

Current efficiency in laboratory aluminium cells

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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



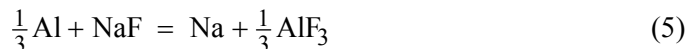
This is not the only possible cathode reaction. According to newer understanding [2, 3], the main reason for the loss in CE is parasitic side reactions "stealing" electrons that would otherwise be used for reduction of AlF_3 , such as



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,

$$\frac{a_{\text{NaF}}^{1/2}}{a_{\text{AlF}_3}^{1/6}} \approx \exp \left\{ -0.815 + \frac{4540}{T} + \left(9.725 - \frac{22850}{T} \right) \cdot \frac{1}{1+r} + \left(-10480 + \frac{7700\,000}{T} \right) \cdot \frac{1}{(1+r)^{12}} \right\} \quad (7)$$

The activities at the cathode can be estimated by

$$\frac{1}{r^* + 1} \approx \frac{2 - (r^\infty + 2) \cdot 1.4 \cdot 10^{-10} (i/k)}{2r^\infty + 2 + (r^\infty + 2) \cdot 1.4 \cdot 10^{-10} \cdot (i/k)} \quad (8)$$

where " ∞ " indicates the bulk of the bath and i is the cathodic current density.

In addition to the theoretical part of the CE model described above, it is necessary to add a term that represents the temperature dependence of the concentration of dissolved metal as well as an empirical term $f(\text{add})$ that describes the effect of bath constituents other than NaF and AlF_3 ,

$$i_{\text{loss}} = k \cdot a_{\text{NaF}}^{*1/2} \cdot a_{\text{AlF}_3}^{*-1/6} \cdot \exp \left(-\frac{22\,000}{T} \right) \cdot f(\text{add}) \quad (9)$$

The empirical function given in Eq. (10) was based on the experimental data shown in Section 4 below. The "chemical model", consisting of Equations (6 - 10), will be discussed in that context.

$$f(\text{add}) = 10^{14} \cdot \left(8.60 - \frac{0.70[\text{CaF}_2]}{1 + 0.08[\text{CaF}_2]} - \frac{2.10[\text{MgF}_2]}{r_\infty^{3/2}} + \frac{0.18[\text{LiF}](r_\infty - 2.4)}{1 - 0.05[\text{LiF}]} + \frac{0.50[\text{KF}]}{1 + 0.02[\text{KF}]} \right) \quad (10)$$

3. Experimental

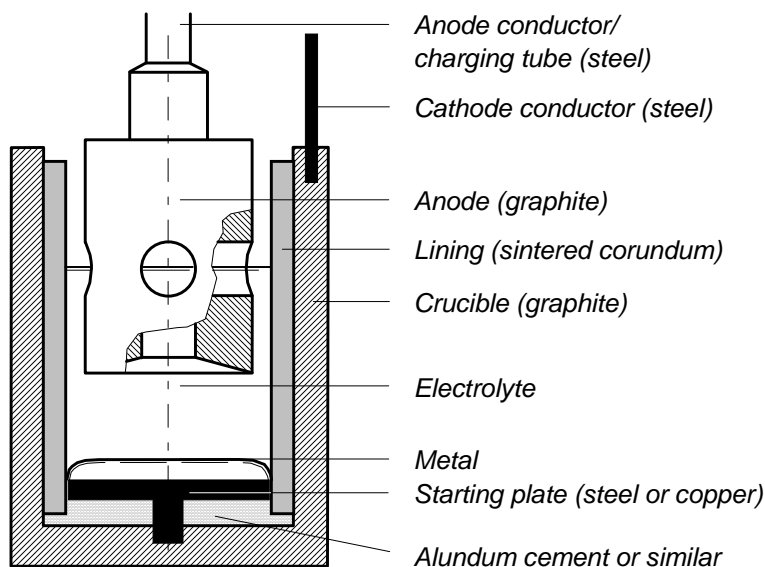
The measurements were conducted in the Sterten-Solli cell, which is sketched in Figure 1. The holes in the anode were made to facilitate gas escape and at the same time allow charging of alumina. With small dimensions, the metal tends to form a sphere due to the high interfacial tension. To counteract this effect, a metallic starting plate was applied at the bottom of the crucible. Carbide formation was eliminated by the use of a sintercorundum lining and alundum cement underneath the starting plate.

