

## EXPERIENCES IN THE DEVELOPMENT OF MAGNESIUM CELL TECHNOLOGY AT CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI

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Research activities on the preparation of magnesium metal by molten salt electrolytic process were initiated in CECRI as early as in 1958. CECRI started its experiments on a bench scale level and further developed into pilot plant scale and finally to the scale of semicommercial unit. Various types of electrolytic cells were developed at CECRI which include externally heated cells with different design modifications, modular cells, bipolar/multipolar cells and new modified monopolar cells. The primary aim of each development was aimed at high current efficiencies energy efficiencies and space time yields. Various types of raw materials like magnesite, sea bitters, and byproduct  $MgCl_2$  from Zr/Ti plants etc. were utilised during the investigations. These studies were carried out with financial grants from Govt. of Tamil Nadu, CSIR, DRDO and Nuclear Fuel Complex. The paper illustrates the design and operational features of different electrolytic cells with consequent gradual decrease in specific energy consumption for magnesium production and increased space time yields with improvement in cell design and operational parameters.

**Keywords:** Magnesium, molten salt electrolysis, bipolar/monopolar cells

### INTRODUCTION

India has very large resources of raw materials for magnesium. It is available in the earth's crust mainly in the form of magnesite and dolomite. It is also available in enormous quantity in seawater in the form of chlorides and sulphates.

Magnesium is a light metal with a density of 1.75; it is 36% lighter than aluminium, 73% lighter than Zinc and 77% lighter than Iron. Apart from high strength to weight ratio magnesium alloys possess good machinability. They are non-magnetic and possess high thermal and electrical conductivities. Magnesium alloys have good corrosion resistance to many chemicals. They have very good dimensional stability and damping capacity. Magnesium also finds use in the production of strategic metals like Zirconium and Titanium.

Considering the strategic importance of magnesium and its alloys, CECRI started its experiments on a bench scale,

which was further developed, into bigger scales of operation employing different types of techniques and electrolytic cells. The development activities are presented in detail in the succeeding pages.

### State of art

The evolution of electrolytic cell technology for magnesium in the world can be classified broadly into four categories. They are

- \* First generation cell - Hydrous cell feed, steel pot containers, external heating
- \* Second generation cell - Anhydrous cell feed, refractory lined, refractory partition between anode and cathode
- \* Third generation cell - Diaphragmless cell, refractory lined, partially dehydrated cell feed
- \* Fourth generation cell - Bipolar/multipolar cells, refractory lined, molten cell feed, totally closed.

The Dow cell comes under the first category while the Norsk Hydro cell comes under the second category. Some of the



later cells developed in Norsk Hydro and CECRI fall under the third category. Multipolar cells of Alcan/Showa Titanium and CECRI belong to the fourth category.

CECRI in the pursuit of magnesium technology development had experimented upon all these type of cells mentioned above. However the cell feed that was used was either spray dried magnesium chloride which contained about 80%  $MgCl_2$ , 15% moisture and 5%  $MgO$  or the byproduct magnesium chloride obtained from Zirconium/titanium production units.

### Cylindrical cell

The earliest cell tried in CECRI was of a cylindrical design. Electrolysis was carried out in a stainless steel clad steel vessel which itself acted as the cathode and cylindrical graphite rod acting as the anode. The cell was externally heated. A current of 700-750 A was passed and the cell voltage was 7 V. The current efficiency obtained with the spraydried magnesium chloride was about 50%. In spite of external heating, the required operating temperature could not be maintained uniform throughout the cell and tenure of the run on most of the occasions was very short. The DC energy consumption was found to be more than 49 kWh/kg.

### Boat type of cell

The next design was a boat type cell. As the previous cell this was also of stainless steel clad mild steel vessel and the entire body was acting as cathode. The cell was wider at the top and narrowed down to the bottom on all four sides of the cell body. The bottom side was given a sloping floor to allow the sludge to slide to one side of the cell and the same was collected from one spot. A bundle of graphite rods of 2.5" dia. was centrally located and resting over refractory bricks placed at the bottom. The cell was provided with a refractory lined lid with hinged doors, at the top. Chlorine gas was sucked through the top with the help of blowers. The cell was run for maximum period of 7 days only. The average energy consumption was around 32 kWh/kg metal.

