A CRITICAL APPRAISAL AND REVIEW OF ALUMINIUM CHLORIDE ELECTROLYSIS FOR THE PRODUCTION OF ALUMINIUM

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ABSTRACT

This paper is an attempt to examine the current state of art of aluminium chloride electrolysis through a review of all the available published literature and patents so that this could help the formulation of the plans of work for any serious R&D effort to develop the chloride technology in this country. Even though the development of technology for aluminium chloride electrolysis is being carried out in a big way by Alcoa and a few other multinational companies for the past several years, many of the data and information are lacking in published literature and the answers to various critical questions have to be found only through inferences from the meagre information available in patents. It was therefore thought fit to undertake a thorough review of all the basic applied and R&D work that are reported in this field and critically assess the various problems to be tackled to evolve a viable technology. This review confines itself to the electrolytic aspect and those relating to the material preparation will be taken up separately later.

Key words: Production of aluminium, Molten salt electrolysis, chlorination of alumina

INTRODUCTION

The need to develop a new technology for aluminium metal production has been felt very much in the major aluminium producing countries and considerable amount of time and money were spent for the research and development efforts in this line.

The Bayer-Hall-Heroult process established about 100 years ago, did not face much competition in the past because of its simplicity and easier technical and practical operations involved even at large industrial scale. Of late the Hall-Heroult process is also being subjected to various improvements so that the energy efficiency and other operating parameters are improved. Use of refractory metal cathodes like titanium diboride or zirconium diboride, inert oxide anodes, modified bath employing different cryolite ratios, improvement in cell linings etc. are some of the fields where much attention is given and considerable research is going on.

Despite these improvements, the other factors such as the low energy efficiency, high capital and operating costs involved, depletion in bauxite and petroleum coke reserves in certain countries and serious environmental problems like fluorine emission from the cell pots etc. have led the producers to think towards the development of an alternate technology for aluminium metal production.

Prominent alternate processes

Of the various processes thought of, the following are considered to be the most significant and leading producers of aluminium metal like the Alcoa, Alcan, Nippon Light Metal etc. have shown considerable interest.

1. Pechiney-Alcoa process (2) Alcan process or sub-halide process (3) Toth process and (4) chloride electrolysis. Details of these processes have been dealt with elsewhere in literature by various authors [1-4].

Out of the four processes mentioned above, the last mentioned one is considered to be the best and attracted the eyes of aluminium producers very much. An attempt is made to describe the salient features of this process in the following pages.

The most obvious advantages of the aluminium chloride smelting are [3]:

1. Substantially lower working temperature (700°C) compared to Hall-Heroult cell (980°C).
2. Relatively higher current densities could be applied since the critical current density for the anode effect is fairly high. By this the throughputs per cell can be considerably increased thereby reducing the capital costs.
3. It does not require a consumable carbonaceous anode which for Hall-Heroult's process accounts for more than 7% of the total cost.
4. Added freedom one can get in the choice of raw materials. Low cost non-bauxite ores can also be beneficially used.
5. No environmental pollution is involved.
6. Chloride process would be the most energy efficient because it is operated at the lowest temperature.
7. Near theoretical power efficiencies are possible in the advanced chloride-bipolar cells thereby providing direct saving in energy costs.
8. The chloride cells can survive power interruptions more easily than the Hall-Heroult cells. This is possible because the chloride cell with its higher efficiency causes little excess heat generation and hence the cell is well insulated. In addition the chloride cell has a much lower temperature liquid range for the electrolyte than the fluoride cells.
9. Chloride electrolysis provides metal of superior purity. Undesirable contamination of sodium as found in Hall-Heroult metal are greatly reduced in this system.

