastructures such as forecasting of renewable generation and demand, real time measurement/monitoring through synchrophasor technology, flexible generation, ancillary reserves, demand-side and demand response management and energy storage, establishment of Renewable Energy Management Centres (REMC) are also identified.

New Technologies in Power Transmission

Transmission sector has consistently adopted relevant global trends to support sustainable growth in the Indian power sector. The increasing maturity of the sector

is evidenced by adoption and indigenization of new technologies across the power transmission sector in general and power sector, in particular.

Transmission utilities are focusing on innovation for development of new transmission technologies and seamless integration in the Indian context. In order to meet the growing power transfer requirement with increased inter-state power transfer requirement and addressing the associated challenges, a two-pronged approach has been adopted on the technology front. In the first approach, capacity and reliability of existing transmission infrastructure is enhanced using new technologies. In this direction, many emerging technologies are already integrated into the transmission system such as FACTS devices (Hingorani and Gyugyi, 2000), e.g. Static VAR compensator (SVC), Thyristor Controlled Series Capacitors (TCSC), Fixed Series Compensation (FSC), reconductoring of transmission lines with higher capacity conductors, etc.

In the second approach, new systems are being designed keeping the long-term perspective utilizing the latest state-of-the-art technologies. In this direction, new technologies such as high capacity 765kV transmission system (765kV double circuit lines), ± 800 kV 6000 MW HVDC and 1200 kV UHV AC technologies, gas insulated substation (compaction), substation automation, compact towers, High Temperature Low Sag (HTLS) conductor, etc. are introduced in addition to existing technical developments.

The country is also establishing the world’s highest transmission voltage level of 1200 kV UHV-AC with the establishment of a national test station at Binain Madhya Pradesh in 2012. This technology has been fully developed indigenously with the collaborative effort of 35 Indian manufacturers under Public Private Partnership (PPP).

Further, the country’s first ± 800 kV HVDC multi-terminal transmission system for bulk power transmission from Biswanath Chariali, in the north-eastern region to Agra in the northern region, about 2000 km, is also under implementation and upon completion, this system will be among the world’s

longest ± 800 kV HVDC multi-terminal system with power transfer capacity of 6000-8000 MW.

To facilitate safe, secure and reliable operation of the large grid so as to avoid frequent outages through openings of lines due to over voltage, which was otherwise found to weaken the grid under emergency situation (Report on grid disturbance in July 2012 in India), and also providing voltage support during various operating conditions under steady state and dynamic conditions, installation of suitable static and dynamic reactive compensation are essential. Static compensation is provided in the form of a bus/line reactor, while dynamic compensation is achieved through SVC/STATCOMs. In this direction, 16 SVC/STATCOMs are now planned at various strategic locations among all regions to meet the dynamic reactive requirement.

With scarce land availability, there is a growing need for reduction of land use for setting up of transmission systems, particularly in metros, hilly and other urban areas. Gas Insulated Substations (GIS), which require less space (about 80% reduction), i.e. 5-6 acres as compared to conventional substation which generally requires an area of 30-40 acres. A number of 400 kV GIS substations are established and many more are under implementation including those of 765 kV level. In special areas, compact towers such as delta configuration, narrow-based tower, etc., which reduce the space occupied by the tower base, are being used. In this direction, 765 kV tower with delta configuration and 400 kV pole structure are quite useful and are being adopted.

To meet various emerging requirements such as achieving controllability/flexibility at grid level, integration of large scale renewable necessitates adoption of other state-of-the-art emerging technologies such as Voltage Source Converter (VSC) based HVDC technology, energy storage technologies, etc.

To improve the efficiency of overall grid management in open electricity market regime, enhanced situational awareness, control at the control centres, and implementation of synchrophasor technology have been planned for wide area

monitoring of state and central grids through placement of Phasor Measurement Units (PMUs) at all HVDCs, 400 kV and above substations/generating stations, PDCs (Phasor Data Concentrators) at strategic locations, along with required analytics based on PMU measurements such as the Unified Real Time Dynamic State Measurement (URTDMS) system.

Smart Transmission Grid Using Synchro-phasor Technology

The existing SCADA/EMS, as shown in Fig. 7, utilizes the Remote Terminal Units (RTUs) for measuring the voltage and current magnitudes. It also measures power flows in the lines. Typically, the RTUs provide measurements at a refresh rate of 2-10 s, which are time skewed. Preprocessing of the data, collected from the RTUs, is carried out at the control centre, which includes the processing of bad data, and carrying out the state estimation. These functions collectively result in estimation of the states, at a typical time interval of 5-10 min. Hence, the SCADA/EMS is suitable for monitoring the system under the steady state, but is not suitable for observing the system under transients or dynamic conditions.

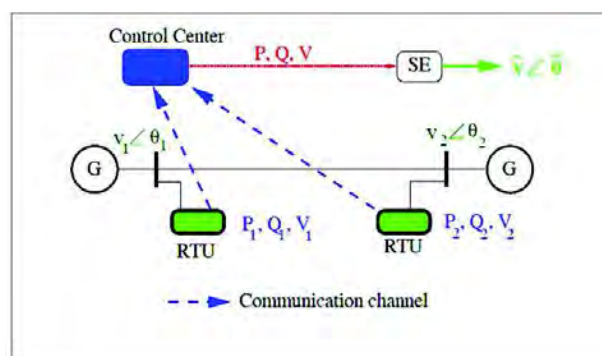


Fig. 7: Typical Conventional SCADA system

With the development of PMU-based Wide Area Monitoring System (WAMS), (Phadke and Thorpe, 2008), as shown in Fig. 8, which utilizes the time-synchronizing pulse (with an accuracy of one microsecond) from the Global Positioning System (GPS), it is possible to measure both the magnitude and the phasor angle of the bus voltages in the power systems. PMU typically provides phasor information once in one or two cycles. This fast refreshing rate

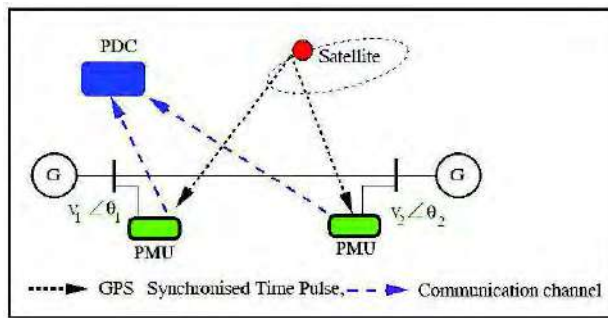


Fig. 8: Typical Wide Area Monitoring and Control System

of PMUs enables them to capture the system states during transient conditions. The data measured from the PMU are sent to Phasor Data Concentrator (PDC) by utilizing the wideband communication channels such as fibre optic channels. These measurements can further be utilized to take some fast control action, to ensure the stable operation of the power system.

