

CURRENT EFFICIENCY AND ALUMINA CONCENTRATION

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A reaction model for the back reaction between carbon dioxide and aluminium is presented. By introducing in the model available data for metal- and gas-solubilities, gas bubble sizes, and the physical-chemical data for the cell electrolyte, we have calculated how the current efficiency should vary with the concentration of dissolved alumina in the electrolyte. These calculations are then utilized in a qualitative discussion of current efficiency behaviour in laboratory cells and different types of plant cells.

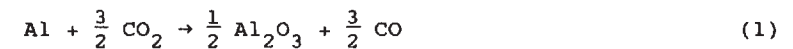
Introduction

Some years ago we applied mass transfer theory to calculate back reaction rates and corresponding current efficiency losses in Hall-Heroult cells for aluminium production (1).

We are, in this paper, using recent physical data and the same approach for calculating how the current efficiency should depend upon the alumina concentration in the bath. The calculated results are discussed in light of published data from laboratory and plant cells. In our first paper, gas bubble areas were not available, and the correlation we then calculated for current efficiency vs alumina concentration needs considerable refinement, especially at low alumina contents.

Calculations

We assume the following reaction to be responsible for the current efficiency loss:



We make the same assumptions regarding this reaction as we did in our first paper (1).

- Reaction (1) occurs between dissolved reactants.
- Simple film theory is valid, and we disregard the transportation of the heat of reaction and the reaction products.
- Al in eq (1) is taken to include dissolved sodium as well, calculated as equivalent amounts of aluminium.
- The chemical reaction between dissolved metal and dissolved gas is instantaneous, and the rate of reaction (1) is considered to be controlled by the mass transfer rates of dissolved reactants through stagnant bath films.

For the dissolution rates, the following relations may be written (1).

$$r_{\text{Al}} = A_{\text{Al}} k_{\text{Al}} (1 + k_{\text{CO}_2} C_{\text{CO}_2} / k_{\text{Al}} C_{\text{Al}}^*) (C_{\text{Al}}^* - C_{\text{Al}}) \quad (2)$$

$$r_{\text{CO}_2} = A_{\text{CO}_2} k_{\text{CO}_2} (1 + k_{\text{Al}} C_{\text{Al}} / k_{\text{CO}_2} C_{\text{CO}_2}^*) (C_{\text{CO}_2}^* - C_{\text{CO}_2}) \quad (3)$$

where

- r = dissolution rate
- A = interfacial area against bath
- k = mass transfer coefficient
- C = concentration of dissolved species in the bulk electrolyte
- C* = thermodynamic solubility

We also assume, in line with experimental data (2) that $C_{Al} > 0$ (which means that $C_{CO_2} = 0$), and further that the stoichiometry of reaction (1) requires

$$r_{CO_2} = \frac{3}{2} r_{Al} \quad (4)$$

Combining (4), (3) and (2):

$$C_{Al} = \frac{k_{Al} A_{Al} C_{Al}^* - \frac{2}{3} k_{CO_2} C_{CO_2}^*}{\frac{2}{3} k_{CO_2} k_{Al} + k_{Al} A_{Al}} \quad (5)$$

Our task is therefore to compute $C_{Al} = f(C_{Al_2O_3})$ by eq (5), insert this in eq (2) to find $r_{Al} = f(C_{Al_2O_3})$ and convert back reaction rates $r = r_{Al}$ to current efficiency by

$$\eta = \left(1 - \frac{r}{r_0}\right) 100 \% \quad (6)$$

where r_0 is the rate of metal production at 100 % current efficiency.

In order to compute $C_{Al} = f(C_{Al_2O_3})$ by eq (5) we need to know how all the parameters vary with the alumina concentration.

Attempts to calculate the mass transfer coefficient for gas bubbles, k_{CO_2} , by correlations given for instance by Winnikow (3), have so far proved unsuccessful, due to lack of experimental data for diffusivity and bubble diameters. As before (1) we therefore assume $k_{CO_2} = k_{Al}$ and furthermore:

$$k_{Al} = 0.023 (D_{Al}/2\ell)(Re^{0.83})(Sc^{0.33}) \quad (7)$$

Where:

- ℓ = interelectrode distance
- $Re = \frac{2\rho V\ell}{\mu}$ (Reynold number)
- $Sc = \frac{\mu}{\rho D_{Al}}$ (Schmidt number)
- ρ = bath density (Kg/m³)
- μ = bath viscosity (Pa • s)
- D_{Al} = diffusivity of dissolved metal (m²/s)
- V = relative velocity bath/metal (m/s)

D_{Al} seems to be relatively insensitive to changes in Al_2O_3 - concentration. We have chosen values from a work by Vetyukov and coworkers (4).