The cell was operated at a current of 2500 A with the cell voltage of 7-8 V. The anode current density was  $0.66 \text{ A/cm}^2$  and cathode current density was  $0.4 \text{ A/cm}^2$ . The average interelectrode distance (IED) was 7.5 cm, however this was not uniform through out the cell. It was less in the lower portions and as the cell body got widened at the top, it was more. It was difficult to maintain the IED constant because of thinning of electrodes during the run, which caused increased voltage and very high bath

temperature resulting in losses of magnesium metal by burning. The high temperature caused deforming of cell body and the cell body developed cracks in the welded portions and electrolyte began to leak out from the cell. The life of the stainless steel cladding was also very much short. A series of failures in this type of cells finally led us to pursue in the direction of refractory lined electrolytic cells.

### Refractory lined cells

The refractory lined cells were of rectangular type. The cathodes employed were of louvre type for aiding ascendance of magnesium metal globules. The anode consisted of a bundle of graphite rods of 3" diameter. High alumina refractory bricks with suitable refractory mortars were used for construction. A mild steel casing provided the mechanical support to the refractory work. The cells were provided with refractory lined mild steel lids and refractory duct arrangements for chlorine removal.

Different arrangement of anodes and cathodes positioning in refractory lined cells were experimented. At first a cell with one centrally located cathode and two side anodes was tried. It was felt that the molten magnesium metal floating over the top could form a single metal pool and could be easily ladled out. However in this arrangement, the metal pool had to remain in the region between anode and cathode and the possibilities of recombination were more and current efficiency was always lower. More over the temperature between anode and cathode was always higher than that between wall and anode, which resulted in burning of metal.

To avoid this problem, in subsequent cells the anode was centrally located and two cathodes of louvre type were employed on either side of the anode, thereby enabling the metal that was formed to be pushed away from the electrolytic zone and get collected in the area behind the cathode and the wall (Fig. 2). Metal removal, feeding of

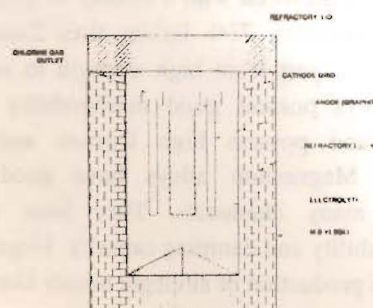


Fig. 1: Magnesium cell - 2000 A centre cathode



MgCl<sub>2</sub>, sludge removal etc were made much easier. A sloping was given at the bottom of the cell from the centre towards the sides of enable the sludge if any formed to get accumulated near the walls so that its removal was easier.

All these refractory lined cells were run with a current rating of 2500 A. The cell voltage was 7-8 V. Periodical change of anodes was done because of thinning of anodes. The interelectrode distance was 7.5 cm and the anode current density and the cathode current density were 0.632 A/cm<sup>2</sup> and 1.29 A/cm<sup>2</sup> respectively. The cell runs were of much longer duration compared to that of boat type cells.

During the operation of several runs, conditions were established for standardisation and optimisation of various parameters and many important data were collected which were vital for scaling up of electrolytic cell at a later date.

Systematic analysis of the performance of various cells revealed that the overall current efficiency obtained was found to be much higher in refractory lined electrolytic cells when compared to earlier Boat type or externally heated cylindrical cells. The specific energy consumption was also much lower compared to what it was in earlier cells.

### 10 kA cells

With the successful completion of smaller scale operations, it was decided to scale up the electrolytic cells to 10 kA capacity, capable of producing about 60 to 70 kg of magnesium metal per day and to run two or more cells simultaneously. The scaled up cells confined more or less to the design of 2500 A cells with central anode and side cathodes. The anode grid consisted of 5 Nos. of 150 mm dia. Graphite rods and around 2000 mm length.

Two cathodes of louvre type were placed on either side of the anode. During the operation, the cathodes were completely submerged in the electrolyte and the mild steel cathode leads were protruded through refractory walls for electrical connections.