The following chemicals were used:

- Cryolite: Selected pieces of handpicked natural Greenland cryolite with melting point 1009.6 °C.
- Aluminium fluoride: Sublimed AlF_3 , made from technical grade AlF_3 by vacuum sublimation at 1000 °C in our own laboratory. The average purity was 99.5 percent.
- Lithium fluoride: Merck No. 5690, *p.a.*
- Magnesium fluoride: Merck No. 5821, optipur.
- Potassium fluoride: Merck No. 4994, *p.a.*
- Calcium fluoride: Merck No. 2840, *p.a.*
- Alumina: Technical grade, calcined at 1200 °C.

The weighed-in amount of alumina was 4 wt%. During electrolysis alumina was usually added manually each 15 minutes, in amounts corresponding to 50 percent CE. Still, the melt was close to alumina saturation due to dissolution of the cell lining.

Electrolysis was run for 4 hours, usually at 26.5 A ($8\,500\text{ A/m}^2$ based on the inner diameter of the cell). The temperature was measured by a Pt-Pt10Rh thermocouple contained in a sintercorundum tube (not shown in Figure 1). The starting plate was weighed before the experiment. After the experiment, the starting plate and aluminium were removed, and the adhering bath was carefully removed mechanically and by an aqueous solution of aluminium chloride. The current efficiency was determined from the weight gain.



**Figure 1. Laboratory cell for determination of current efficiency.
The inner diameter of the sintered corundum lining is 63 mm.**

4. Experimental results and comparison with model

If not otherwise mentioned, or is obvious from the parameter on the abscissa in the figures, the results referred to in the following were obtained with bulk NaF/AlF₃ molar ratio $r = 2.5$, 5 wt% calcium fluoride, alumina concentration near saturation, and cathodic current density $i = 8\,500\text{ A/m}^2$. Much of the data was obtained close to 980 °C, in which case i_{loss} was “normalised” at 980 °C by using the temperature functions in Equations (7) and (9). In the chemical model, represented by Equations (6 - 10), the mass transfer coefficient was set to $1.8 \times 10^{-5}\text{ m}^2/\text{s}$ if not otherwise indicated.

4.1. Effect of aluminium fluoride

A comparison between the experimental data by Solli *et al.* [3] and the current chemical model is shown in Figure 2. It is interesting that the CE can be as high as 99.5 percent in extremely acid bath, which cannot be attained in an industrial cell due to excessive sludge formation and loss of cell control. The latter is related to the very steep slope of temperature versus aluminium fluoride in the NaF-AlF₃ liquidus diagram at high contents of AlF₃, leading to large temperature differences for a small change in the amount of ledge.

4.2. Effect of temperature

Solli *et al.* [3] measured the CE as a function of temperature at three NaF/AlF₃ molar ratios. A comparison between their data and the CE model is shown in Figure 3. As can be observed, a linear

temperature function does not work, except in a narrow temperature range and for a specific NaF/AlF₃ ratio.

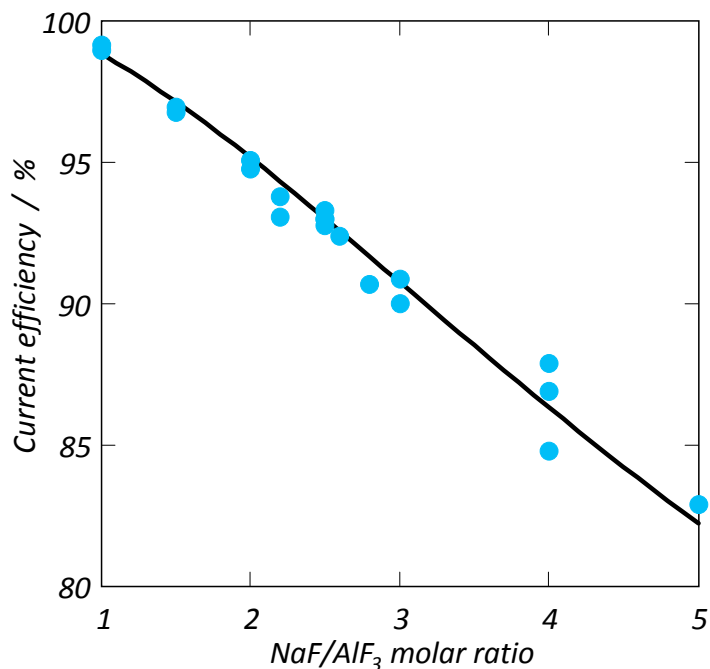


Figure 2. Current efficiency as a function of the NaF/AlF₃ molar ratio. Symbols – experimental data by Solli *et al.* [3], curve – chemical model.

