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 ^oC 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 °C was subtracted to account for impurity elements. It is noteworthy that when one starts at 955 °C liquidus temperature, not much more than 2 wt% LiF can be added without reducing the liquidus temperature.

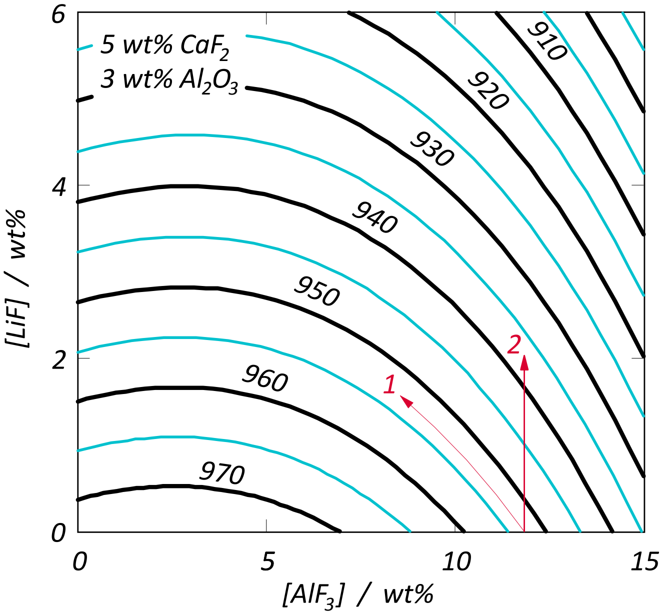

Figure 1. Liquidus isotherms for the system Na_3AlF_6-5 wt% CaF_2-3 wt% Al_2O_3-AlF_3-LiF [7]. Path 1: Constant liquidus temperature, Path 2: constant excess AlF_3 (see the text).

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 °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 is shown in Figure 2. Path 1 gives the highest potential for increase, since the temperature stays constant while the amount of excess AlF_3 decreases, which is also beneficial for the conductivity. Today's standard bath composition has a conductivity of about 215 Sm^{-1}, and it appears to be possible to increase it to at least 240 Sm^{-1} by adding LiF. In a cell running at 9 500 Am^{-2} and at 30 mm ACD, this means that the cell voltage can be reduced by 138 mV at constant ACD, or the ACD can be raised by 3.5 mm at constant voltage.

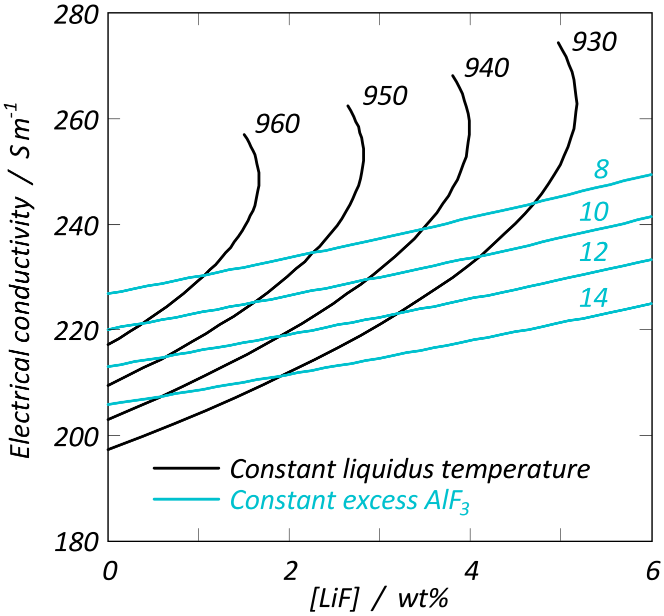

Figure 2. Electrical conductivity as a function of the concentration of LiF [8]. The numbers in the figure denote liquidus temperature and excess AlF_3 [wt%].

