

RESEARCH AND DEVELOPMENTAL ACTIVITIES IN THE FIELDS OF
FUSED SALT ELECTROLYSIS AND ELECTROTHERMAL PRODUCTS
AT CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE,
KARAIKUDI (A REVIEW)

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Work on Fused Salt Electrolysis :

Processes for the extraction of (1) sodium metal from fused bath containing sodium chloride in admixture with other chlorides (2) magnesium metal from fused bath containing anhydrous magnesium chloride in admixture with other chlorides, and (3) misch metal from fused bath containing anhydrous misch metal chloride in admixture with other chlorides of metals have been developed. In all these cases, experimentation was done in a systematic manner employing 500, 1000, 1600, 2500 and finally, in the case of misch metal 4000 ampere cells and in the case of magnesium and sodium 10,000 ampere cells were run successfully and data collected.

Processes on the production of misch metal and sodium metal based on the technology developed at CECRI have been released to parties. The starting material for the production of misch metal is hydrated rare earth chlorides obtained from M/s. Indian Rare Earths left after the extraction of thorium from monazite sands. High quality metals have been obtained.

Under the scheme jointly sponsored by Tamil Nadu Government and CSIR, large laboratory scale work and also pilot trials were successfully conducted for the production of magnesium metal utilising (1) siliceous magnesite and byproduct hydrochloric acid (2) magnesium chloride recovered from bitterns, and (3) anhydrous magnesium chloride obtained as byproduct in the production of titanium and zirconium sponge from their respective anhydrous chlorides at Nuclear Fuel Complex, Hyderabad. The technology has been transferred to Tamil Nadu Industrial Development Corporation, a Government of Tamil Nadu undertaking for setting up a plant utilising the magnesium chloride, recovered from sea bitterns obtained by solar evaporation in backward area with a capacity of producing 2 tonnes of magnesium per day. The magnesium metal produced at the pilot plant was utilised by a number of industries in India including Government Mint, Defence Department and the like. The production of a suitable cell feed from magnesium chloride solutions based on a spray drier technology developed at CECRI is worth mentioning in this connection.

Laboratory scale experiments have been conducted to obtain lead-calcium, lead-calcium-sodium and lead-calcium-barium alloys employing molten lead as cathode. Employing molten aluminium as cathode, aluminium-magnesium alloys have been produced.

Electrochemical Products :

With a view to utilising high grade crystalline limestone which are not usually recommended for the production of calcium carbide in spite of their very high purity, and also the use of charcoal exclusively as a reductant in the production of calcium carbide, systematic experiments have been carried out and conditions have been established for the production of calcium carbide of commercial grade.

Conditions have been established for the production of calcium silicide with calcium content of 18–20 per cent and above 60 per cent silicon employing an improvised 3-phase submerged arc furnace and the process has been released to Defence and to the foundry industry with a combination of 28 per cent calcium and 60 per cent silicon.

Utilising an unlined improvised 3-phase submerged arc furnace with sides and bottom water cooled, conditions were established for the production of fused alumina, suitable for use in abrasive industries employing ferruginous bauxites and also alumina rejects from industries.

Utilising a lined improvised 3-phase submerged arc furnace, conditions were established for the production of titanium slag containing about 80 per cent titanium dioxide in one stage utilising unground ilmenite obtained from both Chawara and Manavalakurichi having 55–62 per cent titanium dioxide content with the production of pig iron as a valuable product. A simple method of upgrading this 80 per cent titanium dioxide slag to about 94 per cent titanium dioxide has also been evolved. This work is of great importance as it eliminates the use of large quantities of hydrochloric and sulphuric acids or chlorine for the beneficiation of ilmenite which pose disposal problems of iron salts. The synthetic rutile thus obtained having 94 per cent titanium dioxide is a good raw material for the production of titanium metal and titanium dioxide through the intermediate production of titanium tetrachloride.

Under the existing conditions in India, it appears economically viable to set up small units capable of producing half a tonne to one tonne per day of calcium carbide, fused alumina, titanium slag from ilmenite and also calcium silicide.