Haupin has published (5) values for $A_{CO_2} = f(C_{Al_2O_3})$ which we will use.

Bratland measured solubilities of carbon dioxide in cryolite with alumina contents from 2,5 % to 9,0 % (weight) almost 20 years ago (6). Bockris (7) has recently recommended Bratland's values, which we will use.

Vetyukov (8) and Arthur (9) have both published measurements of metal solubility in cryolite with varying amounts of alumina. Both find that the solubility is increasing with increasing alumina content, but more precise measurements are needed. We have chosen Vetyukov's data.

Introducing these physical data (appendix 1) in equation (1-7) we obtain the calculated current efficiency correlation shown in figure 1 with a minimum around 4 % Al_2O_3 . The corresponding values of C_{Al} and C_{Al}^* are shown in figure 2.

Discussion

Literature data have been summarized in table 1. For the most modern cells, with central point-feeding, and highly sophisticated computer regulation, no data seems to have been published. General operating experience however suggests that these cells need fairly low alumina contents for maximum current efficiency (10). It is also a fact, that the most successful of these type of cells always operate quite close to anode effect, i.e. at low alumina concentrations, but nevertheless at a higher current efficiency level than even quite small and stable side-break cells seem able to obtain, at a higher average alumina concentration.

Our calculations show that back reaction rates may be limited by gas dissolution at low alumina contents. The rather large gas bubbles are reducing the gas-bath

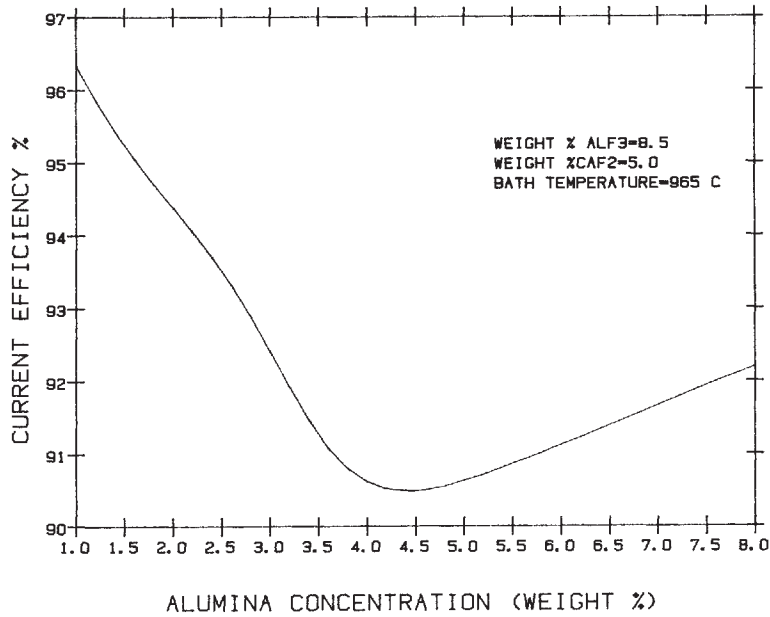
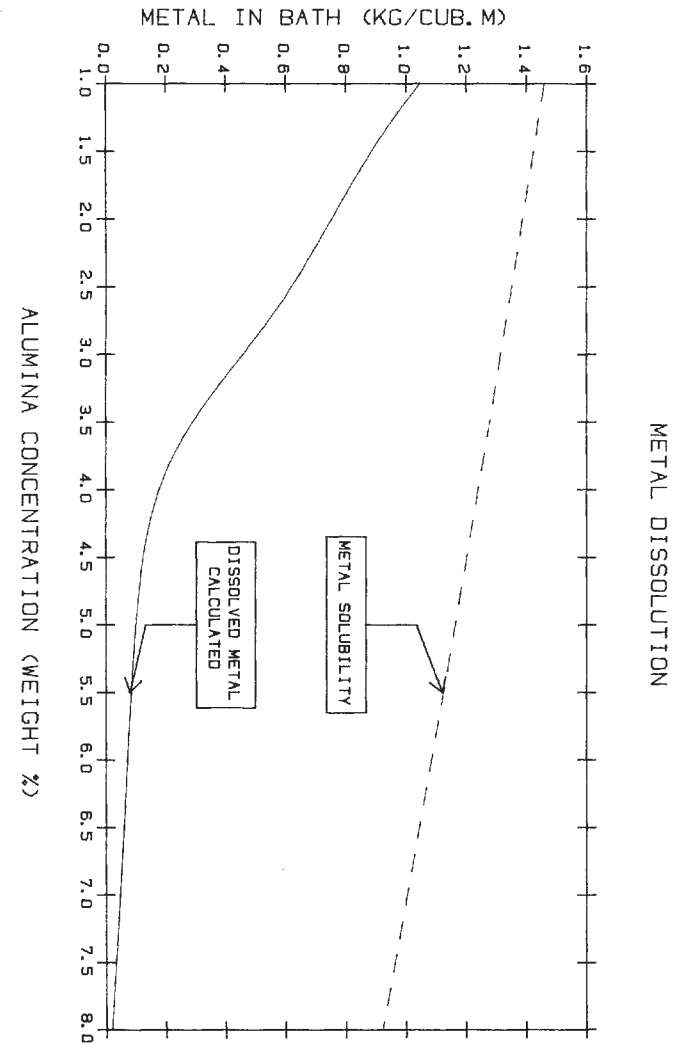


