

MATHEMATICAL MODEL OF FLUORIDE EVOLUTION  
FROM HALL-HÉROULT CELLS

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Abstract

Fluoride evolution from Hall-Héroult cells can be predicted with reasonable accuracy using only thermodynamics, kinetics and the physical properties of the bath. New data have made it possible to improve the previous model<sup>1</sup>. Bath appears to achieve its equilibrium partial pressure in the anode gas. Bath vapor then condenses as it cools to form particulate fluoride. Liquid bath entrained in the pot gas freezes and contributes also to particulate, but is a minor factor if the cell has a good ore cover. Fortunately, kinetics limits the hydrolysis reaction (forming HF) to about 25% of the equilibrium value. The new mathematical model predicted with a RMS difference of only 0.8 kgF/ Metric Ton Aluminum, the previously published total fluoride evolution from a 170kA Alcoa cell<sup>2</sup>.

Introduction

In 1984 Haupin<sup>1</sup> proposed a mathematical model of fluoride evolution based upon thermodynamics, kinetics and the physical properties of the bath. Since then new data have been published on bath vapor pressure<sup>3,4</sup>, activities<sup>5</sup>, liquidus temperature<sup>6,7</sup>, and Gibbs energies of formation<sup>8</sup> for bath components. These new data have permitted our development of an improved mathematical model.

In this paper, fluoride evolution will be defined as the F content (expressed as kg F/ Metric Ton aluminum) of the HF and of particulate that leaves the cell with the cell gas. Most of the evolution will be captured by the cell's hooding and fume treatment system. That which escapes capture will be called fluoride emissions. Hence, fluoride emissions can be calculated by multiplying the evolution by a factor equal to one minus the hooding efficiency. Hooding efficiency generally lies between 0.95 and 0.98.

Fluoride evolution is often classified as gaseous and particulate. Gaseous fluorides are those that continue to be gases at ambient temperature: namely, HF, CF<sub>4</sub>, SiF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub>. Entrained and volatilized bath, on the other hand, become particulate at room temperature. In addition, alumina and carbon dust will sorb HF and, therefore contribute to particulate fluoride. The classification into gaseous and particulate is somewhat arbitrary since the relative amounts depend upon sampling technique, sampling location and analytical procedure. Particulate fluorides may react with water vapor in the air to form HF. Conversely, HF may sorb on nonfluoride particulates and be reported as particulate fluoride. Hence total fluoride evolution is a more meaningful value. Other sources of fluoride emission include fluorides from spent anodes, fluorides from tapping ladles and fluorides from the carbon baking furnaces. These other sources of fluorides and the CF<sub>4</sub>, SiF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub> in the pot gas are not included in this model. Only a small amount of SiF<sub>4</sub> is produced. It is hydrolyzed to SiO<sub>2</sub> and HF by the humidity of the air. The amount produced depends upon the silica content of the anodes.

Cells produce CF<sub>4</sub>, and a trace of C<sub>2</sub>F<sub>6</sub> when they are on anode effect. These fluorocarbon gases previously were considered innocuous, because they are nontoxic and do not contribute to ozone depletion. Recently, however, they have been implicated as "greenhouse gases" which may contribute to global warming. This makes decreasing the frequency and duration of anode effects of prime importance. The fluorocarbon gases deserve their own model. One probably could be developed from non-equilibrium thermodynamics involving electrochemical overvoltages at the anode.

