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EFFECT OF OPEN HOLES IN THE CRUST ON GASEOUS FLUORIDE EVOLUTION FROM POTS

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Abstract

Changes in fluoride evolution from aluminum smelting pots have direct consequences on pot gas scrubber loads and resultant smelter emissions. Changes in fluoride evolution can also have dramatic implications on bath chemistry control and the resulting pot performance. Both of these factors motivate continuing efforts to quantify the effect of pot operating practices on fluoride evolution in order to prioritize the amount of effort to place on any given practice to minimize fluoride evolution. Gaseous fluoride evolution measurements were made at several smelters and demonstrate a strong correlation between the amount of gaseous fluoride evolved from an individual pot and the total area of open holes in the crust. Data from pots of different types suggest that it is possible to normalize the data to allow predictions for other pot sizes and geometries. In almost every case, the additional fluorides lost due to holes in the crust comprise the largest fraction of the total gaseous evolution.

Introduction

Measurements made in the early 1980's by Alcoa demonstrated the qualitative importance of certain pot practices on fluoride evolution from the pots [1, 2]. In particular, the importance of crust integrity (open holes in the crust) in minimizing the fluoride evolution from the pot was well recognized [3]. Although this has been generally appreciated for a long time, the quantitative functional dependence of fluoride evolution on open hole area was not measured or known.

Recent advances in instrumentation have made many measurements easier and more accurate than those in the past, which relied on wet chemical methods. These wet chemical techniques were difficult and expensive to maintain or operate, requiring the full time attention of a highly trained technician to obtain adequate accurate and precise results. Instrument drift made frequent calibrations necessary, while data reduction and interpretation was difficult, since information was collected in an analog or time-averaged fashion. New optical measurement technologies simplify or eliminate these problems, while allowing real-time measurements and higher confidence in the results.

Motivation for the work presented here comes from several diverse sources:

- Social Responsibility: environmental sensitivity and sustainable development are among Alcoa's most strongly held values.
- Governmental Requirements: legislation in all countries where smelters are located is trending toward lower emissions.
- Smelter Financial Performance: improvements in energy efficiency and pot life often depend on tighter bath chemistry control.

Lower fluoride emissions require pot covering practices that are more consistent and at a higher level than ever before. However, simply increasing the thickness of the anode cover to eliminate open holes is often not an option for older pot lines. These older potlines typically run significantly above their original design line currents (30-50%), with characteristically thin sidewall ledge. Aggressive covering practices lead to even thinner ledge and an inevitable increase in pot failures. Thus, a better understanding is necessary to achieve both lower emissions and acceptable financial performance.

We must also make an important clarification and distinction here at the outset: the results reported here are *evolution* numbers, not *emission* numbers. We define evolution as the amount of gas coming off of the pot before any off-gas scrubbing; we define emission as the amount of gas actually released to the environment. No emission data are reported here. For environmental performance reasons, we are interested in evolution rates because they have a direct impact on emission rates. In addition, we are interested in evolution rates as inputs to bath composition control strategies.

Experimental Method

Gaseous HF evolution studies were performed on individual smelting pots by monitoring single pot exhaust ducts using an in-house developed test rig as illustrated in Figure 1. Individual pot exhaust ducts were sampled using a short length of stainless steel inlet tubing as an inlet probe, coupled to a length of Teflon® tubing and an in-house constructed, Teflon®-body gas cell. Using a vacuum pump, duct gas was drawn through a particulate filter and gas cell, while the real-time HF concentration in the gas cell was monitored using a tunable diode laser-based HF monitor (Boreal, Canada). A piece of reflective tape was affixed to the far end of the gas cell in order to provide a return signal to the HF monitor. The ppm-m concentrations of gaseous HF obtained from the HF Continuous Emission Monitor (CEM) were converted to ppm concentrations by dividing the result by the gas cell pathlength.

The inertness of the particulate filter to gaseous HF was verified by performing measurements of smelter exhaust gas with the filter in and out of the sample line. In both cases the observed HF concentrations were unchanged.

HF concentrations were recorded at frequencies ranging from once a second to once every 3 seconds, depending on the duration of the individual sampling trials. Duct air flow velocities were measured by using a pitot tube and digital manometer.

