

Light Metals

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FACTORS AFFECTING FLUORIDE EVOLUTION FROM

Introduction

HALL-HEROULT SMELTING CELLS

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Abstract

Measurements of Hall cell primary fluoride evolution were made over a nine-month period from 1975 December to 1976 August on two smelting pots at Alcoa's Badin, N.C. Works. Observation of primary pot fluoride evolution was made for thirteen 48-hour periods and correlated with process operating parameters, ambient conditions, and raw material composition. Variations in those parameters which are controllable were intentionally introduced and parameters which were not controllable were measured. The resulting equation relating total primary fluoride evolution to operating and raw material parameters for blended alumina and aluminum fluoride feed was as follows: (total primary F evolution, kg/tonne Al) = $-158.5 - 54$ (bath NaF/AlF₃ weight ratio) + 0.244 (bath temperature, C) + 3.77 (ambient partial pressure of water, kPa) + 3.62 (alumina water content, %) - 1.29 (bath alumina content, %) + 0.35 (bath calcium fluoride content, %) + 13.5 (anode effect) - 2.6 (track) + 3.79 (hand fluoride addition) + 9.64 (average anode hydrogen content, %) in which (anode effect) is 1 if an anode effect is occurring and 0 otherwise, (track) is 1 if a track (interruption of alumina feed for feed rate adjustment) is occurring and 0 otherwise, and (hand fluoride addition) is 1 if aluminum fluoride is being added by hand and 0 otherwise.

Previous studies of fluoride evolution from aluminum reduction cells (1,2,3) treat only a few of the important parameters. Reliable data are needed on dependence of fluoride evolution (and, indirectly, emission) on process variable changes in a Hall-Heroult cell. Accordingly, a project (of Badin Works, the Health & Environment Department, Pittsburgh Environmental Engineering, and the Alcoa Laboratories) was undertaken to identify the most promising means for reduction of potroom fluoride emission through process control.

Measurements of primary fluoride evolution were carried out at Alcoa's Badin, NC Works between 1975 December and 1976 August individually on two reduction cells. Parameters expected to affect the evolution were controlled where possible and measured for developing regressions relating evolution to the parameters of the process. A total of thirteen 48-hour observations were made.

Primary evolution of fluoride expresses the amount of fluoride lost by the bath to the hooded area above it. Secondary emission of fluoride is that amount which escapes directly from the potrooms to the environment. The relationship between primary evolution and secondary fluoride emission from the cells to the environment has been named "capture efficiency." This is the fraction of the fluoride evolved by the bath which is subsequently caught by the hooding system during normal operation. The rest of the fume escapes into the potroom atmosphere and ultimately outside.

Previous Studies

Studies of commercial or pilot Hall-Heroult cells (1,2,3) have addressed only a few of the variables affecting fluoride evolution. Grjotheim et al (4) reviewed the results and presented conclusions from the data available in 1972.

Average curves for fluoride evolution from Solntsev (1) and Henry (2) are shown with data from this study in Figure 1 for different bath NaF/AlF₃ ratios at a fixed 15 C delta T (difference between operating and liquidus temperatures). Extrapolations have been made to allow direct comparison. There are significant differences between this study and previous studies in the areas of amount of particulate fluoride generation, overall evolution level, amount of entrainment, and influence of NaF/AlF₃ ratio, bath temperature, and hydrogen sources on evolution.

Experimental Procedure

Control Technique

A primary objective of this investigation was to quantify the effect of lower NaF/AlF₃ ratios on evolution. With the exception of NaF/AlF₃ ratio and anode hydrogen content, parameters of interest were allowed to fluctuate normally and