FIG. 1: Calculated Current Efficiency vs Alumina Concentration

Table 1 Current Efficiency Measurement vs Alumina Concentration: Literature data

Reference	Type of cell	Correlation	Range
Gjerstad (13)	Laboratory cell	Linearly increasing	(0.5-12%)
Belyaev (14)	Laboratory cell	Minimum at 5%	(1 -11%)
Grjotheim (15)	Laboratory cell	Minimum at 4.5%	(0 -11%)
Firsanova (16)	Laboratory cell	Minimum at 9%	(4 -10.5%)
Bersimenko(17)	Laboratory cell	Linearly increasing	(3 -12%)
Szeker (18)	Laboratory cell	Minimum at 4.5%	(2 -12%)
Abramov (19)	Laboratory cell	Linearly increasing	(5 -12%)
Schmitt (20)	Side-break plant cell	Increasing	(2 - 7%)
Thonstad (21)	" " " "	Increasing	(2 - 7%)
Poole (22)	" " " "	Increasing	(2 - 7%)
Lillebuen (1)	" " " "	" or const.	(0.5- 6%)

FIG. 2 : Metal Solubility and Dissolved Metal in Bath vs Alumina Concentration. Weight % AlF3=8.5, Weight %CaF2=5.0, Bath Temperature =965.0 C.



interfacial area to such a degree that the back reaction rates are being reduced and the current efficiency increased in spite of the fact that metal solubility is increased at lower alumina concentrations.

The calculation are based on laboratory data for gas bubble areas. Clearly, the retention time for the gas bubbles and their coalescence are perhaps the most important factors for calculating the effective gas-bath interfacial area, apart from the "pure" size of the bubbles. The retention time will vary from a couple of seconds in small laboratory cells up to maybe ten seconds in the largest Soederberg cells, where the anode width is of the order of 2.5 meters. When the retention time is high, the minimum in current efficiency will be shifted to lower Al_2O_3 - concentrations. This may be part of the reason why side-break cells show no clear sign of minima in the concentration ranges that have been investigated, while most laboratory cells exhibit minima around 4 % alumina, cfr. table 1.

Another aspect is that it is virtually impossible to separate the effect of alumina concentration from the effect of the temperature in plant cells, since temperature will rise as alumina concentration drops in the cell.

The calculations have been based upon a perfectly uniform distribution of dissolved alumina in the bath.

Now, oxygen ions are consumed at the anode, and therefore alumina concentration will be low in the vicinity of the gas bubbles. Near the metal pad, on the other hand, alumina concentration may be higher than in the bulk. As argued by several authors (11, 12) this may be due to the ability of alumina particles, or even "flakes" of alumina-bath composites (liquid or solid) to float upon the metal pad while being dissolved. Also, the bath film near the metal is enriched with sodium fluoride, since sodium ions carry most of the current. This makes the bath film more basic, and able to dissolve more oxide (and less metal).