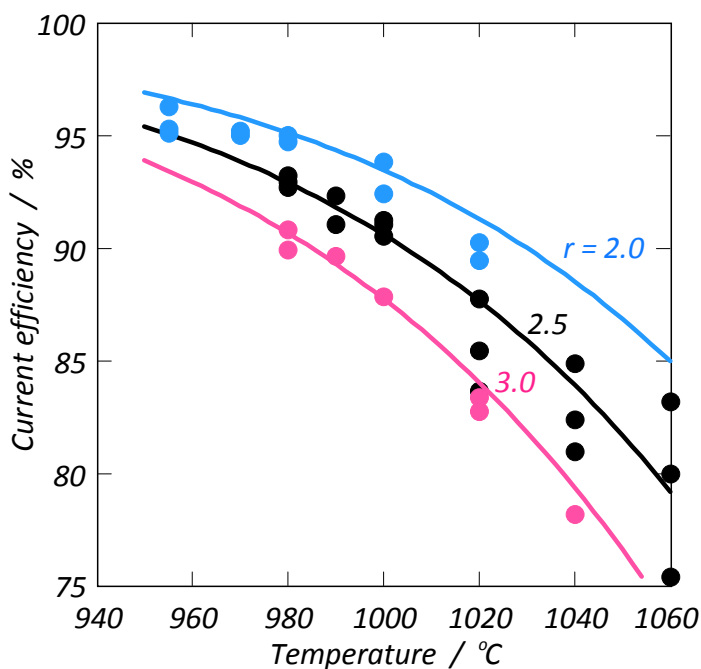


Figure 3. Current efficiency as a function of the temperature at three NaF/AlF₃ molar ratios (r). Symbols – experimental data by Solli *et al.* [3], curve – chemical model.

4.3. Effect of calcium fluoride and alumina

4.3.1. Calcium fluoride

The relationship between CE and the concentrations of calcium fluoride and alumina according to Solli *et al.* [3] is shown in Figure 4. Obviously, additions of calcium fluoride are beneficial (but possible adverse effects of increased bath density are hard to discover in a laboratory cell). Solli *et al.* [3] fitted their data by a straight line; however, a non-linear function as shown in Equation (10) appears to give a better fit.

4.3.2. Alumina

The effect of alumina on the CE has been much disputed. The data by Solli *et al.* [3] do not show any specific trend, and therefore; Equation (10) does not contain an alumina term. It is interesting to note that there is no "chemical" reason to prefer high or low alumina concentration. Possible influence of alumina on the CE appears to be related to other parameters, such as sludge formation, bath temperature, and anode effect frequency. The experimental data by Solli *et al.* [3] is in full agreement with activity data for the system NaF-AlF₃-Al₂O₃ [5]. The combined activities of NaF and AlF₃ are plotted as a function of the alumina concentration in Figure 5. The data indicate a weak trend of decreasing CE with increasing alumina concentration in neutral bath, while there is an opposite tendency in strongly acid bath.