Definition of Terms

- $F_G$  = Total gaseous fluoride (kgF/Ton Al).
- $F_P$  = Total particulate fluoride (kgF/Ton Al).
- $F_T$  = Total fluoride evolution (kgF/Ton Al).
- $F_{VP}$  = Volatilized bath (kgF/Ton Al).
- $F_{EP}$  = Particulate fluoride by entrainment (kgF/Ton Al).
- $F_{GP}$  = Gaseous F formed by hydrolysis of volatilized bath (kgF/Ton Al).
- $T$  = Temperature (Kelvin).
- $T_b$  = Bath temperature ( $^{\circ}C$ ).
- $R_b$  = Weight ratio NaF/ $AlF_3$  in bath.
- $CR$  = Mol ratio (NaF+LiF)/ $AlF_3$ .
- %LiF = Weight % LiF in bath.
- % $CaF_2$  = Weight %  $CaF_2$  in bath.
- % $MgF_2$  = Weight %  $MgF_2$  in bath.
- % $Al_2O_3$  = Weight percent alumina in bath.
- % $Al_2O_3^*$  = Weight percent alumina at saturation<sup>7</sup>.
- $xsAlF_3$  = Wt. % excess  $AlF_3$  over that forming Li and Na Cryolites.
- MFC = Mol fraction  $CaF_2$ .
- MFm = Mol fraction  $MgF_2$ .
- %CE = % Current efficiency.
- $P_B$  = Barometric pressure (kPa).
- Phumid = Absolute humidity of air (kPa).
- VP = Total vapor pressure of bath (Pa).
- $VP_b$  = Total vapor pressure of bath (Bar) =  $VP/1.E5$ .
- $K_P$  = Equilibrium constant for reaction:  
 $Na_2Al_2F_8 = 2NaAlF_4$ .
- $P_M$  = Partial pressure of  $NaAlF_4$  (Bar).
- $P_D$  = Partial pressure of  $Na_2Al_2F_8$  (Bar).
- $P_{NaF}$  = Partial pressure of NaF (Bar).
- SurfT = Surface tension of bath (mN/m).
- $P_{HF}$  = Partial pressure of HF (Bar).
- $\Delta G_n^0$  = Gibbs energy for reaction n (J).
- R = Gas constant = 8.3144 J/(K,mol).
- $P_{H_2O}$  = Partial pressure of  $H_2O$  in pot gas (Bar).
- $F_{GB}$  = Gaseous fluoride by hydrolysis of bath (kg F/Metric Ton Aluminum).
- Wore = %  $H_2O$  in the alumina "ore".
- Han = % hydrogen in anode including moisture.
- $a_{Al_2O_3}$  = Activity of alumina in bath.
- $a_{AlF_3}$  = Activity of solid  $AlF_3$  in bath.
- Catch = Fraction of entrained bath that does not escape.
- HBA = Hydrolysis by air, Weighting factor.

Volatilization of Bath

Most of the particulate fluoride evolved from cells results from vaporization of the bath. In this model the assumption was made that  $CO_2$  and CO leave the bath carrying an equilibrium partial pressure of bath species. As the temperature falls the vapor condenses to form particulate.

The vapor pressure of molten cryolite with additives has been studied extensively and there is good agreement among recent investigators: Guzman, et al<sup>3</sup>, Zhou, et al<sup>4</sup>, Kvande<sup>9</sup>. These data (and those of Kuxmann and Tillessen<sup>10</sup> for the effect of LiF) were combined and fitted by multiple regression to equation (1):

$$VP = \text{Exp} [(-A/T) + B] \tag{1}$$

Where:

$$A = 21011 - 12235 \cdot R_b + 18862 \cdot R_b^2 - 6310.5 \cdot R_b^3 + 116.7 \cdot \%LiF - 55 \cdot R_b \cdot \%LiF - 151 \cdot \%MgF_2 + 1.466 \cdot \%MgF_2^2 - 6.7 \cdot \%Al_2O_3$$

$$B = 25.612 - 9.681 \cdot R_b + 11.854 \cdot R_b^2 - 3.8315 \cdot R_b^3 + 0.025 \cdot \%LiF - 0.013 \cdot R_b \cdot \%LiF - 0.0008 \cdot \%CaF_2 - 0.08696 \cdot \%MgF_2 + 0.001112 \cdot \%MgF_2^2 - 0.11 \cdot \%Al_2O_3 / (1 + 0.193 \cdot \%Al_2O_3)$$

Laboratory measurements show a significant partial pressure of metallic sodium and a small partial pressure of AlF for bath in contact with aluminum<sup>9</sup>. This is not included in equation (1). These species do not appear to exist in the emissions of an operating cell, probably because both are oxidized by  $CO_2$  at the bath bubble interface and redissolve in the bath.

To convert the partial pressure of fluoride vapor (equation 1) to kg F per metric ton of aluminum we need to know the composition of the vapor and that the pot produces [2779.68/ %CE] k mols of pot gas per metric ton of aluminum. Kvande found the major vapor species to be  $NaAlF_4$ ,  $Na_2Al_2F_8$ , and NaF. The NaF may be present partly as other  $xNaF/yAlF_3$  species with  $x/y > 1$ . This does not affect the total F of the particulate.