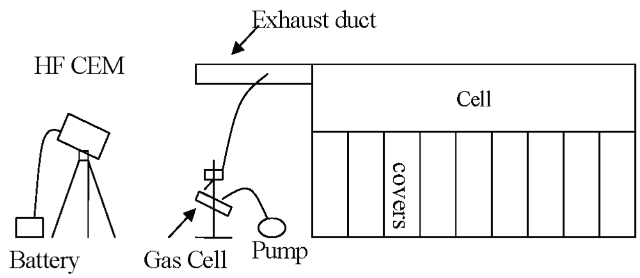


Figure 1. Experimental set-up for monitoring single pot HF evolution.

The vendor performed the initial calibration of the HF CEM and the validity verified by gas cell and permeation oven testing in a lab prior to in-plant use.

The open hole areas in the pots were estimated by briefly pulling the pot covers and visually inspecting the anode cover. After the initial HF measurements, the existing holes were sealed by manually raking loose anode cover material into the holes, and subsequent measurements were made at the new cover condition. In all of the "0" open hole condition cases reported below, the feeder holes were closed either due to the angle of repose of the adjacent alumina, or we intentionally raked cover into the hole. If the feeder holes did not seal after plugging and feeding, we included their actual size in the open hole area reported. The duration of measurements was intentionally designed to include at least one complete underfeed-overfeed cycle.

Results

HF evolution measurements were made on three different point-feed prebake pot types. The first is an older low amperage Alcoa-design pot (AA-small), the second is a medium amperage Pechiney-design pot (AP-medium), and the third is a larger higher amperage Alcoa-design pot (AA-big). Data for Pot Type AA-big included measurements from two different smelters.

Figures 2 and 3 show typical examples of HF evolution measurements, where the HF concentration in the pot off-gas is plotted with time for pot types AA-small and AA-big, respectively. Annotations in the plots show the changes made to alumina feed and pot cover integrity during the measurement time. Placement of the pot covers and the duct flow rate remained essentially constant during each measurement period. Examination of these figures reveals two obvious features: an apparent baseline HF concentration that changes with open holes in the crust and sharp peaks in the concentration occurring at short intervals that change with feed rate. Each of these HF evolution features will be discussed separately.

Fluoride Evolution Spikes and Alumina Feed Shots

In Figures 2 and 3, the fact that the time interval between the peaks is the same as the feed interval leads to the conclusion that the peaks are due to the rapid hydrolysis of the bath by moisture that desorbs from the alumina feed shot as it hits the bath [3, 4]. Closer examination of the individual peaks shows that after each feed shot peak, the HF concentration falls back to the baseline with an apparent exponential decay. This type of decay is typical for a tracer spike in a flow system with appreciable mixing. But the tail is probably stretched out even further from a delayed release of moisture on the alumina. As the cold feed shot enters the bath, it freezes bath around it, which inhibits the release of at least some of the water vapor (especially the hydroxyl groups) on the alumina. Then, as the bath subsequently melts and the alumina dissolves, there is a secondary and slower release of water vapor, which reacts to form HF. This HF is evolved over a more extended time period that lengthens the tail on the feed shot spike. It should be noted that the HF evolution tail roughly corresponds to the known dissolution time for an alumina feed shot; however, independent measurements of the alumina dissolution rate for these feed shots were not made.

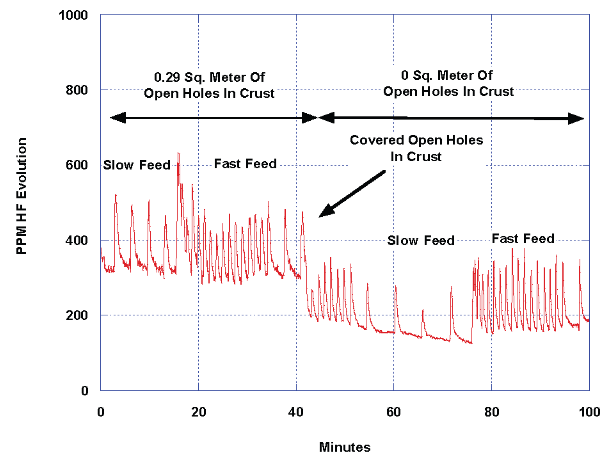


Figure 2. Typical off-gas HF concentration vs. time for Pot Type AA-Small.

