

## Electrolysis of Alumina in a Molten Salt at 760°C

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The electrolysis of alumina at a current density of 0.9 A/cm<sup>2</sup> in a predominantly chloride electrolyte at 760°C has been demonstrated on bench scale. A high surface area anode was used to achieve this result.

### Introduction

Inert anode, cathode and sidewall have been the subjects of much of the past and present Hall cell research. The thrust of these programs has been to reduce the energy consumed in aluminum production by the use of inert materials. There has also been interest in reducing the operating temperature of the process to improve the likelihood of using inert materials for aluminum smelting. But the majority of the candidate electrolytes for low temperature electrolysis are limited by low alumina solubility (<1.0 wt%).

The purpose of this research was to demonstrate that the electrolysis of alumina from electrolytes in which it is only slightly soluble could be achieved by the use of a process that employs a high surface electrode.

### Background

Many authors have investigated the impact of lowering the temperature for aluminum smelting through modified bath composition (1, 2, 3, 4). These baths include cryolite-base melts with as much as 35 wt% excess aluminum fluoride and standard baths with additives such as calcium, magnesium or lithium fluoride. The advantages expected include improved current efficiency, reduced carbon consumption, increased cell life and the enhanced potential for inert materials. Limited alumina solubility has been cited as an impediment to progress in this area.

In aqueous systems, the selective electrolysis of dilute species has been achieved for some time

by the use of high surface area electrodes. A high surface area electrode is one in which the depth as well as the plane area of the electrode become electrochemically active due to favorable overpotentials and permeations of electrolyte into the depth of the electrode. Electrolyte permeation into the electrode can be achieved through design or can occur by virtue of the natural porosity of the material. Three dimensional, high surface area electrodes have found few applications in molten salts. A recent United States patent (4,681,671) by J. J. Duruz reports experiments in which a high surface area inert anode is used in the electrolysis of alumina in a highly acid melt at 750°C. D. J. Fray used packed bed electrodes for electrorefining of aluminum or zinc (5).

Materials researchers at Alcoa during the late 1970s used electrochemical techniques to establish the relative solubility of various refractories in molten salts (6). As a part of that study, steady state polarization measurements (potential versus current curves) were obtained for the anode and cathode reactions associated with electrolysis of alumina saturated in a molten salt. The salt was composed of sodium, lithium and aluminum chloride (68 wt%, 28 wt%, and 4 wt%), and the measurements were made at 710°C. The expected overall reaction was



The half cell reactions were measured relative to a Ag/AgCl reference electrode. The equilibrium voltage, anode to cathode, was 1.28V. The anode to reference voltage was 0.48V and the reference to cathode was 0.8V. All voltages were compensated for the ohmic voltage between the reference electrode and the electrode of interest. The dominant overpotential,  $\eta$ --applied potential ( $E_a$ ) minus the equilibrium potential ( $E_{eq}$ )--was at the

anode. Correlating the anode data in the form of the Tafel relation,

$$\eta = E_a - E_{eq} = a + b \ln(i) \quad (2)$$

resulted in a Tafel slope (b) of 0.24 and an intercept (a) of 1.36. The symbol (i) is current density. The overpotential at the cathode was only a few millivolts at a current density of 1 A/cm<sup>2</sup>. Based on the anode polarization data, the inception of chlorine generation occurred +0.5V from the anode equilibrium half cell potential. This was most likely due to the decomposition of aluminum chloride. Below this voltage it should be possible to electrolyze alumina without generating chlorine.

