Factors Affecting Current Efficiency of Hall-Héroult Process Based on the Variation of Sodium Content in Pot Metal

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Abstract

Sodium concentration in pot metal is known to be an indicator of current efficiency. When current is present, the NaF gradient increases at the bath-metal interface. As the bath ratio at the bath-metal interface is consequently much higher than in the bulk, a film of crystallized cryolite may form. Factors affecting the integrity of this film, and thus the sodium content in metal, are documented in the present study. The cathode concentration overvoltage was calculated using the sodium concentration in the metal. The correlation between sodium and calcium in the metal was confirmed in agreement with thermodynamics. The correlation between the sodium concentration and several bath impurities in the metal was also investigated.

Keywords: Hall-Héroult process; current efficiency; sodium impurities in pot liquid aluminum; cathode overvoltage.

1. Experimental Methodology

Metal samples were collected using the Heraeus Electro-Nite sampler QS3012ACC to avoid sodium loss. Each sample was analysed by Optical Emission Spectroscopy (OES) to determine the concentration of Na and other impurities in the metal. Bath samples were collected simultaneously in order to determine the excess AlF_3 by X-ray diffraction (XRD). CaF_2 was measured by X-ray fluorescence (XRF). Bath temperature measurements were also taken. The carbon content of the bath was determined by LECO analysis.

2. Results

2.1. Cathode concentration overvoltage determination

It is generally acknowledged that the cathode concentration overvoltage, in industrial cells, is of the order of 50 to 140 mV [1, 2]. However, these values concern cells operating with low excess AlF_3, $\leq$ 4 % (bath ratio (BR) $\geq$ 1.35), as was the case in the past decades [3]. Since then, bath chemistry has evolved, and modern cells operate with higher excess AlF_3 targets, $\geq$ 10 % (BR $\leq$ 1.15).

It is possible to calculate the evolution of the overvoltage as a function of bath ratio from the Na concentration found in metal (collected with a Heraeus sampler). The results obtained and the consequences on modern cell operation are set out in this paper.

Cathode concentration overvoltage is given in Equation (1):

$$\eta = -\frac{RT}{F}\ln\frac{a_{Na}}{a_{Na\ eq}} = -\frac{RT}{F}\ln\frac{\gamma_{Na}C_{Na}}{\gamma_{Na}C_{Na\ eq}} = -\frac{RT}{F}\ln\frac{C_{Na}}{C_{Na\ eq}} \qquad (1)$$

where:
- η Cathode concentration overvoltage (V)
- $a_{Na\ eq.}$ Activity of sodium in metal in equilibrium with the bath (without electrolysis)
- $C_{Na\ eq}$ Concentration of sodium in metal in equilibrium with bath (without electrolysis), (mol/m^3)
- a_{Na} Activity of sodium in metal during electrolysis
- C_{Na} Experimentally measured sodium concentration in the metal, during electrolysis, (mol/m^3)
- γ_{Na} Sodium activity coefficient
- T Temperature (K)
- R 8.314 $Jmol^{-1}K^{-1}$
- F 96 485 C

The evolution of sodium concentration in the metal in equilibrium with the bath (Na_{eq}) – as a function of bath ratio – is well documented (Figures 1 - 2) [4]. The evolution of Na concentration (C_{Na}) in the metal of cells, as a function of bath ratio, was measured in industrial pots. One of these pots had a relatively low anode-cathode distance (Pot 1) and the other had a relatively high anode-cathode distance (Pot 2) (Figures 1 - 2). Higher values of sodium content in the metal were measured in the pot having the relatively high ACD.

