

## Effects of electrolyte impurities on the current efficiency during aluminium electrolysis

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### Abstract

Impurities enter the electrolyte mainly from the consumable carbon anode and aluminium oxide. Important impurity elements are iron, silicon, phosphorus and sulfur. Metallic impurities such as iron and silicon tend to codeposit at the cathode, while dissolved phosphorus and sulfur species also affect the current efficiency for aluminium production. In modern industrial cells more impurities end up in the produced metal due to the efficient recycling of impurities within the process. Laboratory experiments were carried out to determine the current efficiency for aluminium deposition and to study the electrochemical behaviour of dissolved phosphorus containing complexes as well as dissolved sulfate. Both additions of phosphate and sulfate to the electrolyte caused a significant reduction in the current efficiency, mainly due to cyclic redox reactions at the electrodes. The behaviour of phosphorus in industrial cells was studied by analyses of data for a large number of cells. Separate measurements were also conducted to study the distribution of impurities during industrial operation. Known amounts of impurity compounds were added to the electrolyte of industrial cells, and chemical analyses of samples of bath and metal as a function of time were carried out.

**Keywords:** Aluminium electrolysis; impurities; phosphorus; sulfur; current efficiency.

### 1. Introduction

About 50 million tonnes of aluminium is produced annually by the Hall-Heroult process. Electrolysis is carried out in molten NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> at approximately 955 °C. Current efficiency with respect to aluminium can be as high as 96 % in modern cells. The primary cell reaction is:



The loss in current efficiency for aluminium deposition is strongly linked to the fact that aluminium is soluble in the electrolyte. Metal solubility is a general phenomenon in molten salts [1]. In molten cryolite based electrolytes dissolved Na must be considered in addition to dissolved Al [2]. 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. Excess electrons from sodium are responsible for a small contribution to electronic conductivity [2]. Solubility studies have been carried out in laboratory experiments, and the metal solubility is generally < ~ 0.1 wt% Al in electrolytes used in industrial cells. The solubility decreases by increasing AlF<sub>3</sub> content and by decreasing bath temperature. Metal solubility data have been published by Ødegård et al. and Wang et al. [3, 4].

The back reaction between dissolved metals (Al and Na) and the anode product is responsible for the major loss in current efficiency:



The rate of the back reaction is limited by diffusion of dissolved metals (Al and Na) through the diffusion layer near the cathode. The rate of the diffusion of dissolved metals depends on the total metal solubility and the diffusion layer thickness. The presence of small amounts of  $\text{CaF}_2$ ,  $\text{LiF}$  and  $\text{MgF}_2$  is known to be beneficial for the current efficiency [1]. It is likely that the total metal solubility is reduced upon these additions.

Impurities enter the electrolyte mainly from the carbon anode and with the added alumina. Most impurities form soluble species in the electrolyte. Metallic impurities that are more noble than aluminium tend to deposit at the liquid aluminium cathode [5]. It has been shown [6, 7] that cations of such impurities are reduced at the cathode at their limiting current densities ( $i_{lim}$ ) given by the following equation:

$$i_{lim} = nFkc \quad (4)$$

where  $k$  is the mass transfer coefficient and  $c$  is the concentration of the dissolved impurity element species in the bulk of the electrolyte. Studies of impurities in industrial cells have been carried out by analyses of samples of electrolyte and metal as a function of time after additions of known amounts of compounds containing impurities [7]. The concentration of the impurity species under investigation versus time after addition can be expressed as follows:

$$c = c^0 \exp\left(-\frac{A}{V}kt\right) \quad (5)$$

where  $A$  is the area of the active cathode,  $V$  is the volume of the electrolyte and  $c^0$  is the background concentration before the addition. The mass transfer coefficient can be determined from the observed relationship between concentration and time after adding the impurity compound. Typical values have been reported to be in the range from  $10^{-5}$  -  $10^{-6}$  m/s [6, 7]. Such mass transfer coefficients will depend more on design, technology and operation of industrial cells. High convection of electrolyte and metal pad or unstable cells will cause higher values.

