

BATH CHEMISTRY CONTROL SYSTEM

David J. Salt

Anglesey Aluminium Metal Limited,
Penrhos Works, P.O. Box 4,
Holyhead, Gwynedd, U.K. LL65 2UJ

Abstract

Bath chemistry of the modern electrolytic cell is dependent on a multitude of variables including alumina composition, cell age, type of break and feed mechanism, type of fume treatment system, cell temperature, bath sampling technique and the analytical precision.

A bath chemistry control system that takes all of the above variables into account has been developed. Deployment of this system has led to a significant improvement in bath chemistry control at Anglesey Aluminium.

Introduction

In order to optimise current efficiency, in addition to optimising the anode cathode distance, it is also important to optimise the bath chemistry.

Natural cryolite $3\text{NaF}\cdot\text{AlF}_3$ has a liquidus temperature of 1010°C . The liquidus temperature is lowered to below 950°C by additions of aluminium fluoride, usually referred to as excess aluminium fluoride, calcium fluoride or fluorspar and aluminium oxide or alumina.

A typical bath composition at AAM Ltd contains:

Calcium fluoride CaF_2	5.0 to 6.0%
Excess aluminium fluoride AlF_3	9.0 to 10.0%
Aluminium oxide Al_2O_3	2.0 to 3.5%
Cryolite $3\text{NaF}\cdot\text{AlF}_3$	balance to 100%

The alumina concentration of the bath is controlled by an adaptive feed strategy. During part of the feed cycle the rate of change of bath resistance is calculated from which the alumina concentration is inferred. The control of the alumina concentration is well known and is not part of the present discussion.

This discussion concerns the control of the fluoride constituents of the bath, in particular the control of ratio of sodium fluoride to aluminium fluoride.

The ratio can be expressed as the weight ratio of sodium fluoride to aluminium fluoride or as the mole ratio of sodium fluoride to aluminium fluoride. It so happens that the weight ratio is exactly half of the

mole ratio because the molecular weight of sodium fluoride (42) is exactly half that of aluminium fluoride (84).

The weight ratio of natural cryolite $3\text{NaF}\cdot\text{AlF}_3$ is therefore 1.50, the mole ratio of course being 3.00.

An alternative mode of expressing the composition is to assume that all the sodium fluoride is present as natural cryolite $3\text{NaF}\cdot\text{AlF}_3$ with weight ratio 1.50 and then aluminium fluoride in excess of that required to make cryolite is referred to simply as excess aluminium fluoride. Excess aluminium fluoride % and weight ratio are related by the equation.

$$\% \text{ Excess AlF}_3 = \frac{2(100 - \% \text{CaF}_2 - \% \text{Al}_2\text{O}_3)(1.50 - \text{Weight Ratio})}{3(1 + \text{Weight Ratio})} \quad (1)$$

Control of Bath Ratio

The control of the weight ratio of sodium fluoride to aluminium fluoride in bath is determined by the rate of sodium absorption into the carbon lining of the cell, the sodium oxide content of the aluminium oxide, the bath temperature, the rate of aluminium fluoride evolution and the amount of aluminium fluoride returned from the exhaust gas scrubbing system.

The accurate analytical determination of bath ratio also relies entirely on the degree of care taken when sampling. Extreme care must be taken to ensure that there is no loss of liquid sample prior to its solidification. Because of fractional crystallisation the liquid always has a lower ratio than the solid with which it is in equilibrium. Any loss of liquid sample, therefore, gives rise to a result which is higher than the true value. Resamples must be taken where results have come back higher than expected.

Sodium absorption by cathode

It is well known that sodium is absorbed into the carbon cathode lining. Initially the rate of absorption is very high such that up to 400Kg of sodium carbonate (soda ash) may be required to be added in the first week of operation.

The soda absorption rate then decreases initially very rapidly ceasing when the cells have reached an age circa, 800 to 1000 days.