Most of the utilities across the world are adopting Smart Grid technologies (Smart Grid report, DOE website; NIST report, 2012) to improve the overall operational and energy efficiency, customer satisfaction, security of the system and adopt greener technology. Some of the building blocks of smart grid are advance metering and communication, which includes smart meters, wide area monitoring system; substation and distribution automation along with distribution and operation management software; renewable integration; utility enterprise applications; and system integration. The smart grid will have distinct features such as *self-healing* to correct problems early; *interactive* with consumers and markets; *optimized* to make best use of resources; *predictive* to prevent emergencies; *distributed* assets and information; *integrated* merging all critical information; and *more secure* from threats from all system and external hazards.

At transmission level, synchrophasor technology based wide area monitoring and control system forms an important part of the smart grid. Its importance has been realized in understanding and analyzing the grid disturbance incidents in July 2012 (Report on grid disturbance in July 2012 in India), even with the data of only few PMU measurements deployed at pilot level.

Fig. 9 shows a typical block diagram of a PMU. The GPS receiver provides two signals, a periodic pulse train at a rate of one pulse per millisecond (1kPPS), and the Inter Range Instrumentation Group time code format B (IRIG-B) signal, which is a periodic pulse train at the rate of one time mark per second. The 1 kPPS signal is utilized by the sampling clock to get synchronized with the GPS clock, whereas, the IRIG-B signal provides the time tag for the estimated phasors. The analogue voltage and current signals obtained from the secondary side of the potential and the current transformers, respectively, are preprocessed by an anti-aliasing filter to remove the presence of alias of the signals from the reconstructed signal. The analogue to digital converter samples the preprocessed analogue data, which are further utilized by the microprocessor-based phasor estimator.

The estimated phasors are finally sent to the PDC using the IEEE C37.118 data format (IEEE C37.118.1, 2011; IEEE C37.118.2, 2011). Synchrophasor technology based Wide-Area Monitoring, Protection, and Control System (WAMPCS) can be effectively utilized for system-wide monitoring, coordinated real time protection and control functions required to counteract the propagation of any major disturbances in the power system. PMU is one of the most vital elements of the WAMPC system. PMU reports time-tagged voltage and current phasors required for the dynamic monitoring functions at a much faster rate than the conventional Supervisory Control and Data Acquisition/Energy Management System (SCADA/EMS). With relatively higher cost of PMUs as on

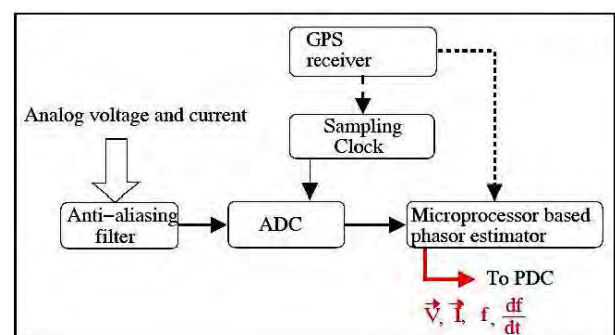


Fig. 9: Typical Block diagram of a PMU

date, these have to be optimally placed to make the system observable (Sodhi *et al.*, 2010a; Sodhi *et al.*, 2011). Utilizing these dynamic measurements, the WAMPC system addresses the automated emergency control functions for various instabilities such as transient, frequency and voltage instabilities. As the conventional protective systems are decentralized and are non-adaptive in nature, a prerequisite for implementing the WAMPCS scheme is to make the protective relaying schemes adaptive. Various possible applications of the synchrophasor-based WAMPCS are as following.

- Phasor-assisted state estimation (Sodhi *et al.*, 2010b)
- Dynamic phasor estimation (Banerjee and Srivastava, 2012)
- Machine rotor angle estimation using phasor measurements for transient stability prediction (Tripathy *et al.*, 2010)
- WAMS-based critical mode identification for small signal stability assessment and control (Tripathy *et al.*, 2011)
- Synchrophasor-based voltage stability assessment (Sodhi *et al.*, 2012)
- Optimal frequency and voltage stability based load shedding (Seethalekshmi *et al.*, 2011a)
- Wide area measurement based adaptive distance protection (Seethalekshmi *et al.*, 2011b; Seethalekshmi *et al.*, 2012)
- Model validation and wide area control (Padhy *et al.*, 2012)

Some of the above analytics are being developed in-house for implementation in the URTDSM system in India.

Role of Smart Grid Technology in Preventing Major Grid Disturbances

In an integrated electricity grid, the power systems in different regions are interconnected and very often an incident initiated in one region may lead to a disturbance in other region also. Grid disturbance may

result in a blackout, which refers to the total loss of power to an area and is the most severe form of the power outage that can occur. Outages may last from a few minutes to a few hours/days depending on the nature of the blackout, configuration of the electrical grid, system restoration time, etc. Some of the major blackout incidents across the world (as also listed in http://en.wikipedia.org/wiki/List_of_power_outages) are as following.

- 1965 US blackout on 9 November 1965 that affected 30 million people.
- 1999 Southern Brazil blackout on 11 March 1999 that affected 97 million people.
- 2003 Northeast blackout in the US and Canada on 14-15 August 2003 that affected 55 million people.
- 2003 Italy blackout on 28 September 2003 that affected 55 million people in Italy, Switzerland, Austria, Slovenia and Croatia.
- 2005 Java-Bali blackout on 18 August 2005 that affected 100 million people.
- 2009 Brazil and Paraguay blackout on 10-11 November, 2009, that affected 87 million people.
- 2012 Indian blackout on 30-31 July 2012 that affected 670 million people.