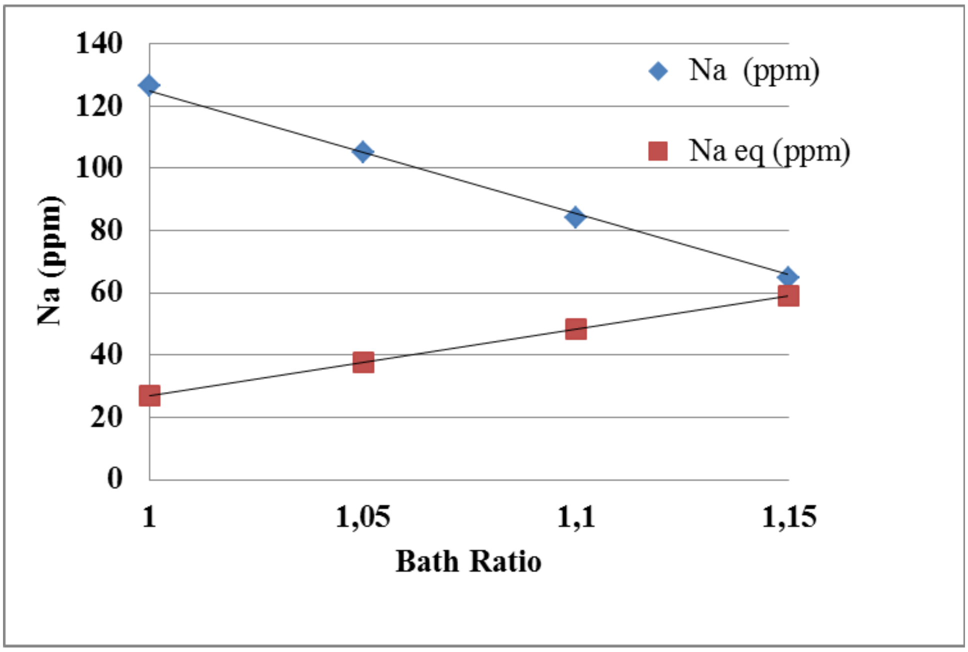

Figure 1. Evolution of the sodium concentration in the metal of Pot 1 as a function of mass bath ratio (red: during electrolysis; blue: at equilibrium).

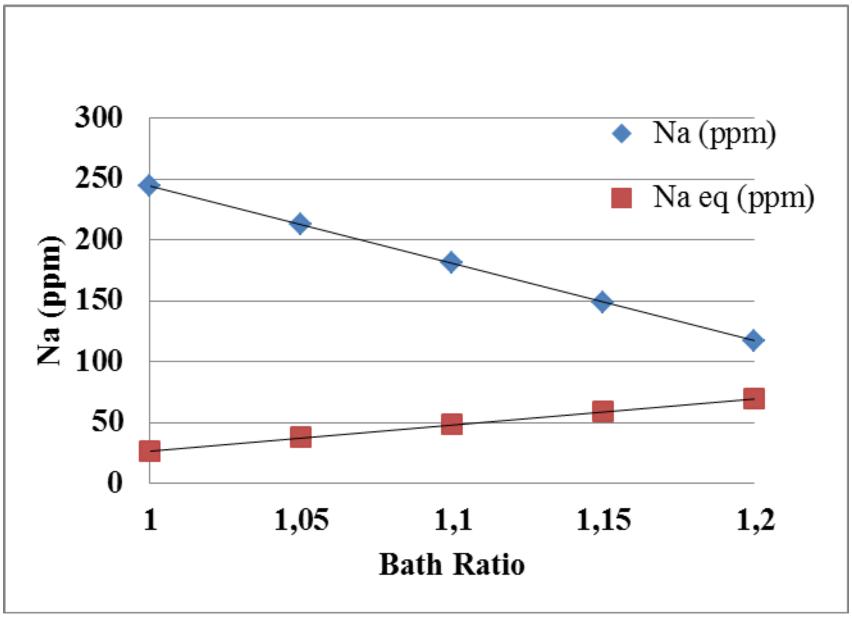

Figure 2. Evolution of the sodium concentration in the metal of Pot 2 as a function of mass bath ratio (red: during electrolysis; blue: at equilibrium).

It is possible to calculate the cathode concentration overvoltage using this data according to Equation 1. The evolution of the cathode concentration overvoltage (absolute value), as a function of bath ratio, is shown in Figure 3 (Pot 1) and in Figure 4 (Pot 2).

