Electrochemical Industries Based on Fused Salt Electrolysis

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ABSTRACT

Sodium, magnesium and misch metal are not produced in India. The technical know-how for the production of these metals had to be developed since attempts made to get pilot plants from foreign countries to test the suitability of Indian raw materials were unsuccessful. The technical know-how for these processes have been developed in this Institute starting from scratch and utilising Indian raw materials and indigenously available equipment and components. Large laboratory scale experiments are in progress.

It is well-known that metals like sodium, magnesium, calcium, potassium, aluminium etc., cannot be recovered by electrolysis of aqueous solutions of salts and therefore they are usually recovered by fused salt electrolysis. The technique of fused salt electrolysis is rather complicated and it involves high temperatures and special techniques. The technical know-how for the production of metals like sodium, magnesium and misch had to be developed since attempts made to get pilot plants from foreign countries to test the suitability of Indian raw materials in their production were unsuccessful. The technical know-how for these processes have been developed starting from scratch and utilising Indian raw materials and indigenously available equipment and components. Large laboratory scale experiments are in progress.

Magnesium Metal

Magnesium occupies an important place in the production of high speed aircraft, commercial highway transportation vehicles, missiles and rockets. In the present age of sputniks, magnesium has got a bright future by virtue of its light weight and amenability to heat treatment when alloyed with other elements like zinc, zirconium etc. Magnesium is employed in the extraction of many strategic elements like titanium, zirconium, beryllium, boron etc., which in turn also find applications in nuclear reactors, aircraft, missiles, space vehicles etc. Magnesium is also used for various military purposes such as construction of radar equipment, radios and accessories, portable alert shelters, wet, dry and water or sea water activated reserve type primary batteries. Great attention is given to its use as a sacrificial anode to prevent corrosion of ships in sea water and for protecting underground pipelines.

In the production of magnesium metal, different procedures have been adopted for the production of anhydrous magnesium chloride. The magnesium chloride solutions employed for the production of anhydrous magnesium chloride are derived (a) from desulphated bitterns (b) by reacting Salem magnesite with byproduct hydrochloric acid and (c) by passing chlorine through a suspension of light calcined Salem magnesite adding potassium chloride with the simultaneous precipitation of potassium chlorate. This last procedure is especially very valuable not only because chlorate is obtained as a valuable byproduct without the use of electric energy or creating problems of disposal of any material such as calcium chloride but also because the anodic chlorine byproduct from magnesium electrolyte cells is utilised in a cyclic process without converting the chlorine into hydrochloric acid. In the first procedure for the production of anhydrous magnesium chloride, the magnesium chloride solution is mixed with small amounts of sodium, potassium and ammonium chlorides and spray-dried to get anhydrous magnesium chloride cell feed for electrolysis. The spray drier as well as the electrolytic cell have been designed in this Institute. In an alternate procedure for the production of anhydrous magnesium chloride, mixtures of magnesite and ammonium chloride are heated recovering ammonium carbonate as a valuable byproduct, leaving anhydrous magnesium chloride for use as cell feed. In a different procedure, a portion of the spent electrolyte is removed, fortified with pure magnesium chloride solution and the mixture heated out of contact with air to produce anhydrous salt composition rich in magnesium chloride suitable for electrolysis. All these experiments have been done in large laboratory scale based on initial success in small scale experiments. In addition, electrothermic chlorination of magnesite or light calcined magnesite has also been attempted.

Several electrolytic cells grouped under the category of either oil-fired externally heated cells employing mild steel container lined inside with stainless steel as cathode, or refractory lined internally heated cells were designed and operated. The internal heating to melt the electrolyte was initially done with a carbon rod as the resistor and in the later stages the bath itself formed the resistor. Low voltage AC of the order of 10-60 V and amperage ranging from 500-1500 amp. were employed. In the case of internally heated and refractory-lined electrolytic cells, the cathode arrangement consisted of a number of stainless steel rods suitably spaced and welded to a single flat at the top for electrical contacts. Experiments were done with and without ceramic diaphragms fitted to metal casings. Electrolysis was conducted at 750°C. The work in a 500 amp. cell was successfully completed and the results were published. The present capacity is 2.2 kg. of metal production in 24 hour. Magnesium metal of suitable purity for trade and defence was produced. A scheme for the production of magnesium metal from Salem magnesite has been sponsored by the Government of Madras. Work is in progress to run a 2000-2500 amp. cell to get at least 12 kg. of metal per day. The anhydrous magnesium chloride production unit is also scaled up in order to feed the 2500 amp. electrolytic cell.