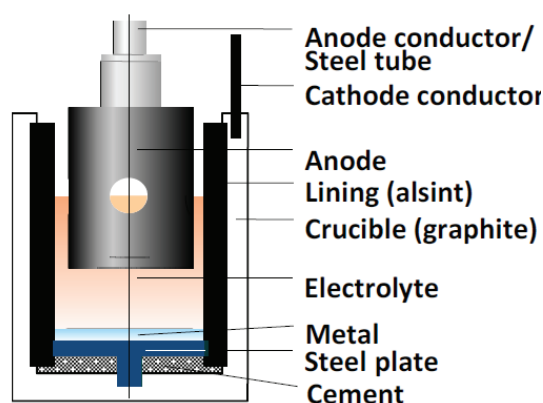
Other impurities that are less noble or do not alloy with aluminium tend to accumulate in the electrolyte. Even species that leave the cells with the anode gas will reenter the electrolyte with secondary alumina, this tendency being more pronounced for modern cells. Such impurities may reduce the current efficiency for aluminium due to cyclic reduction and oxidation reactions at the electrodes. It has been suggested that phosphorus can be regarded as such an impurity [8].

Studies of the behaviour of impurities during aluminium electrolysis are motivated by the possible deterioration of future raw materials and the more efficient treatment of cell emissions which causes more impurities to end up in the produced metal.

## 2. Experimental set-up

Figure 1 shows a sketch of the laboratory cell used to determine the current efficiency by galvanostatic electrolysis. The cell was similar to that used by Sterten and Solli [9 - 12]. 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 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 to ensure that the liquid Al was well wetted. A graphite

anode was immersed about 4 cm into the electrolyte and placed about 4 cm above the steel cathode. The influence of additions of  $\text{AlPO}_4$  and  $\text{Na}_2\text{SO}_4$  was studied in separate experiments. 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 a molar ratio of  $\text{NaF}/\text{AlF}_3$  of 2.5 and 5 wt%  $\text{CaF}_2$  at 980 °C and a constant current density of 0.8  $\text{A}/\text{cm}^2$ . The possible loss of phosphorus and sulphur due to chemical reactions between the added compounds and the electrolyte was also examined by analyses of electrolyte samples taken as a function of time after the additions of impurities.



**Figure 1. Sketch of the experimental cell for electrolysis to determine the current efficiency for aluminium deposition.**

Experiments related to impurities were carried out in industrial cells having prebaked anodes and fed with secondary aluminium oxide. Known amounts of compounds of impurities were added to the same cell at the same time. In this paper the behaviour of dissolved compounds of phosphorus and phosphorus is reported.  $\text{AlPO}_4$  and  $\text{SiO}_2$  were added. Electrolyte samples were taken for analyses before and after the additions at intervals of about 20 - 30 minutes between sampling. Electrolyte samples were analysed by XRF. It was assumed that the compounds dissolved readily in the electrolyte after the additions and that no material was lost in the process.

### 3. Results and discussion

#### 3.1. Laboratory cells

Current efficiencies ranging from approximately 89 % to 93 % were obtained. Good agreement with literature data [9 - 13] was found in pure molten  $\text{NaF-AlF}_3(\text{CR} = 2.5)\text{-CaF}_2(5 \text{ wt}\%)\text{-Al}_2\text{O}_3$  (sat), where CR = cryolite ratio.

After additions of both phosphate and sulfate it was found that the contents of dissolved phosphorus and sulfur in the electrolyte were decreased due to chemical reactions and possible evaporation in experiments without electrolysis. Especially the content of sulfur was rapidly reduced, as shown in Figure 2. In current efficiency experiments the loss of phosphorus and sulfur was compensated for by regular additions of the compounds during electrolysis.