The Indian blackout on 30 and 31 July 2012 is considered to be the most severe in terms of the number of people affected. It caused the loss of power supply for about 14 h in North India on 30 July 2012 and for about 5-8 h the in northern, eastern and north-eastern regions of the country on 31 July 2012. These incidents resulted in a loss of a total load of 36,000 MW on 30 July and 48,000 MW on 31 July respectively, as given in the enquiry committee report (Report on grid disturbance in July 2012 in India). These incidents not only paralyse the life of people affected by the blackout, but also result in huge loss of revenue.

Most of the grid disturbances have been initiated under heavy system loading condition, triggered by the outage of critical line(s), due to natural calamity

or faults, and lack of information and control. Some of the major causes observed in various incidents across the world include lack of situational awareness and real time monitoring tools, inadequate early security assessment/warning system, unintended operation of the protection/improper coordination of control actions, lack of enough reactive compensation, and human error & grid indiscipline.

Continuous large capacity addition and expansion of the grid through increasing interconnections lead to increasing complexity in its management and operation. Open electricity market, wide variation in generation as well as demand on daily/seasonal basis, and increasing penetration level of renewable generation, etc. add to the complexity of the grid management. Maintaining safety, security and stability of such a large grid is posing greater challenges. Hence, it is important to know the dynamic state of the grid in real time to assess angular, voltage and frequency stability of the system; amount of increase in power transfer that can take place at different instances on various transmission elements; initiate control and regulation of power flow to maintain grid

under intact condition; and initiate Remedial Action Scheme(RAS) and System Integrated Protection Scheme (SIPS) in the event of severe contingency or likely condition, which may lead to grid disturbances, to take corrective actions.

The above aspects call for seamless integration of Intelligent/Smart Grid comprising WAMS using synchrophasor measurements provided by PMU at all substations in the grid integrated with high speed communication medium such as fibre optics, and powerful computing facilities at control centres, along with RAS, SIPS. This shall facilitate safety, security and reliability in operation of the large grid as well as ensure efficient utilization of transmission infrastructure. It also improves visualization, enhances situational awareness and controllability and ensures self-healing features. Smart grid implementation facilitates proper automation, information flow and data management, required for assessing the incipient system instability/insecurity condition and initiates emergency control actions to prevent system blackout.

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ACADEMY NEWS

INSA MEETINGS

Council and General Body Meetings

Several meetings were held during July 27-30, 2015 in the Academy premises. The different Sectional Committees met for election of new Fellows of the Academy and selection of the Young Scientist Awardees. The Advisory Boards for the various INSA Awards also met. These were followed by meetings of the Council and General Body on July 30, 2015.

INSA Medal for Young Scientists

The Council at its meeting during July 29-30, 2015 approved the award of INSA Medal for Young Scientist 2015 to 29 young researchers below the age of 35. The award carries a medal, a certificate and cash prize of Rs. 25,000.

The following 29 young scientists were selected for the INSA Medal for Young Scientists.

1. **Dr B Anand** (b 06.01.1981), PhD, Department of Biosciences and Bioengineering, Indian Institute of Technology, Guwahati.

For his novel insights into mode of action of GTPases and diverse cellular functions that they regulate. His work on CRISPR-cas system has potential applications in genome engineering.

2. **Dr Rehna Augustine** (b 18.05.1981), PhD, National Institute of Plant Genome Research, New Delhi.

For her significant work on the manipulation of glucosinolate pathway in oilseed mustard (*Brassica juncea*). Her transgenics for MYB2 gene could be of high agronomic value in developing low glucosinolate varieties and hybrids.

3. **Dr Jyotishman Bhowmick** (b 05.11.1981),

PhD, Stat Math Unit, Indian Statistical Institute, Kolkata.

For his outstanding results on quantum isometry groups of compact quantum groups which have attracted the attention of, and been put to good use by, established experts in the area.

4. **Dr Arup Kumar Das** (b 18.04.1980), PhD, Department of Mechanical and Industrial Engineering, Indian Institute of Technology, Roorkee.

For development of computational algorithms for dispersed two phase flow with complex interfaces and its experimental validation.

5. **Dr Rajendra Singh Dhaka** (b 10.06.1980), PhD, Department of Physics, Indian Institute of Technology, Delhi.

For his unique and significant experiments on rare-gas nanobubbles in metallic surfaces and establishing a general relation between the nanobubbles and the binding energies of the rare gas atoms.

6. **Dr Sumit Ghosh** (b 01.05.1980), PhD, Department of Plant Biotechnology, CSIR-Central Institute of Medicinal and Aromatic Plants, Lucknow.

For having cloned and functionally characterized novel amyrisin synthase genes from sweet basil for the biosynthesis of medicinally important pentacyclic triterpenes. He also engineered slow ripening of tomato by silencing genes that control N-glycan processing.

7. **Dr Jitender Giri** (b 01.07.1980), PhD, National Institute of Plant Genome Research, New Delhi.

For discovering rice genes for stress-associated proteins (SAP 1 and SAP 11) and receptor-like

cytosolic kinase (RLCK 253) that confer abiotic stress tolerance in rice and in transgenic *Arabidopsis* plants.

8. **Dr Ashish Gupta** (b 22.08.1980), PhD, Department of Life Sciences, Shiv Nadar University, Greater Noida.

For discovering functional characterization of the homologue of eukaryotic Origin Recognition Complex (ORC) subunits in *Plasmodium* and for identifying the presence of proliferating cell nuclear antigen (PfPCNA) Interacting Protein (PIP) motif in PfOrcl and confirming the physical interaction between PfORC and PfPCNA by interaction studies and complementation assay.

9. **Dr Nilesh Prakash Gurao** (b 11.03.1983), PhD, Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur.

For his outstanding work in elucidating deformation mechanisms at multiple length scales (from nanometer to millimeter), in particular, his demonstration of the similarity of deformation mechanisms in coarse grained and nanocrystalline Nickel on the basis of misorientation angles determined by electron back scattered diffraction.

10. **Dr Tanvi Jain** (b 17.05.1981), PhD, Indian Statistical Institute, New Delhi.