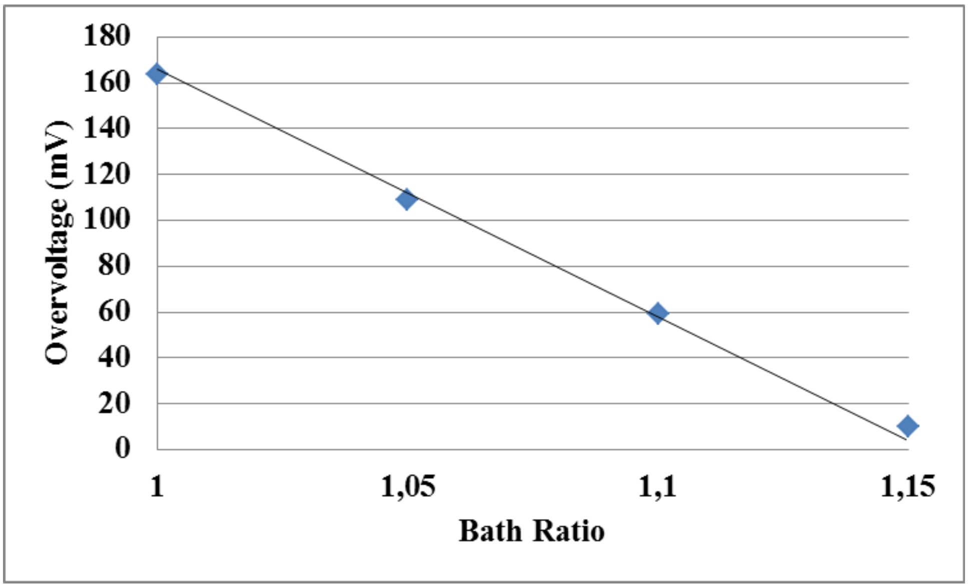

Figure 3. Evolution of cathode concentration overvoltage as a function of mass bath ratio, during alumina electrolysis in Pot 1.

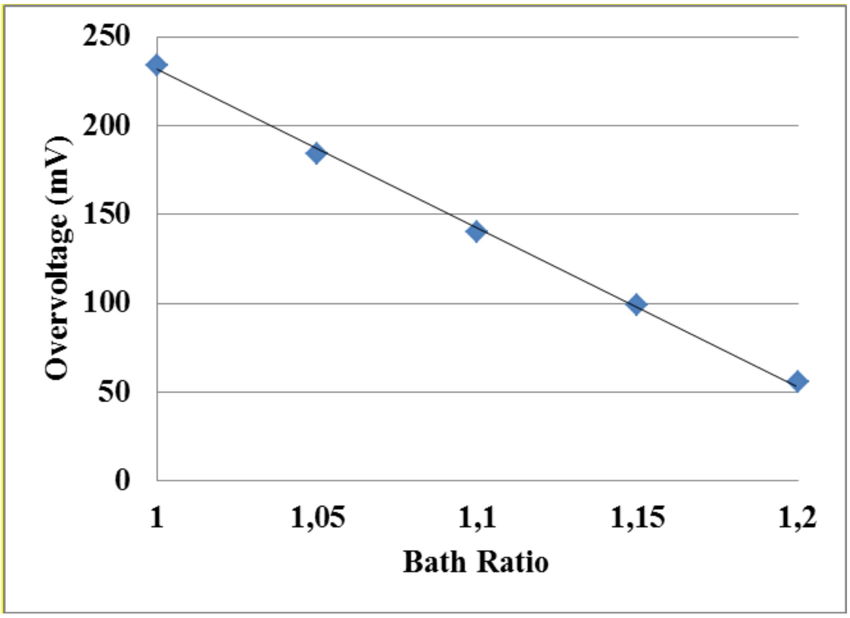

Figure 4. Evolution of cathodic concentration overvoltage as a function of mass bath ratio, during alumina electrolysis in Pot 2.

It can be seen that the overvoltage increases from 60 to 160 mV (Pot 1) and from 100 to 230 mV (Pot 2), for bath ratios varying from 1.15 to 1. Modern cells are operated at target bath ratios varying between 1 and 1.15. This overvoltage that develops at the bath-metal interface should be compensated for by an equivalent reduction in the anode-cathode distance (ACD), when the cell is operated at constant voltage, as it is normally the case. This conclusion leads to the eventual operation of cells with an anode-cathode distance, which could be smaller than that supposed (at bath ratio = 1.05, 3 mm smaller, for Pot 1, and 5 mm smaller, for Pot 2).

In fact:

$$\Delta ACD = \frac{\eta}{\rho j_a} \qquad (2)$$

where: ΔACD ACD decrease (m)

η Overvoltage (V)

ρ Bath resistivity (= 0.0044 Ωm)

j_a Anode current density (= 8 kA/m^2).

2.2. Phenomena occurring at the bath-metal interface

In absence of electrolysis, the sodium content in the metal increases with the bath ratio, according to the chemical equilibrium observed between bath and metal (Figures 1 - 2) [4].