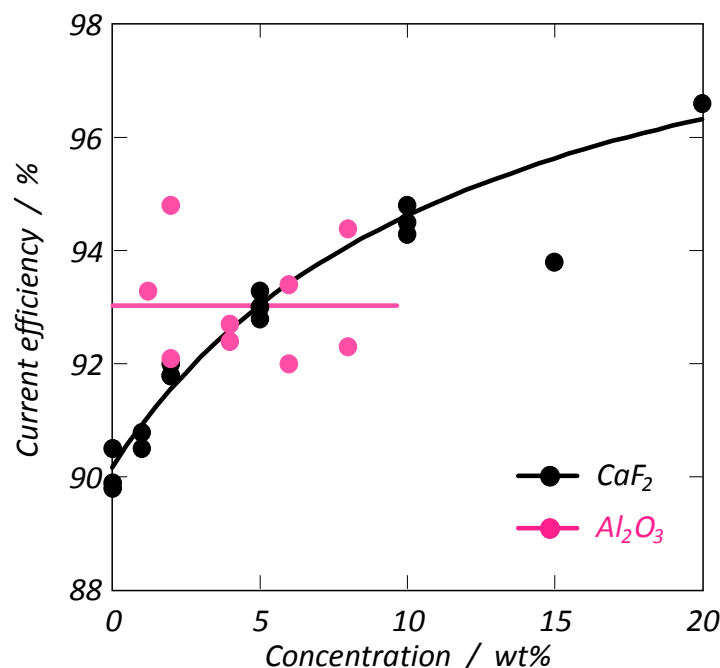


Figure 4. Current efficiency as a function of the concentrations of calcium fluoride and alumina. Symbols – experimental data by Solli *et al.* [3], curve – chemical model.

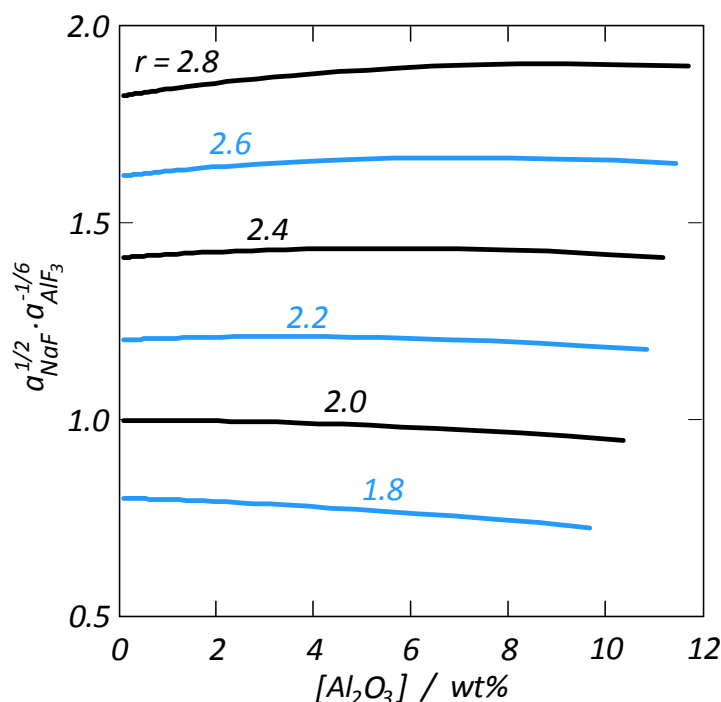


Figure 5. Combined activities of sodium fluoride and aluminium fluoride as a function of the alumina concentration at 1233 K (960 °C), computed from activity data by Solheim and Sterten [5].

4.4. Effect of magnesium fluoride

Magnesium fluoride is always present as a contamination in Hall-Heroult cells, and in some smelters it is added on purpose; particularly, in combination with lithium fluoride. Due to the chemical similarity, magnesium fluoride behaves much like calcium fluoride in the cells. The CE increases with increasing concentration at constant NaF/AlF₃ molar ratio [6].

In many cases, different options should be compared at the same bath or liquidus temperature. Figure 6 a) shows a series of data where the bath composition "follows the liquidus", *i.e.*, increasing amounts of magnesium fluoride is accompanied by reduced excess aluminium fluoride in such a way that the liquidus temperature [7] stays constant.

Bersimenko *et al.* [8] carried out experiments where magnesium fluoride replaced sodium fluoride or aluminium fluoride, weight percent by weight percent. The result is shown in Figure 6 b). All three experimental series shown in Figure 6 were used in the derivation of Equation (10).

There is no doubt that magnesium fluoride is favourable for the current efficiency; on the other hand, the effect is not more than similar to the effect of calcium fluoride. It should be noted that the magnesium fluoride term in Equation (10) also contains the NaF/AlF₃ molar ratio. It can be suspected that the effect of calcium fluoride also is affected by the molar ratio, but this has not been confirmed experimentally.

