

## CURRENT EFFICIENCY FOR ALUMINIUM DEPOSITION FROM MOLTEN CRYOLITE-ALUMINA ELECTROLYTES IN A LABORATORY CELL

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### Abstract

The current efficiency with respect to aluminium can be as high as 96 % in modern Hall-Heroult cells.

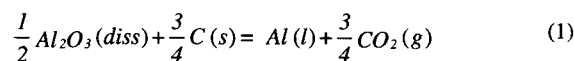
The loss in current efficiency is strongly linked to the fact that aluminium is soluble in the electrolyte. In addition the presence of dissolved sodium must be considered. The back reaction between dissolved metals and the anode product is responsible for the major loss in current efficiency. The rate of the reaction is controlled by diffusion of dissolved metals (Al and Na) through the diffusion layer.

A laboratory cell was used to determine the current efficiency for aluminium during constant current electrolysis. Standard conditions were NaF/AlF<sub>3</sub> (CR=2.5), Al<sub>2</sub>O<sub>3</sub> (sat), 5 wt% CaF<sub>2</sub> at 980°C and 0.85 A/cm<sup>2</sup>.

Current efficiencies ranging from ~ 93 - 96 % were obtained. The current efficiency was found to increase slightly by increasing cathodic current density. Increasing amounts of excess AlF<sub>3</sub> gave higher current efficiencies. Additions of LiF in the range from 1 - 2 wt% did not affect the current efficiency significantly at high current density.

### Introduction

Aluminium is produced by the Hall-Heroult process, where the overall primary cell reaction is:



Alumina is dissolved in a molten fluoride electrolyte based on cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and containing some AlF<sub>3</sub> as well as CaF<sub>2</sub> [1]. Modern cells are operating at ~ 955 - 965 °C. The current efficiency with respect to aluminium can be as high as 96 % and the corresponding energy consumption may be ~14 kWh/kg Al in cells running at ~ 300 kA or higher. The annual production of primary aluminium was about 38 million metric tons in 2007, making it the most important electrowinning process [2]. Although the basic principles of the original process remain unchanged, significant technological developments have taken place. The main improvements have been related to environmental issues and controlling the high induced magnetic fields. The productivity of the process can be increased by increasing the current in existing cells, and such efforts have been implemented in industrial cells in recent years. Another possibility is to increase the current density. The cathodic current density is

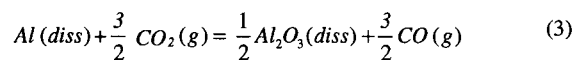
typically in the range from 0.7 – 0.8 A/cm<sup>2</sup> in modern industrial cells.

An important feature of the process is the fact that aluminium dissolves in the molten electrolyte, which is a general phenomenon taking place when a metal is in contact with a molten salt containing the metal cation or other species of the metal [3]. In molten cryolite based electrolytes dissolved Na must be considered in addition to dissolved Al. A small but significant activity of sodium is established at the metal/electrolyte interface due to the following equilibrium:



It is known that the subvalent species AlF<sub>2</sub><sup>-</sup> is formed as well as dissolved Na, the latter being responsible for a small contribution to electronic conductivity. Solubility studies have been carried out in laboratory experiments, and under industrial operation the metal solubility is ~0.06 wt% Al. The solubility decreases by increasing content of AlF<sub>3</sub> and decreasing temperature. Reliable data for the metal solubility have been published by Ødegård et al. and Wang et al. [4, 5].

The loss in current efficiency with respect to aluminium is mainly due to the so called back reaction between dissolved Al and the anode product according to:



The back reaction (3) takes place near the cathode surface, and the rate is controlled by diffusion of dissolved Al through the diffusion layer [1]. Hence, the concentration of dissolved Al at the cathode/electrolyte interface and the diffusion layer thickness is important for the loss in current efficiency.

Sterten presented a theory for the mechanism for the loss in current efficiency for aluminium deposition in the industrial process [6]. Sterten and Solli and coworkers presented experimental results and model calculations for the current efficiency based on laboratory studies [7-10]. The effects of electrolyte impurities and electrolyte composition were included in their investigations. Realistic values for the current efficiency were obtained. The variation of the current efficiency with respect to current density, electrolyte composition and temperature was found to be closely linked to the concentration of dissolved metal.

It is established that the back reaction takes place outside the diffusion layer next to the cathode/electrolyte interface. The rate

of the back reaction is independent of current density, so the current efficiency with respect to Al should increase by increased current density. However, transport phenomena in the electrolyte in the cathode diffusion layer lead to more complex relationship between loss in current efficiency and cathodic current density [1]. The rate of the back reaction can be expressed as follows:

$$v_B = k' (dc/dx) = k' (c^0/\delta) \quad (4)$$

where  $k'$  is a constant including the diffusion coefficient,  $c^0$  is the saturation concentration of dissolved metal at the cathode-electrolyte interface and  $\delta$  is the diffusion layer thickness. Li et al. [11] recently presented a revised model for calculating the current efficiency based on local variations in cathodic current density related to the three-phase flow of electrolyte at the cathode interface. The average current efficiency for a typical 300 kA cell at 960 °C and CR=2.3 was estimated to be 95.0 %.

### Experimental

A laboratory cell similar to that of Sterten and Solli was used to determine the current efficiency for aluminium during constant current electrolysis [7-10]. The current efficiency was calculated from Faraday's law by weighing the amount of deposited aluminium. The electrolysis time was 4 hours for each experiment.