During most of a cell's life, basically from circa 30 days to tap out, aluminium fluoride has to be added to maintain a constant ratio because the soda Na_2O in the alumina forms sodium fluoride. The amount of aluminium fluoride required becomes more or less constant after about 800 to 1000 days once the sodium absorption has virtually ceased or reached a constant low level.

The reaction between soda and aluminium fluoride can be expressed by the equation.



also soda ash dissociates into soda and carbon dioxide



where $R = \text{Weight NaF} / \text{Weight AlF}_3$
Hence

$$1.000 \text{ Kg Na}_2\text{CO}_3 = (0.7923/R) + 0.5282\text{Kg AlF}_3 \quad (5)$$

Soda ash additions made in the early part of a cell's life can now be expressed in terms of minus aluminium fluoride additions and hence it is now feasible to show the relationship of aluminium fluoride usage versus pot age for the whole of a cell's life.

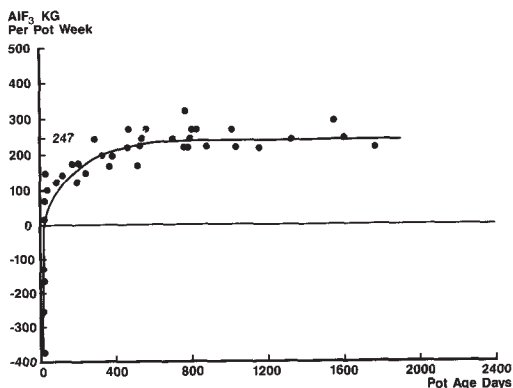


Figure 1: Aluminium fluoride usage versus pot age for half break cell with pure ore.

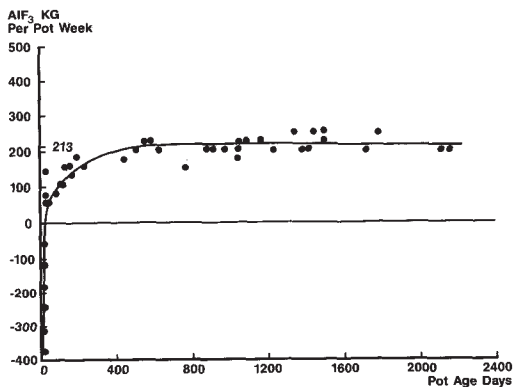


Figure 2: Aluminium fluoride usage versus pot age for half break cell with blend.

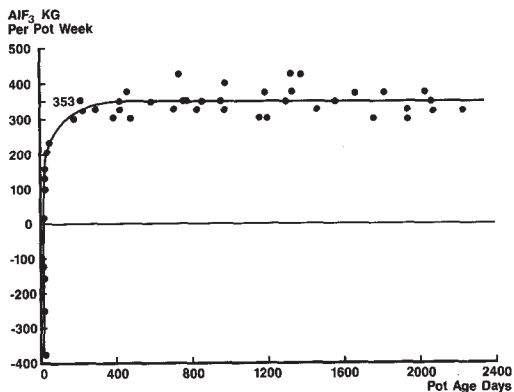


Figure 3: Aluminium fluoride usage versus pot age for point feed cell with pure ore.

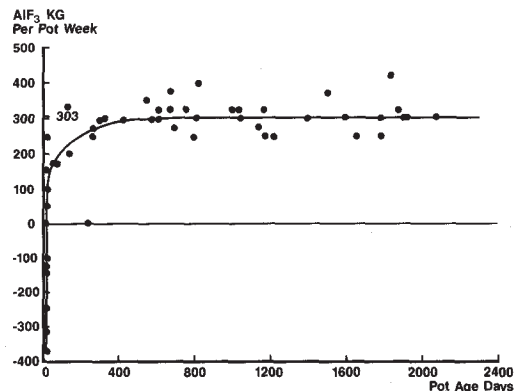


Figure 4: Aluminium fluoride usage versus pot age for point feed cell with blend.