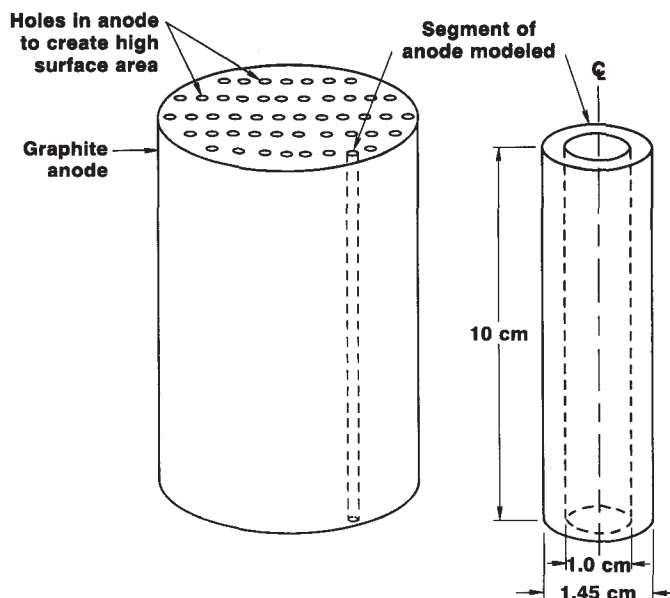
The use of a high surface area anode as a means of selectively extracting aluminum from this salt was evaluated by modeling the anode current distribution. The superficial current density was used as a measure of the effectiveness of an anode design. The superficial current density is the cell current divided by the superficial area of the anode. This approach was used so that the current density reported could be compared to an electrode with a plane surface. A computer code, entitled "Cell Design," a product of L-Chem, Incorporated, was used to determine the current distribution. The program, developed by U. Landau (7), uses a finite difference formulation of Laplace's equation with appropriate boundary conditions to compute primary, secondary and tertiary current distributions. The program can be used for two dimensional or axisymmetric geometries.

One example of a high surface area electrode evaluated was a cylindrical anode 10.0 cm long with a 47% void volume created by a number of 1.0 cm diameter holes placed axially in the electrode. The additional surface area available for electrolysis created by the holes is approximately twenty times the plane area. The current distribution for a segment of this electrode was estimated using "Cell Design." Figure 1 illustrates a typical electrode geometry and the segment modeled. The Butler-Volmer equation,

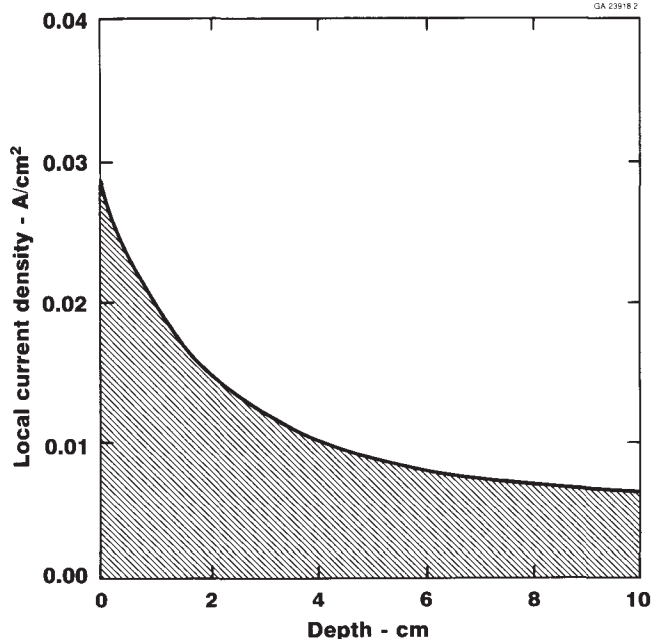
$$i = i_0 [\exp(\alpha n F / RT \eta) - \exp(-\beta n F / RT \eta)], \quad (3)$$

was used for the electrochemical boundary conditions at the anode and cathode surface. The exchange current density ( $i_0$ ) and the transfer coefficients ( $\alpha, \beta$ ) were determined in the conventional manner from the Tafel data previously mentioned. In Equation (3) F is the Faraday constant, R is the ideal gas constant, n is the number of electrons involved in the reaction, and T is absolute temperature. The current density as a function of depth in a hole is shown in Figure 2.

It is assumed that the voltage drop in the anode is negligible. At an overvoltage of 0.48V a superficial current density 8.3 times the current density for a plane electrode is predicted for this design. The current through this segment is 0.34 amperes. The maximum possible at the same overvoltage without the high surface area is only 0.041 amperes.