During alumina electrolysis, the current is transported in the electrolyte by sodium fluoride [5]. As sodium is not deposited at the cathode, the sodium flux at the cathode is nil. Consequently, a concentration gradient builds up at the bath-metal interface to equilibrate the migration current by counter diffusion. The mass transfer coefficient is inversely proportional to this concentration gradient.

$$j_c = \frac{I}{S} = Fk_1 \Delta C_{NaF} \qquad (3)$$

where: j_c Cathode current density (A/m^2)
I Cell current (A)
S Cathode surface area (m^2)
F Faraday constant = 96 485 C
k_1 Mass transfer coefficient of sodium (m/s)
ΔC_{NaF} Sodium fluoride concentration gradient at the cathode (mol/m^3)

As aluminium dissolves in the bath, the current efficiency loss can be expressed as follows:

$$j_c (1-\eta) = 3Fk_{Al} \Delta C_{Al} \qquad (4)$$

where: $1-\eta$ Current efficiency loss (%)
k_{Al} Mass transfer coefficient of aluminium (m/s)
ΔC_{Al} ~ Aluminium saturation concentration in the bath

By combining (3) and (4), the current efficiency loss can be expressed as a function of the sodium fluoride gradient at the cathode:

$$1-\eta = 3\frac{k_{Al}}{k_1}\frac{\Delta C_{Al}}{\Delta C_{NaF}} \qquad (5)$$

The concentration gradient at the bath-metal interface modifies the bath ratio locally. The mass bath ratio, at the bath-metal interface, is more basic than in the bulk:

$$BR_{Int} = 0.5CR_{Int} = 0.5\frac{C_{NaF} + dC_{NaF}}{C_{AlF_3} - dC_{AlF_3}} \qquad (6)$$

where: BR_{int} Bath ratio at metal-bath interface
CR_{Int} Cryolite ratio at the bath-metal interface
C_{NAF} NaF concentration in the bath (mol/m^3)
C_{AlF3} AlF_3 concentration in the bath (mol/m^3)
dC_{NAF} Increase of NaF concentration at the bath-metal interface (mol/m^3)
dC_{AlF3} Decrease of AlF_3 concentration in the bath-metal interface (mol/m^3).

Dividing the numerator and dominator of Equation (6) by C_{AlF3}, one obtains the following expression for the bath ratio at the bath-metal interface:

$$BR_{Int} = 0.5CR_{Int} = 0.5\frac{\frac{C_{NaF}}{C_{AlF_3}} + \frac{dC_{NaF}}{C_{AlF_3}}}{1 - \frac{dC_{AlF_3}}{C_{AlF_3}}} \qquad (7)$$

The current density at the cathode can be expressed as follows:

$$j_c = Fk_1 dC_{NaF} \qquad (8)$$

$$j_c = 3Fk_3 dC_{AlF_3} \quad (9)$$

where: k_3 Mass transfer coefficient of aluminium fluoride, (m/s)

and thus:

$$\frac{dC_{AlF_3}}{dC_{NaF}} = \frac{k_1}{3k_3} \quad (10)$$

moreover:

$$\frac{C_{NaF}}{C_{AlF_3}} = 2BR \quad (11)$$

where: BR Mass bath ratio in the bulk

The bath ratio at the bath-metal interface can finally be expressed as a function of bath ratio in the bulk and sodium fluoride concentration gradient (k_1/k_3 can be expressed as a function of diffusion coefficients according to Equation 13, as mass transfers occurs at the same interface) [6]:

$$BR_{Int} = \frac{0.5(2BR + \frac{dC_{NaF}}{C_{AlF_3}})}{1 - \frac{k_1}{3k_3}\frac{dC_{NaF}}{C_{AlF_3}}} \quad (12)$$

$$\frac{k_1}{k_3} = \left(\frac{D_1}{D_3}\right)^{2/3} \quad (13)$$

where: D_i Diffusion coefficient of the i species, (m^2/s).

The higher is the bulk bath ratio the lower is the bath ratio at the bath-metal interface. This is shown in Table 1. This variation is in agreement with the fact that sodium content in the metal and thus the current efficiency decreases as the bath ratio in the bulk increases [4].

Table 1. Bath ratio at the bath-metal interface vs bath ratio in the bulk.

BR bulk	Na (ppm)	BR bath-metal interface
1	243	1.64
1.05	212	1.57
1.1	181	1.5
1.15	149	1.43

2.3. Behavior of impurities present in the metal

Since calcium fluoride is used as a bath additive, calcium is found in the metal. The evolution of calcium in the metal, as a function of the sodium content in the metal, is presented in Figure 5.