Judged in light of our reaction model, the highest current efficiency is possible if the bath film near the metal pad is saturated with oxide while the bulk electrolyte at the same time has a very low alumina concentration. Clearly, only a point-fed cell with sophisticated computer regulation of the feed may ever come near such a mode of operation.

Also, we would like to mention the possibility of having a different metal-bath interfacial area in the cells than we so far has anticipated. We strive to obtain a cold operation of cells, with the lowest possible super heat (i.e. bath temperature minus liquidus temperature of the bath). In new pointfeeding cells the super heat may be as low as 5 °C. Knowing that the metal reservoir is often a few degrees colder than the bath, there is a chance of solids precipitating on the metal pad, making our calculation of interfacial areas inaccurate, and shifting

the position of the current efficiency minimum to lower alumina concentrations.

Conclusions

- Current efficiency, as a function of the amount of alumina dissolved in the bath has been calculated by a mass transfer approach to the back reaction between dissolved metal and dissolved carbon dioxide, and has a minimum around 4 % (by weight) alumina.
- This correlation is often detected in literature data for laboratory cells.
- The calculated current efficiency is increasing at lower alumina concentrations due to reduced gas bubble area (gas dissolution control) and at higher alumina contents due to lower metal solubility (metal dissolution control).
- The minimum may be shifted to lower alumina concentrations in cells with big anodes due to higher retention times for gas bubbles which means higher gas-bath interfacial areas.
- The position of this minimum along the Al_2O_3 -axis may also be influenced by the degree of uniformity of the distribution of dissolved alumina in the bath, and perhaps by the difference between bath temperature and liquidus temperature of the bath.
- The "ideal" current efficiency cell in this context will be a cell with
 - a) Oxide saturated bath near the metal pad.
 - b) Very low oxide content in the bulk melt.
 - c) Anodes made for easy gas escape.

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Appendix 1:

Physical data equations:

(x = weight% alumina)

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$$1. \quad A_{\text{CO}_2} = (0.02723 + 1.003 \cdot x - 0.3208 \cdot x^2 - 0.05874 \cdot x^3 + 0.03268 \cdot x^4 - 0.1817 \cdot x^5) / (1 - 0.4715 \cdot x + 0.06247 \cdot x^2) \quad [\text{cm}^2/\text{Amp}]$$

for $1 \leq x \leq 8$

$$2. \quad C_{\text{Al}}^* = 0.2877 + 0.0268 \cdot R + 0.0003 \cdot T - 0.0019 \cdot \% \text{CaF}_2 - 0.0043 \cdot (x - 12.5) \quad [\text{weight}\%]$$

Where R is weight ratio NaF/AlF₃, T is temperature in degrees Celsius and CaF₂ is given in weight per cent.

$$3. \quad \rho_{\text{Bath}} = 100 / (\% \text{Na}_3\text{AlF}_6 / (3.049 - 0.000937 \cdot T) + \% \text{AlF}_3 / (1.986 - 0.000319 \cdot T) + \% \text{CaF}_2 / (3.072 - 0.000391 \cdot T) + x / (1.449 + 0.0128 \cdot x)) \quad [\text{kg}/\text{m}^3]$$

(all in weight%)

4. Viscosity equation taken from a work by Tørklep and Øye, given on p 159, *Light Metals* (1980).

$$5. \quad C_{\text{CO}_2}^* = (0.03027 - 0.0006985x) / (1 - 0.08989 \cdot x) \quad [\text{kg}/\text{m}^3]$$

 $1 \leq x \leq 8$

$$6. \quad V(\text{m/s}) = 0.06 \text{ m/s}$$

$$7. \quad \text{Bath composition:} \quad \begin{array}{l} 5\% \text{ CaF}_2 \\ 8.5\% \text{ AlF}_3 \\ 100 - (5 + 8.5 + x)\% \text{ Na}_3\text{AlF}_6 \end{array}$$

$$8. \quad \text{Bath temperature:} \quad 965 \text{ }^\circ\text{C.}$$