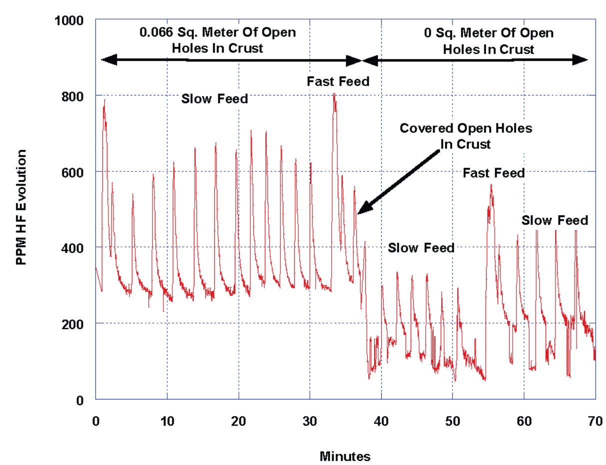


Figure 3: Typical off-gas concentration vs. time for Pot Type AA-Big.

The amount of HF evolved during the initial release of surface water from the alumina can be estimated by integrating the area under each peak down to the apparent baseline. (Of course, this ignores the fact that the peaks merge on the fast feed shots.) The fraction of the total HF evolution due to the feed shot spike is shown for each condition in Table 1. Although the percentage of HF from the feed shot spike is highly variable, Figure 4 shows that it generally decreases as the hole area increases. This is reasonable since more HF bypasses the crust scrubbing as hole area increases.

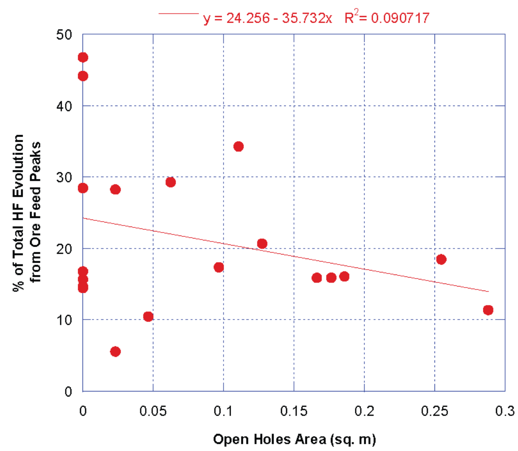


Figure 4: Percent of total HF due to feed shots vs. area of open holes.

The tail of the exponential decay is more obvious for a slow feed condition than a fast feed condition. This is expected since the fast feed shot comes before the previous shot has a chance to decay completely back to the baseline. For the same reason, the apparent baseline for the fast feed shots is higher than for the slow feed shots.

After covering up the open holes in the pot, the baseline also decreases over a relatively long period of time. This observation is especially evident in Figure 2 for the very slow feed condition. The tail is too long to be due to the reduced exposure of humidity in the air, since covering the holes would almost immediately block the AlF_3 and $NaAlF_4$ vapors from the air humidity. There are two possible explanations for this:

1. A very long baseline decay due to poor gas mixing characteristics in the pot hood, as HF slowly bleeds out from remote corners of the hood. This hypothesis could be checked easily with gas tracer residence time distribution studies.

2. An increase in scrubbing efficiency as the cover material put on the open holes sinters into a more solid crust leading to even less by-pass possibilities. Covering the open hole with a material that would not sinter very quickly to a more solid crust could be employed to check this hypothesis.

Fluoride Evolution and the Effect of Open Hole Area

The most important feature in Figures 2 and 3 is the dramatic effect of covering the open holes. For the small pot in Figure 2, the baseline off-gas HF concentration was about 300 ppm for the first 45 minutes followed by a sudden decrease to less than 200 ppm upon covering the open holes. A similar result was observed for the large pot in Figure 3. The baseline HF concentration was about 300 ppm for the first 35 minutes, and then dropped to about 100 ppm immediately after covering the holes in the crust. The lower baseline rates were sustainable for indefinite periods of time. Clearly, covering the holes has a dramatic effect on the HF evolution from the pot and shows that the crust plays a significant role in HF evolution from the pot.

For each condition, the concentration vs. time plot was integrated to get the time-averaged concentration, which was combined with the measured duct flow rate to get the total HF evolution. These values are reported in Table 1 on a per-ton Al basis. Also, in the analyses below, the data set AA-Big-2 is omitted, since these pots were experiencing significant problems with carbon dust and cover consistency. The data is suspect, but is nevertheless listed in Table 1 for the sake of completeness.

