

## STUDIES ON ALUMINIUM CHLORIDE ELECTROLYSIS IN MOLAR CELLS

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With a view to develop an alternate technology for aluminium production preliminary study on the electrolysis of molten aluminium chloride has been carried out in 100A cells at 700°C with different salt systems such as NaCl-KCl-AlCl<sub>3</sub>, LiCl-NaCl-AlCl<sub>3</sub> and MgCl<sub>2</sub>-NaCl-AlCl<sub>3</sub>. Results are reported.

**Key words:** AlCl<sub>3</sub> electrolysis, - monopolar cell

## INTRODUCTION

The need to develop a new technology for aluminium metal production has been felt in the major aluminium industries lately and considerable amount of time and money are spent for the research and development efforts in this field of work. The Bayer-Hall-Heroult process did not face much competition because of its simplicity and easier technical and practical operations. However because of the recent energy crisis and depletion in good bauxite reserves, efforts are intensified to develop an alternate technology which can reduce the operational and investment costs. Of the various alternate routes tried, the following are considered to be significant processes - (1) Pechiney-Alcoa Process (Carbothermal reduction) (2) Alcan subhalide process (3) Toth process and (4) Chloride electrolysis. Of these processes only the last mentioned one seems to be most attractive and has gained sufficient success on a pilot plant scale.

The major advantages of the chloride electrolysis are: (a) lower operating temperature (700°C) compared to the Hall-Heroult cells of 980°C (b) operation at higher current densities (c) elimination of carbonaceous anodes (d) freedom in the choice of raw materials (e) less environmental pollution and (f) higher energy efficiency [1]. It is reported that Alcoa has succeeded in developing a process for aluminium production by electrolysis of aluminium chloride in bipolar cells.

It has been observed [2] in general that the best results are obtained from melts containing alkali chlorides preferably at least two and chloride of the electrowon metal. Various salt systems employing LiCl, NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> with AlCl<sub>3</sub> are reported. Alcoa used baths containing LiCl whereas Japanese [3] workers preferred MgCl<sub>2</sub> or CaCl<sub>2</sub>.

It has been recommended [4] to use special refractories made of nitrides of boron, titanium, aluminium, chromium, zirconium etc. Regarding orientation of the electrode [5] horizontally placed electrodes yielded higher current efficiencies since they offered better wettability and coalescence to the metal.

Preliminary study on the electrolysis of molten aluminium chloride in monopolar cells of 100A capacity has been carried out at CECRI and the details are presented in this communication.

## EXPERIMENTAL

A schematic drawing of the cell is given in Fig.1. The cell consisted

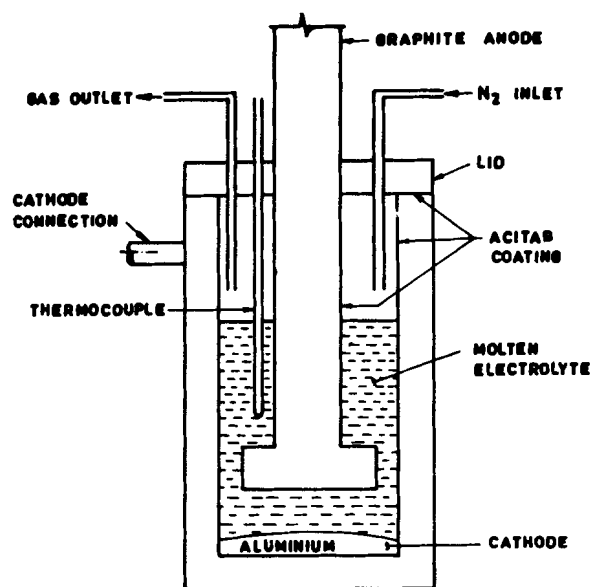


Fig. 1: Aluminium chloride electrolysis Monopolar cell

of a graphite crucible having inner dimensions of 22 cms height and 11 cms diameter. The inner periphery of the crucible was given a refractory coating of alumina-phosphoric acid. The bottom surface acted as the cathode contact. The anode consisted of a cylindrical graphite rod with a disc-like arrangement at the bottom. The lid had provisions for introducing the anode which was suspended over the cathode at a required inter electrode distance. Arrangements were also made in the lid for introducing nitrogen gas into the cell, temperature measurement and outlet for chlorine and other vapours. Copper rings were provided over the crucible and anode rod which served as terminals for D.C. power supply. The whole set up was placed in a resistor furnace to provide external heat and maintain the cell at its operating temperature.