Keywords : Research & Development; Fused Salt Electrolysis; Electrothermal Products; Sodium, Magnesium & Misch Metals; Calcium Silicide; 3 Phase-submerged Arc Furnace—Lined & Unlined

FUSED SALT ELECTROLYSIS

THE author and his group at the Central Electrochemical Research Institute have developed processes for the extraction of (1) sodium metal from fused bath containing sodium chloride in admixture with other chlorides (2) magnesium metal from fused bath containing anhydrous magnesium chloride in admixture with other chlorides, and (3) misch metal from fused bath containing anhydrous misch metal chloride in admixture with other chlorides of metals. In all these cases, experimentation was done in a systematic manner employing 500, 1000, 1600, 2500 and finally, in the case of misch metal 4000 ampere cells and in the case of magnesium and sodium 10,000 ampere cells were run successfully. Processes on the production of misch metal and sodium metal based on the technology developed at CECRI were released to parties, the concerned CECRI staff acted

as consultants for setting up the plant and training their personnel at site. The installed capacity for sodium metal production is 2 tonnes per day. The installed capacity for misch metal is 140kg and multiples of the same. High quality metals have been obtained and are of wide commercial use. The starting material for the production of misch metal is hydrated rare earth chlorides obtained from M/s. Indian Rare Earths left after the extraction of thorium from monazite sands.

The starting material for the production of sodium metal is pure sodium chloride free especially from iron, silica, alumina, sulphur and phosphorous, pure calcium chloride and barium chloride free from moisture, sulphur, phosphate, iron, alumina and silica are also needed in the initial stages for starting up sodium cell and later for addition to the bath to make up the losses. Pure calcium chloride of the above description along with anhydrous misch metal chlorides obtained from hydrated chlorides free of sulphur, alumina, silica and phosphate are required in the production of misch metal by fused salt electrolysis. Solid steel cathode is used for sodium metal extraction. Solid steel cathode or a layer of liquid misch metal on steel cathode is used for recovering misch metal. The anode is graphitic carbon of a quality suitable for fused salt electrolysis in both cases.

Use of Ceramic Diaphragms in the Place of Metal Diaphragms for the Production of Sodium

Improved beta-alumina diaphragms in the form of tubes closed at one end with diameters upto 1.5cm with 15cm high and with about 2mm thickness have been formed in the cold, employing decomposed hydrated melts containing suitable mixtures of aluminium sulphate, sodium sulphate and magnesium sulphate. The formation of the tube in the cold was done by utilising an improvised isostatic pressure equipment. This was followed by careful drying and regulated heating to temperatures upto 1700 °C soaking at the high temperature in the presence of sodium oxide vapour for a required length of time, cooling and then utilising it.

Another sodium conducting solid ion conductor is zirconium-silicate phosphate which has better properties than even modified beta alumina. We have produced cold formed tubes of the same dimensions as that of beta alumina employing suitable oxides of zirconium, silica and sodium carbonate, ammonium phosphate combinations as starting material. The cold formed material was heated also to required high temperature of about 1300 °C and then tested for its porosity and ion conducting properties. Experiments are in progress to construct cells both for the production of sodium metal and also for utilising these diaphragms for use as sodium-chlorine storage battery. The electrolyte in the case of sodium metal production is a suitable mixture of sodium chloride and zinc chloride. In the case of sodium-chlorine battery, the positive mix is a combination of sodium chloride, anhydrous aluminium chloride with antimony chloride and the conducting lead of tungsten molybdenum and the like and with a metallic sodium as the other electrode with mild steel vessel itself as connecting lead.

In the absence of a diaphragm, with molten zinc as cathode, suitable mixtures of pure anhydrous zinc chloride (obtained from primary and secondary sources of

zinc) and sodium chloride on electrolysis gave zinc metal. With molten lead as cathode and with pure lead chloride (obtained from primary and secondary sources of lead) alongwith required amounts of sodium chloride and potassium chloride, molten lead is obtained. In both cases, graphitic carbon was the anode and chlorine was evolved.

Calcium Metal

Employing a suitable calcium chloride-sodium chloride composition in a simple electrolytic fused salt cell at a temperature of 600–700 °C, conditions have been established for the production of calcium metal through the discharge of calcium-sodium alloy at the cathode which, on rising above the cathode reacting with molten electrolyte furnishes calcium metal containing traces of sodium as impurity. This simplified method of production of calcium has found application in the preparation of calcium-silicon-magnesium alloys for use in the production of nodular cast iron. We have produced calcium-magnesium-misch metal alloys with this material and this master alloy could be mixed with different proportions of ferrosilicon and utilised in the manufacture of nodular cast iron. This process for the production of calcium metal has been released to an industry for the production of nodular cast iron.