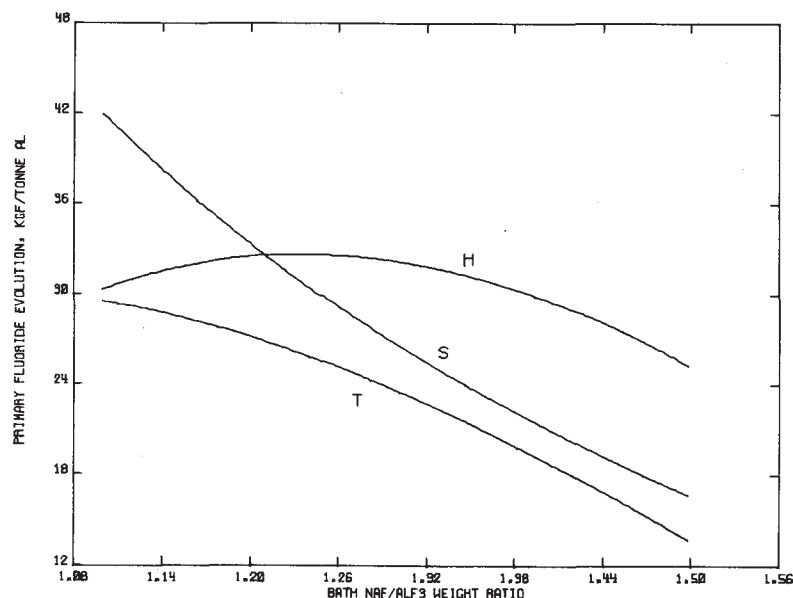


Figure 1. Fluoride Evolution Predictions vs NaF/AlF₃ Ratio for Delta T = 15C
S=Soltsev(1) H=Henry(2) T=This Work

recorded. Anode hydrocarbon content was controlled by selecting anodes from different baking furnace pit locations with temperatures shown to produce variations in hydrocarbon content (5).

Sampling Technique

Sampling of cell gas flow rate, temperature, and offgas fluoride content was made in the exhaust duct just past the elbow above the cell. Gaseous fluoride values were measured continuously by the Alcoa gaseous fluoride analyzer (6). Particulate fluoride samples were obtained from an automatic tape sampler for the first nine tests and a sequential automatic thimble sampler for the last three tests. Fluoride content of the samples collected over 30-minute periods was determined by a semi-automatic technique (Technicon Auto-analyzer). Comparison measurements with Alcoa Standard Method 4075A (6) were made on both systems and calibration factors developed to translate the measured values to 4075A values. The fluoride values were correlated with measured ambient air conditions, bath composition, alumina LOI (fractional weight loss on ignition from 300 to 1200 C) and moisture (fractional weight loss on heating to 300 C) content, anode hydrogen content, bath temperature, and unusual events (anode effects, tracks (interruptions of alumina feed for feed rate adjustment), and additions of aluminum fluoride by hand).

A diagram of the sampling scheme is shown in Figure 2. Bath samples were taken every 2 hours and analyzed for NaF/AlF₃ weight ratio, alumina content, calcium fluoride content, and magnesium fluoride content. The spread in magnesium fluoride content was quite small; therefore, these values were not used. The same is also nearly true for calcium fluoride content and so the predicted values for its effect are erratic.

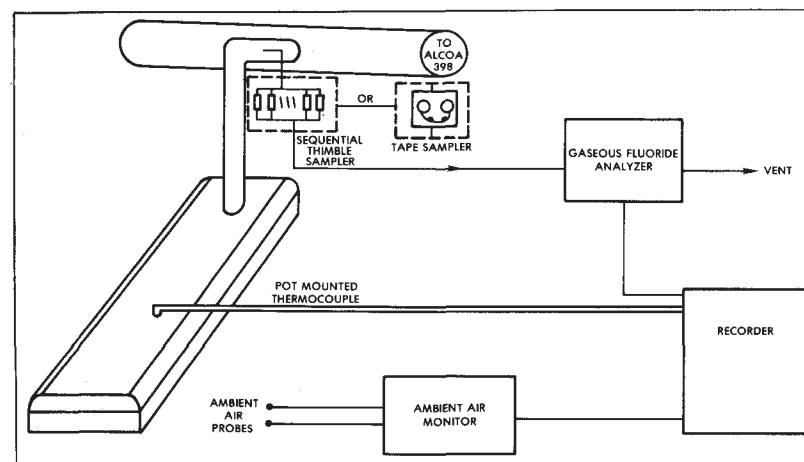


Figure 2. Schematic Diagram of Measuring System

Samples of alumina fed to the pot were taken every 4 hours and LOI and moisture levels determined for each sample. It was found that there was a strong correlation between moisture and LOI, so only the sum of the two was used in the final analysis. This sum represents approximately the total fraction of water in the alumina. Bath temperature was measured continuously with a chromel-alumel thermocouple protected by a KT-silicon carbide sheath immersed in the bath at the center of the cell.

Ambient absolute humidity and temperature were measured continuously with a lithium chloride probe and a thermocouple, respectively. The lithium chloride probe was calibrated to a sling psychrometer. Ambient temperature had little effect on evolution and was not included in the final analysis.

A sample chip was removed from each new anode before it was set in the cell and analyzed for hydrogen (hydrocarbon) content. The average hydrogen content of all 24 anodes in the cell at any time was used as the analysis variable. Gas flow in the duct was measured with a Stauscheibe pitot tube which was set at the average point of a traverse. Gas flow was corrected to normal conditions (25 C, 101.3 kPa) using duct gas temperature measured with a thermocouple.