Various salt systems such as (i) NaCl 50-53, KCl 40-42, AlCl<sub>3</sub>, 5-8, (ii) LiCl 40-42, NaCl 50-53, AlCl<sub>3</sub> 5-8, (iii) MgCl<sub>2</sub> 54-56, NaCl 36-38, AlCl<sub>3</sub> 5-8 mass percentages, were employed during the study. The inter electrode distance was maintained at 2.5 cms. Anode current density was 2.0 A/cm<sup>2</sup>. The temperature during electrolysis was maintained around 700 to 750°C. A current of 100A was passed. Cell voltage was around 4 to 5 volts.

To start with, the electrolyte without aluminium chloride was melted in the crucible. Then a known quantity of aluminium metal was introduced into the cell to provide the metal pad. The anode was introduced into the cell along with the lid. Addition of anhydrous aluminium chloride was done by slightly raising the lid. The aluminium chloride content was maintained about 5-8% in the bath by periodic additions during electrolysis. Nitrogen gas was introduced into the cell to maintain inert atmosphere. The electrolysis was conducted for a period of 4 to 5 hours. Additions of other chlorides were also done to make up the loss of electrolyte during electrolysis. After the electrolysis, the electrolyte and metal were ladled out separately. Metallic globules distributed in the electrolyte were also recovered and increase in weight of aluminium was found out and current efficiency evaluated.

It is also evident from this work that cathode metal pad and inert atmosphere are favourable for better results. Lithium chloride baths were found to be more volatile and in view of their cost, it is not recommended even though the operating cell voltage is reported to be less. Magnesium chloride baths are also not recommended in view of the handling difficulties.

Hence NaCl-KCl-AlCl<sub>3</sub> bath is found to be more suitable.

### CONCLUSION

It is possible to extract aluminium metal by employing NaCl-KCl-AlCl<sub>3</sub> bath in a 100A cell when absolutely oxide free pure anhydrous aluminium chloride is used as the cell feed and an aluminium metal pad with inert atmosphere in the cell is employed.

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Table I: Comparison of current efficiencies for different systems

Bath composition	Current (Amps.)	Cell voltage (Volts)	Inter electrode distance (cm)	Anode current density (A/cm <sup>2</sup> )	Bath temp. (°C)	Current efficiency (%)	Remarks
NaCl-KCl-AlCl <sub>3</sub>	100	5.0	2.5	2.00	700	15	Without cathode metal pad and nitrogen atmosphere
NaCl-KCl-AlCl <sub>3</sub>	100	4.0	2.5	2.00	700	10	With cathode metal pad and without nitrogen atmosphere
NaCl-KCl-AlCl <sub>3</sub>	100	4.0	2.5	2.00	700	57	With nitrogen atmosphere and cathode metal pad
LiCl-NaCl-AlCl <sub>3</sub>	100	4.0	2.5	2.00	700	40	-- do --
MgCl <sub>2</sub> -NaCl-AlCl <sub>3</sub>	100	4.0	2.5	2.00	700	55	-- do --

### RESULTS AND DISCUSSIONS

Experimental data are presented in Table I. From the Table, it is evident that the maximum current efficiency achieved was only 57%. This is very much lower than the reported values. Reasons for this are manifold. Of these two are worth mentioning. One is the oxide content in the bath which might have been from the feed material used and the second is the poor coalescence and wettability of aluminium metal formed which was distributed in the electrolyte itself.

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