Using the data available in Table 1, an attempt is made to generalize the effect of the open hole area on the evolution rate. We start with the commonly held theory that there are two main reactions that result in formation of HF [4]:

1. Hydrolysis under the crust and/or in the bath, where AlF_3 reacts with water from the alumina and hydrogen from the anode to form HF (Haupin and Kvande parameter F_{GB});

2. Hydrolysis above the crust, where bath fumes (primarily $NaAlF_4$) react with humidity in the air to form HF (Haupin and Kvande parameter F_{GP}).

For either hydrolysis reaction it is reasonable to hypothesize that the crust acts in the following ways to reduce HF evolution:

a. As a barrier to prevent moisture in the air from reacting with the bath vapors below the crust.

b. As a packed-bed scrubber for the HF formed below the bath from the moisture on the alumina.

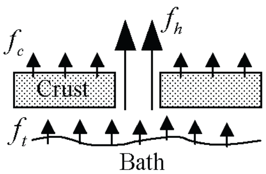
Although both mechanisms are certainly involved, we can determine the dominant mechanism from an analysis of the measured evolution rates.

For the moisture barrier hypothesis (a), as the open hole area increases, there is greater exposure for reaction with air humidity. It is therefore reasonable to expect a linear increase in the HF formation rate on a per-time basis as hole area increases. The slopes should be the same regardless of the current or pot size and depend mostly on the water content of the air (absolute humidity). To test this hypothesis, we plot the total HF evolution rate on a per-time basis vs. area of holes in the crust in Figure 5. Indeed, HF evolution increases linearly with hole area. However, the slopes are clearly not the same for the different pot types; in fact, they differ by a factor of 3. Thus, the observations suggest that the moisture barrier hypothesis (a) is not a totally satisfactory explanation for the effect of holes on the HF evolution rate.

In the case of the packed bed scrubber hypothesis (b), the amount of scrubbing depends on the depth, absorptive capacity and area of the crust. Since changing the area of the holes has only a small effect on the total area of the crust, we would expect little consequence on the amount of scrubbing. However, open holes in the crust also provide a by-pass route for HF-laden gases to escape the pot without passing through the crust. How much by-pass occurs depends on the pressure drop, crust permeability and total area relative to the size of the open holes. In essence, the pot gases have two parallel routes out of the pot and the relative amounts that pass through each depends on the pressure drop-flow characteristics of the crust and the size of the holes. Assuming flow proportional to pressure drop (although actually closer to

$\sim \Delta P^{1/2}$ for the holes), a mass balance on the total gas flows (CO, CO_2, HF, SO_2, etc.) yields:

$$f_t = f_c + f_h$$
$$f_c = \kappa_c A_c \Delta P$$
$$f_h = \gamma_h A_h \Delta P$$



where: f_t = total gas flow (m^3/hr); f_c = gas flow through crust (m^3/hr); f_h = gas flow through the holes in the crust (m^3/hr); κ_c = crust gas permeability (m^3/(hr-m^2-kPa)); A_c = area of crust (m^2); ΔP = pressure drop across crust (kPa); γ_h = pressure-flow coefficient for flow through the holes in the crust (m^3/(hr-m^2-kPa)); and A_h = area of holes in the crust (m^2). But, we also know that the total flow through the crust and holes is proportional to the current:

$$f_t = \phi I$$

where: I = line current (amps); and ϕ = conversion factor that includes current efficiency (m^3/amp-hr). A mass balance on HF flow across the crust boundary yields the following:

$$f_{HF} = x_{HF} f_c (1 - \eta_{HF}) + x_{HF} f_h$$

where: x_{HF} = mole fraction HF in the gas under the crust and η_{HF} = scrubbing efficiency of the crust on HF. One final relationship is required to provide a test against the observations in Table 1. The current yields proportionately more gas flow through the crust, and the holes in the crust act as orifices. Thus, for the sake of simplicity, we assume a constant current efficiency and linear pressure drop as the area of open holes is held constant:

$$\Delta P = \alpha I$$

where α is a constant for a given hole area (kPa/amp). Algebraic manipulation of the equations above yields a relationship between hole area and HF evolution that takes the form:

$$\frac{f_{HF}}{I} = \phi x_{HF}(1 - \eta_c) + (\gamma x_{HF} \eta_c \alpha) A_h$$

Thus, a plot of f_{HF}/I vs. A_h should yield a straight line. Furthermore, the parameters comprising both the slope and the y-intercept we would hope to be relatively constant for different pots and pot types. The only parameters likely to be different from pot-to-pot are x_{HF} (function of water level on the alumina, AlF_3 vapor pressure, etc.) and η_c (function of cover depth, surface area of alumina, absorptive capacity, etc.).