Results

Refer to Appendix I for detailed discussion of relevant statistical definitions.

As a result of the large variability due to unmonitored influences, many observations are flagged as "outliers" by the regression program. Two approaches were used to deaccentuate these outliers. The first was to simply delete them and ultimately arrive at a regression in which no outliers were flagged. This was relatively unsuccessful with these data. All the points relating to hand fluoride additions were deleted in this process (despite the presence of the indicator variable to select them) and, in one case, a set of correlated independent variables was produced from which it was not possible to obtain a regression. Therefore, an alternative procedure called "robust regression" was employed. This procedure does not completely eliminate outlier data points but assigns them lower weight than the central mass of data. In most cases, there was little difference between the ordinary (uniform weight) regression and the robust regression results. Both results are quoted in this paper because outliers may be the result of poor measurement or may be truly meaningful data.

Regressions to predict evolution rate are quoted in Table I. In addition to the regressions listed in Table I, several other techniques were tried to account for or remove the unreasonable negative character of the coefficient of anode hydrogen content. These included the introduction of additional indicator variables and of cross terms. All were unsuccessful. In an attempt to remove the large bath ratio - bath temperature autocorrelation (this reflects the fact that they strongly influence each other), a procedure called "ridge regression" was tried. Its results were not dramatically different from those presented here.

The equation for the robust regression which predicts total evolution is represented in the second column of Table I. This is probably the most significant column in the table as its regression predicts the total evolution rate and its coefficient for anode hydrogen is positive. (It should be pointed out that the t-values for the standard and robust regression coefficients of anode hydrogen (-0.1 and +0.3, respectively) are so small that the true value of the coefficient is near zero. Thus, a negative coefficient, while not physically reasonable, is not surprising. The true value of the coefficient is probably positive, but small.) This is Equation (2) below. Note that evolution rate in g/min can be converted to "specific evolution" in kg F/tonne Al by multiplying by 105/CE, where CE is cell current efficiency in %.

Table II presents regressions to predict "specific evolution" (evolution per unit metal produced, Kg F/tonne Al). Due to difficulty in determining production rates for a single cell in 48 hours, the production rates were determined using a computer program to predict current efficiencies from the measured operating parameters. This program was previously correlated to long term average production rates. Due to measurement error and

TABLE I. Evolution Rate Regressions (Evolution in g F/min.)

	Total		Gaseous		Particulate	
	Standard	Robust	Standard	Robust	Standard	Robust
r ² , %	61.8	61.2	60.9	59.9	45.4	44.4
r ² (d.f.), %	60.3	59.7	59.3	58.3	43.2	42.2
Constant	-143.06	-132.69	-85.99	-85.66	-57.07	-47.03
t-value	-2.7	-2.8	-2.2	-2.2	-2.7	-2.7
Coef. of Ratio	-51.88	-50.24	-32.28	-32.04	-19.60	-18.20
t-value	-5.7	-6.1	-4.6	-4.8	-5.4	-5.9
Coef. of Bath Temp., C	.2237	.2093	.1399	.1375	.0838	.0718
t-value	3.7	3.9	3.0	3.1	3.5	3.6
Coef. of Amb. Abs. Hum., kPa	3.432	3.348	2.983	2.897	.449	.451
t-value	5.3	5.7	6.0	6.1	1.7	2.1
Coef. of Alumina (LOI + moisture), %	2.995	2.967	2.385	2.393	.611	.574
t-value	6.3	7.0	6.5	6.9	3.2	3.6
Coef. of Alumina Content, %	-1.132	-1.189	-.5948	-.6312	-.538	-.558
t-value	-3.3	-3.9	-2.3	-2.5	-3.9	-4.9
Coef. of CaF ₂ Content, %	.3765	.601	.042	.256	.334	.345
t-value	0.2	0.4	0.0	0.2	0.4	0.5
Coef. of Anode Effect +	12.05	11.49	8.098	7.707	3.948	3.786
t-value	4.5	4.8	3.9	3.9	3.7	4.2
Coef. of Track +	-2.037	-2.037	-2.514	-2.485	.477	.448
t-value	-2.0	-2.2	-3.2	-3.3	1.2	1.3
Coef. of Fluoride Addition +	3.252	3.269	3.810	3.970	-.559	-.701
t-value	0.9	1.0	1.4	1.5	-0.4	-0.6
Coef. of Anode Hydrogen, %	-1.499	7.099	-18.84	-10.15	17.35	17.26
t-value	-0.1	0.3	-1.0	-0.5	1.7	2.0

+ 0 = no, 1 = yes (see Appendix I)

TABLE II. Specific Evolution Regressions
(Evolution in kg F/tonne Al)