Figures 3 and 4 show the current efficiency for aluminium during electrolysis at 0.8  $\text{A}/\text{cm}^2$  as a function of the contents of dissolved phosphorus and sulfur species in the electrolyte.

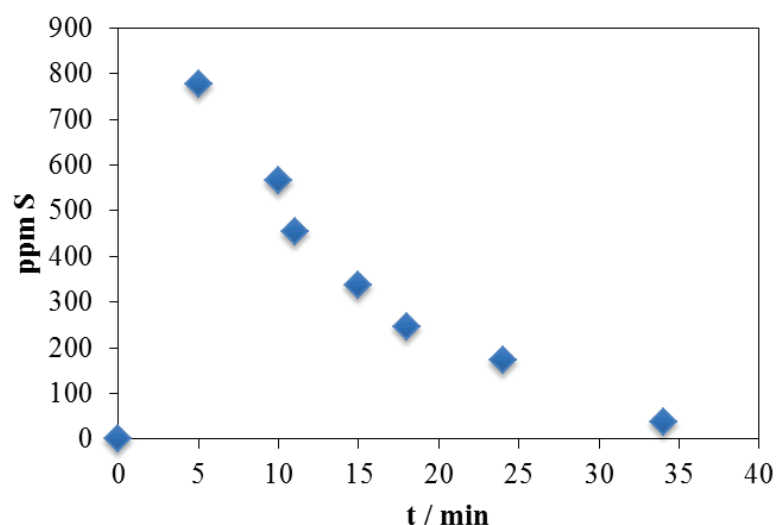


Figure 2. Sulfur concentration in the electrolyte after addition of  $\text{Na}_2\text{SO}_4$  (1000 ppm S).

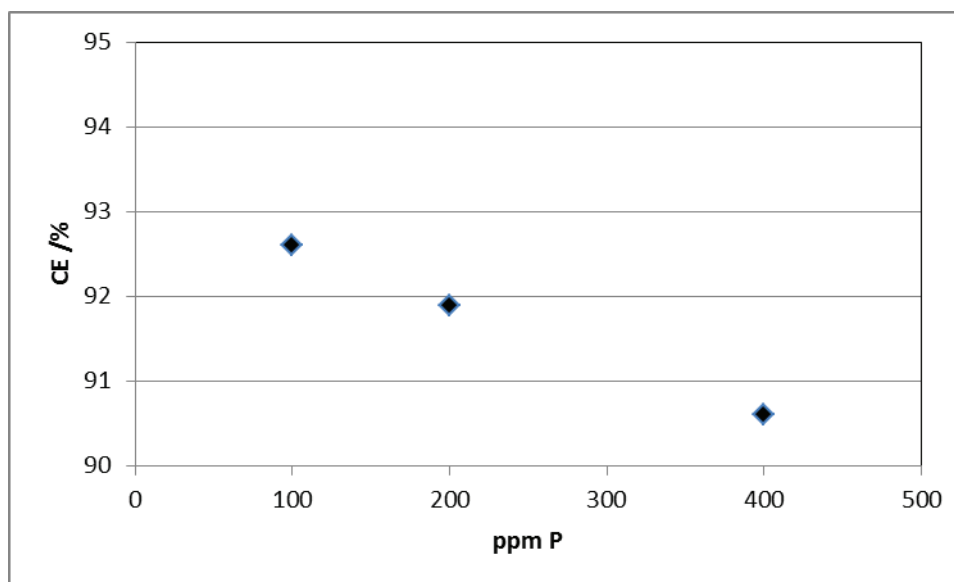
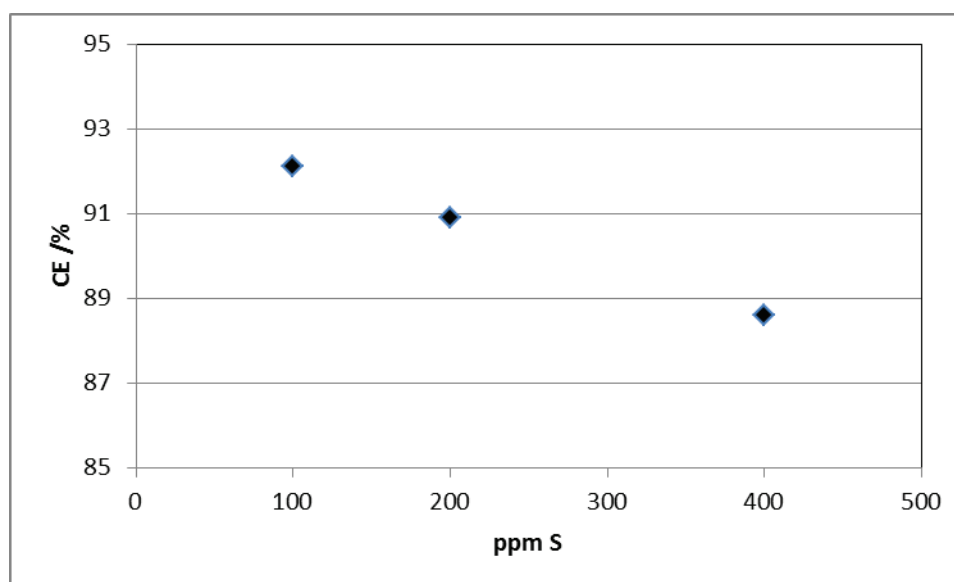