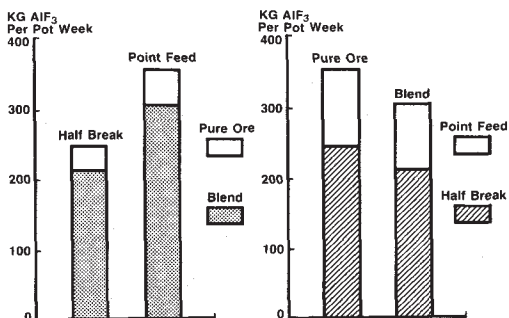
In figures 1 to 4 the aluminium fluoride usage versus pot age is shown for half break cells with pure ore and blend and point feed cells with pure ore and blend. In each case the shape of the curve is the same the only difference being the steady state value reached when soda absorption has virtually ceased. This data can now be used as the basis for calculation of the base addition of sodium carbonate or aluminium fluoride depending on the pot age, for different pot construction and feed types.

Table I Aluminium Fluoride Usage by Cell and Feed Type

		CELL AND FEED TYPE			
		HALF BREAK		POINT FEED	
ORE TYPE		PURE ORE	BLEND	PURE ORE	BLEND
CATCH %			7.3		5.3
CELLS		2B40-77	2A1-39	2A40-77	2A40-77
PERIOD		WK52/88	WK50/88	WK22/89	WK52/88
BATH TEMP DEG C		957	959	957	946
METAL PER POT DAY KG		1151	1107	1191	1159
ORE FACTOR		1.924	1.919	1.901	1.924
Na ₂ O %		0.38	0.38	0.37	0.38
RATIO		1.21	1.13	1.13	1.13
CaO %		0.032	0.039	0.01	0.032
AIF ₃ USAGE	FOR Na ₂ O+CaO	131	131	131	136
KG PER	STEADY STATE	247	213	353	303
POT WEEK	AVERAGE	220	185	345	282
AVERAGE AGE OF SAMPLE DAY		845	847	1099	938

Table 1 summarises the relevant operating parameters pertaining to the data used in figures 1 to 4.

The steady state aluminium fluoride usage is shown by feed type in figure 5a. This shows that when using a blend of alumina and dry scrubber reacted material the usage of aluminium fluoride in both half break and point feed cells is 14 to 15% lower than that required when pure alumina is used. This is because of aluminium fluoride returned from the scrubber.



The steady state aluminium fluoride usage is shown by cell type in figure 5b. This shows that in point feed cells the aluminium fluoride usage is 42 to 43% greater than that required for half break cells irrespective as to whether pure alumina or a blend of alumina and dry scrubber reacted material is used.

Figure 5: Aluminium fluoride usage by feed type. a) feed type b) ore type

Bath Temperature

It is well known that the liquidus temperature of the bath decreases with increasing excess aluminium fluoride i.e. decreasing ratio. Additionally increasing alumina content also decreases the bath liquidus temperature.

Assuming a constant calcium fluoride content the liquidus temperature has been calculated for weight ratios in the range 0.90 to 1.30 for an alumina content of 2.0% (typical minimum) and 3.5% (typical maximum) using the empirical expression:

$$T_{\text{liquidus}} (^{\circ}\text{C}) = 1009.4 + (4.059 \times \% \text{CaF}_2) - (1.167 \times \% \text{CaF}_2^2) + (0.968 \times \% \text{CaF}_2 \times \% \text{AlF}_3) - (0.105 \times \% \text{CaF}_2 \times \% \text{AlF}_3^2) + (0.073 \times \% \text{CaF}_2^2 \times \% \text{AlF}_3) + (0.002 \times \% \text{CaF}_2^2 \times \% \text{AlF}_3^2) - (4.165 \times \% \text{AlF}_3) - (0.054 \times \% \text{AlF}_3^2) - (5.33 \times \% \text{Al}_2\text{O}_3) \quad (6)$$

derived by S.S. Lee, K. Lei, P. Xu and J.J. Brown, Jr. (reference (1)). See figure 6.