High Surface Area Electrode and Segment Modeled  
Figure 1



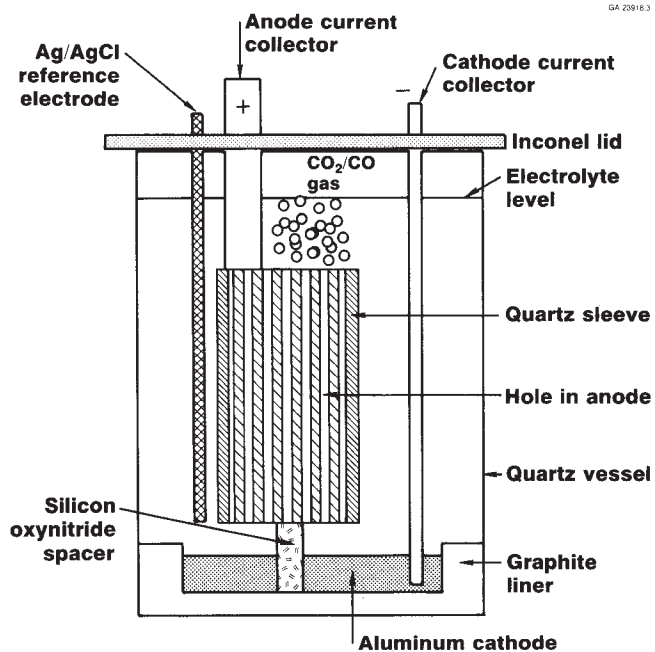
Current Density versus Depth in Electrode Based on "Cell Design"  
Figure 2

This example illustrates that a high surface area electrode would be an effective means of selectively extracting aluminum from an electrolyte with low alumina solubility. The superficial current density computed for this example was  $0.21 \text{ A/cm}^2$ , approximately one quarter of the current density in commercial aluminum production cells. The alumina solubility for this salt is expected to be lower than 0.2 wt%.

### Experimental Procedure

A sketch of the bench scale cell used in this investigation is shown in Figure 3. The cell was enclosed in a quartz vessel and sealed to an Inconel lid using a teflon gasket. The temperature was maintained by an electrical resistance furnace surrounding the quartz vessel. The anode was 14 cm in diameter with 1 cm axial holes to achieve 47% void area. The anode height was 15 cm. A quartz sleeve was placed around the anode to avoid current flow from the perimeter of the anode. The cathode was an aluminum pool approximately two times the cross sectional area of the anode. A graphite cup was used to contain the aluminum. Graphite current collectors were used for both the anode and cathode. The anode and cathode were separated using a silicon oxynitride spacer. The anode-cathode separation was 3.8 cm. A Ag/AgCl reference electrode was placed close to the bottom of the anode and used to control alumina feeding. Alumina was fed to the cell manually through a port in the lid.

The cell was instrumented to log on a computer gas current efficiency, cell voltage and amperes, anode to reference voltage, and cell temperature. Gas current efficiency was established by a balance on the oxygen leaving the cell. The cell was kept under a positive pressure by a nitrogen purge. The nitrogen flow was maintained by a mass flow controller. The nitrogen flow rate and the volume percent  $\text{CO}_2$  and  $\text{CO}$ , measured by infrared analyzers, were used to establish the mass of oxygen flowing from the cell. The cell voltage was measured by probes placed at the top of the anode and in the cathode metal pool. This avoided the external voltage associated with the current collectors. The anode to reference potential was measured from the anode probe to the reference electrode. The anode to reference potential included  $E_{\text{eq}}$ , the anode overpotential and an ohmic component associated with the position of the reference electrode relative to the anode. The ohmic voltage drop was minimized by placing the reference electrode as close as possible to the anode.



**Bench Scale Cell**  
Figure 3

Two methods were used to determine ppm levels of chlorine leaving the cell: a Draeger tube test sensitive to 0.2 ppm, and a potassium iodide (KI) test paper which changed color on exposure to low concentrations of chlorine. Both indicators were validated using 0.5 ppm chlorine standard. Exposure of the KI test paper to the standard gas for 17 seconds caused a noticeable purple tint to the KI paper. The Draeger tube measurement was within 0.1 ppm of the standard gas composition.

Cell operation commenced by a determination of the superficial current density and the anode to reference potential at the inception of chlorine generation. Both were accomplished by incrementally increasing the cell current and testing the gas exiting the cell with the KI paper for a slight color change. Once this information was established, the cell was operated at constant current. The anode to reference potential was used to control alumina feeding. At the inception of chlorine discharge, the anode to reference potential for most salts tested was 0.9-1.0 volts. A material balance was done on the alumina charged. The data logging computer was programmed using coulombs passed and the current efficiency to estimate the alumina concentration in the cell with time and the theoretical alumina feed rate.