	Total		Gaseous		Particulate	
	Standard	Robust	Standard	Robust	Standard	Robust
r ² , %	59.6	58.9	58.6	57.5	43.7	42.6
r ² (d.f.), %	58.1	57.3	57.0	55.8	41.5	40.3
Constant	-158.46	-149.09	-95.49	-96.95	-63.00	-52.17
t-value	-2.7	-2.7	-2.1	-2.2	-2.6	-2.6
Coef. of Ratio	-54.02	-52.54	-32.73	-32.73	-21.30	-19.82
t-value	-5.2	-5.5	-4.1	-4.2	-5.1	-5.7
Coef. of Bath Temp., C	.2436	.2301	.1517	.1511	.0920	.0791
t-value	3.5	3.7	2.9	2.9	3.3	3.4
Coef. of Amb. Abs. Hum., kPa	3.767	3.666	3.303	3.203	.4636	4.633
t-value	5.0	5.3	5.7	5.7	1.5	1.8
Coef. of Alumina (LOI + moisture), %	3.619	3.589	2.887	2.898	.7326	.6916
t-value	6.6	7.3	6.9	7.1	3.4	3.8
Coef. of Alumina Content, %	-1.292	-1.358	-.6676	-.7109	-.6245	-.6476
t-value	-3.3	-3.8	-2.2	-2.4	-4.0	-4.9
Coef. of CaF ₂ Content, %	.3529	.6247	-.0280	.2244	.3800	.4000
t-value	0.2	0.3	-0.0	0.1	0.4	0.5
Coef. of Anode Effect +	13.539	12.921	9.010	8.582	4.524	4.335
t-value	4.4	4.6	3.8	3.7	3.7	4.2
Coef. of Track +	-2.598	-2.598	-3.114	-3.077	.5163	.4798
t-value	-2.2	-2.4	-3.4	-3.5	1.1	1.2
Coef. of Fluoride Addition +	3.794	3.795	4.376	4.541	-.5874	-.7514
t-value	0.9	1.0	1.4	1.5	-0.3	-0.5
Coef. of Anode Hydrogen, %	9.643	19.93	-13.16	-2.834	22.79	22.76
t-value	0.3	0.7	-0.6	-0.1	1.9	2.3

+ 0 = no, 1 = yes (see Appendix I)

to the wide variation of NaF/AlF₃ ratio in these tests, a few cases occurred in which the progPam predicted a frozen or over-insulated cell. Anode effects are also predicted by the program when they did, in fact, occur. These extraordinary conditions were included in the regressions unless the predicted anode-cathode distance was less than 1.27 cm (0.5 in.). It was felt that the current efficiencies might not be reasonable for such small anode-cathode separations. Note that the signs of all the coefficients in both the standard and robust regressions of total specific evolution are the same. Thus, either could be used, but there are fewer uncertainties associated with the standard regression. It is therefore quoted in the abstract and as Equation (1) below.

Table III lists the regression results for total evolution rate for three tests for which anode bridge movement data were collected. Step movements executed by the anode bridge motor were totalled for 6-hour periods. This motor moves all the anodes in the vertical direction and probably damages the crust each time. Approximately 4% of the total variation₂ is accounted for by anode bridge movement. Note also that the r² and r² (d.f.) values for these regressions are low. This would lead one to conclude that anode bridge movements are not significant in determining evolution. Data on anode bridge movement was not available during other tests. No hand fluoride additions were made during these tests and so no coefficient for that variable appears.

Conclusions

The following two equations were felt to be the best of those developed to describe evolution. They apply to cells fed with blended alumina and aluminum fluoride. The first gives "specific evolution" (referenced to production) and the second gives evolution per unit time.

$$\begin{aligned} & \text{(Total primary fluoride evolution, kg F/tonne Al) =} \\ & -158.5 - 54 \text{ (bath ratio) + } 0.244 \text{ (bath temperature, C)} \\ & + 3.77 \text{ (ambient partial pressure of water, kPa) + } 3.62 \\ & \text{(alumina (LOI + moisture), \%)} - 1.29 \text{ (bath alumina} \end{aligned} \tag{1}$$

$$\begin{aligned} & \text{(Total primary fluoride evolution from a 170 KA cell,} \\ & \text{g F/min/cell) =} \\ & -132.7 - 50.2 \text{ (bath ratio) + } 0.209 \text{ (bath temperature, C)} \\ & + 3.35 \text{ (ambient partial pressure of water, kPa) + } 2.97 \\ & \text{(alumina (LOI + moisture), \%)} - 1.19 \text{ (bath alumina} \end{aligned} \tag{2}$$

TABLE III. Total Evolution Rate Regressions Including Anode Bridge Movement Evolution Rate in g F/min.