3.2. Alumina solubility

Reduced alumina solubility is one of the main arguments against lithium modified bath. The current alumina feeding technology requires that the average actual alumina concentration is well below saturation, in order to avoid excessive sludge formation. The alumina solubility as calculated from the equation by Skybakmoen *et al.* [9] is shown in Figure 3. The reduction in the solubility is considerable, particularly when the AlF_3 concentration is kept constant. When the bath is modified at constant liquidus temperature, the detrimental effect of LiF is partly counteracted by the reduced AlF_3 concentration.

3.3. Density

The density was computed using the equation by Solheim [10], and the result is shown in Figure 4. It is a common misconception that the addition of LiF leads to decreased density. While this true when LiF is added to pure cryolite; the density increases, also at isothermal conditions, when the melts contains excess AlF_3. The reason is that the highest densities in the system NaF-LiF-AlF_3 are found close to the line between the cryolites (Na_3AlF_6 and Li_3AlF_6). When starting between Na_3AlF_6 and AlF_3 and adding LiF, the density must "climb the ridge" between the cryolites, as illustrated by the insert in Figure 4.

Common sense suggests that it is beneficial to have large density difference between metal and bath. Still, it is not so easy to predict the consequences of a slight increase of the density.

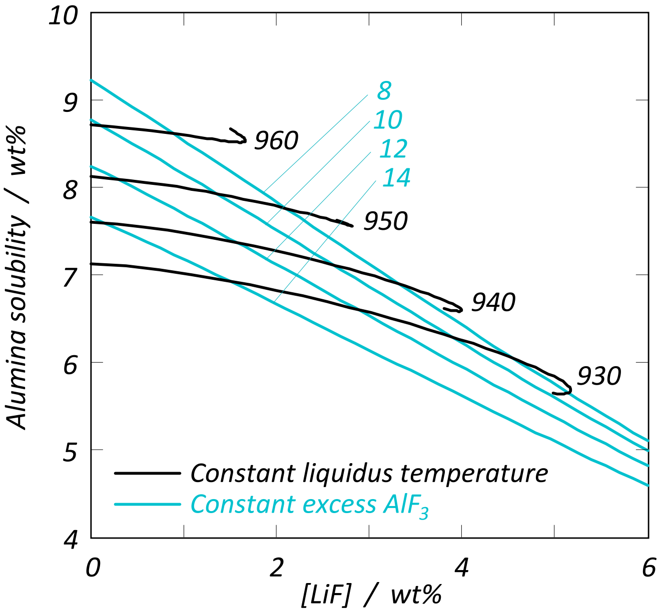

Figure 3. Alumina solubility as a function of the concentration of LiF [9].The numbers in the figure denote liquidus temperature and excess AlF_3 [wt%].

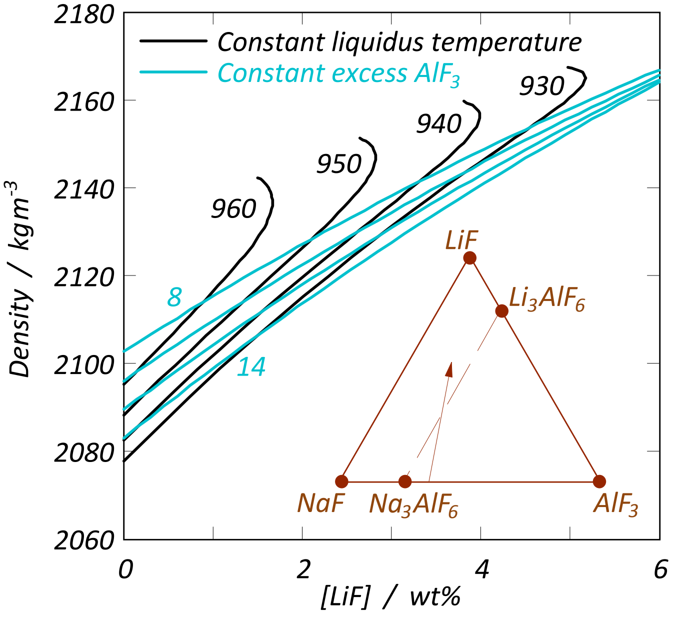

Figure 4. Density as a function of the concentration of LiF [10]. The numbers in the figure denote liquidus temperature and excess AlF_3 (8, 10, 12, and 14 wt%). The insert illustrates that the density increases with increasing LiF because the highest densities in the system are found near the line connecting Na_3AlF_6 and Li_3AlF_6 (see the text).