For her contribution in Matrix Analysis and proof of the variational principle for symplectic eigenvalues of strictly positive real matrices of even order.

11. **Dr Vikas Jain** (b 06.02.1980), PhD, Department of Biological Sciences, Indian Institute of Science Education and Research, Bhopal.

For his understanding of the interactions that occur between a bacterium and its phage. And for developing expression vectors for the rapid cloning and expression of proteins with hexahistidine tag at either termini.

12. **Dr Sameena Khan** (b 23.05.1984), PhD, Translational Health Science and Technology Institute, Faridabad.

For her outstanding work about the structural basis of aminoacylation of tRNA in *Plasmodium falciparum* which has potential application in development of novel therapies against Malaria.

13. **Dr Hima Bindu Kudapa** (b 22.04.1980), PhD, Center of Excellence in Genomics, International Crops Research Institute for the Semi-Arid Tropics, Greater Hyderabad.

For her excellent contributions on gall midge and legume transcriptome which is of high value and useful for breeding of chickpea.

14. **Dr Biman Behari Mandal** (b 07.07.1981), PhD, Department of Biosciences and Bioengineering, Indian Institute of Technology, Guwahati.

For developing innovative use of silk fibre base scaffolds for human tissue engineering and for demonstrating their versatility in applications ranging from skin repair to scaffolds for bone repair.

15. **Dr Athi Narayanan Naganathan** (b 28.11.1980), PhD, Department of Biotechnology, Indian Institute of Technology, Madras.

For developing statistical mechanical models for computational prediction of folding thermodynamics and for comparing predictions with experimental results on biologically important proteins like ACBP, $\text{I}\kappa\beta\alpha$, RNaseH etc.

16. **Dr Rajesh V Nair** (b 24.05.1980), PhD, Department of Physics, Indian Institute of Technology Ropar, Punjab.

For synthesizing and studying high quality photonic crystals in the visible and near infrared wavelength ranges and for obtaining photonic band edge lasing from Si-nanophotonic structures.

17. **Dr Santanu Kumar Pal** (b 18.03.1981), PhD, Indian Institute of Science Education and Research, Mohali.

For his significant contributions on liquid crystal based sensors in detection of cellular analytes.

18. **Dr Vivek Vijay Parkar** (b 06.09.1980), PhD, Nuclear Physics Division, Bhabha Atomic Research Centre, Mumbai.

For his outstanding contributions on experimental measurements of fusion cross sections of weakly-bound nuclei on a range of targets which has opened novel possibilities for studying nuclei away from the line of stability.

19. **Dr Anbarasan Pazhamalai** (b 03.06.1982), PhD, Department of Chemistry, Indian Institute of Technology, Madras.

For his notable work on transition metal catalyzed methodology for synthesis of pharmaceutical and useful molecules through cross coupling reactions.

20. **Dr Vijay Kumar Prajapati** (b 05.07.1984), PhD, Department of Biochemistry, School of Life Sciences, Central University of Rajasthan, Ajmer.

For his important work on nanonization of amphoteresin B, a newer experimental approach in hamster animal model to increase the antileishmanial efficacy.

21. **Dr Upasana Ray** (b 11.10.1982), PhD, National Cancer Institute, National Institutes of Health, Bethesda, USA.

For establishing the existence of switch from translation to replication of HCV RNA and for designing peptide based antivirals that target La protein and HCV NS3 protein and which could inhibit the HCV RNA function.

22. **Dr Nitin Saxena** (b 03.05.1981), PhD, Department of Computer Science and Engineering, Indian Institute of Technology, Kanpur.

For his renowned contributions in the area of algebraic complexity theory and significant studies of the development of important deterministic algorithms for primality testing, polynomial identity testing and construction of hitting sets.

23. **Dr Maheswaran Shanmugam** (b 01.06.1980), PhD, Department of Chemistry, Indian Institute of Technology, Bombay.

For his comprehensive studies of the electronic and magnetic properties of molecular nanomagnets.

24. **Dr Narendra Pratap Singh** (b 23.03.1981), PhD, Stowers Institute for Medical Research, Kansas City, Missouri, USA.

For elucidating the divergence of the developmental roles of Drosophila Abd-a and Abd-b in determining segment identity and proliferation in body segments where they are co-expressed.

25. **Dr Pankaj Kumar Singh** (b 03.02.1980), PhD, Department of Translational Medicine and Neurogenetics, Institut de Genetique et Biologie Moleculaire et Cellulaire (IGBMC), France.

For unravelling cellular functions of Lafora disease proteins and proposing inhibition of SGK 1 as a potential therapeutic strategy for the treatment of the Lafora disease.

26. **Dr Hari Sridhar** (b 28.04.1982), PhD, Centre for Ecological Sciences, Indian Institute of Science, Bengaluru.

For his significant studies leading to the understanding of the relative roles of predation and forging success in driving multi-species flocking in birds.

27. **Shri Shashi Kant Tiwari** (b 10.07.1985), MSc, PhD (Thesis Submitted), Developmental Toxicology Division, Indian Institute of Toxicology Research, Lucknow.

For demonstrating the mechanisms by which Bisphenol A (BPA) affects the endogenous

neural stem cells and oligodendrocyte progenitor cells which lead to the identification of means of its amelioration by curcumin.

28. **Dr Gyana Ranjan Tripathy** (b 05.07.1981), PhD, Earth and Climate Sciences, Indian Institute of Science Education and Research, Pune.

For his significant work on $^{187}\text{Os} / ^{188}\text{Os}$ isotope ratios of the black shale and usefulness of this technique in estimating the atmospheric oxygen levels in the geological past and for focusing on low temperature weathering in the Himalayas and its linkage to the tectonic processes.

29. **Dr Shri Ram Yadav** (b 09.07.1980), PhD, Department of Biotechnology, Indian Institute of Technology, Roorkee.

For his outstanding contributions on the molecular mechanism of action of a gene that regulated floral organ specification and development in rice and for demonstrating the role of gene duplication and diversification of function during evolution of rice floral development.

INSA Medal/Lecture Awards 2015

The Academy announced the following nine medal/lecture Awards for 2015.