Figure 3. Current efficiency for aluminium deposition as a function of the content of phosphorus in the electrolyte after additions of  $\text{AlPO}_4$ . Molten  $\text{NaF-AlF}_3(\text{CR}=2.5)\text{-CaF}_2(5 \text{ wt}\%)\text{-Al}_2\text{O}_3(\text{sat})$  at  $980^\circ\text{C}$  and  $0.8 \text{ A/cm}^2$ .

The current efficiency at  $0.8 \text{ A/cm}^2$  and  $980^\circ\text{C}$  in the pure electrolyte was determined to be approximately 93 %. The effect of phosphorus on reducing the current efficiency was similar to reported results [10, 13], and the main mechanism is the cyclic red/ox reactions of dissolved phosphorus species at the electrodes. The effect of sulfur on the current efficiency has not been widely studied. However, it was shown by Pietrzyk and Thonstad [14] that high amounts of sulfur in the anode caused a significant decrease of the current efficiency. The results in Figure 4 show that dissolved sulfate has a more negative effect on decreasing the current efficiency than dissolved phosphate. Large amounts of sulfate were added during the experiment, and it is believed that dissolved sulfur species are reduced at the cathode while chemical reactions to form  $\text{SO}_2$  also take place.



**Figure 4. Current efficiency for aluminium deposition as a function of the content of sulfur in the electrolyte after additions of  $\text{Na}_2\text{SO}_4$ , Molten  $\text{NaF-AlF}_3$  (CR=2.5)- $\text{CaF}_2$  (5 wt %)- $\text{Al}_2\text{O}_3$ (sat) at 980 °C and 0.8 A/cm<sup>2</sup>.**

### 3.2. Industrial cells

It was found that silicon and phosphorus represent two different behaviours of impurities in modern industrial aluminium electrolysis cells; silicon is reduced at the cathode, while phosphorus has a long residence time in the bath.

Figure 5 shows the concentrations of silicon and phosphorus in the electrolyte as a function of time before and after addition of  $\text{AlPO}_4$  and  $\text{SiO}_2$ . Silicon showed a close to ideal behaviour for a diffusion controlled deposition of a metal. The concentration of dissolved silicon was found to decrease according to Equation (5) indicating that silicon is reduced at the cathode at diffusion controlled conditions. Figure 2 also shows the concentration of phosphorus in the electrolyte as a function of time before and after addition of  $\text{AlPO}_4$ . After an initial increase of phosphorus in both bath and metal due to the addition the changes in phosphorus concentration did not correspond to diffusion controlled reduction of phosphorus species at the cathode. The phosphorus content of the electrolyte was about 10 times higher than that of the metal expressed as ppm P during the experiment. It can be suggested that most of the elemental phosphorus formed initially at the cathode did not alloy with aluminium and was oxidized at the anode and subsequently reduced at the cathode. Such cycles of red/ox reactions will explain the longer residence time of phosphorus in the bath, and it will also cause a loss in current efficiency for aluminium.

