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**Fundamentals –
Electrochemistry and
New Processes**

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MASS TRANSFER REACTIONS NEAR THE CATHODE DURING ALUMINIUM ELECTROLYSIS

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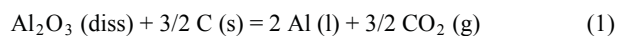
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Abstract

A laboratory cell was used to determine the current efficiency for aluminium during constant current electrolysis at 0.85 A/cm². Current efficiencies ranging from ~ 89 - 93 % were obtained. Effects of additions of KF and LiF were investigated. The presence of dissolved impurity species in the electrolyte may influence key parameters such as current efficiency and metal quality during electrowinning of aluminium. Other electrolyte constituents such as CaF₂, LiF or KF may also have some impact on the electrolysis. The mass transfer of impurity elements to the cathode was studied in industrial cells. Metals that are more noble than Al will deposit at the cathode at their limiting current densities. Mass transfer coefficients for dissolved manganese species were found to be of the order of 10⁻⁵ - 10⁻⁶ m/s.

Introduction

Aluminium is produced by electrolysis in molten NaF-AlF₃-Al₂O₃ at ~955°C. The current efficiency with respect to aluminium can be as high as 96 % in modern Hall-Heroult cells. The total cell reaction is:

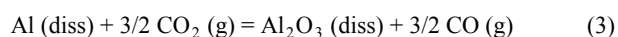


The loss in current efficiency is strongly linked to the fact that aluminium is soluble in the electrolyte. Metal solubility is a general phenomenon in molten salts [1]. In molten cryolite based electrolytes dissolved Na must be considered in addition to dissolved Al [2]. A small but significant activity of sodium is established at the metal/electrolyte interface due to the following equilibrium:



It is known that the subvalent species AlF₂⁻ is formed as well as dissolved Na, the latter being responsible for a small contribution to electronic conductivity [2]. Solubility studies have been carried out in laboratory experiments, and the metal solubility is ~0.06 wt% Al in industrial electrolyte compositions. The solubility decreases by increasing content of AlF₃ and decreasing temperature. Reliable data for the metal solubility 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, and it can be written as follows:



The rate of the back reaction is controlled by diffusion of dissolved metals (Al and Na) through the diffusion layer near the cathode. Additions of relatively small amounts of CaF₂, LiF and MgF₂ are known to be beneficial for the current efficiency [1]. It is likely that the total metal solubility is reduced upon these

additions. In some cases KF is added with the alumina, and the effects of KF on the operation of the electrolysis are not known.

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:

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

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:

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

where *A* is the area of the active cathode, *V* is the volume of the electrolyte and *c*_o is the cbackground 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].

Experimental

A laboratory cell similar to that of Sterten and Solli was used to determine the current efficiency for aluminium during constant current electrolysis [9-12]. The current efficiency was calculated from Faraday's law by weighing the amount of deposited aluminium. The electroysis 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 LiF and KF 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 AlF_3 corresponding to a molar ratio of NaF/AlF_3 of 2.5 and 5 wt% CaF_2 at 980 °C and a constant current density of 0.85 A/cm².

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 manganese is reported. Na_3PO_4 and Mn_2O_3 , MnO_2 and MnO were added. Samples of electrolyte and metal were taken for analyses before and after the additions, at intervals of about 20-30 minutes between sampling. Electrolyte samples were analysed by XRF, while metal samples were analysed by optical emission spectrography. It was assumed that the compounds dissolved readily in the electrolyte after the additions and that no material was lost in the process.

Results and discussion

Liquid Current efficiency

Current efficiencies ranging from ~89-93 % were obtained. The measured current efficiencies versus additions of LiF and KF are given in Figure 1. 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).