There are certain disadvantages also in the chloride electrolysis. The chlorination process is an extra step in the process, while Bayer alumina is the starting material in the Hall's cell. The aluminium chloride and its compounds are highly corrosive to many construction materials. The high volatility of the electrolyte also poses problems for the recovery of aluminium chloride from the fumes. Possibilities are there for the formation of phosgene and other poisonous gases during the chlorination of alumina.
The decomposition potential of aluminium chloride with an inert anode is 1.8 V at 700°C compared to 1.2 V at 1970°C for the aluminium oxide with a consumable carbon anode. However, the operating cell voltage for the chloride electrolysis is much lower (around 3 V) compared to Hall-Heroult cell (about 4.5 V). This is possible because of the lower polarisation voltage, iR and electronic voltage drops in the case of chloride electrolysis. The chloride electrolysis claims less energy consumption to the extent of at least 30% especially when the bipolar cells are operated.

Table 1: Comparison of chloride process with best present Bayer-Hall-Heroult processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Best present Bayer-Hall-Heroult</th>
<th>Future improved Bayer-Hall-Heroult</th>
<th>ALCOA cell (+) (AlCl₃ electrolysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fixed capital investment/annual short ton AI $</td>
<td>1750</td>
<td>1750</td>
<td>1450</td>
</tr>
<tr>
<td>2. Electrical energy kWh/kg of Al</td>
<td>14.3 to 15.4</td>
<td>11-12.1</td>
<td>9.9</td>
</tr>
<tr>
<td>3. Carbon kg/kg of Al</td>
<td>0.44-0.5</td>
<td>0.44-0.5</td>
<td>0.36-0.4</td>
</tr>
<tr>
<td>4. Direct operating costs * per kg of Al (Raw materials and energy only)</td>
<td>35-44</td>
<td>33-40</td>
<td>30-40</td>
</tr>
</tbody>
</table>

(*) Bipolar cell – includes Bayer process for chlorination step (Alcoa)

Electrochemistry of aluminium chloride electrolysis

The electrolysis of aluminium chloride is not a new idea. In fact it can be traced back to as early as 1854 much earlier to the discovery of Hall-Heroult processes, when an electrolysis of fused NaAlCl₄ was carried out to separate aluminium metal. Several workers in this line were continued after the establishment of the Hall-Heroult process. Molten binary and ternary mixtures containing LiCl, NaCl, KCl, MgCl₂ and BaCl₂ in addition to AlCl₃ have also been studied and established as potential electrolytes. The cell reaction in aluminium chloride electrolysis is

\[ \text{AlCl}_3 \rightarrow \text{Al} + 1.5 \text{Cl}_2 \]

For this reaction at 700°C ΔG = +123.6 kilo calories and ΔH = 155.0 kilo calories. Using these values the reversible decomposition voltage works out to about 1.8 volts and the minimum energy consumption of 6.7 kWh/kg. At an actual energy consumption of 10 kWh/kg the energy efficiency would be 67%.

Several researchers have studied the electrochemical reduction of aluminium chloride in alkaline chloride melts. Russian workers have suggested the existence of an Al⁺ and/or Al²⁺ species together with Al³⁺ [6]. Measurements of equilibrium electrode potential of an electrode with varying temperature and AlCl₃ concentration give evidence for the reaction

\[ \text{Al}^{2+} + 2 \text{e}^- = 3 \text{Al}^+ \]

A two step mechanism as shown below has also been proposed for the reduction of AlCl₃ at low current densities.

\[ \text{Al}^{3+} + \text{e}^- \rightarrow \text{Al}^{2+} \]
\[ \text{Al}^{2+} + 2\text{e}^- \rightarrow \text{Al} \]

and one step reduction at high current densities

\[ \text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al} \]

A study on the electrochemical reduction of aluminium chloride in NaCl-KCl equimolar mixture, in the concentration range from 3 x 10⁻⁴ to 3 x 10⁻¹ M for the temperature range of 973°K to 1223°K was carried out using voltamperometric and chronopotentiometric techniques. Vitreous carbon, silver, platinum, tantalum, titanium boroide and liquid aluminum were used as the cathodes. With carbon electrode, the reduction of chloro aluminate occurred simultaneously with the reduction of alkali metal ion and also of the formation of aluminium carbide (Al₄C₃). At the other electrodes like silver, platinum, tantalum, titanium boroide, etc. it was evident that there was the formation of alloy or compound. Chronopotentiotmetric study revealed that the chloroaluminate reduction corresponds to the following equation

\[ \text{AlCl}_3 + 3\text{e}^- \rightarrow \text{Al} + 3\text{Cl}^- \]

Under certain conditions, the reaction is found to be reversible.