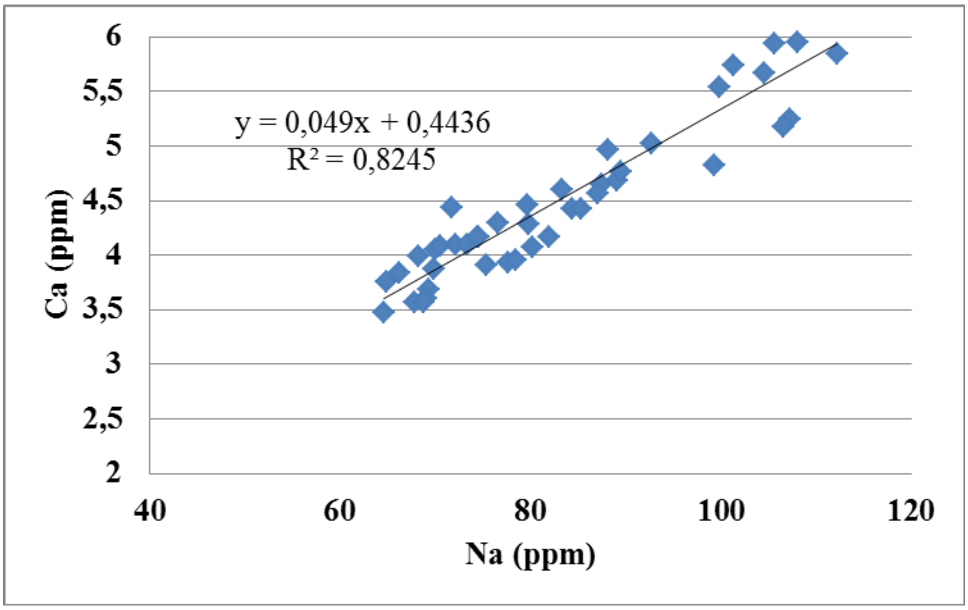

Figure 5. Evolution of calcium content in the metal as a function of sodium content in the metal.

One can observe that the relationship is linear. Some authors already observed this behaviour for calcium and lithium. However, the correlation between sodium and these impurities was not explained [7]. In fact, as already demonstrated by Dewing in the case of LiF used as bath additive [8], this behaviour was verified using thermodynamics. By applying the same reasoning to calcium, one finds:

$$\frac{C_{Ca}}{C_{Na}} = \text{Constant} \qquad (14)$$

The evolution of sodium content in the metal of two pots was monitored during several days (Pot A and Pot B). Bath samples were collected simultaneously. Temperature measurements were also taken simultaneously during metal and bath sampling. Results are displayed in Figures 6 - 7.