The holding capacity of each cell was around 1500 kg of electrolyte in molten state. The electrolyte used was a four component system consisting of MgCl<sub>2</sub> - 20%, KCl - 35%, NaCl-35%, BaCl<sub>2</sub>-10%. A little amount of CaF<sub>2</sub> (not exceeding 2% of the total quantity) was added to have better coalescence of magnesium metal. The bath temperature was around 993 K. The cell voltage was 8 V for a current of 9500 A. The voltage increased gradually, as the graphite electrode became thinner, thus increasing the interelectrode distance, which caused increase in bath temperature. So

periodical replacement of anodes was done to maintain the interelectrode distance. The life of the 10 kA cell was much longer than the smaller cells and the cell runs were more than 100 days duration. It was also possible to clean the electrodes and refractory lining and restart the cell. Nearly 90 tonnes of magnesium metal was produced by operating the 10 kA cells and almost all the metal was sold to various consumers in the country.

During the operation of the 10 kA cells, influence of several factors which affect the current and energy efficiencies were studied. The effect of concentration of MgCl<sub>2</sub> was studied and it was found out that an optimum concentration of 15-18% MgCl<sub>2</sub> would favour higher current efficiencies. A proper operative cycle was evolved to achieve maximum efficiency. The feeding and metal dipping intervals were worked out so that the concentration of MgCl<sub>2</sub> was maintained within the prescribed limits in the bath and metal losses due to recombination was greatly reduced [2].

Even though these cells were operated with fairly good current efficiencies of around 70%, the specific energy consumption was around 22 kWh/kg. More over the cells occupied large floor area with large volume of electrolyte, which caused unnecessary energy expenses to keep the large quantity of electrolyte at the operating temperature. So efforts were taken to evolve new cell designs which could reduce the specific energy consumption and increase the space time yield.

### Modular cells

The theoretical decomposition potential for magnesium at about 973 K is around 2.7 V whereas the cells were operated around 8 V which means more than 60% of the energy input was spent on non-electrolytic purpose. So one of the best possible ways to improve energy efficiency was to bring

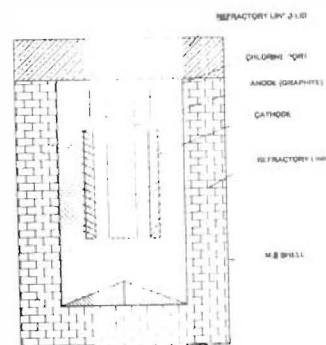


Fig. 2: Magnesium cell - 2500 A side cathodes - centre anode



down the cell voltage. This could be made possible by (i) increasing the conductivity of the bath (ii) lowering the current density and (iii) reducing the IR drop with lower electrode inter electrode gap. In practice the possibility of improving energy efficiency by the first two options was found limited. Therefore the third option of bringing down the inter polar gap had to be explored. The popular belief that larger inter polar gaps were necessary to avoid recombination of metal and chlorine, was the basis of earlier cell designs, which ultimately resulted in higher energy consumption in spite of best operating conditions. However later theories on mechanism of metal losses during electrolysis had undergone substantial changes. The earlier cell designs had not given due consideration to the pattern of electrolyte circulation and gas lift action of chlorine. It was believed a more intensive circulation caused higher metal losses and decreased current efficiencies. But theories on physico-chemical properties of the electrolyte indicated that the metal losses were mainly caused, not by the dissolution of the metal on the cathode surface and its transference through the diffusional layer next to the cathode to the anode, but rather by the dissolution off the surface of a larger number of magnesium droplets which circulate in the electrolyte and also by direct interaction of such small metal droplets with the chlorine gas evolved at the anode. Hence it became clear that metal losses could be minimised by increasing the sizes and reducing the number of droplets afloat in the electrolyte by ensuring their effective coalescence and speedy removal from the reaction zone. This could be achieved by adjusting the electrolyte composition so as to have maximum surface tension with respect to cathode and also more importantly by effective utilisation of the hydrodynamic forces created by chlorine evolution for pushing away the metal globules from the reaction zone to a collection chamber within the electrolyser. Contrary to the previous belief, the reduction in the inter polar gap proved to be beneficial towards maintaining reasonable current efficiencies, but at the same time could reduce the cell voltage substantially, provided the design and disposition of the electrodes could ensure a proper pattern of electrolyte circulation [2,4].

The greatest achievement of CECRI in magnesium technology was the development of Modular cell by which specific energy consumption was brought down to around 14 kWh from around 22 kWh with an energy saving of 30%. In this cell design provision to take advantage of the gas lift action of chlorine had been made possible by having narrow inter polar gap and suitable cathode designs.