4.5. Effect of lithium fluoride

The effect of lithium fluoride on the CE is shown in Figure 7. It appears that the trend in the CE curves depends on the NaF/AlF₃ molar ratio, in such a way that lithium fluoride is beneficial in an

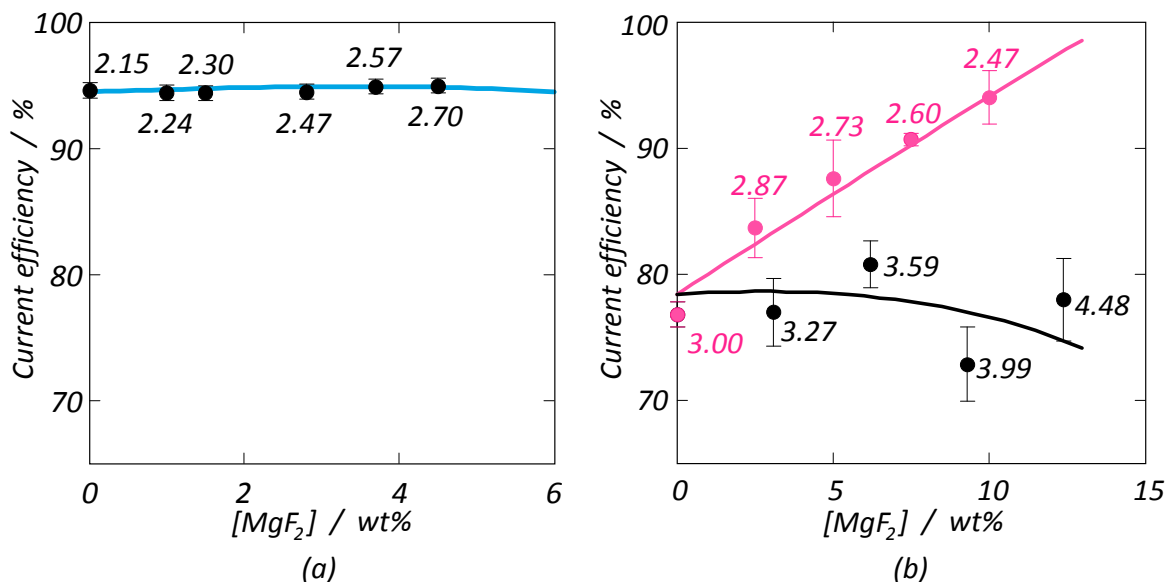


Figure 6. Current efficiency as a function of the concentration of magnesium fluoride. The numbers in the figure represent the NaF/AlF₃ molar ratio and the symbols represent experimental data. a) – amount of excess aluminium fluoride adjusted to keep the liquidus temperature constant at 3.5 wt% alumina [7], experimental data from the current study. b) – magnesium fluoride replacing sodium fluoride (red curve) or aluminium fluoride (black curve), weight percent by weight percent. No calcium fluoride present, current density 3537 A/m², temperature 955 °C, alumina close to saturation. Experimental data by Bersimenko *et al.* [8], curves – chemical model, assuming mass transfer coefficient $k = 1.4 \times 10^{-5}$ m/s.

acid bath and harmful in neutral bath. As a general advice, the behaviour of a bath additive often depends on the chemical environment, which is reflected in cross terms between substances in empirical equations for calculating physicochemical properties. Therefore, parameters measured at only one NaF/AlF₃ molar ratio may be misleading. Unfortunately, the precision in the data shown in Figure 7 appears to be lower than normal. A striking feature in these measurements was the shape of the solidified metal pool after the experiment. In many cases, the metal on the starting plate shown in Figure 1 was very asymmetric, and in some cases, it even formed a distinct sphere at the cathode instead of spreading out on the starting plate. Some pictures are shown in Figure 8 below. While the exact reason for this peculiarity is not clear, it must be caused by some kind of de-wetting at the cathode, possibly related to sludge formation due to excessive alumina feeding or crystallisation of alumina and cryolite at the cathode. The phenomenon was observed from time to time in the past, but never dominating an experimental series.

4.6. Effect of potassium fluoride

The use of KF as a major addition has not been reported until recently. Frolov *et al.* [9] proposed the following alternative bath composition: 2.1 wt% LiF, 4.7 wt% KF, 1.2 wt% MgF₂, 4.0 wt%

CaF_2 , the rest NaF/AlF_3 and Al_2O_3 . The NaF/AlF_3 weight ratio was 1.328, which corresponds to approximately 4.5 wt% excess AlF_3 . This composition has better electrical conductivity and higher alumina solubility compared with a traditional bath composition. Nothing was mentioned about CE in the work by Frolov *et al.* [9].