We can estimate from Kvande's data the partial pressure in kPa of NaF:

$$P_{NaF} = VP_b \cdot (0.2073 - 182/T) \cdot (-0.6366 + 1.449 \cdot CR - 1.068 \cdot CR^2 + 0.2556 \cdot CR^3) \tag{2}$$

Kvande found the equilibrium constant  $P_M^2 / P_D$  for:

$\text{Na}_2\text{Al}_2\text{F}_8 = 2\text{NaAlF}_4$ , to be:

$$K_P = \text{Exp} [(-21085 / T) + 15.45] \quad (3)$$

Solving the quadratic for  $P_M$  gives:

$$P_M = \{-K_P + [K_P^2 + 4 \cdot K_P \cdot (VP_b - P_{\text{NaF}})]^{1/2}\} / 2 \quad (4)$$

$$P_D = VP_b - P_{\text{NaF}} - P_M$$

$$F_{VP} = 5351000 / \%CE / P_B \cdot (4 \cdot P_M + 8 \cdot P_D + P_{\text{NaF}}) \quad (5)$$

### Entrained Bath

Liquid bath entrained in the pot gas freezes and becomes particulate as the gas cools. Early measurements indicated 20 to 40% of the particulate came from entrainment<sup>11,12,13</sup> based upon microscopic examination of the particles. Wahnsiedler et al<sup>2</sup> using the  $\text{CaF}_2$  content of the particulate as a tracer, found only 5 to 9% of the particulate was entrained bath.

The entrainment mechanism has been described<sup>14</sup> as follows: When a gas bubble reaches the surface, its dome breaks producing tiny droplets that will be carried away if the gas velocity is sufficient. The liquid rushing in to fill the cavity formed by the breaking bubble ejects a single larger droplet. Since these droplets are larger, a higher gas velocity is needed for entrainment. It has been shown<sup>14</sup> that entrainment varies directly with gas velocity and the ratio (gas density) / (liquid density - gas density) and inversely with the surface tension of the liquid. In our case only the surface tension varies significantly, but a new variable can be added. The crust acts both as a filter to remove entrained liquid and a long exit path giving more time for entrained droplets to settle out. We named the crust effect "Catch." To accommodate the earlier data we set Catch = 0.9 when calibrating against Wahnsiedler's data<sup>2</sup>. This led to the following empirical relationship for entrained bath:

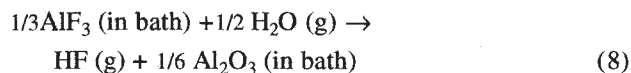
$$F_{EP} = 76000 \cdot (1 - \text{Catch}) / (\text{SurfT} \cdot \%CE) \quad (6)$$

An equation for surface tension was developed from data by Bratland et al<sup>15</sup>:

$$\begin{aligned} \text{SurfT} = & 270 - 0.137 \cdot T_b - 3.29 \cdot \% \text{Al}_2\text{O}_3 - 0.19 \cdot \% \text{CaF}_2 - \\ & 2 \cdot \ln(\% \text{Al}_2\text{O}_3) + 0.00329 \cdot T_b \cdot \% \text{Al}_2\text{O}_3 + \\ & 0.00056 \cdot \% \text{CaF}_2 \cdot T_b - x \text{AlF}_3 \end{aligned} \quad (7)$$

### Formation of HF

Gaseous fluoride is produced by hydrolysis of bath and hydrolysis of pot vapor. The partial pressure of HF in the pot gas can be calculated from the reaction:



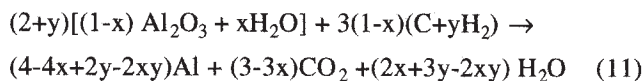
It was assumed that moisture reacts with aluminum fluoride rather than cryolite or any other component of the bath because the equilibrium constant is over a thousand fold higher for aluminum fluoride. The equilibrium constant for the above reaction leads to the following expression for the partial pressure of HF:

$$P_{\text{HF}} = \text{Exp} \left[ -\Delta G_8^0 / (RT) \right] P_{\text{H}_2\text{O}}^{1/2} a_{\text{AlF}_3}^{1/3} a_{\text{Al}_2\text{O}_3}^{-1/6} \quad (9)$$