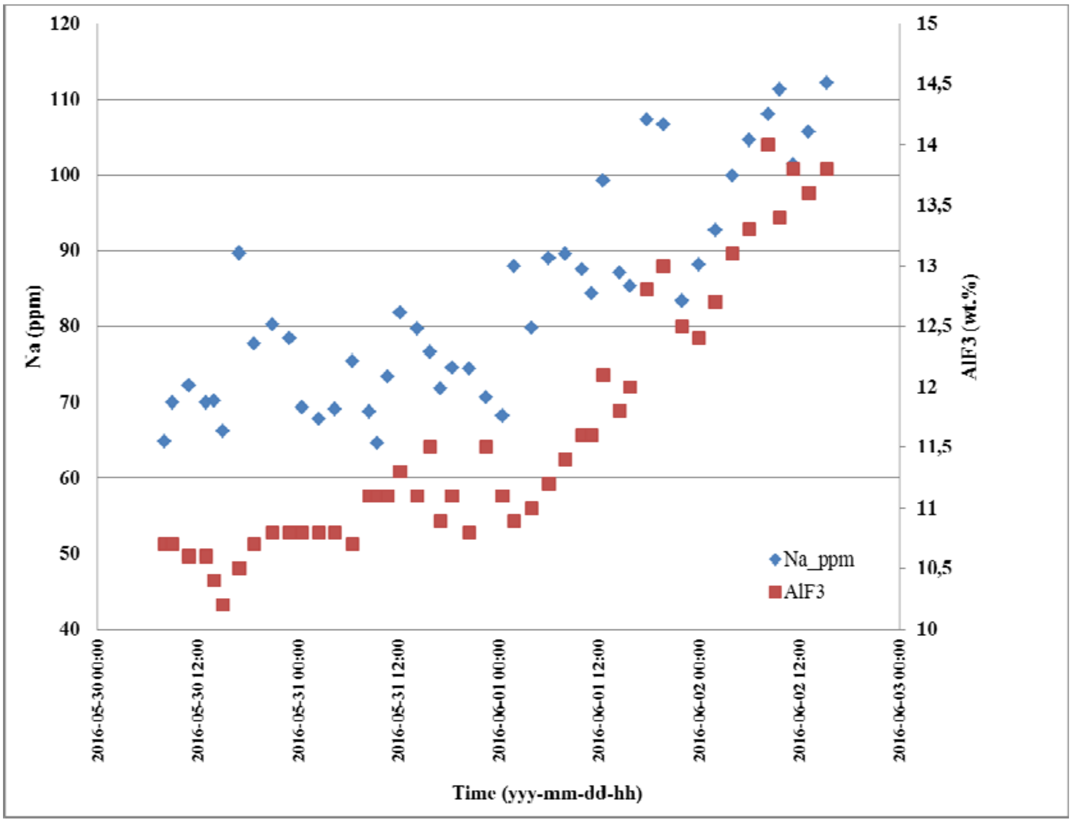

Figure 6. Evolution of sodium content in the metal and aluminium fluoride excess as a function of time (Pot A).

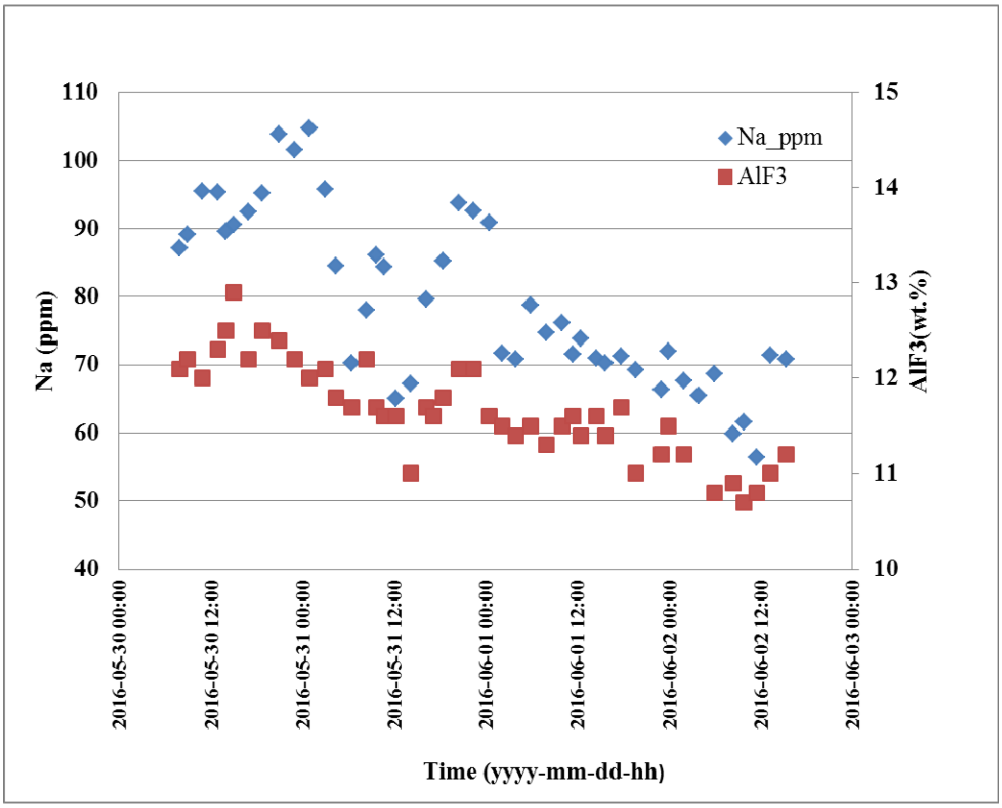

Figure 7. Evolution of sodium content in the metal and aluminium fluoride excess as a function of time (Pot B).

The correlation between the evolution of sodium in the metal with the bath ratio (or AlF_3 excess) is good. This is in agreement with the theory mentioned in Section 2.2 (Figures 8 - 9).