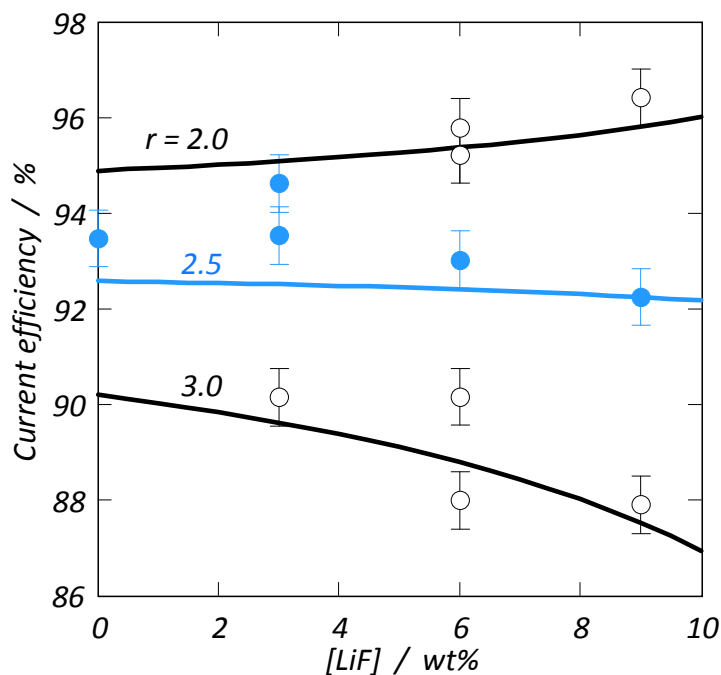


Figure 7. Current efficiency as a function of the concentration of lithium fluoride at three NaF/AlF_3 ratios. Symbols – experimental data from the current study (assuming an uncertainty of $\pm 0.6\%$ as suggested by Solli *et al.* [3]), curve – chemical model. 4 weight percent calcium fluoride.



Figure 8. Solidified metal pool on the starting plate after the experiment. From left to right: Normal appearance, asymmetric metal, and formation of sphere.

Not entirely unexpected; the results presented here showed that the current efficiency decreases strongly upon addition of potassium fluoride, as shown in Figure 9. By using the chemical model with $k = 3 \times 10^{-5} \text{ m}^2/\text{s}$; the CE will be 94.2 percent in a traditional bath ($r = 2.2$, 5 wt% CaF_2 , 960 °C, 8 500 A/m^2) and 92.1 percent for the bath composition suggested by Frolov *et al.* [9] at 940 °C, other parameters being equal.

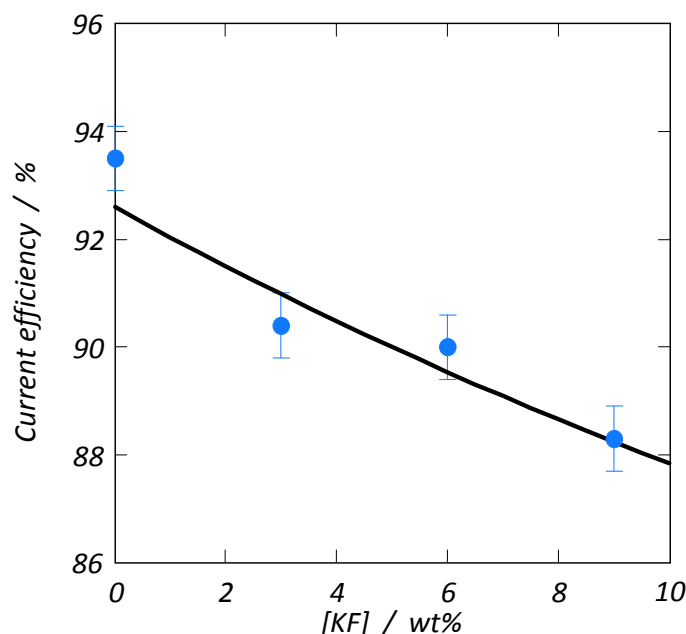


Figure 9. Current efficiency as a function of the concentration of potassium fluoride. Symbols – experimental data from the current study (assuming an uncertainty of ± 0.6 % as suggested by Solli *et al.* [3]), curve – chemical model. 4 weight percent calcium fluoride.

5. Acknowledgement

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6. References

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