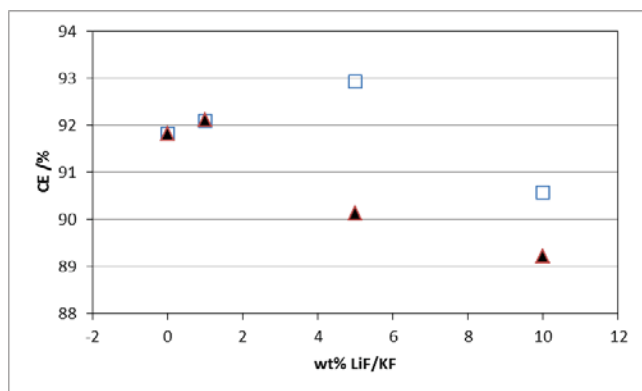


Figure 1. Current efficiency for aluminium deposition as a function of additions of LiF (open symbols) and KF (filled symbols) in molten $\text{NaF-AlF}_3(\text{CR}=2.5)\text{-CaF}_2(5 \text{ wt}\%)\text{-Al}_2\text{O}_3$ (sat) at 980 °C and 0.85 A/cm².

There was essentially no effect of additions of 1 wt% LiF and KF on the current efficiency. Further addition up to 5 wt% LiF caused a significant increase of the current efficiency, whereas 10 wt% LiF caused a considerable decrease of the current efficiency. The solubility of Li is negligible in cryolite based electrolytes at 1 wt% LiF [8]. At moderate contents of LiF the activity of NaF is probably lowered so that the total metal solubility is lowered, which should lead to a higher current efficiency. At 10 wt% LiF the solubility of Li might be so high that the rate of the back reaction increases. Dewing [14] and Tabereaux et al. [15] reported that the loss in current efficiency in industrial cells increases

somewhat with increasing LiF content up to 3 wt% LiF. However, industrial measurement campaigns may lead to other changes of the electrolysis operation, so that industrial data for the current efficiency may not be reliable.

KF additions above 1 wt% were found to reduce the current efficiency considerably. The reason for this could be the influence of the solubility of potassium.

Impurities behaviour

It was found that manganese and phosphorus represent two different behaviours of impurities in modern industrial cells for producing aluminium; manganese is reduced at the cathode, while phosphorus has a long residence time in the bath. Of special interest regarding manganese it was found that essentially all the added manganese was found to end up in the metal regardless of the compound that was added to the electrolyte; Mn_2O_3 , MnO_2 or MnO .

Figure 2 shows the concentration of manganese in the electrolyte and metal as a function of time before and after addition of Mn_2O_3 . Manganese showed a close to ideal behaviour. The concentration of dissolved manganese was found to decrease according to equation (2) indicating that manganese is reduced at the cathode at diffusion controlled conditions. Figure 2 shows the concentration of phosphorus in the electrolyte and metal as a function of time before and after addition of Na_3PO_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 this experiment. It can be suggested that most of the elemental phosphorus formed initially at the cathode did not alloy with aluminium and was oxidized by the electrolyte and again reduced. Such a cycle will explain the longer residence time of phosphorus in the bath, and it will also cause a loss in current efficiency for aluminium.

Plots according of the logarithm of concentration of manganese and phosphorus in the electrolyte as a function of time after additions of Mn_2O_3 and Na_3PO_4 according to equation (2) were found to be linear in the case of manganese. As expected the phosphorus data did not resemble a straight line, so no mass transfer coefficient could not be calculated based on phosphate additions. From the results in Figure 2 the mass transfer coefficient was determined to be $6.7 \cdot 10^{-6}$ m/s, which is of the same order of magnitude as reported [6,7] for other metallic impurities. By adding MnO_2 , a value of $8.3 \cdot 10^{-6}$ m/s was found. Possible side reactions are associated with partial reduction of the metal containing species to a lower valency. Such reactions will cause a longer residence time in the bath and give a lower mass transfer coefficient. Possible interactions between different impurity species added in the same experiment were not studied.