	Standard	Robust
$r^2, \%$	42.9	41.7
$r^2(\text{d.f.}), \%$	34.3	33.0
Constant	63.43	90.15
t-value	1.0	1.7
Coef. of Ratio	2.843	8.162
t-value	0.2	0.7
Coef. of Bath Temperature, C	-.0271	-.0578
t-value	-0.4	-0.9
Coef. of Ambient Absolute Humidity, kPa	2.454	2.725
t-value	2.0	2.6
Coef. of Alumina (LOI + moisture), %	3.483	3.746
t-value	2.7	3.5
Coef. of Alumina Content, %	-1.287	-1.193
t-value	-2.1	-2.3
Coef. of CaF_2 Content, %	-1.853	-2.478
t-value	-0.4	-0.6
Coef. of Anode Effect*	15.75	16.66
t-value	3.4	4.2
Coef. of Track*	-2.923	-2.762
t-value	-2.2	-2.5
Coef. of Anode Hydrogen, %	-109.33	-120.26
t-value	-1.5	-1.9
Coef. of Anode Bridge Moves	.0306	.0241
t-value	0.5	0.5

* 0 = no, 1 = yes (see Appendix I)

+ Totalled for 6 hour periods

The (track), (anode effect), and (hand fluoride addition) variables assume values of 0 or 1. They assume 1 if the indicated operation is occurring (see Appendix I for further discussion) and 0 if not.

Anode bridge movements were also studied in relation to primary evolution in Tests 5, 6, and 7. Less than 5% of the observed variation was attributed to anode bridge movement. The crust integrity is no doubt significant in determining evolution, but anode bridge movement is not the only variable which affects it.

Figures 3 and 4 plot the influence of NaF/AlF_3 ratio and bath alumina content in the standard regression for total specific evolution in Table II (Equation 1).

Discussion

Mechanism of Evolution

This section will focus on the regressions quoted in Table I in an effort to provide understanding of the mechanism of fluoride evolution. Since the distinction between gaseous and particulate evolution is blurred by two processes which can convert one to the other (namely, adsorption of HF onto alumina and hydrolysis of particles to HF by water in the air), the main consideration here will be total evolution. The robust regression from Table I will be used since it gives results whose coefficient of anode hydrogen content is more reasonable.

Several mechanisms exist which can cause loss of fluoride-bearing material from the bath: (1) vaporization of bath, either directly into the air sweep or into the anode gases; (2) entrainment of bath droplets by the air sweep or anode gas; (3) direct hydrolysis of bath to HF by hydrogen (as water or hydrocarbon) entering the bath from (a) alumina, (b) anode carbon, and (c) air sweep; (4) direct fluoridation of anode carbon which apparently occurs only during anode effects; and (5) direct entrainment of feed material. Calculation of the amount of F attributable to all the submechanisms of (3) is possible from the regression coefficients in Table I if a few assumptions are made. The contribution of mechanism (2) cannot be determined from Table I but separate measurements of calcium levels in particulate provide a basis for calculating it. Calcium has no volatile compounds at bath temperature and can only be taken up in the offgas by entrainment. Mechanism (4) will be assumed negligible during the bulk of pot operation and mechanism (5), which is not easily measured, will be ignored. Thus, the contribution of mechanism (1) can be determined by difference. This difference will be compared with the values predicted by vaporization into saturated anode gas alone.

Table IV lists raw material requirements for the Badin P155A cell design and some other pertinent information about the P155A. These data were used to calculate the contribution of mechanism (3). Hydrogen entering the cell is expressed as water equivalent