Lead Calcium-Sodium Alloy

Employing molten lead as cathode we have standardised conditions on a laboratory scale for the preparation of lead-sodium, lead-calcium, lead-sodium-calcium, alloys. The work is of importance for the production of metals like calcium, magnesium, sodium etc. because the lead alloys could be heated out of contact with air to recover the metals and the molten lead containing small quantities of these metallic impurities could be fed back to the electrolytic cell. This two-stage process of producing metals like sodium, calcium, magnesium is also of importance because of the fact that the electrolytic cell designed is very simple, no diaphragm is employed and the discharge of metals onto molten cathode is very favourable electrochemically also. In an alternative procedure, lead-sodium, lead-calcium, lead-magnesium alloys could be used as anodes and the metal can be recovered. Greater efficiency in the production of these metals is possible because of the fact that there is no recombination between metals and chloride.

Magnesium Metal

Under the scheme jointly sponsored by Tamil Nadu Government and CSIR, large laboratory scale work and also pilot plant trials were successfully conducted for the production of magnesium metal utilising (1) siliceous magnesite and byproduct hydrochloric acid (2) magnesium chloride recovered from bitters, and (3) anhydrous magnesium chloride obtained as a byproduct in the production of titanium and zirconium sponge from their respective anhydrous chlorides at Nuclear Fuel Complex, Hyderabad. The technology has been transferred to Tamil Nadu Industrial Development Corporation, a Government of Tamil Nadu undertaking for setting up a plant utilising the magnesium chloride, recovered from sea

bitterns obtained by solar evaporation in a backward area with a capacity of producing 2 tonnes of magnesium per day. The magnesium metal produced at the pilot plant was utilised by a number of industries in India including Government Mint, Defence Department and the like. The production of a suitable cell feed from magnesium chloride solutions based on a spray drier technology developed at CECRI is worth mentioning in this connection.

The spray drier that has been specially designed, fabricated and operated at CECRI converts a 30–33 per cent solution of magnesium chloride straightaway to a fluffy powder having approximately $\text{MgCl}_2 \cdot 1.25 \text{H}_2\text{O}$. In addition to its use as the cell feed, the dehydrated magnesium chloride of the above composition has also been found to be useful in the manufacture of fluxes suitable for melting magnesium and magnesium alloys.

Aluminium-Magnesium Alloys

Aluminium-magnesium alloys have been produced employing molten aluminium cathode onto which magnesium has been discharged from a fused bath. Experiments have been conducted on a laboratory scale and conditions have been standardised. This work is of specific significance as a brittle alloy containing about 30 per cent magnesium could be utilized in fire works. It can also be used as a master alloy for diluting the aluminium-magnesium/magnesium-aluminium alloys to the required degree. One important application can also be that aluminium-magnesium alloys when reacted outside the electrolytic cells with pure anhydrous aluminium chloride derived from any source such as from clay could yield aluminium resulting in the production of magnesium chloride which can be fed back to the cell along with a required portion of aluminium for use as molten cathode.

Massive Manganese

The possibility of employing low grade ore to produce manganese metal by fused salt electrolysis at 1200–1300 °C was investigated. The metal can be employed in alloy steel industry. Experiments were conducted in 400 ampere cell in manganese fluoride-calcium fluoride bath. The feed material is dried manganese ore of –100 mesh size. The metal obtained contained 80.6 per cent manganese, rest iron and 0.2 per cent phosphorus. As the phosphorus is a deleterious impurity, only when pure cheap manganese oxide got as a byproduct in any industry is available, then this process may be attractive. In one of the experiments in which pure manganese oxide is obtained from calcined manganese carbonate, the metal obtained was 99.3 per cent pure.

ELECTROTHERMAL PRODUCTS

Production of Calcium Carbide in a Three-Phase Electric Arc Furnace

With a view to utilise the high grade crystalline limestone which decrepitates (becomes powdery) when heated to high temperatures (and hence considered unfit normally for the production of calcium carbide) experiments were undertaken to

utilise it along with the locally available raw materials in South India viz., charcoal and/or lignite char. Conditions have been established and the product quality conforms to Grade B Specifications even when petroleum coke is not utilised. The phosphorus content of calcium carbide is within limits.

Employing the improvised facility available at this Institute we have conducted experiments in a 380kVA arc furnace for testing the suitability of U.P. limestone (a very high class amorphous limestone) for calcium carbide production and given the test report. We are able to undertake similar trials for meeting the requirements of any private or government bodies.