(A) Medals Instituted by the Academy

1. **The Satyendranath Bose Medal to Professor J Maharana, FNA**, Institute of Physics, Bhubaneswar.
2. **The Darashaw Noshervanji Wadia Medal to Professor S Sengupta, FNA**, INSA Senior Scientist, Department of Geological Sciences, Jadavpur University, Kolkata.
3. **The Golden Jubilee Commemoration Medal (for Animal Sciences) to Professor MD Gadgil, FNA**, DD Kosambi Visiting Research Professor, Goa University, Goa.

(B) Endowed Medals

4. **Vishwakarma Medal to Dr AB Pandit, FNA**,

UGC Research Scientist C (Professor Grade), Chemical Engineering Department, Institute of Chemical Technology, Mumbai.

5. **Professor GN Ramachandran 60th Birthday Commemoration Medal to Dr Amitabha Chattopadhyay, FNA**, JC Bose National Fellow and Outstanding Scientist (Director Level), CSIR-Centre for Cellular & Molecular Biology, Hyderabad.
6. **Professor Krishna Sahai Bilgrami Memorial Medal to Dr Yadvinder Singh, FNA**, INSA Senior Scientist, Department of Soil Science, Punjab Agricultural University, Ludhiana.

(C) Endowed Lectures

7. **Dr Nitya Anand Endowment Lecture to Professor TK Kundu, FNA**, Transcription and Disease Laboratory, Molecular Biology and Genetics Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru.
8. **Professor Vishnu Vasudeva Narlikar Memorial Lecture to Professor SK Khanduja, FNA**, Indian Institute of Science Education and Research, Mohali.
9. **Professor Vishwa Nath Memorial Lecture to Professor Subrata Sinha, FNA**, Director, National Brain Research Centre, Manesar.

Award Lectures Delivered

Professor Shyam Bahadur Saksena Memorial Medal Lecture (2011): Professor LC Rai, Centre of Advanced Study in Botany, Molecular Biology Section, Banaras Hindu University, Varanasi delivered Professor Shyam Bahadur Saksena Memorial Medal Lecture on *Decoding Cyanobacterial Survival under Arsenic Stress through Proteomic, Genomic and Bioinformatics Approaches* at Allahabad University, Allahabad on August 22, 2015.

The Syed Husain Zaheer Medal Lecture (2014): Professor B Yegnanarayana, International Institute of Information Technology, Hyderabad will be delivering The Syed Husain Zaheer Medal Lecture

on *The Problem in Signal Processing –Need to relook at the time frequency analysis of speech signals* at University of Hyderabad, Hyderabad on September 22, 2015.

INTERNATIONAL ACTIVITIES

Nominations/Election of Indian scientists for various positions at International Council for Science (ICSU) and its different Unions

- **Dr Anita A Rampal**, Department of Education, University of Delhi has been nominated for the membership of the Executive Committee of the International Commission on Mathematical Instruction (ICMI) which is commission of the International Mathematical Union (IMU).
- **Dr Sivaramakrishnan Rajan**, Director, National Centre for Antarctic and Ocean Research (NCAOR), Goa has been nominated for the membership of Ad-hoc Panel for the Joint review of the Scientific Committee on Antarctic Research (SCAR) and Scientific Committee on Oceanic Research (SCOR).
- **Professor SC Lakhotia**, Vice-President, INSA and Professor Emeritus & DAE-Raja Ramanna Fellow, Banaras Hindu University, Varanasi has been nominated as the National Focal Point for IAP's Science Education/Science Literacy activities from India. Professor Lakhotia is also a member of Science Education Programme of the Academy.
- **Dr Anindita Bhadra**, Indian Institute of Science Education and Research, Kolkata has been selected by IAP as IAP Young Scientist to attend the IAP Young Scientists Side Event on *Scoping the future: views and ideas of young scientists to tackle global challenges* and the World Science Forum (WSF) to be held during November 4-7, 2015 in Budapest.
- **Dr Mahesh Kumar**, Indian Institute of Technology Jodhpur was nominated to attend the workshop on *Realizing a Sustainable Energy Future: Roles and Tasks for the World's Academies* which was organised by the Royal

Netherlands Academy of Arts and Sciences on June 26, 2015.

- **Professor RB Singh**, Head, Department of Geography, Delhi School of Economics, University of Delhi has been nominated for the membership of Integrated Research on Disaster Risk (IRDR) programmes of ICSU and also as an expert for IAP International Committee to assist with implementation of the Sendai Framework on Disaster Risk Reduction.
- **Dr Ranjini Bandyopadhyay**, Raman Research Institute, Bengaluru has been elected as a Member of ICSU Committee on Freedom and Responsibility in the Conduct of Science for the term 2015-2018.
- **Professor LS Shashidhara**, Indian Institute of Science Education and Research, Pune has been re-nominated for the membership of IUBS Executive Board.
- **Professor Rohini Godbole**, Centre for High Energy Physics, Indian Institute of Science, Bengaluru has been nominated by the Academy to participate in the 11th AASSA Regional workshop on *Gender Issues in Science Research and Education* held during August 26-27, 2015 in Seoul, South Korea.
- **Professor AK Singhvi**, Physical Research Laboratory, Ahmedabad, has been elected as Vice-President, International Union of Quaternary Research (INQUA) for the term 2015-2019.

Workshop/ Symposia/ Conference supported by the Academy

The 15th SCA Conference on *Science and Technology for Culture* was organized by Institute of Technology of Cambodia in cooperation with the Ministry of Education, Youth and Sport of Cambodia, Ministry of Culture and Fine-Arts of Cambodia, and the Science Council of Japan. Professor Rajendra Prasad, Vice-President, INSA attended the conference in Siem Reap, Cambodia held during May 15-16, 2015 as an observer.

Support for Visiting Scientists during May – August 2015

- 13 Indian scientists were supported by the INSA for attending various ICSU sponsored international conferences abroad.
- 32 Indian scientists visited abroad under INSA Bilateral Exchange Programme.

