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

M. J. Chollier-Brym[1], **A. Bergeron**[2], **D. Dufour**[2], **G. Gagnon**[2],
D. Ringuette[2], **L. Dubé**[2], **G. Perron**[2]
1. Research Scientist
2. Technician
Rio Tinto Aluminium, Arvida Research and Development Centre, Jonquière (Québec),
G7S 4K8, Canada
Corresponding author: marie-josee.chollier@riotinto.com

Abstract

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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, ≤ 4 % (bath ratio (BR) ≥ 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, ≥ 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.

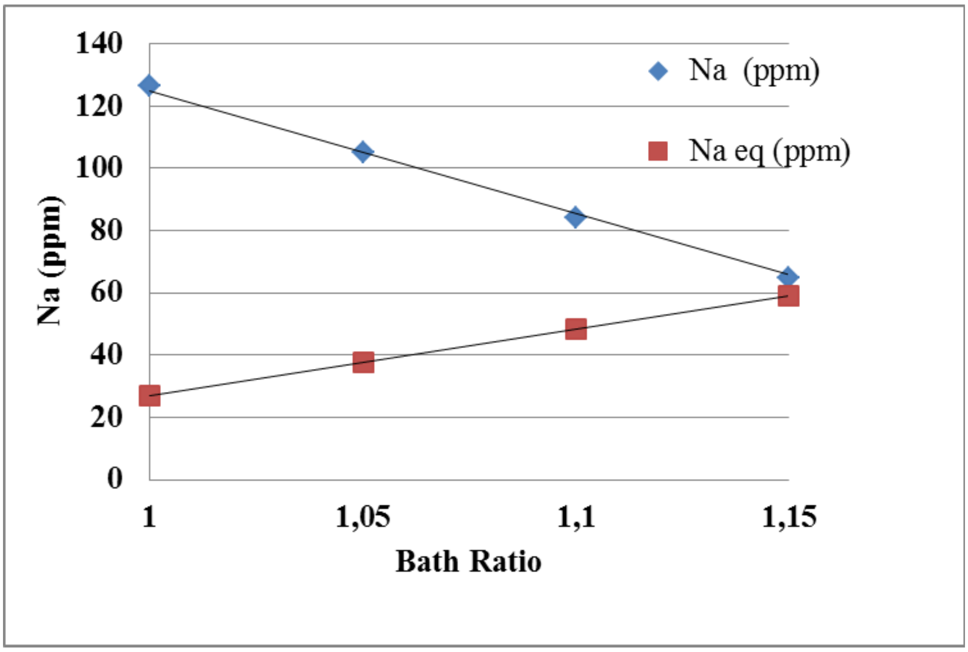

Figure 1. Evolution of the sodium concentration in the metal of Pot 1 as a function of mass bath ratio (red: during electrolysis; blue: at equilibrium).

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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