We have undertaken the contract to instal a 380kVA arc furnace in Burma at Rangoon before the end of this year for the production of calcium carbide at the instance of National Research Development Corporation of India under Indo-Burma Technical Co-operation Agreement.

This process will later be released to industries in India on the same scale with the complete technology pack. Taking into account the future industrialisation envisaged on a small and a medium scale in various rural areas and the necessity for the use of acetylene in many welding operations, small units of this capacity capable of giving 1/2 to 3/4 ton per day would be very attractive.

Production of Calcium Silicide in a Three-Phase Electric Arc Furnace

Calcium silicide having a calcium content of 18–20 per cent, above 60 per cent silicon, is of a specific requirement by Defence. We have established conditions on a small scale and released the process free of cost to the Defence.

Calcium silicide containing about 30 per cent calcium, 60 per cent silicon, 4 per cent iron is needed for the production of mehanite casting and the like in foundries. We conducted experiments on a small scale employing a 60kVA arc furnace. The three well-established procedures for the production of calcium silicide viz., (1) reaction of calcium oxide/carbonate with quartz and carbon, (2) reaction between calcium oxide, calcium carbonate and ferrosilicon having a silicon content of not less than 75 per cent and (3) reaction between calcium carbide and quartz were tried extensively. In addition to the three processes, some countries also employ reaction between silicon and calcium oxide.

We have established that the process dealing with reaction between calcium oxide and quartz in the presence of carbon at high temperatures gives a poor yield. A maximum of 25 per cent of theoretical yield is alone possible. The reaction between calcium carbide and quartz with or without carbon was inferior to the reaction between calcium carbide and ferrosilicon. By the process involving reaction between calcium oxide and ferrosilicon (75 per cent Si), we were able to produce calcium silicide of acceptable quality. The product has been tested and utilised by Messrs India Pistons and by Sayee Enterprises, Trichy. This product was sent by M/s. Advani Oerlikon to France and the French company have also tested the quality of the product for use in foundry.

Initially our pilot plant trials were confined to the production of 25 to 27kg of calcium silicide in a batch of three hours. These experiments were conducted in an unlined water cooled furnace. We were having in our programme to adopt this process by employing a bogie-hearth furnace wherein after conducting experiments for three hours, the furnace will be shifted and allowed to cool and another furnace ready will take its place. Recently, we have established conditions for producing calcium silicide in carbon/graphite lined furnace and continuous tapping has also been successful. As improvement to this process we are investigating the use of bauxite as addition to the calcium oxide/calcium carbonate/ferrosilicon mixtures and to see whether it is possible to obtain a better product containing calcium-aluminium silicate slag which can be easily separated out from the calcium silicide product and also to examine its usefulness as a cement. The process has been demonstrated to Messrs Silical Metallurgic Private Limited, Coimbatore, to whom we have released the process. The party is proposing to set up a plant capable of producing about 150 to 200kg/day of calcium silicide having a calcium content ranging from 28-30 per cent based on our process at Industrial Estate, Hosur, Dharmapuri Dist. Two more parties have recently been licensed also to exploit our process on calcium silicide.

Fused Alumina

In an unlined arc furnace with sides and bottom water-cooled, we were able to produce fused alumina starting from ferruginous bauxites and also alumina derived from non-bauxitic resources. The alumina thus produced was found to conform to the commercial specification. We were able to utilise the products from the byproduct slag obtained in the aluminothermic reaction for the production of metals like manganese and chromium and also from the low grade emery powder produced on a small scale as a byproduct in the manufacture of abrasives by private parties, in the production of fused alumina. We have successfully conducted a few experiments in 380kVA arc furnace and produced fused magnesium oxide, aluminium oxide mixtures. Capacity for fused alumina production is 30kg/hr in a batch process of 3 hours.

We have taken up recently a sponsored work for the production of fused alumina based on the material sent by M/s. Alirox Industries Limited, Yercaud. In a batch, we have produced 200kg of fused alumina and we have sent about 100kg for testing its usefulness by the party. A few variations, if found necessary, would be effected to produce fused alumina of the grade required by the firm.