3.4. Vapour pressure

The total vapour pressure was computed from the equation derived by Haupin and Kvande [11]. The result is shown in Figure 5. In both cases shown in the figure, the total vapour pressure decreases considerably, which is beneficial. If the amount of excess AlF_3 is kept constant, the vapour pressure decreases mainly due to the reduced temperature. At constant liquidus temperature, the reduced pressure is mainly caused by the reduced excess AlF_3.

Reduced vapour pressure contributes to a less harmful working atmosphere. The amount of lithium in the vapour is commented on in a subsequent section.

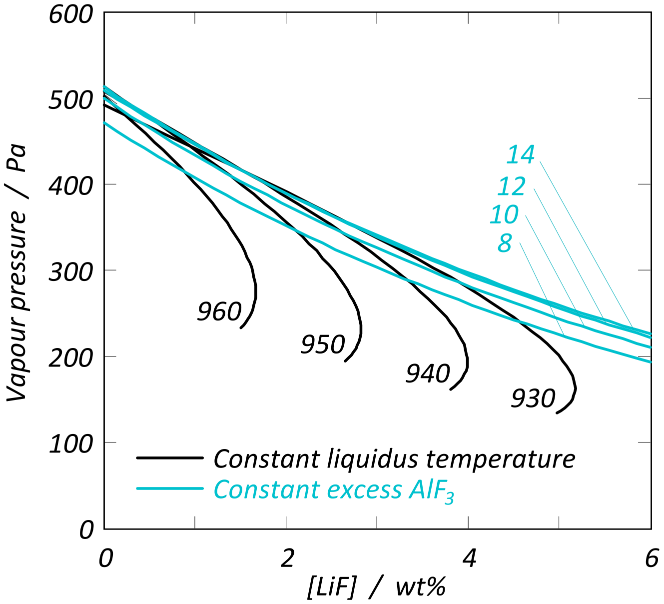

Figure 5. Vapour pressure as a function of the concentration of LiF [11]. The numbers in the figure denote liquidus temperature and excess AlF_3 [wt%].

3.5. Viscosity

The most precise equation for computing viscosity for the system $NaF\text{-}AlF_3\text{-}Al_2O_3$ is probably the one published by Herzberg *et al.* [12]. However, the equation by Herzberg *et al.* does not contain terms for LiF. The effect of LiF was studied by Chrenkova *et al.* [13]. For the present purpose, it was found adequate to use the Herzberg equation as basis and modify it by using the LiF-terms taken from the equation by Chrenkova *et al.* [13], which produced 5 - 6 relative percent increased viscosity per weight percent LiF for both modifications paths shown in Figure 1.

The effect of viscosity is normally small at turbulent conditions, and it is likely that the effect of a change to LiF-modified bath is negligible. It is possible that the mass transfer coefficient at the cathode will decrease slightly (which is beneficial for the current efficiency). It is also possible that the amount of gas accumulated underneath the anode will increase slightly. It is not easy to decide if the total effect of increased viscosity is beneficial or not.

3.6. Surface tension

An equation for calculation of the surface tension between bath and gas was published by Danek *et al*. [14]. The equations showed increasing surface tension with increasing concentration of LiF, particularly when the liquidus temperature was kept constant. According to the fluoride evolution model by Haupin and Kvande [11], this would lead to decreased bath loss into the flue gas in the form of entrainment of droplets.

3.7. Current efficiency

A semi-empirical current efficiency (CE) model was recently published, based on theory as well as numerous measurements in the so called "Sterten-Solli cell" [16]. It appeared that the effect of LiF depends on the NaF/AlF$_3$ molar ratio (r), in such a way that the effect is positive in acid bath and negative in neutral bath. At today's industrial composition (r ≈ 2.2) there is almost no direct effect of LiF. It should be emphasized that the CE model was based on laboratory data, where some important parameters such as sludge and the sideledge situation cannot be reproduced.