Using data from JANAF tables<sup>8</sup>,  $\Delta G_8^0$  for reaction (8) can be expressed as a linear function of temperature over the range 1200 to 1300K:

$$-\Delta G_8^0 / RT = 7.494 - (8401/T) \quad (10)$$

To calculate the partial pressure of  $\text{H}_2\text{O}$  in the pot gas we must convert weight % water in the alumina to mole fraction,  $x$ , water in the alumina, and the weight % hydrogen in the anode to mole fraction,  $y$ , of hydrogen in carbon. Then we can determine the quantities of moisture and  $\text{CO}_2$  that would be formed by the cell reaction:



Because  $x$  is small and  $y$  very small, the  $xy$  terms can be neglected. Reaction of  $\text{CO}_2$  with aluminum dissolved in the bath does not change the gas volume, hence we do not have to consider the CO content. Simplifying and solving for the mole fraction  $\text{H}_2\text{O}$  gives the following expression for the partial pressure of  $\text{H}_2\text{O}$  in the pot gas:

$$\begin{aligned} P_{\text{H}_2\text{O}} = & (\% \text{H}_2\text{O in Ore}) / [25.96 + 1.237(\% \text{H}_2\text{O in Ore})] + \\ & (\% \text{H in anode}) / [17.67 + 0.8(\% \text{H in anode})] \end{aligned} \quad (12)$$

The pot produces (2779.68/%CE) k mols of CO + CO<sub>2</sub> per metric ton of aluminum produced. Multiplying this by the partial pressure of HF, the molecular weight of F and ratio of reference state pressure to barometric pressure gives equilibrium gaseous F production. When this was compared with actual measured HF evolution we found that hydrolysis proceeded only 26.8% toward thermodynamic equilibrium at 2.20 CR and 21.6% at 2.60 CR. Entering this kinetic data into the relationship gave:

$$F_{GB} = \left( \frac{2914000 - 1364000R_b}{(\%CE)(P_B)} \right) \text{Exp} \left( \frac{7.4941 - 8401}{T} \right) \left( \frac{\text{Wore}}{25.96 + 1.237\text{Wore}} + \frac{\text{Han}}{17.72} \right)^{1/2} a_{\text{AlF}_3}^{1/3} a_{\text{Al}_2\text{O}_3}^{-1/6} \quad (13)$$

### Activities

The model requires equations for the thermodynamic activity of alumina and aluminum fluoride. Activity data for Al<sub>2</sub>O<sub>3</sub> in the bath<sup>16,17</sup> (reference state α-Al<sub>2</sub>O<sub>3</sub>) was fitted by the expression:

$$a_{\text{Al}_2\text{O}_3} = (\% \text{Al}_2\text{O}_3 / \% \text{Al}_2\text{O}_3^*)^{2.77} \quad (14)$$

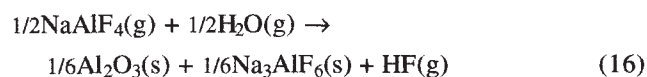
The percent alumina saturation, %Al<sub>2</sub>O<sub>3</sub>\*, was calculated using the equations of Skybakmoen et al<sup>7</sup>.

Activity data for AlF<sub>3</sub> in the bath<sup>5,9</sup> (reference state solid AlF<sub>3</sub>) was fitted by the equation:

$$a_{\text{AlF}_3} = \text{Exp}(1.9656 - 4.7237*CR + 0.51281*CR^2) (1 - \text{MFC} - \text{MFM})(1 - 0.375*a_{\text{Al}_2\text{O}_3}) \quad (15)$$

### Hydrolysis of Pot Fume

Another source of gaseous fluoride arises from hydrolysis of NaAlF<sub>4</sub> vapor by moisture in the air brought in by the pot's exhaust draft:



Treating this reaction similar to the previous hydrolysis gives:

$$P_{\text{HF}} = \text{Exp}[-\Delta G_{16}^0/(RT)] (P_{\text{NaAlF}_4})^{1/2} (P_{\text{H}_2\text{O}})^{1/2} \quad (17)$$