Beneficiation of Ilmenite

After several laboratory scale experiments employing a 60kVA single phase arc furnace, we have established conditions for the production of 80 per cent titanium dioxide slag in one stage even from unground ilmenite of both Chawara and Manavalakurichi, in a three phase 380kVA arc furnace. While normally, in direct reduction process in an arc furnace 70 per cent titanium dioxide slag alone is possible (being produced commercially and marketed) we have succeeded

in obtaining in one stage 80 per cent titanium dioxide through the addition of proper amounts of sodium carbonate and converting the portion that would normally be fixed up as ferrous titanate into sodium titanate. The 80 per cent titanium dioxide product when ground and reacted with nitric acid yields not less than 92 per cent titanium dioxide and from the resulting liquor by reaction with sodium carbonate high grade iron oxide suitable for use even in ferrite manufacture is obtained with the simultaneous production of sodium nitrate solution as a product (sodium nitrate could be converted into potassium nitrate by double decomposition with potassium chloride and thus a valuable mixed fertiliser is obtained). The sulphuric acid requirements for processing this 92 per cent titanium dioxide to obtain high grade titanium dioxide will be far less compared to starting with ilmenite containing about 60 per cent titanium dioxide from Chawara. The great advantage of this process is pig iron obtained as a valuable byproduct. It eliminates the necessity of (i) grinding the ilmenite to fine powder, (ii) reduction of the ferric oxide at least to ferrous oxide, if not to iron stage, in a rotary kiln, (iii) cooling of the product out of contact with air, and (iv) pressure leaching with large volumes of hydrochloric acid in rubber-lined equipment at temperatures of 105 °C, filtering of the material and washing it to get 92 per cent titanium dioxide. Thus, production of enormous amounts of ferrous chloride-hydrochloric acid would be eliminated in production of 92 per cent titanium dioxide from Manavalakurichi ilmenite containing above 52 per cent TiO_2 .

In the case of sulphuric acid treatment, since the requirement of sulphuric acid would be much smaller compared to the direct use of finely powdered ilmenite (in the electrothermal process, we are utilising the ilmenite as such and therefore powdering costs are eliminated), the volume of ferrous sulphate-sulphuric acid obtained as a waste product is very much less. Hence, the cost of acids in processing ilmenite and the cost of disposal of waste without polluting the waters add significantly to the importance of electrothermal process. The 92 per cent titanium dioxide slag obtained by the electrothermal process appears to be ideal for chlorination as it has a deposit of carbon on it which is retained even after mild leaching with acids.

In the initial stages, we were obtaining about 100kg of 80 per cent titanium dioxide in a batch process lasting four hours in a 380kVA arc furnace by manipulating the operating conditions. Pig iron was a byproduct. Both Chawara and Manavalakurichi ilmenite which have different structures have been utilised successfully when used as such without any grinding as a feed along with carbon and sodium carbonate to the electric arc furnace.

Recently, we have conducted some trials with 380kVA lined carbon/graphite arc furnace to tap out molten pig iron and slag. This tapping of materials from lined arc furnace would prove to be more economical than the batch process in which unlined improvised arc furnace has been employed by us.

We have so planned our work that whenever the process is released to the industry, the transformer, the arc furnace, busbar and other facilities could be utilised for the production of one or the other electrothermal product depending

upon the demand for the products either in a water cooled unlined furnace (especially in the case of fused alumina and calcium silicide) or in the lined arc furnace for the production of titania slag and iron or calcium carbide.

We have in our programme of doubling the capacity and conducting these trials by connecting another transformer to the existing one and establishing the optimum conditions since at a later stage it might be expected that doubling the capacity of production of the said materials would be more economical and advantageous to produce these materials on a small scale. Thus a turnkey offer could be made available.

Discussion

S. GURUSWAMY (*Central Electrochemical Research Institute, Karaikudi*): Sodium is a very active element. Any scope to tame the violent reaction for slow useful reactions to release the hydrogen of water ?

V. ARAVAMUTHAN : One could try utilising suitable alloys of sodium with other metals such as lead-sodium to get a regulated supply of hydrogen, keeping temperature, pressure and pH of the medium at the optimum values which would vary depending upon the time for which hydrogen is tapped and also the impoverishment of sodium due to liberation of hydrogen continuously.

H. C. GAUR (*Centre of Advanced Study, Department of Chemistry, University of Delhi, Delhi*): Has some work been done at CECRI to produce alloys by fused salt electrolysis ?