Studies regarding anodic overvoltages of chlorine liberation at carbon electrodes in melts containing aluminium chloride had been found to be helpful, to calculate energy and heat balances [7]. The study on reaction mechanism at carbon electrode helps to understand the nature of interactions between the electrode products and anode material and to foresee and prevent the oxidation and destruction of electrodes and so also to reduce the anodic overvoltage. The anodic overvoltage is found to be mainly dependent on aluminium chloride content in the melt.

References are cited in literature regarding electrochemical studies on certain low temperature molten salt systems containing aluminium chloride which undergoes a series of Lewis acid base reactions with other chlorides [8]. They form low melting chloro-aluminates with alkali chlorides. The most important equilibria in the melts can be represented by the equation:

\[ 2\text{AlCl}_3^- \rightarrow \text{Al}_4\text{Cl}_6^- + \text{Cl}^- \]

The sodium chloride containing aluminium chloride melts at 175°C, the equilibrium constant being 1.96 x 10⁻⁵. Some metal chlorides dissolve in the melt enabling codeposition to form alloys of aluminium.

Electrolysis of aluminium chloride has been carried out by several research workers employing different salt systems and operating parameters [4, 9, 10, 11, 12]. Operating temperatures ranging from 150°C to 760°C and current densities varying from 0.9 to 2.8 A/cm² are reported.

Factors influencing the ideal operation of electrolytic cell

If an electrolytic cell has to be operated under ideal conditions many factors such as cell design, operating temperature, electrode materials, refractory lining, bath composition and control etc. are to be carefully studied and the best conditions are to be incorporated.

Cell design

Based on energy and production considerations on ideal electrolytic cell should satisfy the following requirements [13]:

a) The cell should be operated at a voltage very near to the theoretical voltage.

b) The electrodes should be dimensionally stable and the designs of the same should facilitate minimum losses in current efficiency.

c) Provision for easier separation of anodic and cathodic products should be made.

d) Adequate circulation of the electrolyte should be maintained to maintain uniform concentration within the cell.

e) At a given volume it is always advantageous to have the maximum electrode area.

The chloride electrolysis permits most of the parameters to be incorporated in the cell design especially in bipolar cells. It permits small interelectrode gaps to the extent of 1 cm and the cell voltage is thereby reduced considerably. The voltage loss in the electrode is considerably reduced in the bipolar cells. As aluminium metal is formed over the horizontal electrode gas is carried down to the metal collection chamber at the bottom and the chlorine gas rises to the top. Provisions can be made to recover the volatile aluminium chloride in the anodic gases having condensers and separators outside the electrolytic cell. Feeding of aluminium chloride is also a tough task to be handled. There may be an excessive loss of aluminium chloride because of its high volatile nature. These vapours are to be recovered and recycled. The feeding hopper is to be so designed that it allows continuous
feeding either in solid or vapour form. Some inert gases like nitrogen, argon etc. can also be employed as carrier gases for aluminium chloride vapours for feeding into the cell.

**Electrode design**

The design of electrodes is also important, from such stand points of view as noted below [14]:

1. The electrodes should have good electronic conductivity.
2. Low solubility or reactivity with molten aluminium or chloride melts.
3. Cathodes should have more wettability by molten aluminium.
4. At the anodes the chlorine gas formed should be enabled to grow into bigger bubbles, which helps to improve the coalescence of the metal.
5. Small interpolar gaps are beneficial since the gas bubbles evolved provide better circulation of the electrolyte for maintaining the bath composition uniform.