To test this hypothesis, we can use the observed evolution on a per-ton basis (kg HF/MT Al) in Table 1 as a surrogate for f_{HF}/I, since they differ by only a conversion constant.

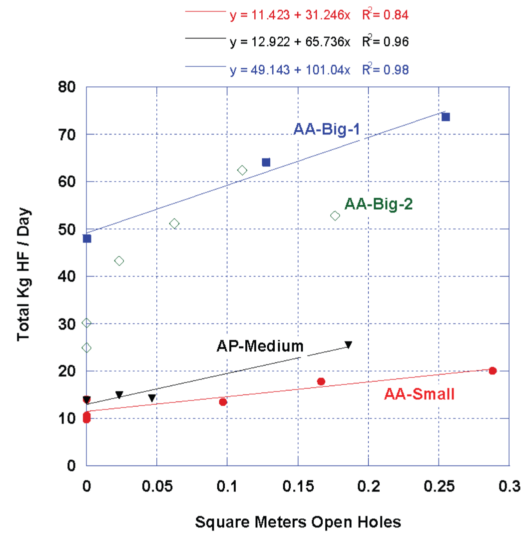


Figure 5. Total HF evolution rate (on a time basis) vs. area of open holes in the crust.

The resulting plot in Figure 6 shows that the range of slopes is much smaller than the case with evolution on a per-day basis. The slopes here vary by only a factor of 1.4 (from 42 to 58 kg HF/MT Al-m^2) compared to a factor of 3 on a per day basis. Notice also that the range for the intercepts is also smaller (from 11 to 27 kg HF/MT Al). Thus, normalizing the HF evolution rates with respect to the amount of Al produced appears to be a very feasible approach to generalize the effect of open hole area on gaseous HF evolution. The mechanistic rationale above suggests that the HF formation rate is dominated by moisture on the alumina underneath the crust, and the effect of holes is to offer an undesirable by-pass for the HF-laden gases to escape without being scrubbed through the crust.

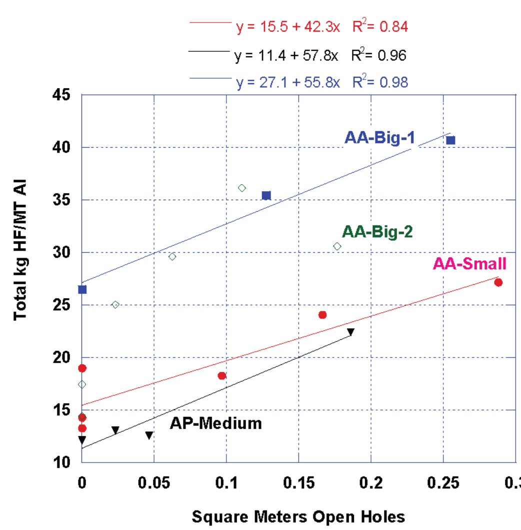


Figure 6. HF evolution rate on a per ton Al basis vs. area of open holes in the crust.

Also in Figure 6, the AP-Medium data is generally lower than the others. For this data set, the plant typically has a much higher alumina content in the anode cover material (80-90%), compared to about 50% for the other pot types. The higher alumina results in better scrubbing efficiency of the crust (η_c), so the slope in Figure 6 would be expected to be slightly higher and the intercept slightly lower than the others. This is indeed the case, lending even more credibility to the model.

Finally, in an attempt to collapse the curves in Figure 6 even further, we would like to somehow normalize or correct for the other conditions that changed among the data sets in Table 1, such as bath ratio, temperature, etc. The mathematical model by Haupin and Kvande [4] makes such a correction possible. Their parameter F_G (total gaseous fluoride evolution) quantifies the effect of these other conditions on the hydrolysis reactions based on thermodynamics and kinetics tuned with measured data. The efficacy of the model was reported recently as a soft sensor for fluoride losses in a bath chemistry control strategy [5].

