Properties of Lithium Modified Baths for Hall-Héroult Cells

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Abstract

Some aspects concerning the use of lithium-modified baths in aluminium electrolysis cells were considered. Based on literature data, a number of physical and chemical properties were calculated for two cases: i) the bath composition was assumed to follow a liquidus temperature isotherm by adding lithium while at the same time reducing the amount of excess aluminium fluoride, or: ii) the bath was modified by adding lithium fluoride while keeping the amount of excess aluminium fluoride constant. Compared with normal bath compositions, lithium modified baths have higher electrical conductivity, lower alumina solubility, lower vapour pressure, higher density, higher viscosity, and higher surface tension. The current efficiency decreases when the composition follows a liquidus isotherm, but increases when lithium fluoride is added at constant aluminium fluoride. The main way for lithium out of the process is with produced bath. Using alumina containing 0.4 wt% sodium oxide and 0.04 wt% calcium oxide, the stationary consumption of lithium carbonate was estimated to be 0.32 kg/t Al.

Keywords: Electrolyte; lithium fluoride; physical data; current efficiency.

1. Introduction

The use of lithium fluoride (LiF) modified bath in aluminium electrolysis cells was more common a few decades ago. Until about 1970 - 1980, baths with only 5 wt% excess aluminium fluoride (AlF_3) were standard, and temperatures around 980 °C was considered normal. The temperature can be reduced by any fluoride, but adding more AlF_3, LiF, magnesium fluoride (MgF_2), or a combination of those have been considered to be the best options. The main benefit with LiF is the strongly increased electrical conductivity. Some of the older literature also refers to increased current efficiency (CE), while newer data indicate that the CE will be constant or reduced.

Pechiney changed the bath composition in the acid direction (more excess AlF_3) in 1978. Trials with LiF modified bath in 180 kA cells were performed in the 1980s, but these tests were not pursued [1]. Some tests were also performed in Pechiney's 280 kA cells some years later [2], but also in this case, it was found that the use of LiF was not profitable. Venalum used LiF-modified bath in the 1980s. After the introduction of point feeders, the composition was changed in the acid direction without LiF [3, 4].

Although the use of lithium modified bath is not a hot topic today, it is an idea that is being reconsidered from time to time. In the few cases where addition of LiF has been tried in modern cells [5, 6], the motivation has been to increase the amperage, to obtain better stability by increasing the anode-cathode distance (ACD), or to reduce the specific energy consumption (in spite of slightly reduced current efficiency). According to Tabereaux *et al.* [5] the optimum LiF concentration may be about 1 wt%.

The purpose of the present work is to quantify and illustrate the consequences of introducing LiF in modern cells. The author does not intend to give specific advice or recommendations concerning the use of LiF-modified bath. Hopefully, the data and considerations presented here may be helpful during the first part of a decision process concerning bath modification.

2. Bath Modification Paths

Bath modification can take place along two paths: i) by replacing AlF_3 by LiF in such a way that the liquidus temperature remains constant, or: ii) by simply adding LiF while keeping the excess AlF_3 constant (all combinations of these paths are, of course, possible). The paths are illustrated in Figure 1. The liquidus isotherms were calculated from the equation by Solheim *et al*. [7], from which 3 ^{o}C was subtracted to account for impurity elements. It is noteworthy that when one starts at 955 ^{o}C liquidus temperature, not much more than 2 wt% LiF can be added without reducing the liquidus temperature.

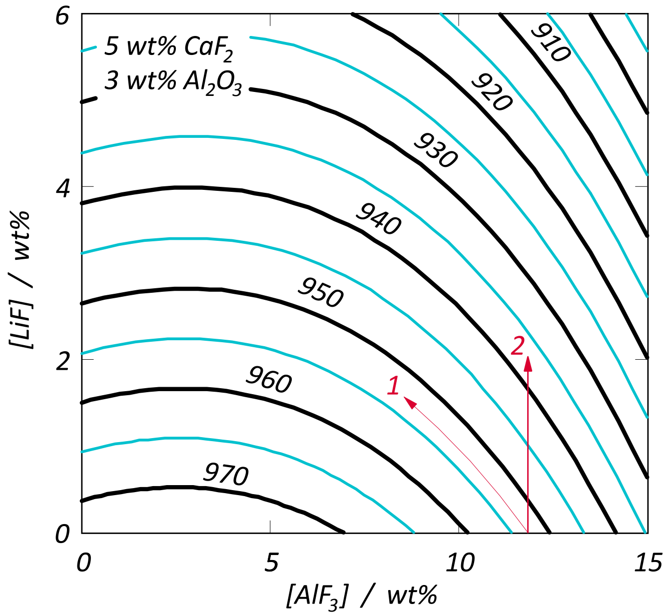

Figure 1. Liquidus isotherms for the system Na_3AlF_6-5 wt% CaF_2-3 wt% Al_2O_3-AlF_3-LiF [7]. Path 1: Constant liquidus temperature, Path 2: constant excess AlF_3 (see the text).

3. Some Physical and Chemical Properties

The figures in this section show different physical and chemical properties as a function of the concentration of LiF. The bath composition was supposed to follow the two paths shown in Figure 1. In all cases, the superheat was assumed to be 10 ^{o}C, and the bath always contains 5 wt% CaF_2 and 3 wt% Al_2O_3. The data obtained with Path 1 (constant liquidus temperature) show "hooks" at the end of the curves, which is related to the fact that the liquidus isotherms pass through maxima.

3.1. Electrical conductivity

Increased electrical conductivity is the strongest motivation for introducing LiF modified bath. The electrical conductivity was calculated from the equation suggested by Hives *et al*. [8], and the result

8. References

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