It has been observed that vertical electrodes yield lower current efficiencies since droplets do not wet the aluminium electrolytes thereby reducing the tendency for the metal to coalesce [15]. The horizontally placed electrodes yield better effects for wettability and coalescence thereby increasing the current efficiency. It is also stated when the cathode is completely covered by a layer of aluminium the current efficiencies are much higher.

Metal cathodes like iron, steel, titanium, zirconium, etc. are easily wetted by aluminium (the wetting angle of liquid aluminium approaches zero) and thereby offer very high current efficiencies close to 100% even when arranged vertically. But the most metal cathodes get deteriorated after some time during electrolysis and hence not found to be useful as cathodes. However, cathodes made of titanium boride do not show any deterioration and offer higher current efficiencies.

**Refractory**

The life of the cell depends mainly upon the refractories, which have to withstand the corrosive chloride metals circulating within the cell with a high turbulence. Many refractories commonly insensitive to fluoride bath are highly sensitive to chloride electrolysis and the electrolyte tends to penetrate and react with the conventional refractory materials and ultimately forms sludge [16]. The presence of sludge not only decreases the efficiency of aluminium chloride electrolysis but also requires shut down at cleaning of the cells and removal of sludge. The conventional refractories used in Hall cell such as silica or silica based refractories or alumina or alumina based refractories and even nitride bonded silicon carbide are opposed to be used in the chloride electrolysis for aluminium metal production. These refractories pose problems because of their solubility particularly in that oxygen values therein operate to consume the carbon. In the case of silica based refractory, silicon from the refractory contaminates the aluminium metal being produced.

Refractory materials having a nitride material as its base either alone or associated with a mixture or in compound or in combined form of an oxide of silicon, boron, aluminium, wherein the nitrogen concentration of the nitride is between 25% and about 60% by weight of the nitride are used. Even though nitrides of silicon, boron and aluminium are preferred, other nitrides such as those of titanium, chromium, hafnium, gallium, zirconium, etc. are also found to be suitable. The use of such refractories are useful in most of the non-conducting materials that interfacially bind the electrolyte within the cell.

**Operating temperature**

Aluminium has the melting point of 650°C. If the cells are operated below this temperature, only solid metal could be deposited. For easier operations and control it is always better to conduct the electrolysis above the melting point of aluminium.

**Monopolar and bipolar systems**

Though it could be possible to extract the metal in monopolar electrolytic systems, it is conceived that better results could be obtained in bipolar cells where the space time yields are always higher. Since bipolar cells require a completely closed system better utilisation of heat balance can be worked out. Moreover bipolar systems provide greater circulation of the electrolyte and permit very small interpolar gaps. The interpolar gaps can also be maintained throughout the same by allowing the metal to flow off from the cathode surface to the reservoir kept at the bottom of the cell. Only a thin film of aluminium metal is retained constantly during the electrolysis.

**Bath composition and control**

It has been observed that best results are obtained in the electrowinning of metals from fused chloride melts in ternary systems of electrolytes that contain at least two alkali metal chloride components in addition to the chloride of the electrolyte metal [11]. This is because these ternary systems are expected to exhibit more extensive regions of complete liquid miscibility and lower vapour pressures of chlorides of electrowon metal at similar temperatures.

Studies on the electrical conductance of chloride melts containing LiCl, KCl, CaCl₂, MgCl₂, NaCl and AlCl₃ at temperatures of 700-750°C reveal that these melts deviate negatively from the additive conductivity law and it is also possible to predict the conductivity of complexes like LiCl-AlCl₃, NaCl-AlCl₃, NaCl-KCl, KCl-AlCl₃, NaCl-LiCl, KCl-LiCl etc. The densities of the mixtures agree well with the additive law [17].

The conductivity of pure molten LiCl is 6.18 ohm⁻¹ cm⁻¹ at 700°C and the highest of all melts at that temperature. By the addition of aluminium chloride the conductivity of LiCl is much more lowered than would be expected based on dilution by an inert nonconducting species. From 0-15% each molecule of aluminium chloride appeared to block the conduction between one and nine Li⁺ ions depending on aluminium chloride concentration. It is also observed that KCl-NaCl formed more stable complexes with LiCl than with AlCl₃.