By application of the CE model to bath composition changes along the two paths considered in this paper, it appeared that the detrimental effect of reduced excess AlF$_3$ will dominate if the liquidus temperature is kept constant, while the beneficial effect of reduced temperature dominates when the AlF$_3$ concentration is kept constant. This is illustrated in Figure 6.

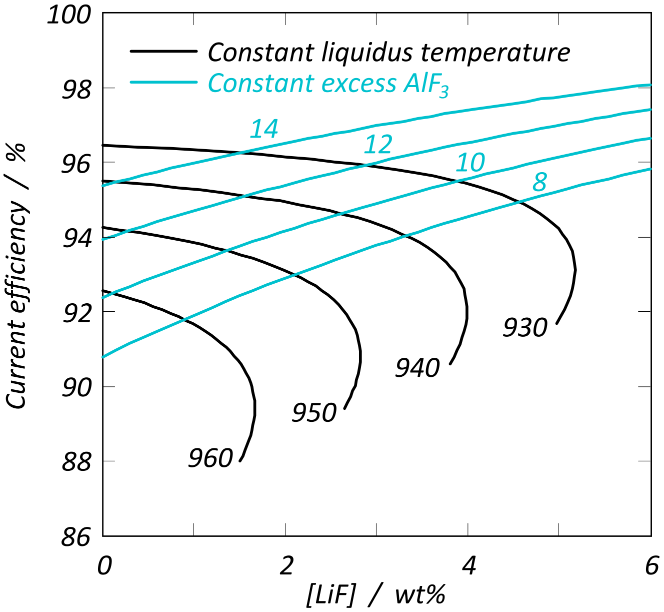

Figure 6. Current efficiency as a function of the concentration of LiF, calculated from a CE model [15]. The numbers in the figure denote liquidus temperature and excess AlF$_3$ [wt%].

4. Lithium in the Produced Metal

Lithium fluoride is reduced by aluminium at the cathode, leading to small amounts of lithium in the produced metal. This is probably the main argument against the use of lithium fluoride. In principle, Li can be removed by the same methods as used for the other alkali metals and calcium. However, this is very demanding, since the Li tolerance is very low in certain applications, such as aluminium foil manufacturing (< 1 ppm Li).

The empirical equation derived by Peterson and Tabereaux [16] indicates that there will be around 5 ppm Li in the metal per weight percent LiF in the bath; this goes for constant liquidus temperature as well as for constant excess AlF_3.

5. Hydrogen Fluoride Generation

Hydrogen fluoride (HF) is generated by reaction between bath and humidity. The humidity mainly stems from the alumina, but also from humid air entering the cell:

$$\tfrac{1}{3}\mathrm{AlF_3} + \tfrac{1}{2}\mathrm{H_2O} \;=\; \mathrm{HF} + \tfrac{1}{6}\mathrm{Al_2O_3} \qquad (1)$$

The HF pressure for a given water vapour pressure can be calculated by:

$$p_{HF} \;=\; p_{H_2O}^{1/2} \cdot a_{AlF_3}^{1/3} \cdot a_{Al_2O_3}^{-1/6} \cdot C \qquad (2)$$

where *C* is the equilibrium constant for the reaction above. The activity of AlF_3 decreases with increasing LiF when the liquidus temperature is kept constant (Path 1 in Figure 1). When the amount of AlF_3 is kept constant, the temperature decreases (Path 2), which gives smaller *C*. In both cases, the HF pressure becomes lower. This is in accordance with observations made in industrial cells by Mizoguchi and Yuhki [17] as well as by Stejer *et al.* [6].

6. Lithium Carbonate Consumption

6.1. Loss mechanisms

Lithium is commonly added in the form of lithium carbonate (Li_2CO_3) which is readily available and easy to dissolve due to the turbulence caused by gas evolution,

$$\tfrac{1}{2}\mathrm{Li_2CO_3} + \tfrac{1}{3}\mathrm{AlF_3} \;=\; \mathrm{LiF} + \tfrac{1}{2}\mathrm{CO_2} \qquad (3)$$

LiF is gradually lost from the bath, and must be replaced by adding more Li_2CO_3. There are several loss mechanisms, which are shortly commented below. The cost of Li_2CO_3 is one of the major objections against LiF-modified baths. The following mechanisms have been identified,

Loss with the produced metal: As mentioned above, the produced metal contains about 5 ppm Li per wt% LiF in the bath. This corresponds to a stationary consumption of 0.027 kg Li_2CO_3/t Al per wt% LiF.