The incoming air supplies moisture but also cools the pot gas, limiting hydrolysis. HBA is an adjustable factor between 0 and 3 used to allow for variations in the kinetics resulting from changes in ore cover. HBA=1 represents average conditions. The kinetics factor was calibrated for an exhaust draft of 0.5 m<sup>3</sup>/min, kiloampere at 30°C. A higher air flow would bring in more moisture but would also cause more rapid cooling. Hence little overall change in hydrolysis would be expected.

$$F_{\text{GP}} = \frac{380000(\text{HBA})}{(\%CE)(P_B)} \text{Exp} \left( \frac{13.746 - 14370}{T} \right) P_M^{1/2} \left( \frac{\text{Phumid}}{102.9} \right)^{1/2} \quad (18)$$

While hydrolysis of pot fume changes the ratio of gaseous to particulate fluoride, it does not change the total fluoride evolution.

### Summary

Total particulate fluoride is given by:

$$F_P = F_{VP} + F_{EP} - F_{GP} \quad (19)$$

Total gaseous fluoride is given by:

$$F_G = F_{GB} + F_{GP} \quad (20)$$

Total fluoride is given by:

$$F_T = F_{VP} + F_{EP} + F_{GB} \quad (21)$$

### Discussion

This model attempts to calculate the fluoride evolution from a point fed, prebaked anode cell during normal operation with a good ore cover. It is not known how well it predicts evolution from other types of cells. Anode changing, anode effects, tracks (shutting off the alumina feed and tracking the resistance rise), and manual feeding of aluminum fluoride will affect the fluoride evolution. Wahnsiedler et al<sup>2</sup> found the influence of the following operations on the fluoride evolution:

$$\Delta F = 0.55 \cdot \text{AEPD} + 0.12 \cdot \text{FADPD} - 0.35 \cdot \text{TRACPD} \quad (22)$$

Where:

$\Delta F$  = Increase in total fluoride evolution  
(kg F / Ton Al ).

AEDP = Anode effects per day.

FADPD = Manual fluoride additions per day.

TRACPD = Cell tracking operations per day.

Of course this is only an approximation, since the duration of each event as well as its frequency must be important.

The predictions of this model were compared with the total fluoride evolution measured from a 170kA Alcoa cell during normal operation as bath ratio (weight ratio NaF/AlF<sub>3</sub>), moisture content of the alumina, and the hydrogen content of the anodes were varied. Other variables affecting fluoride evolution were allowed to fluctuate normally but were measured. Unfortunately the original data is no longer available, therefore the comparison was against regression equations<sup>2</sup> representing the original data. Over the range 1.10 to 1.40 bath ratio and 3 to 5% alumina the RMS (root mean square) difference in total fluoride evolution was 0.8 kg F/metric ton aluminum. At lower alumina concentrations the model gives a higher fluoride evolution than the regression equation. This is to be expected because linear regression was used, but the true relationship is nonlinear.

Predictions of the mathematical model are shown in figures 1 – 4. The  $\Delta T$  labels on the curves is the difference between bath temperature and the liquidus temperature, often called superheat. The equations of Sterten and coworkers<sup>6,7</sup> were used to calculate the liquidus.

The following conditions were held constant for all of the curves: barometric pressure 97 kPa, absolute humidity 1.41 kPa, 2.8% H<sub>2</sub>O in Al<sub>2</sub>O<sub>3</sub>, 0.093% H in anodes, 6.5% CaF<sub>2</sub> and 0.15% MgF<sub>2</sub> in the bath.

Figures 1a and 1b show how fluoride evolution increases as bath ratio is lowered while holding the superheat constant. Figure 2 demonstrates the increase in evolution as alumina is decreased. Figure 3 shows the rather dramatic lowering of evolution produced by adding 3% LiF to the bath at a constant 15°C superheat. Figure 4 predicts the entrained bath evolved from a modern cell. It is a minor factor and mainly a function of alumina concentration.

Macintosh computer users may obtain a copy of the model in Quick Basic by sending W.E. Haupin a formatted blank Macintosh 3.5" 800K disk with return postage.