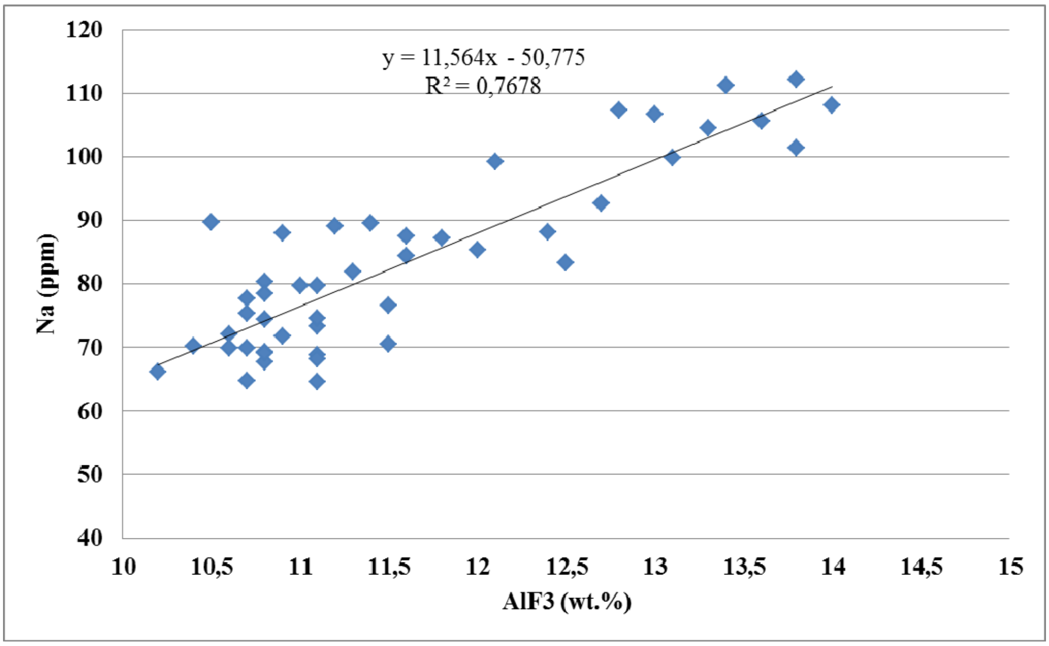

Figure 8. Correlation between sodium content in the metal and bath chemistry (Pot A).

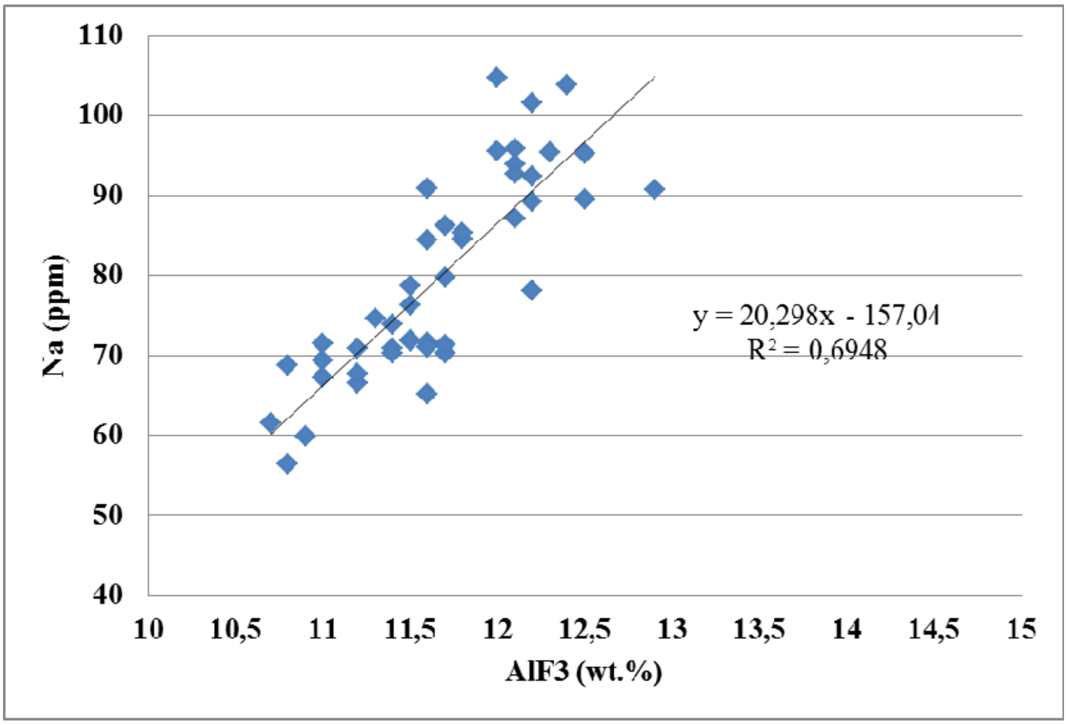

Figure 9. Correlation between sodium content in the metal and bath chemistry (Pot B).