Charging loss: Due to violent gas evolution during charging (Equation (3)), a considerable part of the batch will be thrown back from the melt, forming dust. According to Kuschel and Welch [18], the charging loss could be reduced by adding pellets instead of powder.

Evaporation loss: The main part of the vapour above the bath consists of $NaAlF_4$ and its equivalent $LiAlF_4$. The total vapour pressure decreases when LiF is present (Figure 5). From thermochemical data [19] it can be calculated that the vapour pressure of $LiAlF_4$ at 1300 K is only 26 percent of the $NaAlF_4$ pressure when compared with equal activities of LiF and NaF. It can, therefore, be predicted that the vapour pressure of $LiAlF_4$ will be relatively low.

Entrainment loss: When gas bubbles break at the bath surface, bath droplets with bath composition are formed. Some of those are small enough to be entrained with the gas.

Loss with produced bath: The alumina contains small amounts of sodium and calcium in the form of Na_2O and CaO. These react with the bath to form fluorides,

$$\tfrac{3}{2}\mathrm{Na_2O} + \mathrm{AlF_3} \;=\; \tfrac{1}{2}\mathrm{Al_2O_3} + 3\,\mathrm{NaF} \tag{4}$$

$$\tfrac{3}{2}\mathrm{CaO} + \mathrm{AlF_3} \;=\; \tfrac{1}{2}\mathrm{Al_2O_3} + \tfrac{3}{2}\mathrm{CaF_2} \tag{5}$$

In order to keep the bath composition constant (the NaF/AlF_3 molar ratio, r), the production of NaF and consumption of AlF_3 must be compensated for by charging AlF_3. This leads to production of bath, which is treated below.

The further discussion concerning Li_2CO_3 consumption will be limited to plants with hooded cells and equipped with efficient gas treatment centres. In that situation, lithium compounds entering the flue gas ducts will be returned almost quantitatively from the dry scrubber. Depending on the hooding efficiency; small amounts of lithium may be lost as roof emissions, but the quantities will normally be negligible. This means that lithium losses take place only with produced metal and produced bath in modern electrolysis plants.

6.2. Bath production

The following mass balances related to Equations (4) and (5) apply, where m_a is the mass of alumina added [kg/t Al], w is the mass fraction of Na or Ca in the alumina, and the numbers are stoichiometric factors:

Produced NaF:

$$m_{NaF} \;=\; m_a w_{Na} \cdot \frac{42}{23} - \tag{6}$$

Consumed AlF_3:

$$m_{AlF_3} \;=\; -\,m_a w_{Na} \cdot \frac{1}{3} \cdot \frac{84}{23} - m_a w_{Ca} \cdot \frac{2}{3} \cdot \frac{84}{40.1} \tag{7}$$

Produced CaF_2:

$$m_{CaF_2} \;=\; m_a w_{Ca} \cdot \frac{78.1}{40.1} \tag{8}$$

Added AlF_3 to keep the molar ratio (r) constant:

$$m_{add} = m_{NaF} \cdot \frac{2}{r} - m_{AlF_3} \tag{9}$$

The factor 2/*r* is the weight ratio between NaF and AlF_3. By inserting m_a = 1895 kg alumina/t Al (slightly above the theoretical value) we obtain:

Added AlF_3:

$$m_{add} = \left(\frac{6921}{r} + 2307\right) \cdot w_{Na} + 2646 \cdot w_{Ca} \tag{10}$$

Total bath production:

$$m_{prod,\,bath} = \left(\frac{6921}{r} + 3460\right) \cdot w_{Na} + 3691 \cdot w_{Ca} \tag{11}$$

As a typical example, we take $w_{Na} = 0.0030$ (0.4 wt% Na_2O) and $w_{Ca} = 0.00029$ (0.04 wt% CaO). At $r = 2.2$, 17.1 kg AlF_3/t Al must be added, and the total bath production becomes 20.9 kg/t Al. The above numbers were not corrected for the fraction of sodium removed with the metal (100-200 ppm Na corresponding to typically 0.15 kg/t Al, which is less than 3 percent of the amount added with the alumina).