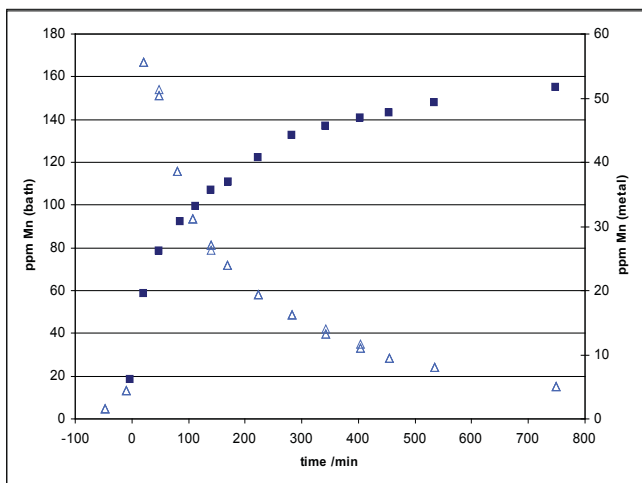


Figure 2. Concentration of manganese in bath and metal as a function of time before and after adding 2 kg Mn_2O_3 . The addition was made at $t = 0$.

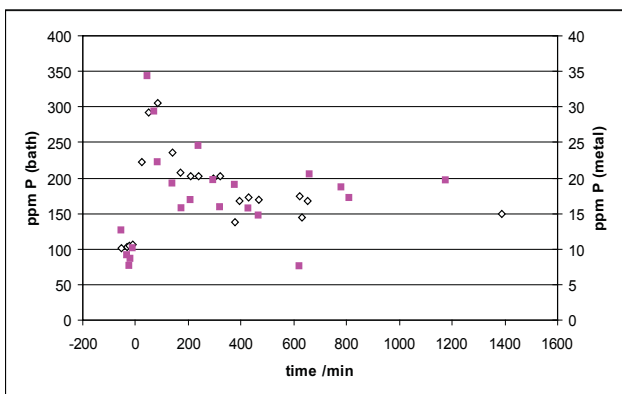


Figure 3. Concentration of phosphorus in bath and metal (filled squares) as a function of time before and after adding about 5 kg Na_3PO_4 . The addition was made at $t = 0$.

Transport processes near the cathode

It is known that transport number of sodium ions is close to unity in molten cryolite based electrolytes [2]. Since Al (III) species and not Na^+ ions are reduced at the cathode, concentration gradients with respect to AlF_3 and NaF are established near the cathode. The CR is higher at the cathode/electrolyte interface than in the bulk of the electrolyte. Hence the total metal solubility increases slightly with increasing current density. The convection affects the diffusion layer thickness, which will influence both the current efficiency and the rate of codeposition of other metals. The rate of diffusion of dissolved metals (Na and Al) determines the current efficiency. The presence of LiF and KF as well as dissolved impurity species may influence the diffusion of dissolved metals, and dissolution of both Li and K complicates the whole matter. Both Li^+ and K^+ may be able to carry some of the current due to their small size. Therefore the metal solubility is affected. It is known from studies in pure molten KF and NaF that dissolved potassium causes the component of electronic conduction in the electrolyte to increase much more. The interactions between

different ionic species in the boundary may cause additional impact on the current efficiency.

Conclusions

The current efficiency for aluminium deposition was found to be ~92 % in molten NaF- AlF_3 (CR=2.5) - CaF_2 (5 wt%)- Al_2O_3 (sat) at 980 °C and 0.85 A/cm². Additions of LiF up to 5 wt% were found to improve the current efficiency. Additions of more than 1 wt% of KF were found to reduce the current efficiency significantly.

The transport of the metallic impurities such as manganese from the electrolyte to the cathode is mass transfer controlled. By additions of known amounts of compounds of these impurity elements and analysing samples taken from the bath as a function of time, mass transfer coefficients for dissolved impurity species can be determined. The mass transfer coefficient for Mn was found to be of the order of 10^{-5} - 10^{-6} m/s. Dissolved phosphorus species were found to be transferred to the cathode much slower than metallic impurities because only a small fraction of phosphorus primarily being reduced at the cathode alloys with aluminium.

Mass transfer of ionic species in the boundary layer near the cathode is an important mechanism for the rate of the back reaction and the rate of the codeposition of metallic impurities. The measured mass transfer coefficient can be linked to the convection of the electrolyte near the cathode.

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