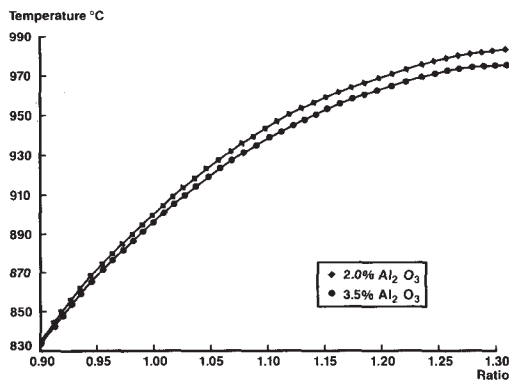


Figure 6: Liquidus temperature versus ratio (calcium fluoride % = 5.5).

Very typically the actual bath temperature is some 8° to 12°C higher than the liquidus temperature and figure 7 shows a typical plot of bath temperature versus ratio based on temperature measured at the time of sampling.

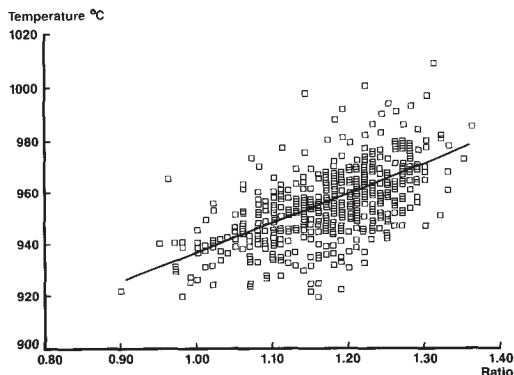


Figure 7: Bath temperature versus ratio.

Because of fractional crystallisation the liquid bath in a cell always has a lower ratio than that of the solid bath (ledge) with which it is in equilibrium. Hence warming a cell will melt some ledge and increase the ratio of the liquid, conversely cooling a cell will decrease the ratio of the liquid. Changing bath temperature therefore changes the ratio of the liquid even though there has been no chemical additions of either aluminium fluoride or soda ash. In any system of control of bath chemistry, and in particular the ratio, it is essential that the bath temperature is known at or about the time of sampling. It is also essential that when defining target ratio the bath temperature is also defined. For example at AAM for half break cells the target ratio is 1.18 ± 0.07 within the temperature range 948° to 968°C.

The bath temperature is taken into account when calculating the number of bags of aluminium fluoride required to bring the ratio back to target. Basically a cell is defined as being cool when bath temperature is more than 10°C below aim, normal when the bath temperature is aim $\pm 10^{\circ}\text{C}$ or warm when the bath temperature is more than 10°C above aim.

Table II Number of bags (25Kg) of aluminium fluoride for ratio adjustment (add to base)

Actual - Target Ratio	Number of Bags of AlF ₃		
	Bath Temperature		
	Cool >10°C Below Aim	Normal Aim $\pm 10^{\circ}\text{C}$	Warm >10°C Above Aim
+0.18 to +0.22		+4	+3
+0.13 to +0.17	+4	+3	+2
+0.08 to +0.12	+3	+2	+1
+0.03 to +0.07	+2	+1	0
-0.02 to +0.02	+1	0	-1
-0.03 to -0.07	0	-1	-2
-0.08 to -0.12	-1	-2	-3
-0.13 to -0.17	-2	-3	-4
-0.18 to -0.22	-3	-4	

	Target Ratio	Aim Temperature °C
Half Break	1.18	958
Point Feed	1.15	952

Table II shows the number of bags of aluminium fluoride that have to be added to bring the ratio back to target. This assumes for example equivalence of 1.13 ratio/<948°C, 1.18 ratio/948 to 968°C and 1.23 ratio/>968°C.

Alumina Composition

The prime reason for the regular addition of aluminium fluoride to control ratio is to compensate for the continuous addition into the bath of sodium oxide from the alumina.

As has been shown earlier the reaction between soda and aluminium fluoride can be expressed by the equation.



