

SOME CONTRIBUTIONS FROM CECRI IN THE FIELD OF ELECTROMETALLURGY (AQUEOUS)

R. SRINIVASAN

Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu, India

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R&D efforts of CECRI have a natural bias in the direction of utilisation of indigenous resources and import substitution. Studies on new/improved techniques as well as competence building in conventional methods have been the motive behind the activities.

A base for studies on amalgam metallurgy techniques has been created as a result of investigations on electrolytic recovery of gallium using sodium amalgam. Basically the process includes the step of sodium deposition and displacement of gallium by sodium as a secondary process. Amalgam metallurgy techniques have a good potentiality in respect of preparation of high purity metals and recovery of valuable metals in low concentration streams as potentiostatic control is possible with mercury cathodes wherein the metal could dissolve as an amalgam.

Chloride metallurgy is another field in which pioneering work has been done in CECRI in this country. Leaching of sulphide concentrates with ferric chloride as a direct hydrometallurgical approach has been investigated. Electrolysis of chloride solutions have advantages in certain instances, provided suitable materials of construction are available.

Process improvements through the use of rotating cathodes have been found possible in some cases. Electrowinning of manganese and refining of gold are two typical examples. Use of high current density using rotating cathodes, has resulted in cutting down the inventory costs in the refining of gold, which in present day costs could be very significant.

Development of suitable processes for the utilisation of indigenous resources in the case of electrowinning of manganese, chromium, production of metallic powders of iron and copper, electrorefining of lead, antimony, silver and tin have resulted in advancement of import substitution efforts and in the build-up of competence in these areas to undertake trouble-shooting and consultancy work whenever the need arises.

Electrowinning of chromium from hexavalent baths has been developed to a prototype scale of a unit to make 4 kg of the metal per day. Preparation of chrome alum starting from sodium chromate, and electrolysis of the alum solutions to get chromium metal have been investigated. Refining of lead, silver and tin from impure materials arising from secondary workings have been carried out to satisfy the needs of specific industries.

Keywords : Electrometallurgy (Aqueous); Indigenous Resources; Import Substitution; Amalgam Metallurgy; Chloride Metallurgy; Electrowinning; Hexavalent Bath

INTRODUCTION

'ELECTROWINNING and refining' is probably the most significant area of activity in the field of electrochemistry judging from the value of turnover of products in this area as compared to other areas. Electrolytic recovery of metals, as is well known, could be classified under two broad headings, viz., aqueous media and molten salts with distinct technologies involved in the two categories. Some of the contributions from CECRI on process development in the field of aqueous electrometallurgy are highlighted in this article.

Research and development efforts of CECRI have a natural bias in the direction of utilisation of indigenous resources and import substitution. Studies on new and improved techniques as well as competence building in conventional methods have been the motives behind the activities.

AMALGAM METALLURGY

Amalgam metallurgy techniques have a good potentiality in respect of recovery of valuable metals in low concentration streams, particularly in cases where there are no other viable methods. One typical instance is the recovery of gallium (a metal of far reaching importance due to its application in the form of intermetallic compounds and alloys in the field of semi-conductors, solar energy converters etc.) from the circulating sodium aluminate liquors in the bauxite processing plants. The concentration of gallium in these liquors ranges between 150mg and 300mg per litre and electrolysis with mercury cathode is resorted to for recovering the gallium content. It has been found that, basically sodium deposits on mercury and by a process of exchange (commentation), transfers gallium into the mercury phase. This led to the studies on the comparative use of sodium amalgam in the recovery of gallium both as a reactant and as a cathode (Abdul Kader *et al.*, 1975). As a reactant for comen-tation of gallium, 0.5 per cent sodium amalgam was employed from practical considerations. Table I summarises the results obtained.

TABLE I

Process	Callium extracted per cent (average)	Rate of extraction mg/hr/dm ² of cathode area	Remarks
Cementation	85	30	Area of cathode does not come up here
Electrolysis	80	80	—
Pulse electrolysis	75	60	—

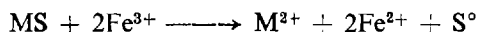
The current efficiency and energy consumption of the process is not a significant factor in the overall economics. The rate of extraction becomes a factor of prime

importance due to the charges on investment on the plant and mercury. The choice of the process, therefore, fell on electrolysis and further scale up was undertaken for operations on a semipilot plant level (50g gallium per day). Design of a suitable stirring device to facilitate diffusion of sodium and gallium on to mercury, presented problems, and a planetary type stirrer was found to be adequate for the job. Commercialisation through a pilot plant stage has been taken up.

Hence, a base has been created for further work on amalgam metallurgy processes, that may find use also in purification and separation of metals which are otherwise difficult to achieve. It is well known that the deposition potentials on mercury cathodes shift in a favourable manner for effecting separation of closely related metals.