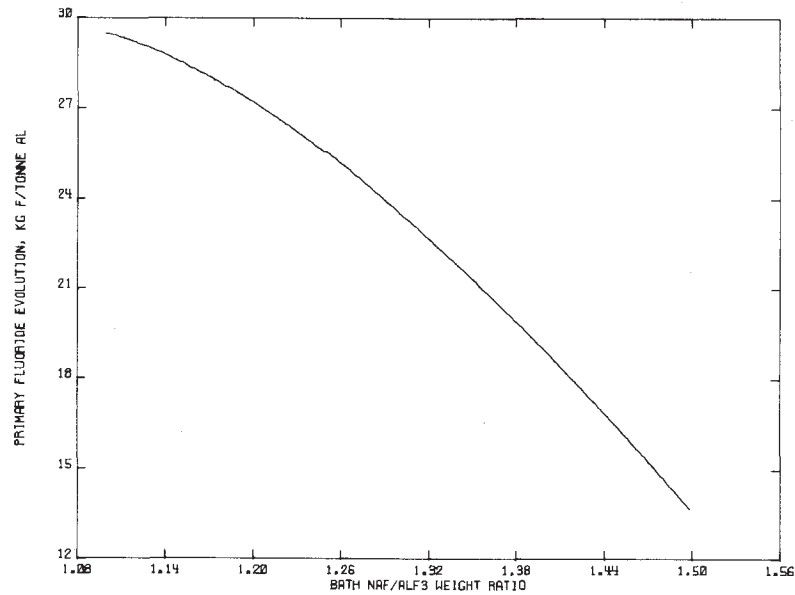


Figure 3. Eq. 1 F-Evolution vs NaF/AlF₃ Ratio for Delta T = 15C
Other Variables Fixed at Means

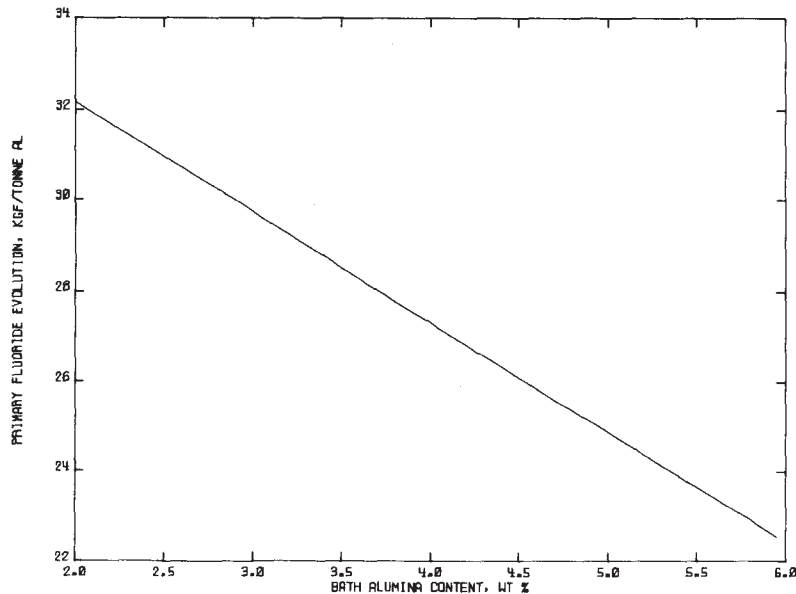


Figure 4. Eq. 1 F-Evolution vs Bath Alumina Content for
Delta T = 15C Other Variables Fixed at Means

TABLE IV. Average Raw Material Requirements for P155A Hall Cell

Current	170,000 A
Alumina	1640 g/min
Anode Carbon	435 g/min
Air Sweep	85 m ³ /min (3000 ft ³ /min) @30 C
Alumina (LOI + moisture)	2.8%
Alumina Water	46 g/min F equivalent 97 g/min
Anode Hydrogen Content	.093%
Anode Hydrogen as Water	3.6 g/min F equivalent 7.6 g/min
Pressure of Water in Air	1.41 kPa
Barometric Pressure at 500 ft Elevation	99.6 kPa
Weight of Air Sweep	98.8 kg/min
Weight of Water in Air Sweep	871 g/min F equivalent 1839 g/min
Anode Gas Volume Produced	2.47 m ³ /min @950 C 0.60 m ³ /min @25 C

which is converted to F (as HF) equivalent on the same line of the table. Note that the cell is far over-supplied with hydrogen for the amount of HF given off. Enough hydrogen to make 1944 g/min of F is taken in whereas the actual total evolution is 24.3 g F/min.

Table V lists the fractions of hydrogen taken in from the three main sources that are converted to HF calculated from the regression coefficients. These "incremental conversion fractions" express the amount of conversion of a small amount of extra hydrogen added when the system is running at near its average hydrogen intake. It is assumed that these conversion fractions apply to all the hydrogen taken in. Using the data in Table V, one can then calculate the amount of F from each source separately. These values are listed in Table VI.

The total for mechanism (3) is then 13.69 g F/min. Measurements of CaF₂ in offgas compared to CaF₂ levels in the bath indicate that entrainment accounts here for 2.5% of the total F or 0.61 g F/min for mechanism (2). Mechanisms (4) and (5) are ignored. Thus, mechanism (1) is responsible for 10.0 g F/min of evolution. These results are summarized and broken into percentage fractions in Table VII.