The vapour pressure measurements reveal that the loss of electrolyte through the volatilisation is more in LiCl bath. It is reported that nearly 0.8 kg aluminium chloride is lost through volatilisation per kg of aluminium produced from a melt containing 5% AlCl₃ [18] and equimolecular mixture of LiCl and NaCl. However, the lithium chloride baths always offer a lower cell voltage because of their very high conductivity.

It is also reported that the loss of electrolyte would be around 50 kg/ton of aluminium when the molar ratio of NaCl : KCl is around 9-1 and AlCl₃ content is around 10 mole%. The composition and the estimated value would be approximately AlCl₃ 80% and KCl + NaCl 20% [19].

The current efficiencies obtained are always higher in the bath containing NaCl or MgCl₂ than LiCl bath [20]. Systems like AlCl₃-MgCl₂-NaCl, AlCl₃-CaCl₂-NaCl, AlCl₃-DiCl₃-MgCl₂-NaCl have an effect on inhibiting the reverse reaction from such standpoints as the solubility of aluminium in the bath, viscosity of the bath and wettability of aluminium with the bath. It is also reported that the addition of BaCl₂ up to 10% helps to reduce the interfacial tension of aluminium metal-bath so as to effectively promote the flow of the metal from the cathode surface though it is not effective for improving the current efficiency.

The surface characteristics and bath compositions seem to have a dominant role in the process. The composition of the bath has been found to be very critical. Presence of oxides more than 0.03% in the bath adversely affects the life of the graphite electrode. The presence of aluminium layer in the metal melt interface may also pose problems of passivation and ultimately affect current and electrical efficiencies [21,22]. Chlorine gas dissolved in the melt decreases the current efficiencies by reoxidation of dispersed aluminium. Increased aluminium chloride content in the melt enhances solubilities of chlorine and decreases the current efficiency. The increase in temperature is also observed to yield the same adverse effect [15].

It is always important to keep the aluminium chloride concentration at the desired level and should not be low enough for the formation of alkali metals. For if alkali metal chlorides are reduced, they form compounds with graphite and ultimately break the electrodes. Hence it is always important to keep aluminium chloride concentration within the desired level and not low enough for the formation of an alkali metal at the cathode. Maintenance of

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Kannan and Desikan - Aluminium by aluminium chloride electrolysis

The ALCOA Bipolar cells

the aluminium chloride content is rendered very difficult especially because of its high vapour pressure and escape along with the anodic chlorine gas. The bath resistance is found to be a function of aluminium chloride concentration and in electrolytic cells the feeding of aluminium chloride is based on continuous measurements of effective resistance, current and voltage. Decreases in resistance are relayed by computerised controls to the feeding mechanism and the feeding is discontinued as soon as the resistance is restored to the optimum value [23].

The chloride process may be broadly classified into the following steps:

a) Preparation of aluminium chloride by chlorination of aluminium oxide in the presence of carbon and its subsequent purification.

b) Electrolytic separation of aluminium chloride into aluminium metal and chlorine gas at 700°C.

Chlorine gas produced from the cell is recycled for production of aluminium chloride.

Chlorination of alumina (preparation of aluminium chloride)

Alumina can be chlorinated in the presence of a reductant such as carbon according to the equation:

\[ \text{Al}_2\text{O}_3 + 3/2\text{C} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3 + 3/2\text{CO}_2 \]

The temperature range is around 700-900°C. Other reductants such as CO can also be used with a little variation in the operating temperature. In the initial stage, bauxite is refined to alumina via Bayer process, taking care to control physical form such as surface area, crystal structure etc. for optimum conditions in the chlorination. The alumina is then impregnated with carbon and chlorinated in the presence of a catalyst. These conditions ensure that the gas evolved is predominantly \( \text{CO}_2 \) thus minimising the total energy requirement. It has been estimated that approximately 20 GJ./metric ton is required per metric ton of aluminium content for chlorination in spite of the reaction being exothermic. This is an addition to 45 GJ./metric ton required for mining operations and processing of Bayer alumina [13].

