# EFFECT OF CURRENT DENSITY AND PHOSPHORUS IMPURITIES ON THE CURRENT EFFICIENCY FOR ALUMINUM DEPOSITION IN CRYOLITE-ALUMINA MELTS IN A LABORATORY CELL

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## Abstract

The current efficiency in industrial Hall-Heroult cells for aluminum production may be up to 96%. [1]. The back reaction between the dissolved metals (aluminum and sodium) and the anode product play the major part in the loss in current efficiency. Also impurities, such as phosphorous, which participate in cyclic red/ox reactions at the electrodes contribute significantly to reduced current efficiency. Phosphorous and other impurities are recycled with secondary alumina. Further potline amperage increase in industrial cells may require higher current densities. Thus the current efficiency dependence on current density and phosphorous content was studied at current density ranging from 0.85 - 1.5 A/cm$^2$ in a laboratory cell. Current efficiencies from 90 - 97% were obtained and increased slightly by increasing cathodic current density. The current efficiency decreased by about 3.8% per 100 ppm of phosphorus in the electrolyte.

## Introduction

The current efficiency in industrial Hall-Heroult cells, for aluminum production may be up to 96% [1]. The back reaction between dissolved metals (aluminum and sodium) and the anode product plays the major part in the loss in current efficiency. However, impurities also have impact on reduction of current efficiency. They are introduced to the electrolyte bath with the alumina or fluoride salts or come from carbon anodes and tools. Impurities have gained significant attention since the cell design has changed and dry scrubbers have been implemented, as airborne impurities will be captured in the dry scrubber and recycled to the reduction cell with secondary alumina. Phosphorus is an example of how impurities can have a negative impact on the operation of the Hall-Heroult process for aluminum production. It has been reported by several authors that phosphorus lowers the current efficiency by about 1% for each 100 ppm in the electrolyte [2,4]. Figure 1 shows previously published results on the effects of phosphorus on the current efficiency for aluminum deposition measured at a current density of and 0.85 A/cm$^2$ from Solli[2] and Thisted[4]. Figure 2 shows the current efficiency as a function of current density over a current density range from 0.4 to 1.3 A/cm$^2$ as published by Sterten [5]. These figures are reproduced in this paper for comparison to the results presented in this paper.

Phosphorous has several oxidation states from 3- to 5+. It has been suggested that three valent and five valent phosphorus species exist in fluoride melts. Dissolved complexes of phosphorus are reduced at the cathode and reoxidized at the anode, consuming electrical current without producing aluminum. By this mechanism phosphorous in the bath reduces current efficiency.
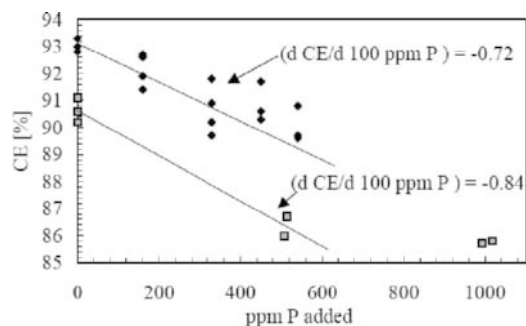


Figure 1. Current efficiency for aluminum deposition versus the amount of P added. Solli [2] - filled symbols, Thisted [4] - open squares. Molten $Na_3AlF_6$-$Al_2O_3$(sat)-$AlF_3$(7 wt%)-$CaF_2$(5 wt%) + $Na_3PO_4$ at 980 $^\circ$C and 0.85 A/cm$^2$.
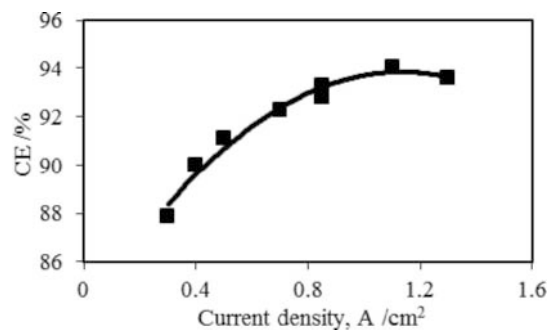


Figure 2. Current efficiency for aluminum deposition versus the current density [5].

## Experimental setup

Tests were conducted in an experimental cell with a controlled impurity level in the electrolyte at 980 $^\circ$C for 2-4 hours and the resulting current efficiency was determined by measuring the amount of deposited aluminum. All the parameters which affect current efficiency such as electrolyte composition, temperature, and cathodic current density were kept as constant as possible in order to study the influence of impurities on current efficiency.