The modular type cell essentially consists of a plurality of individual modules wherein a central cylindrical graphite anode is surrounded by a square steel cathode frame (Fig. 3). The cathode frames have horizontal and transverse members. Both sides of the steel cathodes are effectively utilised for electrolysis. The entire set up of individual modules is arranged side by side in a form of checkers so that a separate electrolytic zone is formed within the refractory lined cell. The hydrodynamic force due to chlorine evolution pushes the magnesium metal formed from the electrolytic zone into the tranquil non-electrolyte zone. The cathodes are so designed that there is free communication and circulation of electrolyte between electrolytic and non- electrolytic zones. This helps to maintain the concentration of  $MgCl_2$  and temperature uniformly throughout the cell at desired levels.

The main advantage of the modular design was that it could be scaled up to any capacity by increasing the number or size of modules. Thus at CECRI, 8 kA cells with 16 modules of 500 A each as well as 4 modules of 2 kA each were successfully tried. Taking advantage of the successful results, CECRI set up a scaled up version of 30 kA capacity 12 module magnesium cell at DMRL, Hyderabad and successfully operated under a collaborative programme. Prototype cells of this capacity were also operated at TMML, Valinokkam, Tamil Nadu where commercial scale plant was set up. Where as the conventional cell was operated at about 7.5 V the modular cells employed a cell voltage of 4-4.5 V with current efficiencies remaining more or less same in both type of cells. The energy consumption was brought down from 22 kWh/kg to 13- 15 kWh/kg. [5,6]

### Bipolar/multipolar cells

The latest technology development reported in the field of magnesium metal production has been the emergence of bipolar and multipolar technology by which it has been proved that the specific energy consumption could be

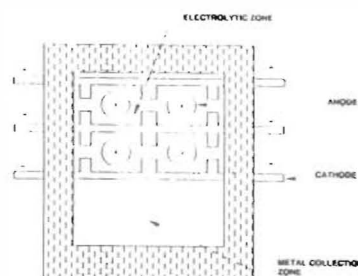


Fig. 3: Modular cell - 10 kA



brought down to 10 kWh/kg. Two multinational companies namely Osaka Titanium Company, Japan in collaboration with Alcan and Showa Titanium, Japan had successfully operated multipolar magnesium cell and it has been reported that the energy consumption was brought down to the levels of 10 kWh/kg of metal produced.

The principle of bipolar cell system is that if an electrically conducting plate is inserted between the conventional anode and cathode of an electrolytic cell, the side of the plate facing the cathode becomes anode and the other side becomes cathode as the current flows through the plate. The plate thus becomes a bipolar electrode and the production is nearly doubled for the same quantity of current flow through the cell. If there are 'n' bipolar electrodes employed in the cell, the production increases nearly by 'n+1' times. A judicious combination of a number of modules of bipolar system through series and parallel connection within the electrolyser to optimise the total current and voltage will lead to commercial capacity multipolar electrolytic cells [7,8].

The advantage of this system is that it allows narrow inter polar gaps and permits higher current densities to achieve reduction in energy consumption and higher space-time yield. Substantial saving can be achieved in the capital costs and operating costs because of its compact nature, less complicated bus bar connections, substantial saving in the bus bar requirement and reduced voltage drops.

Keeping in mind the vast experience gained in this field CECRI had undertaken the task of upgrading and updating the electrolytic process through the development of multipolar cell technology. DRDO and NFC extended financial support for developing bipolar and multipolar cell designs and study various parameters.

The multipolar cell technology involved several intricate factors which include the development of stable bipolar electrodes, minimising the bypass current, optimising the cell design with proper flow pattern of electrolyte, metal

channeling arrangement, identification of suitable electrolyte etc., for obtaining best results.

CECRI had taken care of all these basic concepts and developed spacer type of bipolar electrodes. Metallic spacers were first fitted tight into the graphite plate at one end and welded to mild steel louvres of the cathode part of the bipolar electrode thereby forming a cavity in between.

In the earlier experiment [9], the bipolar cells were constructed with a terminal anode at the back and terminal cathode at the front and bipolar electrode placed in between anode and cathode. Since the flow of electrolyte was over the bipolar electrodes, the liberated magnesium metal had to pass through chlorine bubbles across the cell before reaching the metal collection chamber. The possibilities of recombination of products were more and hence current efficiency realised in such cells was always lower.