TABLE V. Fractions of Incoming Hydrogen Converted to HF

Source	Fraction
Alumina	8.6 %
Anode Carbon	8.7 %
Air Sweep	0.26%

TABLE VI. F from Hydrogen Sources Directly

Source	Evolution Rate, g F/min
Alumina	8.31
Anode Carbon	0.66
Air Sweep	4.72
Total	13.69

TABLE VII. HF Source Breakdown

Mechanism Number	Source	Evolution Rate g F/min	Fraction
1	Vaporization	10.0	41 %
2	Bath Entrainment	0.6	2.5%
3a	Alumina Hydrolysis	8.3	34 %
3b	Anode Hydrolysis	0.7	2.9%
3c	Air Hydrolysis	4.7	19 %
4	Anode Fluoridation	--	--
5	Feed Entrainment	--	--

The figure of 10.0 g F/min in Table VII obtained by differencing the other mechanisms from the total evolution rate can be compared with the value of vaporization predicted by consideration of vaporization into dry anode gas only; the NaAlF_4 vapor pressure is 2.24 mm Hg or 0.299 kPa at the average bath composition and temperature of the tests. The anode gas volume is about 2.5 m³/min at 950 C. Therefore, NaAlF_4 is vaporized at a rate of 9.25 g/min, equivalent to 5.58 g F/min in saturated anode gas. There is a difference of 4.42 g F/min between the predicted figure and that obtained by difference in Table VII.

One means of explaining this difference is to postulate direct contact between the bath and the air sweep. This is consistent with the observation of correlation between ambient humidity and total evolution rate since the air must contact the bath directly if its composition is to influence the total evolution. Since 0.26% of the air sweep hydrogen is converted to HF, one may assume that about 0.6% of the air sweep volume

contacts the bath. (Equilibrium conversion of H₂O to HF is 40% complete for the test conditions (7)). This gives an additional vaporization volume of 0.51 m³/min at 30 C or 2.1 m³/min at 950 C which allows for the vaporization of an additional 4.6 g/min of F equivalent, bringing the predicted total to 10.2 g/min of F. There is then a possibility that 0.6% (or more if equilibrium conversion is not attained) of the intake air does contact the bath. Solid bath may contribute vaporization and hydrolysis products. Also, this data is averaged over times when the crust was broken for cell working.

A possible alternative explanation is that ambient humidity influences alumina moisture content. Since alumina moisture content was included in the regression, this influence should already have been accounted for. However, a separate regression between alumina (LOI + moisture) and ambient partial pressure of water was made and gave the equation

$$(\text{Alumina (LOI + moisture, \%)})) = 2.1 + 0.49 (\text{ambient partial pressure of water, kPa})$$

Using the listed effect of alumina (LOI + moisture), 3.6 kg F/(tonne Al-%), one can calculate that a 1 kPa increase in ambient partial pressure of water would cause a 0.49% increase in moisture content, which would raise evolution by 1.8 kg F/tonne Al. The corresponding regression coefficient indicates that a 1 kPa increase in ambient partial pressure of water brings about an increase of 3.8 kg F/tonne Al. Thus, 50% of the observed effect may be accounted for in this way.

According to Table V, 91.4% of the alumina water and 91.3% of the anode hydrogen is not converted to HF. At equilibrium, about 40% (7) of either should convert assuming oxidation of the hydrocarbon to water. The most reasonable explanation here is that the kinetics of the conversion are sluggish compared to the rate of removal by the anode gas and air sweep.

Thus, the picture of evolution which emerges is rather complex, involving all the mechanisms to some degree except possibly bath entrainment, anode fluoridation, feed entrainment, and anode hydrolysis. Vaporization takes place into anode gas and into the air sweep directly and hydrolysis by the air sweep and the ore are significant.

Other Discussion

Table I shows a more pronounced effect of all the variables on gaseous evolution than on particulate evolution with the possible exception of anode hydrogen. However, particulate evolution is only 25% as large as gaseous evolution so the fractional effect of many of the variables on particulate evolution is as large or larger than the corresponding fractional effects on gaseous evolution. The bath alumina content seems to have about equal effect on both types of evolution which may be due to some residual influence of anode effect which was not

Appendix IDefinitions

In several of the tables, "weight %" has been abbreviated to "%" when referring to composition variables.

Three "indicator variables" were included in the data analysis. Indicator variables are used to mathematically code statements about the conditions prevailing at a given time which are not numerical in nature. These are usually "yes/no" type statements and so the variables associated with them assume two values, one for "yes" and one for "no." It is usual practice to use 1 and 0 for these, respectively. If this is done, then the regression coefficient of the indicator variable is the difference in evolution between a "yes" and a "no" condition, other things being equal. Three "yes/no" variables are included here, (track), (anode effect), and (hand fluoride addition). When any of these assumes 1 as its value, it signifies that the condition named is occurring.