V. ARAVAMUTHAN : Yes. We have been conducting large laboratory scale experiments on the following (1) lead-calcium (2) lead-sodium (3) lead-sodium-calcium (4) aluminium-magnesium (5) magnesium-barium and (6) magnesium-silicon alloys.

A. V. GORODYSKY (*Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, USSR*): 1. How can you estimate the perspectives and advantages of both electrochemical and electrothermal processes ? Probably, electrochemistry is convenient when electrothermal process does not go or when it is necessary to have very pure product ? 2. What are the perspectives for some changing of hydro electrometallurgy to the high temperature one ? 3. If I have understood you correctly, chlorides are more preferable molten electrolytes, isn't it ? And what about the others, such as fluorides, bromides, silicates ?

V. ARAVAMUTHAN : 1. Depending upon the availability of raw material, electric energy, fossil fuels and water at economic rates and in abundance, one could choose chemical, thermal, electrothermal, electrochemical or also combination processes. Taking the example of production of acetylene through an electrothermal product *via* calcium carbide, in tropical countries like India, one could think of obtaining cheap methane by the anaerobic digestion of waste cellulosic materials, animal refuse and the like or mixtures of these and utilise about two-thirds of methane for meeting the energy requirements for decomposing methane out of contact with air to obtain acetylene in good yield from the remaining one-third of the methane. This procedure would be attractive especially when quality lime is not available and also electric energy is costly, in tropical countries like India.

Although aluminium silicide from clay could be produced by electrothermal process, yet employing cheap source of oxygen from air through the use of manganese-phosphonium compounds in a cyclic process and also cheap source of carbon monoxide such as the one obtained even from low grade coal, coke fines with plenty of ash and even sulphur, when they are subjected to fluidization after suitable admixture with calcium oxide in a current of oxygen could help obtain high temperatures economically and therefore, could replace electrothermal procedures under the said favourable conditions. The purity of the product is also a factor. However, even impure product

such as aluminium silicide produced without the use of electric energy as indicated before, in a cyclic process employing either anhydrous aluminium chloride or molten zinc could give aluminium of purity which is normally obtained by fused salt electrolysis. Alloys like titanium boride could be produced by fused salt electrolysis as well as by electrothermal procedures. Depending upon the expertise available, one could choose either the fused salt technology of the electrothermal procedure.

2. If I have understood the question correctly, I am to frame the question as follows : For one and the same metal whether electrolytic recovery by fused salt electrolysis or aqueous electrolysis could be decisive. The answer is : Zinc is a typical example of a metal which can be obtained both by aqueous electrolysis and by the fused salt electrolysis. In the latter case, as already pointed out, high current densities of the order of say $4-6\text{A}/\text{sq. in.}$ of cathode area can be employed in contrast to about a maximum of $60\text{A}/\text{sq.ft.}$ in the case of aqueous chloride electrolysis. This would make the size of the electrolytic cells very compact while dealing with fused salt electrolysis. However, one should obtain anhydrous chloride of the metal without impurities at economic rates. In the case of aqueous chloride electrolysis a diaphragm is a must to separate out anodic chlorine from the cathodic zinc. In the case of molten metal cathodes such as the molten zinc cathode, zinc can be deposited onto the molten cathode and without diaphragm the chlorine can be sucked out (Fused salt electrolysis for the production of zinc metal employing molten zinc cathode, with an electrolyte of anhydrous zinc chloride in admixture with alkali metal chloride).

3. Yes. Molten chlorides are preferable for fused salt electrolysis. Fluorides are used at high temperatures, when the metal is to be deposited or to be plated from the oxide or oxide fluoride melts, such as for example electrodeposition of tantalum, from tantalum fluorine-tantalum oxide mixtures, production of aluminium metal by the electrolysis of aluminium oxide dissolved in molten cryolite, production of titanium boride employing mixtures of titanium dioxide, boron oxide and alkali metal fluoride alone or in admixture with the fluoride of titanium. Mixtures of fluorides and chlorides in suitable proportion are employed for fused salt electrolysis for the electrodeposition of zirconium and titanium. Silicates require very high temperatures for melting and maintaining conductivity (generally, far above 1250°C and under some special circumstances, one could think in terms of using silicate electrolyte medium for obtaining metals from their oxides). Bromide compositions are normally preferred for electrorefining of metals and even in these cases, mixtures of bromides with iodides could be used advantageously. One example in this connection is that of obtaining sodium metal from sodium amalgam employing low temperature molten electrolyte containing mixed bromides and iodides.