The electrolysis cell was placed in a closed furnace with dry argon atmosphere. A graphite crucible with a sintered alumina lining served as the container for the molten electrolyte. A steel plate was placed at the bottom of the crucible acting as the cathode. A graphite anode was immersed about 4 cm into the electrolyte and placed about 4 cm above the steel cathode.

The influence of changing the cathodic current density and electrolyte composition including excess  $\text{AlF}_3$  and  $\text{LiF}$  additions was studied. The electrolyte was saturated with respect to alumina. Standard experimental conditions were  $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  (sat) with excess  $\text{AlF}_3$  corresponding to CR (molar ratio of  $\text{NaF}/\text{AlF}_3$ ) being 2.5 and 5 wt%  $\text{CaF}_2$  at 980 °C and 0.85  $\text{A}/\text{cm}^2$ .

### Results and discussion

Liquid aluminium was deposited on the solid steel cathode plate. Steel was used to achieve good wetting of liquid aluminium, which does not wet the solid graphite.

Current efficiencies ranging from ~ 92 - 96 % were obtained. The measured current efficiency versus current density is given in Figure 1. Good agreement with literature data was found at "normal" current densities. The current efficiency was found to increase slightly by increasing cathodic current density. This is in accordance with theory, since the main reason for loss in current efficiency is the back reaction between the primary products. The slight increase in current efficiency at high current densities is likely to be due to the fact that the transport phenomena at the cathode boundary layer cause a higher metal solubility, thus giving a slightly increased rate of the back reaction at increasing current density. However, the main reason for increased current efficiency at high current densities is due to the fact that the back reaction is almost independent of the current density.

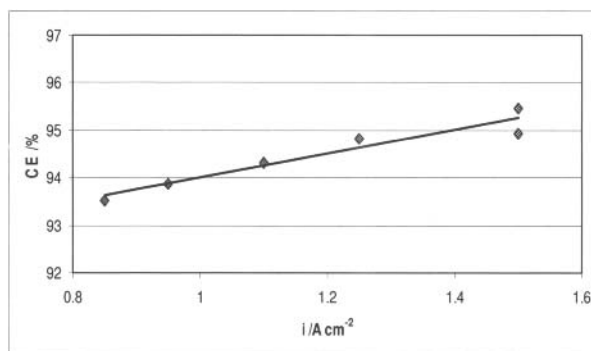


Figure 1. Current efficiency for aluminium deposition as a function of cathodic current density in molten  $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  (sat) with excess  $\text{AlF}_3$  corresponding to CR (molar ratio of  $\text{NaF}/\text{AlF}_3$ ) being 2.5 and 5 wt%  $\text{CaF}_2$  at 980 °C.

Figure 2 shows the effect of varying electrolyte composition ( $\text{AlF}_3$  content) on the current efficiency for aluminium. Increasing amounts of  $\text{AlF}_3$  gave higher current efficiency. This is also in agreement with previous investigations carried out at lower current densities.

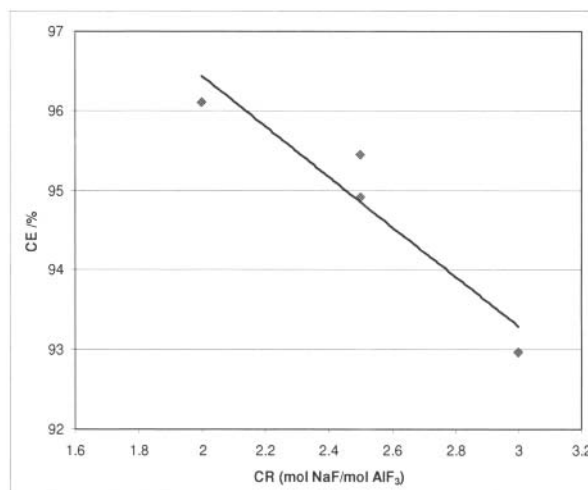


Figure 2. Current efficiency for aluminium deposition as a function of the electrolyte composition in molten  $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$  (sat) at 980 °C and 1.5  $\text{A}/\text{cm}^2$ .

The effect of  $\text{LiF}$  additions of 1 and 2 wt% did not give any significant change of the current efficiency, which was determined to change from 94.2 % to 94.4 % and 94.0 % respectively. This is not in accordance with literature, where Dewing [12] and Tabereaux et al. [13] reported that the loss in current efficiency in industrial cells increases somewhat with increasing  $\text{LiF}$  content. However, theoretical considerations may suggest that the current efficiency should not depend on relatively small additions of  $\text{LiF}$ . Additions of  $\text{LiF}$  in industrial cells may

lead to other changes of the electrolysis operation, so that industrial data for the current efficiency may not be reliable. The presented laboratory results for the current efficiency may not be directly applicable to industrial operation. Industrial cells have some constraints with respect to the design which is largely given by the energy and heat balance. An increase of the current density may not be feasible because it will imply a decrease of the interpolar distance in order to reduce the heat production.

### Conclusions

The current efficiency with respect to aluminium was found to increase slightly by increasing the cathodic current density in the range from 0.85 - 1.5 A/cm<sup>2</sup> during galvanostatic electrolysis in molten cryolite based electrolytes. The current efficiency was found to increase by increasing the content of AlF<sub>3</sub> in the electrolyte. Additions of 1 and 2 wt% LiF did not cause any significant change of the current efficiency.

### Acknowledgment

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