

SOME EXPERIENCES IN ELECTRO-WINNING OF  
ALUMINIUM FROM FUSED CHLORIDE BATH (\*)

P.A. Ravindran and  
Dr. V.A. Altekar,  
University Department of  
Chemical Technology, Bombay.

Although the electro-winning of aluminium from out of a fused chloride bath dates back to 1854, when Bunsen first isolated the metal, the interest in the process since then has been sporadic.

Earlier work in this laboratory had not only confirmed the results reported in the literature, but had gone a step ahead in proposing and conducting electrolysis on extended time schedule with periodic additions of the trichloride. This work however was conducted at an optimum temperature of 400°C i.e. below the melting point of the metal, which was obtained mostly as loosely adherent flakes. The recovery of such a deposit had been problematical and the cell operation had to be interrupted because the fluffy deposit would soon accumulate to short circuit the electrodes. Further it would drop off the cathode while the same was being removed, thus further complicating the procedure.

This work which was in the nature of continuation of the previously reported work set up its aims in overcoming this draw-back. It sought to maintain the scale of operation between 1 to 2 litres of cell volume in trying to obtain continuous runs.

#### Experimental

In view of the aims set forth for this investigation, the approach was divided into two sections: (i) To operate at a temperature below the melting point of Al, and to manipulate conditions of electrolysis so as to obtain a coherent and yet strippable deposit on the cathodes; and (ii) to operate at temperatures above the melting point of aluminium with arrangement for periodic collection of the molten metal.

---

(\*) Paper for presentation at the Symposium on "Recent Developments in Non-Ferrous Metals' Technology" - 4th to 7th December, 1968, Jamshedpur.

Certain procedures were commonly followed throughout the investigations and these are outlined here. Deviations or additional features appear at appropriate places.

Electrolyte-Components: These investigations mainly pertain to the  $\text{NaCl-AlCl}_3$  system. The sodium chloride used was of A.R. grade of B.D.H. and Merk makes. The Aluminium trichloride was obtained from M/s. Indian Dyestuff Industries. Their grade II, which is more granular was found to be more suitable. In many of the melt preparations, the trichloride was sublimed before use. Fresh stocks were periodically obtained from the factory and stored in chambers desiccated with  $\text{CaCl}_2$ .

Electrolyte Preparation : For better results, the sodium chloride was heated to about  $300^\circ\text{C}$  for over an hour to make it as dry as possible. A pyrex beaker preheated to over  $100^\circ\text{C}$ . The weighed amount of trichloride was poured in, and the same immediately covered up by the hot sodium chloride. It requires some practice to obtain clear, transparent, colourless, melts with practically no fuming and no loss of the trichloride. Presence of iron, in the melt colours it, but a little addition of aluminium powder removes this colouration. It is advisable to keep the melt hot to 'homogenise' it and to filter it through hot glass wool into another hot pyrex beaker.

Electrodes and Their Care: The anodes used were either graphite and carbon, depending upon the temperature. The behaviour of these two in a fused chloride electrolyte is rather anomalous. Hard carbon has been recommended, and found to be excellent anode material below  $600^\circ\text{C}$ , while the graphite electrodes disintegrated under similar conditions. However, the role is reversed above this temperature when hard-carbon tended to disintegrate, and varieties of graphite stood up well.

For longevity, the anodes require a meticulous but routine care. This comprises of immediate washing after electrolysis, leaching out the chlorides in boiling water, alcohol-wash, and oven drying. Similarly, they were heated to about  $200^\circ\text{C}$  for one hour before immersion in an electrolyte. Any laxity in this routine resulted in swelling, flaking, and general disintegration of the anode.

The cathodes tried in this investigation, varied from hard carbon, graphite, aluminium steel, nickel and others. The metallic cathodes were used in the lower temperature range as at higher temperatures it seems to form non-strippable intermetallic compounds with nickel and steel; whereas the aluminium cathode sheet

tended to warp and deform. In the high temperature range, only graphite was used as cathode. The care of graphite cathode is similar to that of the anode.

The Electrolysis-Cells: For low temperatures up to 600°C, 'Pyrex' glass beakers could be used without any mishap. They were wound directly with nichrome heating element, which was fed from an auto-transformer to regulate its temperature. The beaker was then kept in an insulated chamber.

For higher temperatures, graphite cells were used. The graphite was closely machined to fit into a stainless sheet vessel, which was externally heated by an electric furnace. In one series of experiments the pot itself served as the cathode. The care and maintenance of these was similar to those of graphite electrodes described earlier.

Other Accessories: A.C. - D.C. motor-generator sets, one of 0 to 50 amps and another of 0 to 500 amps were used. The generated voltage could be controlled by a rheostat in the field windings.

Auto-transformers were used to control the furnace heating and the bath temperature, which was measured by thermocouples in glass or silica sheath.

The chlorine evolved at the anode was lead out of the system with the help of a water ejector, through a series of absorption towers containing NaOH. In order to avoid contact of the bath with the moist air, dry nitrogen was used as a flushing gas under the cell lid.

Experiments below melting point of Aluminium: Use of rotary cathode:

The idea of using a rotating cathode was taken up from the practice of electro-aluminising. It was thought that the stirring effect created by the rotating cathode would prevent concentration gradient with low trichloride content at the cathode, which might help in codeposition of sodium and thus prevent three dimensional growth of the deposit.

: 4 :

The tabulated values of the current efficiencies show a much lower peak value of about 74% as against the peak efficiency of 84% obtained with stationary cathode, under similar conditions. The deposit continued to be flaky, fluffy, if bright and lusturous and non-adherent. It was surmised that instead of producing the desired adhesion and a coherent deposit, the rotary action of the cathode might be responsible for throwing away the flakes towards the anode due to centripetal force.

\*\*\*\*\*