Similarly the reaction between calcium oxide and aluminium fluoride can be expressed by the equation.



from equations (2) and (7) the amount of aluminium fluoride required for reaction with the sodium oxide and calcium oxide in the alumina can be calculated.

Aluminium fluoride required for Na₂O and CaO in alumina in Kg per pot week

$$= 7 \times \text{Kg Al per pot day} \times \text{Ore Factor} \times \left(\left(\frac{\%Na_2O}{100} \times 1.355 \right) \times \left(1 + \frac{2R}{3} \right) / R + \left(0.9983 / 100 \times \%CaO \right) \right) \quad (8)$$

The ore factor, weight of ore/weight of metal can be calculated from the chemical analysis of the alumina according to the equation

$$\begin{aligned} & 100 / \left((0.5293 \times (100 - \%SiO_2 - \%Fe_2O_3 - \%ZnO \right. \\ & - \% \text{ Loss on Ignition to } 1000^\circ\text{C} - (0.4516 \times \%Na_2O) \\ & - (0.3940 \times \%CaO)) \left. \right) + (0.4674 \times \%SiO_2) \\ & + (0.6994 \times \%Fe_2O_3) + (0.8034 \times \%ZnO) \end{aligned} \quad (9)$$

Where the alumina equivalent of soda

$$= 0.5484 \times \%Na_2O \text{ (from equation (2))}$$

and the alumina equivalent of lime

$$= 0.6060 \times \%CaO \text{ (from equation (7))}$$

Combining equations (8) and (9) it is now possible to calculate the amount of aluminium fluoride required to react with the soda and lime in the alumina knowing the analysis of the alumina, the metal production rate and the bath ratio.

The aluminium fluoride usage "versus" pot age data given in Figures 1 to 4 assumes a soda content of the alumina of 0.38%. This typically gave an aluminium fluoride usage of around 130 Kg per pot week for soda and lime in alumina.

By calculating the amount of aluminium fluoride required to react with the soda and the lime in the alumina for each new alumina delivery it is now possible to make an adjustment to the base addition based solely on pot age, cell and feed type.

TABLE III. ALUMINA ANALYSIS 1980-89.