Comparison with 1984 mathematical model

The greatest difference between the new model and the old lies in its prediction of particulate fluoride. The new model predicts, for a constant superheat, a rather flat

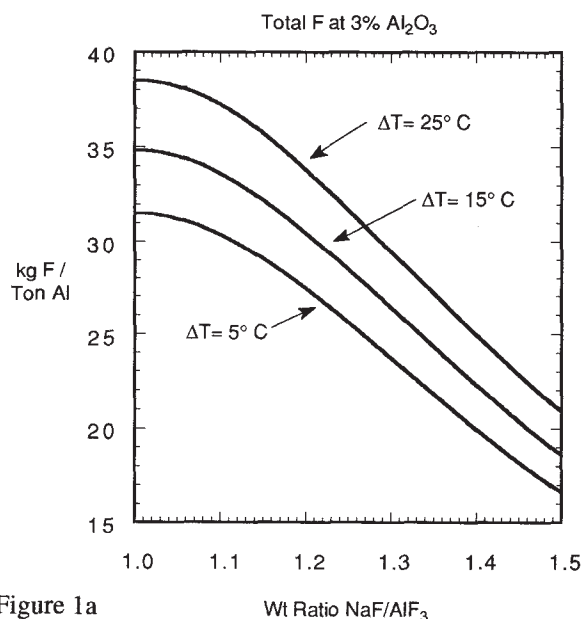


Figure 1a

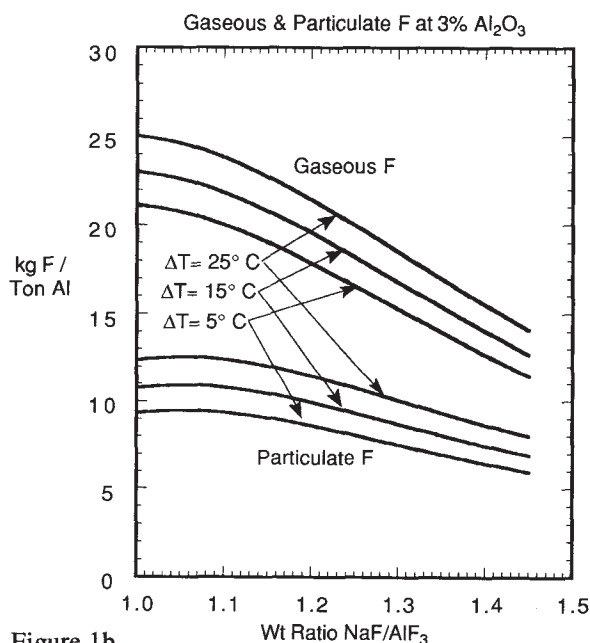


Figure 1b

maximum at 1.07 bath ratio. The previous model predicted for constant superheat, a marked peak in particulate fluoride emission at a bath ratio of 1.15. The difference is a result of the new vapor pressure model, Figure 5.