Plots of the logarithm of the concentration of silicon in the electrolyte as a function of time after addition of  $\text{AlPO}_4$  according to Equation (5) were found to be linear. The mass transfer coefficient was determined to be  $3.1 \times 10^{-5}$  m/s, which is of the same order of magnitude as reported [6, 7] for metallic impurities.

Routine data of analyses of produced metal from industrial cells over a long period was examined. It was found that the content of phosphorus in produced aluminium decreased during periods of increasing bath temperature. Also anode effects and operation of newly started cells led to lower phosphorus levels.

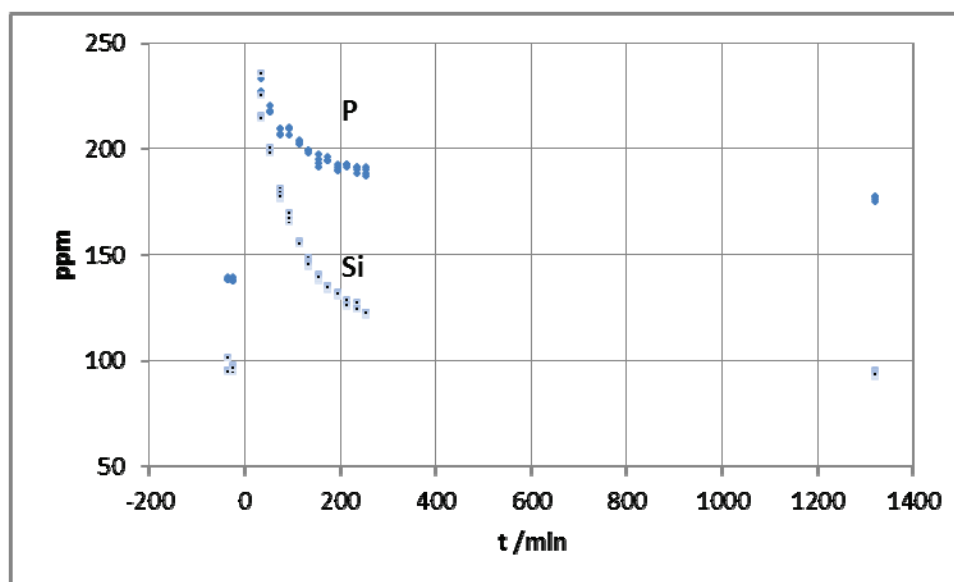


Figure 5. Concentrations of phosphorus and silicon in the electrolyte as a function of time before and after additions of  $\text{AlPO}_4$  and  $\text{SiO}_2$  in an industrial cell.

#### 4. Conclusions

Laboratory experiments were carried out to determine the current efficiency for aluminium deposition. Both additions of phosphate and sulfate to the electrolyte caused a significant reduction in the current efficiency, mainly due to cyclic redox reactions at the electrodes. Loss of phosphate and sulfate due to interaction with the electrolyte was compensated for. The behaviour of phosphorus and silicon impurities was studied in industrial cells by adding  $\text{AlPO}_4$  and  $\text{SiO}_2$ . Analyses of electrolyte samples showed that phosphorus has a long retention time in the electrolyte, while silicon was deposited at its limiting current density.

Recycling of impurities with secondary alumina and possible deterioration of raw materials represent future challenges with respect to achieving high current efficiency and good metal purity during aluminium electrolysis.

#### 5. Acknowledgments

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