ALUMINA TYPE	ALUMINA A	ALUMINA B	ALUMINA C	ALUMINA D	ALUMINA E	ALUMINA F	ALUMINA G	ALUMINA H
ANALYSIS								
%SiO2	0.010	0.010	0.009	0.014	0.013	0.010	0.012	0.015
%Fe2O3	0.013	0.013	0.022	0.018	0.024	0.011	0.016	0.019
%ZnO	0.015	0.010	0.001	0.001	0.001	0.001	0.008	0.001
%Na2O	0.480	0.430	0.340	0.390	0.340	0.330	0.320	0.440
%CaO	0.047	0.027	0.008	0.004	0.018	0.018	0.036	0.040
%MnO	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
%V2O5	0.007	0.001	0.004	0.001	0.002	0.001	0.001	0.004
%TiO2	0.001	0.001	0.001	0.001	0.001	0.004	0.001	0.002
%P2O5	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
LOI 0-300 DEG C	1.280	0.910	0.670	0.810	1.150	1.280	0.820	1.200
LOI 300-1000 DEG C	0.620	0.640	0.530	0.410	0.800	0.490	0.710	0.810
BULK DENSITY LB / CU FT	59.8	61.7	61.2	61.8	59.1	62.1	63.6	62.2
%+150 MICRON	2.9	1.6	0.7	1.1	0.3	6.0	0.5	2.8
%-150+106 MICRON	20.3	21.4	15.6	28.6	8.8	19.0	12.0	9.8
%-106+90 MICRON	17.7	20.8	19.4	19.3	14.9	13.0	23.5	28.2
%-90+75 MICRON	22.1	19.0	23.4	17.8	22.5	18.0	16.5	25.0
%-75+53 MICRON	25.1	19.4	23.6	17.1	31.6	27.0	23.7	17.2
%-53+45 MICRON		6.1	6.1	3.6	9.8	8.0	8.2	9.3
%-45 MICRON	13.2	11.9	11.1	12.5	12.1	9.0	15.7	7.5
%-20 MICRON	1.0	3.0	2.4	3.8	1.0	1.4	3.8	1.5
MEDIAN PARTICLE SIZE MICRON	64.0	86.0	81.0	86.0	75.0	80.0	75.0	84.0
ANGLE OF REPOSE DEG	31.8	30.6	31.1	32.5	32.0		31.2	33.8
% ALPHA AL2O3	19.4	6.8	8.6	4.0	14.8	2.0	13.1	18.5
SURFACE AREA SQ M / GM	64.0	62.7	61.3	4.0	71.7	72.7	58.8	55.5
ATTRITION INDEX	22.8	8.6	13.2	14.2	25.5	10.7	23.0	
CALCULATED VALUES								
ORE FACTOR	1.930	1.923	1.915	1.916	1.930	1.926	1.922	1.932
%CaF2 FROM Na2O AND CaO IN ORE	5.2	3.4	1.3	0.6	2.9	2.9	5.9	4.8
AlF3 KG PER POT WEEK FOR Na2O AND CaO IN ORE	160	140	108	124	111	107	107	146
CRYOLITE KG PER POT WEEK FROM Na2O IN ORE	186	166	131	150	132	128	123	171
CaF2 KG PER POT WEEK FROM CaO IN ORE	10	6	2	1	4	4	8	9
BATH KG PER POT WEEK FROM Na2O AND CaO IN ORE	196	172	132	151	136	131	131	179
%Si IN METAL FROM ORE	0.009	0.009	0.008	0.013	0.012	0.009	0.011	0.014
%Fe IN METAL FROM ORE	0.018	0.017	0.029	0.024	0.032	0.015	0.022	0.026
%Zn IN METAL FROM ORE	0.023	0.015	0.002	0.002	0.002	0.002	0.012	0.002

Table III shows the average analysis for the period 1980-89 of all aluminas used at AAM. The aluminium fluoride usage for the soda and lime in the alumina has been calculated for each ore type. (It should be noted that Alumina A only refers to the period 1980-84 because of plant shut down in 1984). It can be seen that the highest aluminium fluoride requirement is for Aluminas A, B and H. The lowest usage is for Aluminas C, F and G.

Control of Calcium Fluoride

Calcium fluoride concentration is maintained at 5.5 ± 0.5 % on an empirical basis. Additions of calcium fluoride CaF_2 are made if the level of calcium fluoride in the bath is below 5.0% for two consecutive week. The frequency of additions however can be estimated from the calculation of the amount of calcium fluoride produced in the bath originating from the soda and lime in the alumina.

The percentage CaF_2 in the generated bath can be calculated from:

$$\begin{aligned} \% \text{CaF}_2 \text{ in bath} = & (1.392 \times \% \text{CaO} \times 100) / ((1.392 \times \% \text{CaO}) \\ & + (1.355 \times ((1+R)/R) \times \% \text{Na}_2\text{O}) \quad (10) \end{aligned}$$

Table III shows that the highest calcium fluoride generation rate is with Aluminas A, G and H and lowest generation rate is with Aluminas C and D. Frequent fluorspar additions are required when Aluminas C and D are used.

Conclusion

A knowledge of the historical usage of aluminium fluoride/soda ash versus pot age for different feeding modes and different types of feed (pure ore versus blend) coupled with a knowledge of the bath temperature when the bath sample is taken and the analysis of the alumina in use allows accurate calculation of aluminium fluoride and soda ash additions. The calculation of the amount of calcium fluoride in the generated bath gives an indication of the frequency additions of calcium fluoride.

References

1. S.S. Lee, K. Lei, P. Xu and J.J. Brown, Jr., "Determination of Melting Temperatures and Al_2O_3 Solubilities for Hall Cell Electrolyte Compositions", *Light Metals*, 1984, 841-855.