Sodium Metal

Sodium finds extensive use in the manufacture of sodium cyanide, sodamide, sodium hydride, sodium azide, sodium peroxide, lead-tetraethyl etc. It is employed as a heat-transfer medium in nuclear reactors and the like. Rarer metals such as thorium, zirconium and titanium are produced in a pure state by the reduction of chlorides with sodium. A well-known use is in sodium-vapour lamps and in similar discharge lamps.

In the production of sodium metal from sodium chloride, different salt bath compositions were tried. Absolutely sulphate-free pure sodium chloride available in India from an alkali-chlorine industry was utilised as a source of sodium chloride. The other components of the electrolyte were potassium and barium chlorides and also small amounts of calcium fluoride. It is now established that a composition containing 30-35 per cent barium chloride on anhydrous basis, 35-40 per cent sodium chloride on dry basis, 20-25 per cent potassium chloride on dry basis and 5 per cent calcium fluoride on dry basis is the best of all electrolyte compositions tried so far. This composition is not very sensitive to temperature fluctuations unlike other baths and the bath composition can also be easily corrected. The electrolysis is conducted at 600-620°C.

Several electrolytic cells grouped under the category of either oil-fired externally heated cells employing a mild steel container lined with monel as cathode or refractory-lined internally heated cells were designed and operated. Internal heating to melt the electrolyte was initially done with a carbon rod as a resistor and in the later stages the bath itself formed the resistor. Low voltage AC of the order of 10-60 V and amperage ranging from 500-1500 amp. were employed.

In the vertical cylindrical type of cells wherein the mild steel vessel was lined with monel, cathode connections were given to the vessel itself. The bottom graphite anode arrangement was employed. A top circular sleeve arrangement of monel for collecting sodium metal was also provided. With this type of cell, work was done employing 500 amp. DC and 2.2 kg. was obtained in 24 hour. Sodium metal of suitable purity for trade and defence was produced. The results have been published.

In the case of refractory-lined internally heated rectangular vessels, the cathodes were of stainless steel suitably spaced, preferably encased by wire-gauze of suitable mesh and with a hood arrangement at the top for collecting the sodium metal. Graphite plate anodes were kept on either side of the cathode. Stepped monel cathodes in place of stainless steel rods have also been tried. With this type of arrangement 820-850 amp. DC was passed and more than 5 kg. of metal was obtained in 24 hours. The work is in progress to reduce the consumption of graphite. Further scaling up to produce 12 kg. per day is being undertaken.

Misch Metal

Misch metal containing 45-50 per cent cerium, about 40 per cent other rare earths such as lanthanum and up to 10 per cent iron is used widely in the manufacture of sparking flints for lighters. It also finds use in tracer bullets. It is employed to deoxidise steel and harden magnesium alloys. Very small amounts of misch metal added to aluminium improves its properties for use in the manufacture of pistons. It is also used as a getter in vacuum tubes. Its use in the production of nodular cast iron is well-established. In the case of jet engines it replaces batteries and provides a very satisfactory ignition.

The residues left after the extraction of thorium from the monazite sands of Travancore forms the starting material for the production of misch metal. The hydrated mixed chlorides of cerium and other rare earths like lanthanum are first dehydrated, preferably in the presence of small quantities of ammonium chloride and alkali metal chlorides. Several bath compositions have been tried containing different proportions of mixtures of anhydrous cerium chloride with alkali and alkaline earth chlorides. The best of all compositions is 80 per cent cerium chloride on anhydrous basis, 15 per cent potassium chloride on dry basis and 5 per cent barium chloride on dry basis.

Several electrolytic cells grouped under the category of either oil-fired externally heated cells employing mild steel container as cathode or refractory-lined internally heated cells were designed and operated. The internal heating to melt the electrolyte was initially done with a carbon rod as a resistor and in the later stages the bath itself formed the resistor. Low voltage AC of the order of 10-60 V and amperage ranging from 500-1500 amp. were employed. In the case of externally heated or internally heated mild steel vessel only the bottom portion of the vessel was allowed to function as cathode. The sides were either protected by refractory lining or the electrolysis was prevented between the sides of the vessel and the carbon or graphite anode by having a truncated conical bottom. Thus, it was possible to have the electrolysis between the bottom of the vessel (narrow portion of the vessel) and the carbon anode dipping in the molten electrolyte. A separate mild steel plate cathode arrangement resting on the bottom of the vessel was also employed. However, it was found advantageous to have the bottom itself functioning as cathode and replacing the worn-out bottom by welding a mild steel plate of suitable dimensions and thickness. Misch metal was produced in a batch process and electrolysis was conducted at 950°C. Before stopping the electrolysis, the electrolyte was removed as far as possible and only after cooling the metal was removed from the cell. Misch metal of composition suitable for trade and defence was produced. Work conducted in a 500 amp. cell was published. It is proposed to scale up the work to obtain 12 kg. per day.