The impurities content of Pots A and B as well as their bath composition/temperature are shown in Table 2. One can note that the mean sodium content is the same for the two pots as well as the aluminium fluoride excess. Pot A, displaying the lowest temperature and the lowest carbon content in the bath, presents the highest phosphorus, iron and vanadium content in the metal.

Moreover, the ratio of the bath vs metal impurity is higher in Pot B (Table 3). As far as phosphorus is concerned, the ratio is higher than one, since this impurity is mainly present in the bath. As far as metallic impurities are concerned (iron and vanadium), the ratio is lower than one, since these metallic impurities are more noble than aluminium.

Table 2. Impurities in the metal and bath composition/temperature.

		Pot A	Pot B
Metal	Na (ppm)	59.7	56.1
	P (ppm)	13.3	0
	Fe (ppm)	928.3	665.0
	V (ppm)	118.6	46.4
Bath	Temperature (^oC)	963.3	970.5
	AlF_3 (wt.%)	11.6	11.7
	CaF_2(wt.%)	5.56	5.75
	Carbon (wt.%)	0.063	0.165

Table 3. Distribution of impurities between bath and metal.

	Pot A	Pot B
P bath/ P metal	7.0	22.1
Fe bath / Fe metal	0.054	0.165
V bath / V metal	0.089	0.332

2.4. Impact of cell operation on the sodium content in the metal

The impact of cell operation on the sodium content of Pot 2 is depicted in Figure 10. At constant aluminium fluoride excess, one observes a drastic decrease of the sodium content in the metal after an anode change. Moreover, tapping has no negative impact on the sodium content in the metal.

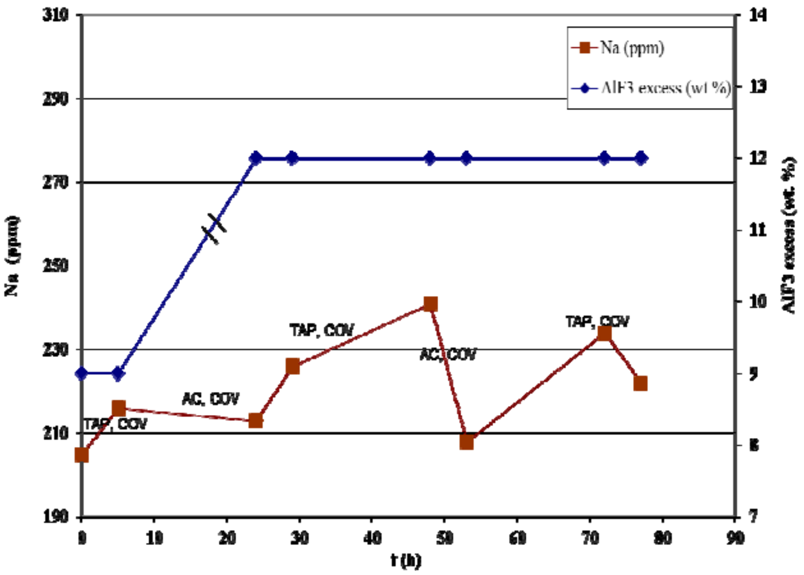

Figure 10. Impact of cell operation on the sodium content in the metal (Pot 2) (AC = anode change, TAP = metal tapping, COV, anode covering).

3. Summary and Conclusions

The cathode concentration overvoltage can be calculated using the sodium concentration found in the metal. This overvoltage varies with the bath ratio and becomes higher with more acidic baths. The overvoltage decreases the ACD.

The current efficiency can be expressed as a function of mass transfer coefficients and of the sodium fluoride gradient at the bath-metal interface.

As far as impurities are concerned, there are different behaviors. The sodium content in the metal is linked to the aluminium fluoride excess. Using thermodynamics, it was observed that there is a linear relationship between calcium and sodium found in the metal. The presence of iron, vanadium and phosphorus, in the metal, can vary from one pot to another. Pots having higher temperatures and contents of carbon in the bath will present less of these impurities in the metal.

The impact of cell operation on the sodium content in pot metal was investigated, and it was observed that only anode changes has a detrimental impact on the sodium content in the metal.

4. References

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