Several procedures have been adopted for the chlorination process, but the majority of them are employing fluidised bed for best results.

Electrolysis - Cell description and operation

The ALCOA Bipolar cells

Even though the preliminary work as described above gave an idea about the feasibility of the chloride electrolysis, the real breakthrough was achieved by the ALCOA when it developed the bipolar cell. It took nearly 15 years of R & D efforts and consumed more than $25 million for ALCOA to develop this technology. A pilot plant of capacity 15000 T/year had been installed by the ALCOA in Anderson Country Texas.

It is reported that ALCOA has solved many problems connected with the electrolysis of aluminium chloride. Complete information of the process developed is not still disclosed but based on the informations from their patents one can understand to a limited extent about the salient features.

The cell (Fig. 1) consists of a steel mantle lined with thermally insulating refractory materials which resist the attack by the chloride electrolyte [4].

A graphite compartment is provided at bottom for the collection of liquid aluminium. The cell lid is also made of a refractory material which has openings for the addition of aluminium chloride and other salts, for
Electrode polarisation

Table

Ionic resistance drop (electrolyte)

A number of graphite electrodes, which are placed in a vertical pile in the cell at a distance of about 1 cm, act as the bipolar electrodes. The top and bottom electrodes are connected to the positive and negative terminals of the power supply. The operating temperature is about 700°C and has the bath composition of NaCl 50 - 53, LiCl 40 - 45, AlCl₃ 5 - 7 mass percentages with possible additions of MgCl₂, CaCl₂, KCl etc. in meagre quantities.

The common and very narrow anode - cathode compartment is an outstanding feature of the cell design [25 - 26]. By this, the chlorine gas formed escapes only on one side of the compartment and leads to a defined movement of the electrolyte and the liquid aluminium between the electrodes, setting up a circular motion of the electrolyte in the cell, resulting in a continuous supply of new electrolyte to the cell compartment. The aluminium metal formed sinks towards the bottom and the chlorine gas rises to the top thereby minimising the chances of recombination. The saturation of chlorine in the electrolyte is also a necessity for better operating conditions because the chlorine increases the ability of aluminium droplets to coalesce and thereby reducing back reaction. It is also reported that aluminium chloride content in the bath also has an effect on the size of chlorine bubbles.

A current density of 0.8 - 2.3 A/cm² and cell voltage of 2.7 to 2.9 are reported for the ALCOA cells. Current efficiency of the order of 90% is normally obtained and the energy efficiency is claimed to be around 60% which for Hall cell is around 45%. The specific energy consumption is reported to be about 9 to 10 kw/h kg of aluminium metal and hence at least 30% energy is saved compared to Hall - Heroult cell. However, the claim is referred to the electrical energy consumed for the electrolysis and does not include energy requirements for the chlorination of alumina.

Table II gives a comparison of voltage and energy consumption for Hall - Heroult cell and ALCOA bipolar cell [13].

2. Nippon Light Metal's Bipolar cell

Japan's Nippon Light Metal Company which has also experimented upon the electrolysis of aluminium chloride, has adopted a modified design for their bipolar cell. The schematic diagram of the same is given in figure 2.