The primary purpose for inclusion of these indicator variables was to allow the regression to separate out the exceptional conditions known to affect evolution and thereby obtain a relation representative of normal operation (all three "yes/no" variables equal to 0 or "no"). However, useful information can be obtained from the regression coefficients of these variables. In interpreting these coefficients, however, one must bear in mind the nature of the system they attempt to represent.

The effects of an anode effect, track, or hand fluoride addition are not uniform with time. An anode effect, for instance, produces a rather sharp, symmetrical peak, whereas a track produces first a drop and then a partially-compensating rise in evolution.

Since the primary objective was to separate out the data which was in any degree affected by these unusual conditions, the appropriate indicator variables were set to 1 throughout the occurrence of the condition with a little extra leeway on each side. This situation is graphically illustrated in Figure 5 for an anode effect.

With this arrangement, the regression coefficient of (anode effect) does not represent the evolution peak height. It represents the difference between normal and anode effect operation averaged over the period during which (anode effect) was 1. The same is true of (track) and (hand fluoride addition) as well. The time spans for these variables were as follows:

removed by the anode effect variable. The increase in particulate evolution due to a track is reasonable since fast feeding releases much dust. However, the negative coefficient of hand fluoride addition is unreasonable and must result from random error. The large difference in anode hydrogen influence is probably also the result of random error.

Table III represents a very small portion of the data and is presented here only to illustrate the effect of anode bridge moves. Anode bridge movement accounts for about 4% of the observed variation in total evolution. Hence, bridge movement does not account for the remaining 40% of the variation which is unexplained by the regressions. Undoubtedly, some of this variation is due to crust integrity variations, but more factors than anode bridge movement contribute to crust integrity.

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<u>Variable</u>	<u>Time Span</u>
(anode effect)	The center of the anode effect \pm 30 minutes; 60 minute total
(track)	Starts at computer-logged start of track and continues for 2 hours after completion of track (the aftereffects of a track are long-lived); average total 3.6 hours
(hand fluoride addition)	Starts 15 minutes before (to allow for timing error - these values are hand-logged) and continues for 30 minutes after the addition; 45 minutes total

equation. The $r^2(\text{d.f.})$ is an attempt to compensate for the inherent variability introduced when new terms are added to the equation (more independent variables considered). $r^2(\text{d.f.})$ is, in principle, a more realistic number than r^2 for a 12-term equation; however, the method used to obtain $r^2(\text{d.f.})$ is only approximate. Therefore, both values are given.

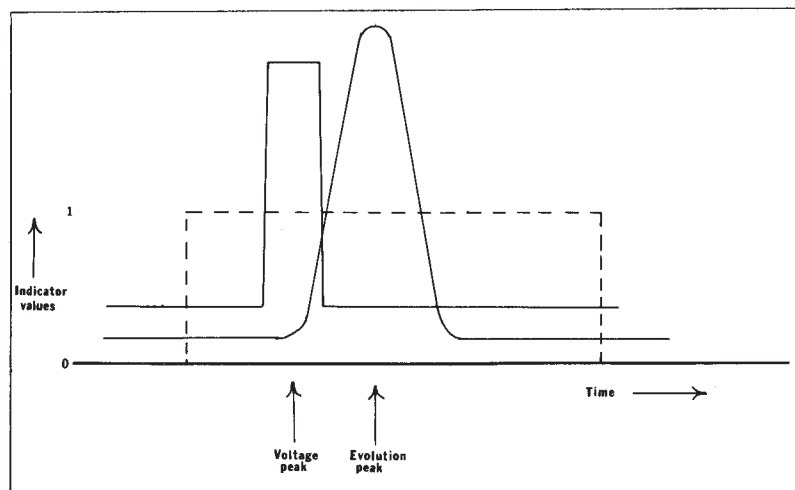


Figure 5. Relationships During Anode Effect

A useful interpretation of the regression coefficients of these variables is obtained by multiplying the regression coefficient by the appropriate time span. The result is the total amount of excess evolution created by the event (for (track) this product is negative, signaling a net decrease in evolution). Thus, the regression coefficient of (anode effect) in Equation (2) is $11.5 \text{ g/min} \times 60 \text{ min}$ (total time span for (anode effect)) = 690 g additional fluoride evolved for the average anode effect. Corresponding values are -441 g F for the average track and 147 g F for the average hand fluoride addition.

In the tables which represent the results of the analysis, several terms are used which may require definition. The "t-value" listed is the ratio of each regression coefficient to its estimated standard error. This is the familiar "student's t" test for significance. r^2 and $r^2(\text{d.f.})$ are the amount of the observed variation in the data which is accounted for by the