Hence in subsequent cells, the design was changed with facility for parallel flow of electrolyte. In this type of cells, the terminal electrodes were on two sides of the cell with bipolar electrodes placed in between them. A separate metal collection chamber was provided along the side of the electrodes. The electrolyte chamber and metal collection chamber was separated by a partition wall. Openings were provided in the partition wall in the bottom and on the top for electrolyte circulation. The bipolar electrodes were placed vertically over refractory pillars. The electrodes were held in position by confining the two sides in the vertical grooves made in the refractory walls on one side and in the partition wall on the other side. Refractory cement mortar was applied to fill the gaps in the refractory grooves so that electrodes were not displaced during the run. To minimise the bypass current, refractory curtain plates were provided below and above the electrodes. The top curtain plates were of refractory hood type to guide the metal towards the metal ports and into the metal collection chamber. Current efficiency was improved by such arrangements. Two melting chambers were provided on either side of the cell for having premelting of the cell feed. The multipolar cell was designed

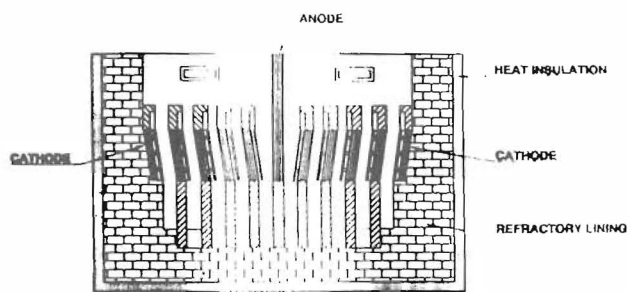


Fig. 4: Multipolar cell - 1.2 KA

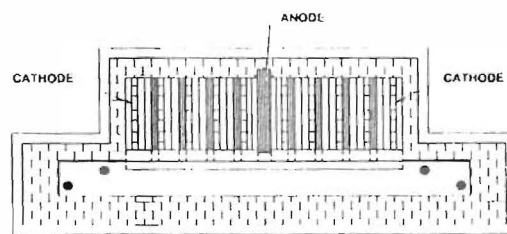


Fig. 5: Multipolar cell - 1.2 KA

with a central anode and two terminal cathodes and the bipolar electrode place and supported in between cathode and anode as in a single module cell. Partition walls, metal collection chamber and melting chamber were common for both modules. (Figs. 4,5)

The metal port arrangements at the top of partition wall was so designed, that there was easy flow of electrolyte with metal globules into the metal collection chamber and at the same time providing a liquid seal in between the electrolytic chamber and metal collection chamber, so that air entry into the electrolytic chamber and chlorine gas escape through metal collection chamber were prevented. Suitable lids were provided at the top to make the cell air tight.

Several models of bipolar and multipolar cells were designed and operated. The major operating parameters that were studied during the cell operations are: a) Optimisation of number of bipolar electrodes, b) Electrolyte circulation, c) Inter polar gap, d) Current density, e) Premelting arrangement, f) Metal port arrangement, g) Metal channelling, h) Design and testing of different types of snugfit bipolar electrode with a view to make the cell more compact, i) Voltage measurements for each bipole unit of the cell. A larger version of multipolar cell of 42 kA capacity was operated successfully at DMRL, under optimum operating conditions the energy consumption was found to be around 12.0 to 12.5 kWh/kg of magnesium metal.

#### Modified monopolar cell

By the experience gained in the operation of modular cells and bipolar cells, one has to consider the positive and negative aspects of both these designs. While modular cells were simple and could be operated with replaceable anodes, there were certain disadvantages also. The square cathode and cylindrical graphite anodes did not ensure uniform current distribution. The electrolyte circulation was hindered by the gas evolution in the adjacent modules causing possibilities of recombination. The absence of liquid seal arrangement enabled air entry into the electrolytic area and anodes exposed above the electrolyte level often got eroded and reduced the life of the anodes and increased the stub losses. The absence of metal channeling arrangement and regulation of electrolyte circulation often caused reduction in current efficiencies.