Visit of Overseas Delegates to INSA

- Dr Vincent Caudrelier, City University London, Northampton Square, London recipient of Dr V Ramalingaswami Chair of INSA (2015-16) visited Saha Institute of Nuclear Physics, Kolkata; Jawaharlal Nehru University, New Delhi and Delhi University.
- Dr Saibal Roy, Tyndall National Institute, Cork, Ireland recipient of Dr AS Paintal Chair of INSA visited Indian Association for the Cultivation of Science, Saha Institute of Nuclear Physics, SN Bose National Centre for Basic Sciences and CSIR-Central Glass & Ceramic Research Institute, Kolkata.
- Professor Neelima R Sinha, University of California, USA recipient of Dr BP Pal Chair of INSA visited Delhi University, Indian

Institute of Science, Bengaluru and IISER Pune. During her visit, she delivered a lecture on *Heteroblasty and Heterophylly - What Happens When Two Programs Collide?* at Department of Botany, Delhi University on September 3, 2015.

SCIENTIFIC MEETINGS DURING MAY-AUGUST 2015

- An interactive session of Science Academies' Summer Research Fellows and their mentors was organized at the INSA premises on June 22, 2015. The meeting was chaired by Professor R Gadagkar, President INSA along with Professor Dipankar Chatterji, Molecular Biophysics Unit, Indian Institute of Science, Bengaluru. Professor Dipankar Chatterji, delivered a lecture on *Chance and Necessity: Nurturing the Young Talent*. A large number of summer research fellows, working in Delhi/ New Delhi, and their mentors interacted with the panel after the lecture. The fellows and mentors, while applauding the programme initiated by the three Academies viz., INSA, IASc and NASI, also discussed some problems faced by them during the period of research. Some local fellows of INSA also attended the session.



Interactive session of Summer Research Fellows and their mentors

- Annual meeting of the ICSU National Committee was held on July 28, 2015 at INSA premises.
- A discussion meeting of the Organizing Committee for the forthcoming INDO-US Workshop 2016 was held on August 5, 2015 at Jawaharlal Nehru University. The meeting was attended by Professor Rakesh Bhatnagar, Professor Pawan K Dhar and Ms. Jaishree from Jawaharlal Nehru University; Dr VS Reddy, International Centre for Genetic Engineering and Biotechnology (ICGEB), New Delhi and Dr James LeDuc and Dr Rita S Guenther of US National Academy of Sciences.

SCIENCE & SOCIETY PROGRAMME

Indian National Young Academy of Sciences (INYAS)

The newly established Indian National Young Academy of Sciences (INYAS) meeting was held on June 20, 2015 in the Academy premises. During this meeting the 20 founding members of INYAS selected by the council met for the first time for the selection of seven core committee members (one chair and six members) from among the founding members for regular activities of INYAS. They discussed future activities, the *modus operandi* for inducting new members, and the short and long term goals of INYAS etc.

The following seven were elected as the core committee members to run the activities of INYAS:

Anindita Bhadra (Chair), Assistant Professor, IISER Kolkata; **Vijay Pal Yadav**, Assistant Professor, JNU, New Delhi; **Ranjani Viswantha**, Faculty Fellow, JNCASR, Bengaluru; **Sudarshan Ananth**, Associate Professor, IISER, Pune; **UK Anandavardhanan**, Associate Professor, IIT Bombay; **Rajeev Saraswat**, Scientist, NIO, Goa and **Saptarshi Mukherjee**, Associate Professor, IISER Bhopal as members of INYAS.

AWARD AND HONOUR TO INSA FELLOW

- Professor R Rajaraman, Emeritus Professor of Theoretical Physics, School of Physical Sciences, Jawaharlal Nehru University, New Delhi was honoured by the Governor of the Hiroshima prefecture, H.E. Hidehiko Yusaki for his efforts on nuclear disarmament at the 70th Anniversary Commemoration ceremony of the Bombing of Hiroshima on August 6, 2015 at the Hiroshima Peace Park built at “Ground Zero” of the bomb explosion.



Professor Rajaraman with Ambassador Lalit Mansingh, a fellow invitee, in front of the “Dome”, the iconic building which survived despite being located directly below the exploding bomb

- Professor Raghavendra Gadagkar, President INSA, has been awarded the highest civilian honour of the Federal Republic of Germany, the “Cross of the Order of Merit” by the Consul General Joern Rohde for his contribution in the field of behavioural ecology and socio-biology as well as strengthening research linkages between India and Germany.



Mr. Joern Rohde pinning the Cross of the Order of Merit to Professor Gadagkar

RECENT PUBLICATIONS OF THE ACADEMY

Proceedings of the Indian National Science Academy

Volume 81, No.3 (June 2015) issue has been published. This issue contained five review articles, two book reviews, one research paper and a

commentary besides the Editorial. The issue also included a medal lecture by Professor VS Borkar, Department of Electrical Engineering, IIT Mumbai on *Playing Dice with the Universe: Algorithms for Random Environments*.

Indian Journal of History of Science (IJHS)

Volume 50, No. 2 (June 2015) of the 50th Anniversary year of *IJHS* has been published. The issue contains papers on classification of cancer in the Ayurvedic text, medicinal plants of Indian *purāṇas*, substances in medieval *Vaidyanighaṇṭus* (medical lexicons) ancient Indian mathematical sciences in Chinese compilation of Gautam Siddha, *Nārāyaṇā*'s generalisation of *mātrā-vṛtta-prastāra* and Virahāṅka-Fibonacci representation of numbers, rationale for *Vākyas* pertaining to the Sun in *Karanapaddhati*, Lālah Bulhomal Lāhorī and the production of traditional astronomical instruments, use of Ambergris in perfumery, traditional healing practices of North East India, historical antecedents of cancer surveillance and scientific exploration of the snow fungus. The issue also contains report on history of science project on metrological traditions of south India and review of the book *Indian Astronomy—Concepts and Procedures* apart from news from history of science.

Indian Journal of Pure and Applied Mathematics (IJPAM)

Volume 46, No.3 & 4 (June & August 2015) issue of *IJPAM* has been published.

OBITUARY**Fellows****Sarmukh Singh Bir**

Sarmukh Singh Bir (*b* 28 August 1929; *d* 26 August 2015) obtained his PhD from Punjab University. He began his career at Punjab University, Chandigarh and shifted to Punjabi University, Patiala in 1967 as Reader and Head, Department of Botany.