Table I: Summary of Measure Data and Results

Pot Type	Open Hole Area (m^2)	Bath Temp (C)	Bath Ratio	Bath Al2O3 (wt%)	Ore Moist. (MOI <300C) (wt%)	Air Humidity (kPa)	Avg. PPM HF	Duct Flow Nm^3/hr	% HF from Feed Shot	Total Meas'd. kg HF/ MT Al	Total Model* kg HF/ MT Al
AA-Small	0.17	962	1.14	3.2	1.51	2.19	339	2449	15.9	24.1	19.5
AA-Small	0.00	962	1.14	3.2	1.51	2.19	260	2520	28.5	19.0	19.5
AA-Small	0.29	954	1.20	2.7	1.30	2.19	368	2547	11.4	27.2	16.4
AA-Small	0.00	954	1.20	2.7	1.30	2.19	185	2664	15.7	14.3	16.4
AA-Small	0.10	948	1.19	2.8	1.41	2.19	190	3316	17.4	18.3	15.9
AA-Small	0.00	948	1.19	2.8	1.41	2.19	136	3370	14.7	13.3	15.9
AP-Med.	0.19	953	1.08	3.5	1.73	1.88	305	3903	16.1	22.4	19.0
AP-Med.	0.05	953	1.08	3.5	1.73	1.88	171	3903	10.5	12.6	19.0
AP-Med.	0.00	953	1.08	3.5	1.73	1.88	165	3903	14.5	12.1	19.0
AP-Med.	0.02	955	1.10	3.5	1.73	1.88	178	3903	5.6	13.1	18.5
AA-Big-1	0.25	965	1.10	1.8	1.53	2.03	569	6052	18.5	40.7	27.0
AA-Big-1	0.13	965	1.10	1.8	1.53	2.03	489	6130	20.7	35.4	27.0
AA-Big-1	0.00	965	1.10	1.8	1.53	2.03	363	6179	16.8	26.5	27.0
AA-Big-2	0.11	966	1.13	3.0	1.67	1.91	487	5985	34.3	36.1	20.8
AA-Big-2	0.00	966	1.13	3.0	1.67	1.91	231	6091	44.2	17.4	20.8
AA-Big-2	0.18	977	1.19	3.0	2.01	1.91	421	5857	15.9	30.6	21.0
AA-Big-2	0.02	977	1.19	3.0	2.01	1.91	343	5887	28.3	25.0	21.0
AA-Big-2	0.06	967	1.19	3.0	1.57	1.91	392	6091	29.3	29.6	18.1
AA-Big-2	0.00	967	1.19	3.0	1.57	1.91	190	6125	46.8	14.4	18.1

* Assumptions for Haupin-Kvande Model calculations:
Total water on ore = MOI = LOI; where LOI represents the loss 300-1000 C = 0.8 wt%
H_{an} = 0.09 wt%

The predicted HF evolution rate from the Haupin-Kvande model is listed in Table 1 for each data set. (Exercising the model equations shows that water content of the alumina, bath ratio and temperature are the most sensitive variables.) Since the Haupin-Kvande model does not consider the effect of open holes, the same HF evolution rate is predicted when the holes are covered. We are interested in how the area of open holes affects the measured evolution relative to the Haupin-Kvande prediction. Thus, we plot the ratio of the measured-to-predicted evolution rates against the open hole area in Figure 7. Unlike the previous plots, the data from the different pot types and conditions now overlaps much more in this plot, suggesting the corrections were effective. Note also in Figure 7 that the open hole area corresponding to where the line-fitted ratio is equal to one is about 0.07 m^2, which is presumably the open hole area that was implicit in the Wahnsiedler calibration data Haupin and Kvande used. This is a very reasonable open hole area for the two feeder P-155 pot on which the original measurements were made.

We also considered the differences between the measured and predicted evolution rates instead of the ratio plotted in Figure 7. Using the difference resulted in a slightly lower correlation coefficient than that obtained using the ratio. Thus, the effect of the open holes appears to be a multiplicative effect, rather than an additive effect on the Haupin-Kvande F_G parameter. Thus, for every 0.1 m^2 (~1 ft^2) increase in the open hole area, the actual HF evolution rate increases by about 25% over the Haupin and Kvande model.