The bipolar cells of course are energy efficient. It has a regulated path for electrolyte circulation. The liquid seal arrangement prevents air entry into electrolytic chamber. The cells can be operated at high current densities and with

increased productivity. But it suffers from certain basic disadvantages: the first and foremost is that the bipolar electrodes are not replaceable. The life and stability of the electrodes determine the life of the cell. Therefore the electrodes should be positioned firmly so that they are not distorted during the operation. Failure of even one bipolar electrode may ultimately cause in failure of the entire cell. The cell feed should be absolutely free from moisture. The presence of moisture reduces the life of the bipolar electrodes, which in turn shortens the cell life. In spite of the best efforts any oxide inclusion in the cell feed gets accumulated at the bottom as sludge which finally hinders the electrolysis and thereby reduces the current and energy efficiencies. The complexity of electrode fabrication, cell design and constructional aspects make the operations of the cell more difficult.

To obviate these drawbacks, a modified cell which was monopolar in type and at the same time more compact than modular cells and as energy efficient as that of bipolar cell was designed. The replaceable type of anodes, provision for metal channeling, uniform current distribution, suitable metal port with liquid seal arrangement made the cell more attractive from the points of longevity, energy efficiency and better operating conditions.

An electrolytic cell with the above features and of 2.5 kA capacity was designed and operated. (Fig. 6). The cell essentially consisted of two chambers, one for electrolysis and the other for metal collection separated by a refractory partition. Three steel plate cathodes and two graphite plate anodes were vertically mounted alternately. A sloped bottom

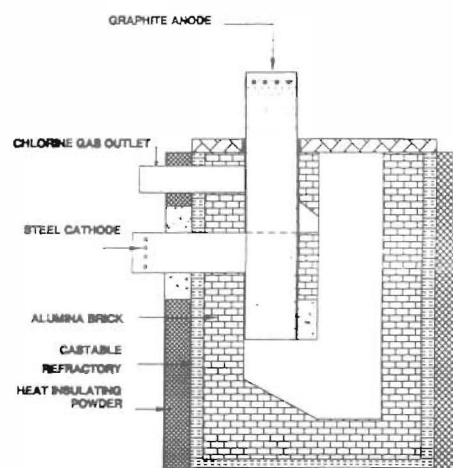


Fig. 6: Magnesium cell  
Modified monopolar - plate type - 2500 A



was provided below the electrodes to enable the sludge if any formed to slide into the bottom of the metal chamber through the openings below the partition. While the cathodes were submerged in the electrolyte, the current leads of the cathode protruded through the refractory walls. The anode plates were suspended from the top with suitable sealing arrangements in the lid to prevent air entry into the cell from the top. Suitable port arrangements in the refractory partition just above the cathode top level provided liquid seal between the two chambers and prevented air entry into the electrolytic chamber, thereby protecting the graphite anodes from the atmospheric air at high temperatures.

The anode plates were positioned in such a manner that they cover the entire width of the electrolytic chamber and were projected through the lid of the cell. This arrangement helped channeling of metal and guiding the electrolyte into the metal collection chamber rapidly along with the metal globules. The partition wall in between the two chambers enhanced the velocity of electrolyte circulation. The narrow interpolar gap enabled to lower the cell voltage and the use of plate type electrodes made the cell more compact and provided uniform current distribution.

The cell was operated for more than 45 days and current efficiencies ranging from 70-75% were obtained. The cell voltage was ranging from 3.9 to 4.1 V. The average energy consumption worked out to be around 11.5 to 12 kWh/Kg of metal produced.

### CONCLUSION

If one go by records, it could be seen the growth of magnesium technology had been very slow and there are only a few producers in the world. Process research and development works have largely been conducted by the producers and the results have often been shrouded by secrecy [10]. Little information about the process has been published except for patents. Dow stated that a large percentage of failures were necessary to solve complex problems. "We have a right to be wrong" states Willard Dow [11]. The above statement fits very well to the developmental activities at CECRI. Many practical problems like

mechanisation of metal removal and sludge removal stood very much in the way of successful operations of electrolytic cells. In spite of these difficulties CECRI was able to update the technology and make it at least as energy efficient as that of most updated technologies in the world. The key to further development of electrolytic cell is to be sought in the optimisation of the chemistry of cell feed and improved materials. CECRI has also done useful experiments for evolving suitable electrolyte composition for different types of electrolytic cells operated. The efforts of CECRI in this direction had been well appreciated by external agencies that had funded the project activities ever since 1963.

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