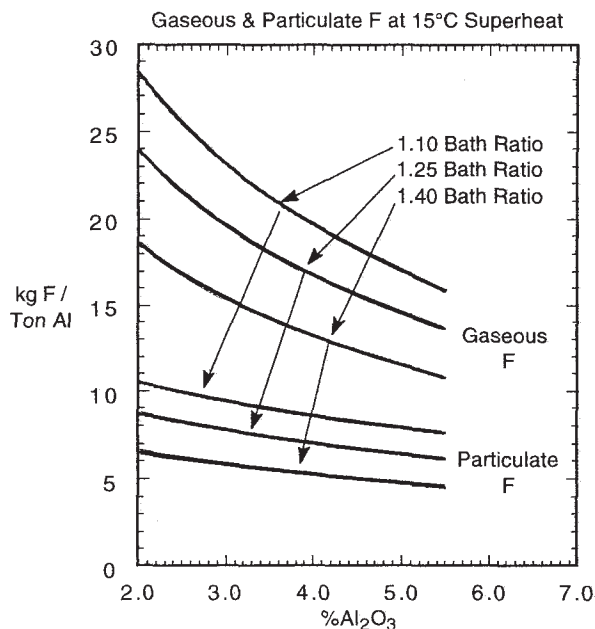


Figure 2

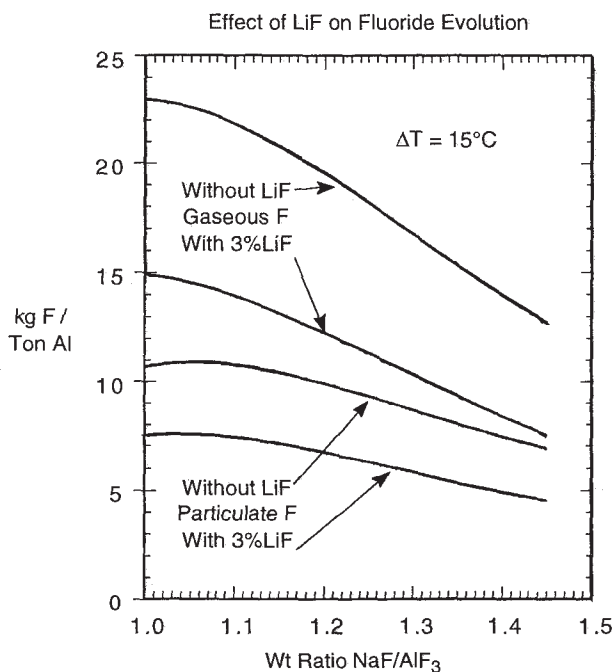


Figure 3

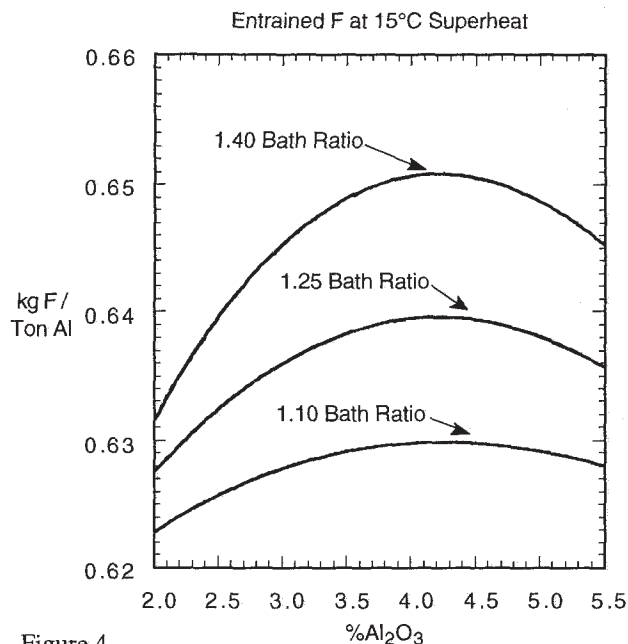


Figure 4

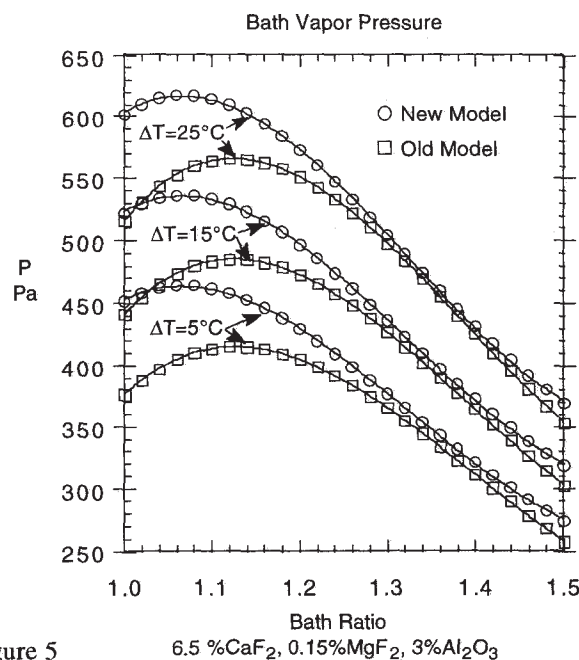


Figure 5

The new model includes hydrolysis of bath vapor by moisture in the air. This was not included in the old model. It converts some particulate to gaseous F. Entrainment of bath in the anode gas is now modeled mathematically based upon surface tension, a major factor in bubble size, and crust integrity. In the previous model it was calculated using a linear regression model. These latter changes produced only minor changes in the predictions.

This new mathematical model is believed to be superior to the 1984 one, but it has been checked only against actual measurements from one cell. The authors hope others will check the model against fluoride evolution measurements from their cells and let them know the degree of agreement or disagreement.

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