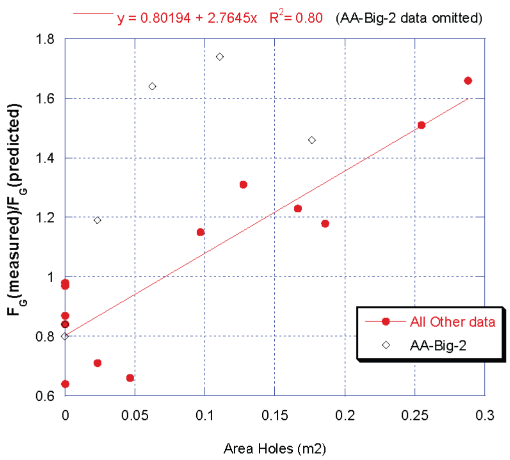


Figure 7. Ratio of measured to predicted evolution rates vs. open hole area, where predicted evolution rates are from the Haupin-Kvande model.

Discussion

A significant source of variability remains in the HF evolution data reported here. This variability might be due to the impact of "worm-holes" on HF evolution. "Worm-holes" refers to the small tunnels that form under the crust surface, wherein an open hole of a given area may actually be directly connected to a much larger area of bath surface. While open-hole area is easily assessed by visual inspection of the crust, it is difficult to estimate worm-hole area and its effect as a by-pass around the crust scrubbing. From a practical pot-tending perspective, worm-holes can be minimized by tamping in the crust surface to collapse these sub-surface tunnels, prior to dressing the pot cover.

Besides the environmental impact, open holes in the crust can also have a significant detrimental effect on the heat balance of the pot. Each 0.1 m^2 can lose as much as 10-12 kW energy. So covering open holes is a win-win proposition for both energy savings and the environment.

Finally, the danger of over-covering the pot was pointed out earlier. Based on the foregoing, it would seem appropriate to increase the anode cover to maximize the scrubbing efficiency of the crust. But over-covering can result in thinner ledge and premature pot failures. To obtain reduced HF evolution without suffering additional pot failures in older potlines especially, a workable compromise is reached by keeping the holes covered while not over-covering the anodes.

Conclusions

Feed shots lead to HF spikes in the off-gas that result from the initial flashing of surface water off of the alumina as it hits the bath. The sizes and shapes of these spikes is dependent on the feed shot frequency, the residence time distribution of the gases in the pot and the rate of release of water and hydroxyl groups off of the alumina.

The impact of open holes in the crust on HF evolution is remarkable. Despite the fact that low bath ratio and high temperature increase the vapor pressure of the bath and increase HF evolution, these factors are minor compared to the overwhelming effect of open holes in the crust. HF evolution from the pot can nearly double for what some would consider modest increases in open hole area. Conversely, the ability of the crust to act as an in-situ scrubber for HF is critical. Reducing the area of open holes in the crust can dramatically reduce HF evolution, and by extension, significantly reduce actual emissions of HF to the environment.

A mechanistic rationale for the effect of open holes on HF evolution has been proposed, yielding a relatively simple mathematical model. The HF formation rate is dominated by the rate of release of moisture from the alumina. The primary effect of open holes is to offer an undesirable by-pass for the HF-laden pot gases to escape without passing through the crust, which acts as an in-situ scrubber. The model was tested against HF evolution measurements and found to fit the data quite well. The model was combined with the Haupin-Kvande model to account for bath composition, temperature and other effects, resulting in a comprehensive model that improved the fit with measured data even more. For every 0.1 m^2 (~1 ft^2) increase in the open hole area above their 0.07 m^2 basis, the actual HF evolution rate increases by about 25% over the Haupin and Kvande model.

The present work has shown a promising comprehensive understanding of the effect of open holes on HF evolution. At this time the biggest gap in our understanding is the effect of open holes on particulate evolution. Although it is reasonable to assume similar mechanisms for particulate evolution for modest changes in open hole area discussed in this paper, other explanations must be employed as the open hole area reaches the extremes [3]. It is our hope both more HF evolution and particulate evolution data will be added to what is reported here so that a more rigorous test of the model is provided to advance our understanding even further.

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