The electrolyte was saturated with respect to alumina. Standard experimental conditions were $Na_3AlF_6$-$Al_2O_3$ (sat) with excess $AlF_3$ corresponding to CR (molar ratio of NaF/$AlF_3$) being 2.5 and 5 wt% $CaF_2$.
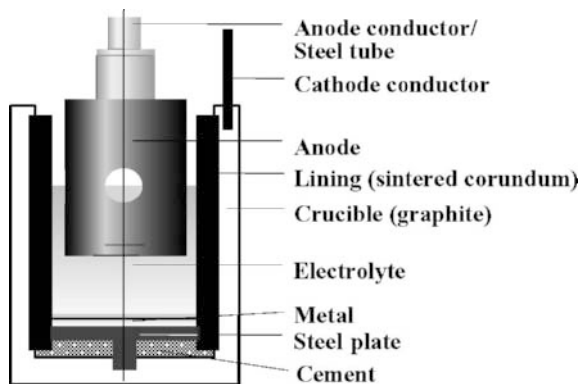
Figure 3. Electrolysis cell used to investigate effect of impurities on current efficiency

The laboratory cell, similar to that of Solli [2] was used to determine the current efficiency for aluminum during constant current electrolysis. Figure 3 is a schematic illustration of the cell. The advantage of this type of cell is that it provides a good convective pattern and maintains an almost flat cathode surface by using a steel cathode which is wettable for the liquid aluminum. Thus the cathodic current density stays constant and is distributed evenly. This is important for current efficiency studies because current efficiency is sensitive to the cathodic current density.

The cell was placed in a furnace with a controlled atmosphere, flushed with nitrogen gas at a flow rate of 0.2-0.3 $dm^3$/min to prevent air burn of the cell. A graphite crucible with a sintered alumina lining served as the container for the molten electrolyte.

The stainless steel tube was connected to the graphite anode, fitted with vertical holes and horizontal channels to facilitate convection in the cell.

The cathode was liquid aluminum deposited on the solid steel. Alumina additions were made manually through a steel tube every 15 min.

The duration of each experiment was aimed at producing the same amount of aluminum, so at high current densities, and corresponding high total cell current, the duration would be shorter than at low current densities. The length of the experiment therefore ranged from 2-4 hours, After termination of the electrolysis, everything was switched off and left to cool down. Then the crucible was broken and aluminum was cleaned mechanically and left in an aqueous solution of $AlCl_3 \cdot 6H_2O$ for 30 minutes. The current efficiency was calculated by weighing the amount of deposited aluminum and comparing it with the theoretical amount calculated from Faraday's law. Estimated loss because of metal handling is assumed to be 0.9%.

Two series of measurements are reported in this paper.

CE as a function of current density

In this series of experiments, the current efficiency was measured for a number of values of total imposed current with a constant electrolyte composition of $Na_3AlF_6$-$Al_2O_3$ (sat) with excess $AlF_3$ corresponding to CR (molar ratio of $NaF/AlF_3$) being 2.5 and 5 wt% $CaF_2$. The electrolyte was saturated with respect to alumina. This represents a corresponding range in cathode current density from 0.85 up to 1.5 $A/cm^2$, as the geometry of the experimental setup remained constant for all the experimental runs.
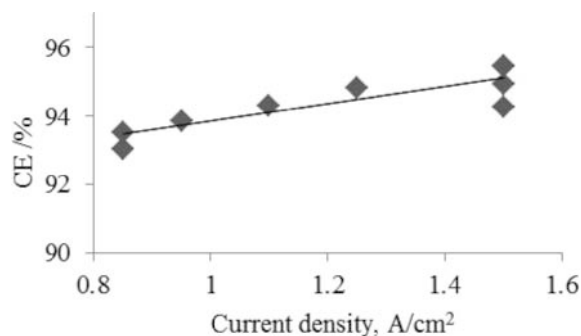


Figure 4. CE as a function of cathodic current density

CE as a function of phosphorous content at high current density

During this series of experiments the electrolysis cell was run with a 1.5 $A/cm^2$ current density. A predetermined amount of phosphorus was added to the electrolyte at the start of the experiment. Additions of $AlPO_4$ were made manually every 15 min, along with the alumina feeding in order to compensate for the loss of phosphorus. From experience and reported results this loss of phosphorus was estimated to be 10%. [4]. After the end of each experiment the phosphorous concentration in the electrolyte bath was measured using HR-ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometry).

**Results and Discussions**

Effect of current density

The measured current efficiency versus current density is given in Figure 4. Two tests were run at 0.85 $A/cm^2$ and three at 1.5 $A/cm^2$ to determine the reproducibility of the determined CE. The values show good reproducibility with a standard deviation of 0.25 and 0.48 respectively. Good agreement with literature data [5] was found at 0.85 $A/cm^2$ and 1.2 $A/cm^2$.

It was observed that the current efficiency increases slightly by increasing cathodic current density. This is expected, since the main reason for loss in current efficiency is the back reaction between the primary products, which has a constant rate with low dependence on current density. An increase in current efficiency at high current densities is likely to be counteracted by 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, this effect is not strong enough to prevent increased current efficiency at high current densities.