He was appointed Professor of Botany in 1969 and retired as Senior Professor in 1989. Professor Bir after retirement spent nearly 20 years at Punjabi University, Patiala as Professor Emeritus. He had been a CSIR Emeritus Fellow; INSA Senior Scientist (1995-2000) and Honorary Scientist (2001-04, 2006-09).

Professor Bir significantly contributed to the advancement of botanical knowledge about Indian flora. He was known for his comprehensive cytological, biosystematic, phytogeographic, taxonomic and morphological studies on more than 500 species of higher plants, ferns and fern allies from different floristic regions of India in Himalaya, Pachmarhi, Nilgiris and Palni Hills. Professor Bir's discovery and naming of over a dozen new taxa of Indian ferns is highly significant in pinpointing the vast diversity and richness of Indian vegetation. His postulate about the existence of polyploidy in ferns, ferns allies and woody taxa of forests has been well received by flora scientists.

Professor Bir was recipient of Professor P Maheshwari Memorial Medal (Indian Botanical Society), Professor DD Pant Medal & Oration Award (Society of Bionaturalists, India); Platinum Jubilee Lecture of Indian Science Congress; Birbal Sahni Foundation Medal to name a few. He was elected as fellow of National Academy of Sciences (India), Allahabad.

Professor Sarmukh Singh Bir was elected to Fellowship of the Indian National Science Academy in 1981 and served as its Council member during 1993-95.

Satyendra Nath Ghosh

Satyendra Nath Ghosh (*b* 15 August 1918; *d* 24 June 2015) obtained his DSc degree in Physics from Calcutta University. He was appointed as Head, Department of Physics, Senior Professor, Department of Electronics and Communication, Allahabad University and Sir Rashbehari Ghose Professor of Applied Physics, Calcutta University. After superannuation from Calcutta University, he joined as INSA Senior Scientist from 1985-87.



Professor Ghosh's studies focused mainly on Applied Physics, Communication, Space Science and Microwave Spectroscopy. He received many distinguished scholarships, such as Adir Dutt Research Scholarship and was ICI Research Fellow; Post-doctoral Research Fellow, Duke University; Scientist, Wentworth Institute; Post-doctorate Fellow, Harvard University; and Scientist, Geophysical Research Centre, USA. Professor Ghosh was recipient of Sampurnanand Prize of National Academy of Sciences, Allahabad. He was President of Engineering and Metallurgy Section of Indian Science Congress. A Lecture Hall is set up in Allahabad University in his name and a lecture, known as "Professor SN Ghosh Lecture", is delivered every year at Allahabad by a selected Eminent Scientist.

Professor Satyendra Nath Ghosh was elected to the Fellowship of Indian National Science Academy in the year 1968 and served the Council as an additional member during 1972-73.

Sethunathasarma Krishnaswami

Sethunathasarma Krishnaswami (b 21 May 1945; d 20 July 2015) obtained his PhD from Bombay University specializing in Geochemistry. He did his post doctoral research work on the applications of U-Th series nuclides in aquatic systems from Yale University. He then



joined Physical Research Laboratory (PRL), Ahmedabad. After his superannuation from PRL, he was an INSA Senior Scientist. He served as Vice-President of IAPSO (International Association for the Physical Sciences of the Oceans), SCOR (Scientific Committee on Oceanic Research of ICSU) and as Executive Member and Treasurer of IGBP (International Geosphere-Biosphere Programme of ICSU).

Professor Krishnaswami's research focused on the applications of environmental radioactive and radiogenic isotopes to study the earth surface processes. His contributions in isotope geochemistry have provided new and powerful environmental radioactive and radiogenic tracers and approaches to understand and quantify natural processes, such as sedimentation and particle mixing in lakes and coastal oceans; growth history of marine and fresh-water ferromanganese deposits; contaminant transport in sea water and sub-surface aquifers; weathering and erosion in the Himalaya and Deccan traps and their influence on global change, etc.

Professor Krishnaswami received several awards including INSA Young Scientist Medal (1975), Krishnan Medal (1981) and SS Bhatnagar Prize (1984). He was a Fellow of the Indian Academy of Sciences, Bangalore, National Academy of Sciences (India), Allahabad, The Academy of Sciences for the Developing World, Trieste, American Geophysical Union, Geochemical Society and European Association of Geochemistry.

Professor Sethunathasarma Krishnaswami was elected to the Fellowship of the Indian National Science Academy in 1989 and served as Council

member during 2002-04.

Adusumilli Srikrishna

Adusumilli Srikrishna (b 01 January 1955; d 20 January 2013) obtained his PhD from Hyderabad University and carried out postdoctoral research in the Universities of Chicago and Columbia, USA. He joined the Department of Organic Chemistry, IISc, Bangalore, in 1985, as a



Lecturer and later rose to be a Professor (1999). He also served the Department as the Chairman during 2003-05.

Professor Srikrishna made significant contributions in organic synthesis covering development of synthetic methodologies, total synthesis of natural products both in racemic and enantiomeric forms, development of new reagents for selective organic transformations, and investigation and application of molecular rearrangements in organic synthesis. He accomplished the total synthesis of a large number of sesquiterpenes, both in racemic as well as optically active, and in the process confirmed/established the absolute configuration of several natural products.

Professor Srikrishna received many awards and recognitions, including the INSA medal for young scientist, Dr SH Zaheer Young Scientist Award, BM Birla Science Award, Shanti Swarup Bhatnagar Prize, RD Desai Commemoration Medal, AB Kulkarni Endowment Lecture and Professor S Swaminathan Endowment Award. He was also DST JC Bose National Fellow. He was elected to the Fellowship of Indian Academy of Sciences, Bangalore and National Academy of Sciences, Allahabad. He was a member of the Editorial Board of the *Proceedings of the Indian National Science Academy* and *Indian Journal of Chemistry*.

Professor Adusumilli Srikrishna was elected to the Fellowship of Indian National Science Academy in the year 2003.