**Results and Discussion**

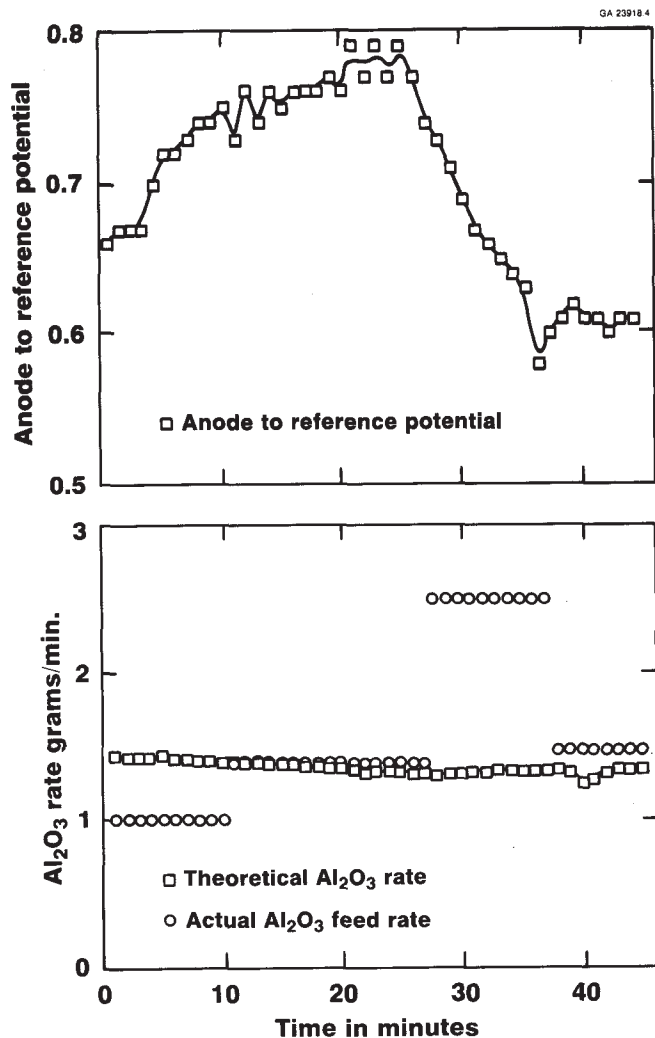
One of the electrolytes evaluated in this program was composed of 44 wt% sodium chloride, 44 wt% potassium chloride and 12 wt% cryolite. The cell was operated at 760°C. The liquidus temperature of this salt mixture without the cryolite present was 670°C. Alumina solubility for this salt was not known but was expected to be below 0.5 wt%. At both a 0.5 and 1.0 wt% alumina, it was possible to operate at 145 amperes without any indication of chlorine in the gas leaving the cell. The superficial current density was 0.9 A/cm<sup>2</sup>. The CO<sub>2</sub>/CO ratio was typically 5.5. The anode to reference potential varied depending on alumina concentration. Figure 4 is a plot of the alumina feed rate and the anode to reference potential versus time. The sequence illustrates alumina under-

feeding, then overfeeding, and finally feeding at the theoretical rate. Underfeeding resulted in an increase in the anode to reference potential to 0.78 volts. Increasing the feed rate dropped the anode to reference potential to 0.61 volts. At this point, the feed rate was returned to near theoretical.