The produced bath can find its way out of the process along several paths:

- As bath tapped off for sale (*e.g.*, for the start-up of new smelters)
- As bath tapped off for deposit
- As bath tapped off with the metal and disposed of with dross from the foundry
- As bath entering the bottom- and side linings and disposed of with spent pot lining (SPL)
- As diffuse losses, *e.g.*, with dust spreading from the potroom (minor amounts)
- As particulate fluoride loss over roof (minor amounts, depending on the hooding efficiency)

Anode cover material and bath adhering to the anode butts will be recycled to the cell. The same will be true for bath removed with tools used in the cell.

As long as the total bath mass and composition stay constant, the rate of LiF removal and, thereby, the Li_2CO_3 consumption, is independent of how the bath is removed.

6.3. Total stationary lithium carbonate consumption

The loss of Li_2CO_3 can be calculated by:

$$m_{loss} = m_{prod,bath} \cdot w_{LiF} \cdot 1.424 \text{ [kg/t Al]} \tag{12}$$

where the number 1.424 is the stoichiometric ratio between ½ Li_2CO_3 and LiF. By using 5 ppm Li in the metal per wt% LiF and the bath production rate estimated above (20.9 kg/t Al), the total lithium carbonate consumption becomes 0.32 kg/t Al per wt% LiF in the bath. The lithium loss is a direct function of the composition of the alumina, which determines the bath production rate.

The above estimate is generally lower than the values compiled by Peterson and Tabereaux in the 1980s [20]. Apparently, large amounts of lithium were lost with the flue gas. This can, possibly, be attributed to immature dry scrubber technology at the time. The ductwork losses increased strongly for LiF concentrations above 2 wt%, which may explain that the plots of Li_2CO_3 consumption rate *vs*. wt% LiF in the bath were non-linear. Peterson and Taberaux did not identify produced bath as a separate reason for Li_2CO_3 consumption.

It is important to consider that the lithium carbonate consumption measured in a limited number of test cells will not be representative. Most of the lithium that disappears into the gas ducts will not be returned to the test section – which also implies that the rest of the plant will be contaminated by lithium. LiF removed with the anode cover material (ACM) will also be spread to the rest of the plant, unless a separate ACM cycle for the test section is established.

When lithium modified bath is introduced in the entire plant, it will take time before the consumption is down at the level indicated above. Large amounts of Li_2CO_3 must be added in the beginning to attain the desired level of LiF in the bath, and also to reach stationary levels in the sideledge and anode cover material.

6.4. Time perspective

When LiF modified bath has been introduced in a plant the die has been cast – in the sense that it will take a long time to reverse the decision. Assuming that the stationary Li_2CO_3 consumption is 0.32 kg per ton Al and wt% LiF in the bath, the rate of LiF removal will be 0.22 kg LiF/(t Al · wt% LiF) after stop of the feeding. In a cell that contains 7 000 kg bath and produces 2.2 t Al/day the removal rate becomes:

$$\frac{d[LiF]}{dt} = -\frac{0.22\cdot[LiF]\cdot 2.2\cdot 100}{7000} = -0.0069\cdot[LiF] \qquad \text{[wt\% / day]} \qquad (13)$$

where the brackets denote concentration in wt%. Integration gives:

$$[LiF]_t = [LiF]_{t=0}\cdot\exp(-0.0069\,t) \qquad (14)$$

where t is the time [days]. The half-life of LiF, *i.e.*, the time needed to reduce the concentration to 50 percent of the original concentration, is close to 100 days. By taking into account the amount of LiF present in the sideledge and anode cover material, the half-life will be considerably higher. This means that it may take up to a few years to remove LiF from the process.

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