

Current efficiency in laboratory aluminium cells

Asbjørn Solheim¹, Henrik Gudbrandsen², Karen Sende Osen³, and Jannicke Kvello⁴

1. Chief Scientist, 2. Research Engineer,
3. Research Scientist, 4. Senior Engineer
SINTEF Materials and Chemistry, Trondheim, Norway
Corresponding author: asbjorn.solheim@sintef.no

Abstract



The current efficiency (CE) in aluminium cells is mainly related to transport of dissolved metal from the cathode and into the electrolyte. The transport rate depends on the equilibrium concentration of dissolved metal at the cathode as well as the effective mass transfer coefficient. The CE was studied experimentally, using the so called "Sterten-Solli" laboratory cell. It was found that the CE increases with decreasing temperature and increasing concentrations of aluminium fluoride, calcium fluoride, and magnesium fluoride. Potassium fluoride is detrimental to the CE, while the alumina concentration apparently is of no importance. The effect of lithium fluoride depends on the concentration of aluminium fluoride; lithium fluoride affects the CE positively in acid bath while it is harmful in neutral bath. The results are expressed by a semi-empirical equation taking the mentioned variables into account.

Keywords: Current efficiency; bath composition; laboratory cell.

1. Introduction

It is well established that the main reason for loss of CE in aluminium electrolysis cells is related to dissolved metal in the electrolyte, which is formed at the cathode and re-oxidized at the anode. The rate of metal loss appears to be governed by transport across the boundary layer at the cathode. The CE loss can be explained by simple concepts, but the underlying chemistry is very complicated.

Arguably, the best knowledge concerning mechanisms for loss in CE stems from experiments in the laboratory. Still; in the aluminium community there is a certain degree of scepticism when it comes to laboratory cells. When considering older literature concerning the effect of different variables on the CE, the laboratory data are scattered [1], and some of the data show much lower values than for industrial cells. The discrepancies can partly be attributed to the method of CE determination (weighing of produced metal is more accurate than gas analyses), and partly to cell construction (some of the work was performed in cells where extensive formation of aluminium carbide is unavoidable). There is reason to be more confident in data generated in laboratory cells that give high CE values, such as the "Sterten-Solli cell" [2, 3].

An industrial aluminium cell is an extremely complex device, where nearly all parameters are coupled through the energy balance and ledge formation. Parameter studies in the "real" system are, therefore, very difficult. As an example; when determining the effect of alumina concentration on CE, it is impossible to distinguish between the effects of alumina *per se* and the reduced temperature. Also, the variation in freeze geometry and the amount of sludge are important. The strength of laboratory cells is that it enables the study of one parameter at a time, owing to external heating and the absence of ledge. Moreover, the chemical conditions can be accurately reproduced and closely controlled. The main weakness of laboratory cells is that the small dimensions and low

amperage make it impossible to reproduce the types and levels of convection prevailing in industrial cells, although convection can be varied by stirring and gas bubbling.

2. Theory. "Chemical" current efficiency model

The main cathode reaction in the aluminium electrolysis cell is



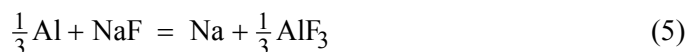
This is not the only possible cathode reaction. According to newer understanding [2, 3], the main reason for the loss in CE is parasitic side reactions "stealing" electrons that would otherwise be used for reduction of AlF_3 , such as



The metal species formed (sodium and aluminium with reduced valence) dissolve in the electrolyte and are transported towards the anode, where they are oxidized. The current efficiency can be calculated from the parasitic or "loss" current density i_{loss} ,

$$\text{CE} = 100 \cdot (1 - i_{\text{loss}} / i_{\text{tot}}) = 100 \cdot i_{\text{Al}} / i_{\text{tot}} \quad (4)$$

Sodium appears to be the most important dissolved metal species, since a melt with dissolved sodium has electronic conductivity. Sodium is at equilibrium with metal and bath at the cathode,



The CE loss is governed by the transport rate of dissolved metal from the cathode towards the bulk of the bath. Therefore, i_{loss} is a function of the dissolved metal concentration at the cathode (represented by sodium) and a transport coefficient; the latter representing ordinary mass transfer as well as electronic conduction.

It appears that i_{loss} as well as the electronic conductivity is nearly proportional with the square root of the sodium activity at the cathode, which has been theoretically justified [2, 4],

$$i_{\text{loss}} \propto k \cdot \sqrt{a_{\text{Na}}^*} \propto k \cdot a_{\text{NaF}}^{*1/2} \cdot a_{\text{AlF}_3}^{*-1/6} \quad (6)$$

where k is the mass transfer coefficient (in the present version of the model it should be regarded as the mass transfer coefficient for AlF_3) and the asterisk indicates the cathode.

The activities in Equation (6) can be computed from Solheim and Sterten's data for the system $\text{NaF}-\text{AlF}_3-\text{Al}_2\text{O}_3$ [5], but the system of equations is very complex. The following empirical equation was derived, representing the original activity data in a wide range of composition and temperatures,

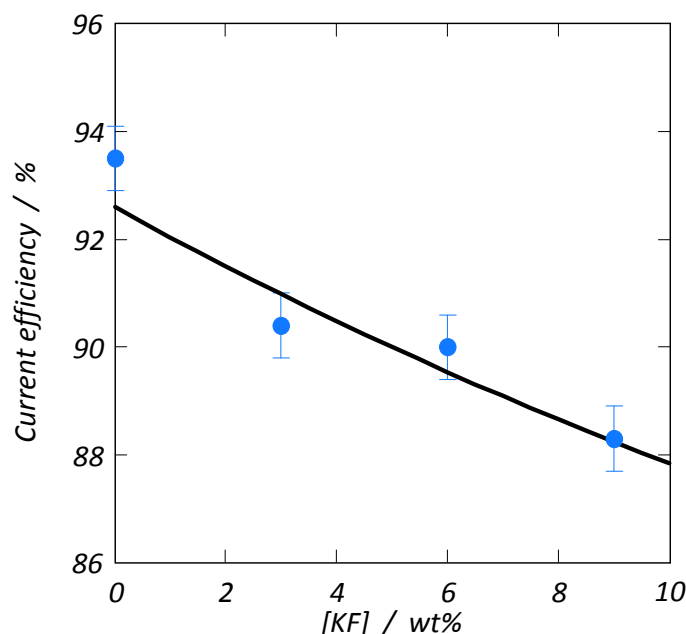


Figure 9. Current efficiency as a function of the concentration of potassium fluoride. Symbols – experimental data from the current study (assuming an uncertainty of ± 0.6 % as suggested by Solli *et al.* [3]), curve – chemical model. 4 weight percent calcium fluoride.

5. Acknowledgement

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