Table II: Comparison of voltage and energy parameters in Hall Heroult process and chloride process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hall - Heroult ALCOA</th>
<th>Bipolar cell (Estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition voltage</td>
<td>1.18 V</td>
<td>1.85 V</td>
</tr>
<tr>
<td>Electrode polarisation</td>
<td>0.50 V</td>
<td>0.40 V</td>
</tr>
<tr>
<td>Ionic resistance (electrolyte)</td>
<td>1.60 V</td>
<td>0.55 V</td>
</tr>
<tr>
<td>Electronic (electrode) resistance</td>
<td>1.02 V</td>
<td>0.02 V</td>
</tr>
<tr>
<td>Total cell voltage</td>
<td>4.30 V</td>
<td>2.90 V</td>
</tr>
<tr>
<td>Current efficiency</td>
<td>90 %</td>
<td>90 %</td>
</tr>
<tr>
<td>Energy efficiency</td>
<td>45 %</td>
<td>60 %</td>
</tr>
<tr>
<td>DC kWh/kg</td>
<td>14.2</td>
<td>9.6</td>
</tr>
</tbody>
</table>

The N.L.M. cells are almost similar to Alcoa cells in their design excepting the variation in shape of bipolar graphite electrodes which are inclined towards the interior in a kind of funnel shape [27]. The angle of inclination is normally between 10 and 45°. It is said that more than 50° inclination would reduce the current efficiency. The electrodes are so spaced apart as to provide the electrolysis in the in-between space. The aluminium metal produced on the cathode surface will descend centripetally towards the centre holes along the slope of the upper surfaces of the funnel and fall into the molten metal reservoir. On the other hand the chlorine gas evolved at anode will diffuse radially in a radial direction along the sloped lower surfaces of the funnel and passing through the peripheral clearances (gas rising passages). The electrolytic bath contained in the gas rising passages will develop rising flow current due to buoyancy of chlorine gas and a falling flow current will be produced in the centre hole. The N.L.M. claims to have reduced the chances of recombination very much less compared to ALCOA cells in their cell designs. It is reported that the electrodes are separated and held in position by having separators made of alumina. The direct contact between the bath and refractory brick structure is prevented by cooling the latter to a temperature lower than the solidification temperature of the bath so as to form a film of bath over the inside walls of the structure [28]. By this the structure is electrically insulated from the bath.

The aluminium chloride is fed into the bath by a rotary feeder with vibrating facility [29]. The solid aluminium chloride through the feeder is mixed with a small quantity of sodium chloride present in a low melting point high concentration solvent which helps the vapourisation of aluminium chloride. The vapours are transported to the electrolytic bath by the nitrogen carrier gas.

The chlorine gas generated at high temperature along with carrier gas and other vapours produced in the melt is transported towards the exhaust. The aluminium chloride and alkali compounds are separated in a cooled trap provided before the chlorine collector. The exhaust and separators are made of acrylic materials.

The N.L.M. aluminium cells have dispensed with the use of expensive lithium chloride in the electrolytic bath, instead they employ bath containing CaCl₂, MgCl₂ or BaCl₂ along with NaCl and AlCl₃. A number of systems of different combinations of the salts mentioned above have been studied, in detail and it is reported that the current efficiency obtained was over 95%. The operating temperature is around 680 - 750°C and the current density employed is between 0.5 and 2.0 A/cm². The interelectrode distance varies from 1 to 2.5 cm. The cell voltage is about 3.2 to 3.4 volts. It is reported that a 100 kg/day aluminium plant has been installed in N. L. M. Kambra smelter. The energy consumption is said to be around 10000 kWh/tonne of aluminium metal [30].

CONCLUSION

The task of the chloride process to establish itself against the conventional Hall-Heroult process may be very tough. Its success lies mainly in the economic production of anhydrous aluminium chloride in a very pure state to avoid sludge formation and attack on electrodes. However, it is heartening to note that the ALCOA has already successfully overcome all these tasks in their new venture and has built a plant of capacity 15000 T/year. Major advantages such as less energy requirement, no carbon requirement for the electrolysis, avoidance of fluoride pollutions, reduction in operation and working costs, higher space-time yields, adaptability for the use of non-bauxitic ores etc. have put the process in the front line among the alternate processes for aluminium production. A better understanding in the physico-chemical properties such as phase diagrams of the melt, vapour pressure of components, effect of impurities, cell designs, etc. may perhaps put the process ahead of the established Bayer-Hall-Heroult Process.

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