Effect of phosphorous

Figure 5 shows measured current efficiency for aluminum deposition as a function of phosphorus additions to the electrolyte in experiments run at a constant current density of 1.5 $A/cm^2$, where 10% of the initial phosphorus batch was added at 15 minute intervals throughout the electrolysis period. The impact of phosphorus appears to be non-linear as can be seen in Figure 5. Increasing phosphorus content causes a seemingly linear reduction in current efficiency at lower phosphorous levels, while the effect seems to flatten out at higher levels, the average slope
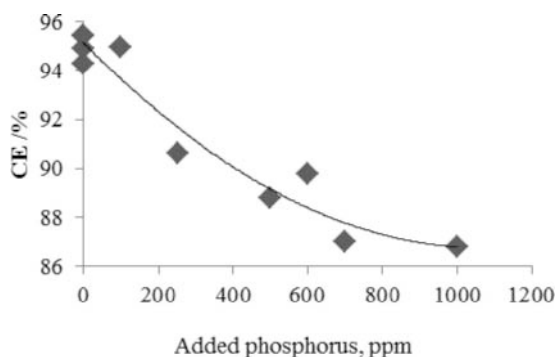
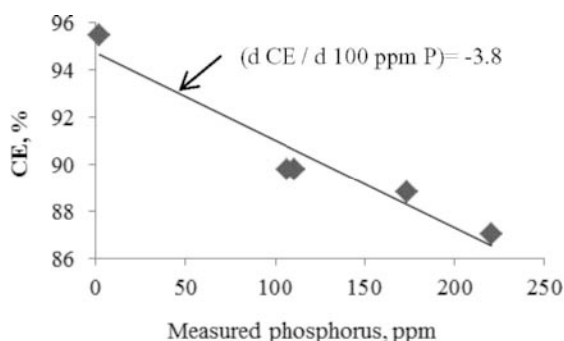Figure 5. Current efficiency for aluminum deposition as a function of the added phosphorus at 1.5 A/cm².



Figure 6. Current efficiency for aluminum deposition as a function of the phosphorus concentration in the electrolyte measured at the end of each experimental run at a current density of 1.5 A/cm².

corresponding to a 0.81% decrease in the CE per 100 ppm of phosphorous. This data is partly presented previously [6,7].

After the termination of each electrolysis run, the bath was removed from the crucible and analysed for phosphorous and other elements using HR-ICP-MS. Figure 6 is a plot of the current efficiency as a function of measured phosphorous concentration from this analysis. The phosphorous concentration measured by ICP was considerably lower than the estimates based on the phosphorous addition. As a result of this, plotting the CE as a function of measured phosphorous concentration shows a considerably higher impact of the phosphorus concentration on the current efficiency, a 3.8% decrease in the CE per 100 ppm of phosphorous in the bath. This underlines the importance of verifying the impurity concentration with reliable chemical analysis of bath samples. This effect on the current efficiency is significantly higher than previously reported values, as shown in Figure 1, but those results are derived from CE as a function of estimated phosphorous content based on additions and are thus comparable to Figure 5, which is in much better agreement. Industry experience may agree with the results from Figure 6.

It can be seen from the data in Figure 6 that the reproducibility is very good as the same current efficiency was found at similar contents of phosphorus determined by the HR-ICP-MS analyses.

It is believed that Figure 6 gives more accurate results than Figure 5 since it is based on chemical analyses of the electrolyte. However, the real effect of phosphorus can only be determined when the phosphorus content is known at any time during the course of electrolysis. Loss of added phosphorus during the experiments may have many causes, and the estimated effect on the CE from Figure 6 is probably somewhat exaggerated because the phosphorus content decreases as a function of the electrolysis time, so a chemical analysis after it's termination will give a value lower than the average. This is not the first time such discrepancy has been reported. Thisted [4] found that the real phosphorus content in the bath was significantly lower than the added amount. Note that the CE curve in Figure 6 shows no sign of levelling out at higher phosphorous concentrations, as observed in Figure 5. This is probably an indication that at higher concentration the phosphorous depletion from the bath is faster, so the higher rate of addition does not produce a correspondingly higher bath concentration.

Comparing the curves for CE as a function of added phosphorous to the reported data from Solli[2] and Thisted[4] it is observed that the higher cathodic current density in this work leads to a higher CE, but does not significantly change the slope of the curve. A reduction in the slope would have been expected since the amount of deposited aluminum should be proportional to the current density while the effect of phosphorous should be proportional to its concentration, but independent on the current density.

## Conclusions

Results from the present study support previous findings that the current efficiency for aluminum deposition increases with current density. This is mainly due to the fact that the loss reactions are non-electrochemical. The current efficiency was found to continue to increase slightly even at high current densities up to 1.5 A/cm².

As expected phosphorous in the bath was found to decrease the current efficiency. The current efficiency shown as a function of the estimated phosphorous content based on additions to the bath conforms well with previously reported data using the same method, with a decrease in current efficiency by 0.81% pr 100 ppm of phosphorous addition.

The current efficiency as a function of phosphorous concentration in the bath, as measured after termination of the experiments show a decrease in current efficiency by 3.8% pr 100 ppm of phosphorous in the bath. This is a considerably higher impact of phosphorus than previously reported. This shows the importance of carefully monitoring the actual concentration in the bath during the whole experiment, as while the estimate based on measurement at the termination of the experiment is presumably more accurate than the estimate based on addition, it will probably give and over-estimate of the slope. This is due to the fact that the average phosphorous concentration is probably higher than the final concentration.

## Acknowledgements

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