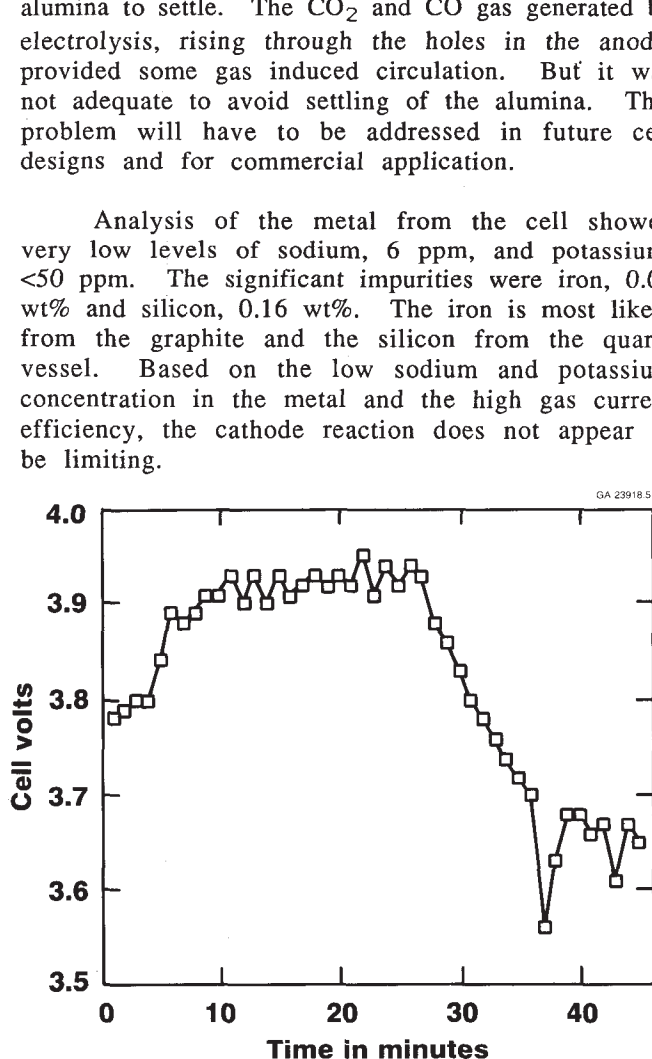
Figure 5 shows the cell voltage, and Figure 6 the CO<sub>2</sub>/CO ratio and the predicted gas current efficiency during the same time period, as reported in Figure 4. The average oxygen current efficiency for this period was 89%, the cell current was constant at 145 amperes and the alumina was being controlled to 0.5 wt%. The cell was also operated at 1.0 wt% alumina with similar results.

The cell was not designed to insure suspension of undissolved alumina. Operating at 1.0 wt% increased the tendency for undissolved alumina to settle. The CO<sub>2</sub> and CO gas generated by electrolysis, rising through the holes in the anode, provided some gas induced circulation. But it was not adequate to avoid settling of the alumina. This problem will have to be addressed in future cell designs and for commercial application.

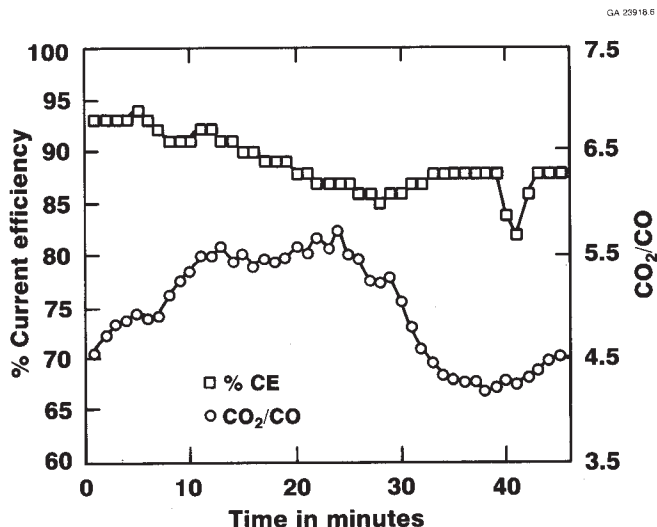
Analysis of the metal from the cell showed very low levels of sodium, 6 ppm, and potassium, <50 ppm. The significant impurities were iron, 0.08 wt% and silicon, 0.16 wt%. The iron is most likely from the graphite and the silicon from the quartz vessel. Based on the low sodium and potassium concentration in the metal and the high gas current efficiency, the cathode reaction does not appear to be limiting.



**Effect of Alumina Feed Rate on Anode to Reference Potential**  
Figure 4



**Cell Volts versus Time**  
Figure 5



**Current Efficiency and CO<sub>2</sub>/CO versus Time**  
**Figure 6**

**Conclusions**

A theoretical model and a bench scale experiment have demonstrated that aluminum can be electrochemically extracted from fused salts with low alumina solubility (<1.0 wt%), using a high surface area anode. This was accomplished without the decomposition of the supporting electrolyte and the resultant generation of chlorine. We believe that this approach would be viable for other oxides as well.

**Acknowledgment**

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