Among the industrially important metals prepared by fused salt electrolysis, aluminium, sodium, magnesium and misch metal occupy a prominent place. For magnesium, sodium and misch metal, technical know-how as stated earlier has been developed and work is in progress on large laboratory scale. In the case of aluminium, the industry is well-established in India and more plants are being built. Therefore, research work on the production of aluminium metal was concentrated towards the utilisation of clay as alternate raw material to bauxite in the production of aluminium metal and also towards the development of an electrolytic procedure which will give chlorine as anode product instead of oxygen as in the commercial cells which consumes the carbon anode.

It was thought worthwhile studying fused salt electrolysis of mixtures of sodium or potassium cryolite with varying amounts of alkali or alkaline earth chlorides to get chlorine as anode product and aluminium as cathode product. With this aim in view, work was started towards the production of cryolite from bauxite and clay. Two different procedures have been developed. The first procedure deals with the reaction between soluble aluminium salt such as chloride, sulphate or nitrate obtained from clay or bauxite and silica-free pure ammonium fluoride solutions obtained from the hydrofluosilicic acid byproduct (of superphosphate industry) in the presence of alkali metal chlorides. In the second procedure, sodium aluminate is reacted with ammonium fluoride in a cyclic process and the ammonia evolved is utilised in the production of pure ammonium fluoride from hydrofluosilicic acid byproduct. This latter procedure has been handed over to eight parties on a non-exclusive basis and also the requirements of defence for cryolite are being met in a unit at Madras capable of producing 30 kg./day. Thus, this step relating to alternate methods for extraction of aluminium has incidentally helped to meet economically the requirements of cryolite for the well-established procedures for the production of aluminium metal in India. In addition, work is also in progress to obtain aluminium fluoride needed both in the well-established procedure for the production of aluminium metal and also for correcting the composition in the cryolite-alkali metal chloride compositions for the production of aluminium metal by the alternate routes. After successfully completing the work on aluminium fluoride production, electrolytic experiments will be taken up.

Production of alkali and alkaline earth metals, especially sodium, through the intermediate formation of lead alloys in a cyclic process is of late being extensively investigated in different parts of the globe. The significance of this process lies not only in meeting the demand for lead alloys containing alkali or alkaline earth metals in various industries but also to reduce the electric energy requirements in the production of these, especially sodium (and hence sodium hydroxide also) by fused chloride electrolysis. After establishing the conditions on a laboratory scale, it is proposed to step up this line of investigation.

An attempt has been made to indicate the lines on which research work is being conducted in the Fused Salt Division of this Institute. It will be our endeavour to bring all these processes to a satisfactory stage of completion to enable the industries to put higher capacity units based on the work.

The future programme of work also includes development of processes for the production of materials considered so very indispensable in the space age such as titanium and zirconium metals and also borides and silicides of titanium, zirconium, vanadium and chromium by fused salt electrolysis. Work has already been started on the fundamental aspects of fused salt electrolysis relating to the recovery of metals and metallic compounds.

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DISCUSSION

on Paper by

V. ARAVAMUTHAN

(Presented by V. Aravamuthan)

H. V. K. UDUPA: Pure magnesium is in great demand for alloys of magnesium which find extentive use.

The preparation of barium metal could be also useful to the country though its uses are on a smaller scale and perhaps not revealed by some industries like tube-light manufacture.

V. ARAVAMUTHAN: Barium is not known to be used as such but might be used as phosphors along with those of other metals.

H. V. K. UDUPA: Barium is used as a getter in vacuum tube industry.

V. ARAVAMUTHAN: If the requirement is small, it can be produced even in experimental cells.

H. GANESAN: Is beryllium-copper, needed by electrical industries, produced in India? Can it be done?

V. ARAVAMUTHAN: It is not necessary to use pure beryllium in the preparation of beryllium-copper alloy. The alloy can be prepared by heating beryllium oxide with coke and copper, in an arc furnace.