CHLORIDE METALLURGY

Hydrometallurgical processes, involving the use of ferric ion for leaching sulphide minerals, have been proposed mainly from the viewpoint of avoiding roasting operations that give rise to pollution and eliminating the need for sulphuric acid plants as necessary adjuncts. The redox reaction occurring during leaching in acidic media is represented by the equation,



Possible regeneration of the ferric ion either electrolytically or by chlorine gas is an attractive feature. Conventional agitated reactors could be used.

Investigations carried out in CECRI have established the leachability of indigenous sphalerite (Aravamuthan & Srinivasan, 1960) and galena (Aravamuthan & Balasubramanian, 1960) concentrates by hot ferric chloride solutions. Temperature and ferric ion concentration were the main controlling factors. The dissolution rate was independent of the zinc concentration of leaching medium, in the case of zinc concentrates. The optimum conditions were, —250 mesh size of the concentrates, 70g/l Fe^{3+} and boiling for 75 minutes in the case of zinc concentrates and —100 mesh size of the concentrates, 100g/l Fe^{3+} and boiling for 60 minutes in the case of lead concentrates. Lead concentrates were dissolved with almost 100 per cent efficiency while the extraction from zinc concentrates amounted to about 75 per cent.

A direct spin-off of these programmes has been the knowledge on chloride electrolysis with diaphragm arrangements. In the case of lead, electrolysis has to be done with hot sodium chloride solution as electrolyte to keep lead chloride in the dissolved state. Electrolysis of chloride solutions can result in saving of power, provided suitable materials of construction are available.

Leaching with acidic ferric chloride solutions has also been proposed for treatment of complex polymetallic sulphide ores, which are otherwise difficult to process.

ROTATING CATHODES

Use of rotating cathodes in electrosynthesis and deposition of metals has enabled employment of higher current densities of several orders of magnitude as compared

to conventional practice. Increased convection and reduction in the diffusion layer thickness overcome the difficulties due to the impoverishment of the relevant ionic species near the cathode.

Electrowinning of manganese from sulphate solutions could be carried out at 7 to 8 times the normal cathode current densities (Udupa & Dey, 1961) but the usefulness has been restricted to short durations. It is in the field of refining of precious metals that the rotating cathode shows up a distinct advantage. Investigations on gold refining (Shenoi *et al.*, 1963) have revealed the possibility of not only using a high current density but also a high current concentration, with a rotating cathode. An idea of the possible operating parameters with stationary and rotating cathode is given in Table II.

TABLE II

System	Cathode current density (amps/dm ²)	Current concentration amps/litre
Stationary cathode	13.5	8
Rotating cathode	108	80

Increase in the speed of deposition and reduction of the quantity of gold locked up are the obvious advantages of a rotating cathode. Reduction of the inventory on gold, in present day costs, could be very significant.

INVESTIGATIONS ON INDIGENOUS RESOURCES AND COMPETENCE BUILDING

Utilisation of the manganese and chrome ores of India has been the motive behind the investigations on electrowinning of manganese and chromium. Semi-pilot plant level studies on electrolytic recovery of manganese have been carried out (Jogaroo *et al.*, 1955). Extensive studies on the reduction, leaching and deposition of electrolytic grade manganese dioxide (EMD) from chloride electrolytes, on a pilot plant level, have given valuable data, useful for commercialisation of the process. Use of titanium anodes in place of graphite for the deposition of EMD is another significant achievement of this laboratory.

Electrowinning of chromium from hexavalent baths has been developed to a prototype level of 4kg of the metal per day per unit. The investigations on trivalent bath for the recovery of chromium involved the preparation of chrome alum using a modified route and its electrolysis. Sodium chromate was reduced on a mercury cathode and the resultant chromium hydroxide was converted into the useful violet modification of chromium-ammonium sulphate. Reduction of a number of purification steps associated with the processing of chromite ore and avoidance of impurities from the starting point itself are the advantages. The grade of chrome alum produced by this method is quite comparable to that obtained by the digestion of chromite and processing by a series of fractional crystallisation steps (Table III).

TABLE III

Product	Content per cent									
	Cr	Fe	Al	Mg	Pb	Si	Ni	Ti	V	NH ₃
Chrome alum from conventional process	10.6	0.02	0.01	0.001	0.001	0.01	0.0008	0.005	0.004	3.53
Chrome alum prepared from sodium chromate	10.7	0.01	0.02	—	0.001	0.01	0.0005	0.0005	0.0005	3.52

Electrorefining of lead, antimony, silver and tin have been carried out mainly from the viewpoint of import substituting efforts and building up competence in these areas to undertake trouble-shooting and consultancy work whenever the need arises. As a result, methods for the recovery of lead, tin and silver from impure materials arising as secondary sources could be worked out to satisfy the needs of specific industries. Some of the instances where technical help was rendered to industries are shown in Table IV.

TABLE IV

Metal recovered	Source Material	Outline of method
Tin	Dross from hot dip tinning operations	Roasting, leaching of impurities, reduction, dissolution and cementation
Silver	Cemented copper from silver refineries	Roasting and selective leaching and cementation
Lead	Lead sulfate waste from batteries	Washing with soda and reduction

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