Foreign Fellows

Vladimir G Kadyshevsky

Vladimir G Kadyshevsky (b 5 May 1937; d 23 September 2014) obtained his PhD in 1962. He was a well-known theoretical physicist in the elementary particle and quantum field theory. Since 1970 Professor Kadyshevsky had been Professor of the Physics at Moscow State University. He was the Director of JINR Laboratory of Theoretical Physics (1987-92) and Director of the Joint Institute for Nuclear Research (1992-2005). Since January 1, 2006 he was Scientific Leader of the Joint Institute for Nuclear Research.



Professor Kadyshevsky wrote a number of papers on the relativistic theory of elementary particles in the quantized space-time that anticipated the research in “non-commutative geometry” in the 1990s. His name was connected with the elaboration of a specific diagramme technique for the amplitudes on mass shell. Relativistic 3D equations, established in this framework, are known in the literature as “Kadyshevsky equations”. They are applied to calculate interactions of particles, nuclei and to describe the quark structure of hadrons. In recent years Professor VG Kadyshevsky had developed a new approach to describing strong and electroweak interactions beyond the scope of the Standard Model. Professor Kadyshevsky was a member of the Russian Programme for Science & Technology and the IUPAP Commission on Particles and Fields. He was the President of the Union of the Russian Scientific Societies (1993-99).

Professor Vladimir G Kadyshevsky was elected to the Foreign Fellowship of the Indian National Science Academy in the year 2004.

Charles Hard Townes

Charles Hard Townes (b 28 July 1915; d 27 January 2015) obtained his PhD from California Institute of Technology, USA specializing in Spectroscopy, Quantum Electronics and Astrophysics. He was the Chairman, Department of Physics, Columbia University (1952-55), Vice-President and Director of Research, Institute for Defence Analysis (1959-61), Provost, Massachusetts Institute of Technology and later from 1986, he was Professor Emeritus in University of California.



Professor Townes' principal scientific work was in microwave spectroscopy, nuclear and molecular structure, quantum electronics, radio astronomy and infrared astronomy. He won the Nobel Prize for Physics in 1964 for original contributions to the maser and laser. Professor Townes' work in astrophysics included development of new infrared techniques (and work in a high flying NASA airplane), discovery of stable molecules in galactic clouds, and evidence for a large black hole in the centre of our galaxy. He developed a pair of movable telescopes, for obtaining much more detailed infrared images of astronomical objects than had previously been possible.

Professor Townes was recipient of several awards including Nobel Prize in Physics (1964). He was a Fellow of National Academy of Sciences; Royal Society, London; American Physical Society (President 1967) and American Philosophical Society.

Professor Charles Hard Townes was elected to the Foreign Fellowship of the Indian National Science Academy in the year 1993.

ANNOUNCEMENTS

Nomination for Election of Fellows

The last date for receiving nominations for election of Fellows is **October 15, 2015**. Nominations received on or before October 15 will be included for consideration in the year 2016, while those received after October 15, will go for the year 2017. Nomination form can be downloaded from the INSA website **www.insaindia.org**.

Nomination for Election of Foreign and Pravasi Fellows

Nominations are invited from the Fellows of INSA for election of Foreign Fellows and Pravasi Fellows for the year 2016. Nomination form can be downloaded from the INSA website **www.insaindia.org**.

INSA Medal for Young Scientists - 2016

Nominations are invited for **INSA Medal for Young Scientists – 2016**. Those born on or after **January 1, 1981** are eligible for consideration in the year 2016. The awardee shall receive a **certificate**, a **bronze medal** and cash award of **Rs. 25000/-**. Proposals may be submitted by a Fellow of the Indian National Science Academy or by earlier recipients of this award. Scientific societies of national standing, university faculty, post-graduate departments of research institutions may also nominate eligible candidates. The last date for receiving nominations for INSA Medal for Young Scientists is **October 31, 2015**. Nomination proforma can be downloaded from the website **www.insaindia.org**.

Proposal by INSA Fellows for lectures to young students and teachers of schools and colleges in the remote/rural areas

The Academy has launched a programme under which INSA Fellows are encouraged to deliver Popular Lectures to young students and teachers of schools and colleges in remote/rural areas. Proposals are invited from Fellows with details like name and address of the school/college where they wish to deliver the lecture, title/s of lecture/s, proposed dates and the quantum of required travel support. Proposals may be sent to Executive Director, INSA at **esoffice@insa.nic.in**, **insacouncil@gmail.com** with a copy to **sci-soc@insa.nic.in** at the earliest.

Call for Research Proposal in History of Science

The Indian National Commission for History of Science approves, under the guidance of a Research Council, Research Projects on various subjects pertaining to history of science and technology in India. Through this programme, the Investigator can take up source and theme oriented study and compilations of important sources with commentaries; translation of important technical primary sources on mathematics, astronomy, medicine, alchemy, agriculture, natural products, life sciences, scientific traditions including oral traditions of scientific nature, metals and metallurgy, architecture and irrigation technology, for critical assessment relating to ancient and medieval periods. The Commission gives equal emphasis for historical evaluation of science and technology scenario in India during the 19th and 20th centuries. Study of pioneering institutions, popular perceptions of science development, tools, techniques and how the knowledge in each area of science has grown conceptually on the basis of International perspectives, are some examples of the research areas. Themes may also be selected depending on candidates' own aptitudes and specializations.

The last date for submitting research proposals is December 31, 2015. For all other details and application form, visit the website www.insaindia.org or mail at ijhs@insa.nic.in.

Nomination for INSA Awards

The last date for receiving nominations for the following INSA Awards due for the year 2016 is **October 15, 2015**:

1. INSA-Vainu Bappu Memorial Award
2. JC Bose Memorial Lecture
3. The Srinivasa Ramanujan Medal
4. The Jagadis Chandra Bose Medal
5. The Silver Jubilee Commemoration Medal
6. The Golden Jubilee Commemoration Medal (*for Chemical Sciences*)
7. Professor Brahm Prakash Memorial Medal
8. Professor K Naha Memorial Medal
9. The Chandrakala Hora Memorial Medal
10. Professor S Swaminathan 60th Birthday Commemoration Lecture
11. Professor Darshan Ranganathan Memorial Lecture
12. Dr Biren Roy Memorial Lecture

Nomination form can be downloaded from the INSA website www.insaindia.org.