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DRY SCRUBBING for MODERN PRE-BAKE CELLS

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Abstract

The two fundamental "raw materials" for pot room gas treatment systems are alumina, and process off-gases. Modern dry scrubbing systems offer very efficient removal technology. However, increases in the kilograms per ton of fluoride evolution from reduction cells and increases in fume evacuation rates can challenge the abilities of existing dry scrubbers. This is especially so if the goal is to provide both state of the art removal efficiency and alumina at the pot that is low in fines content. In this paper the authors discuss trends in our industry and propose solutions that include more efficient utilization of alumina and process gas flow to meet emerging needs.

Introduction

When existing reduction technology is stretched to new limits by increases in pot line load it is often necessary to revisit cell design fundamentals. Boost rectifier groups are commonly used to test these fundamentals and assure good performance of cells due to changes in current density, magnetic stability, or the thermal balance of the cell.

There is also a need to revisit the fundamentals for dry scrubbing technology that services the pot line when an increase in pot line load is planned. However, the frequency with which this type of due diligence is performed is not as common as that which may be done to evaluate reduction cell performance at higher line loads.

Challenges to dry scrubbing technology may also occur when the portion of a pot line dedicated to pure metal production is increased. A configuration that uses dry scrubbers to support pure metal production shifts the fluorides evolved from these pot groups onto the alumina that is consumed by other sections of the pot line.

Higher line loads and reduced alumina utilization from purity groups will synergistically drive the weight percent of fluoride on alumina closer to its effective saturation point, thereby reducing the scrubbing efficiency of the gas treatment center, or GTC. Amperage increases not only drive up HF evolution rates per ton Al produced, but increased pot heat loss can increase off-gas temperatures which also serves to compromise the efficiency of the GTC.

On occasion, changes in pot line load may also lead to upgrades in the design of the GTC. The aim of these upgrades may be to boost average pot exhaust rates or to provide very high exhaust flow rates during specific process activities such as anode changing. Potroom ventilation may also be improved by add-on systems that collect fume from hot anode butts or from hot bath materials that are removed from the pots.

Increases in process gas flow can challenge the fundamentals of dry scrubber designs either with regard to surface area that is available for highly efficient removal of fluorides or with regard to linear air flow, velocity, and the attrition of alumina particles into undesirable fines, <45μ, and superfines, <20μ.

Some aluminum producers approach higher temperatures and process gas flow rate by adding additional filtration capacity to keep the gas velocity at the filter media below a maximum value.

An alternative approach is to cool the off-gases to the GTC. This can be achieved by; using an in-duct chiller,[1] which may also accelerate hard gray scale formation,[2] using an energy recovery system to remove heat from the pot off-gases for use elsewhere in the plant, or adding dilution air thereby requiring additional fan and filtration capacity, or by pulling less air from pot rooms.

Under these conditions one must re-examine the most effective use of available alumina and its surface area and the most efficient use of process exhaust.

The pursuit of higher line loads or increases in total process gas flow rates without a thorough re-examination of the gas treatment process may lead to results that are either self-limiting or partially counter-productive.

Discussion

Scrubbing Capacity of Alumina

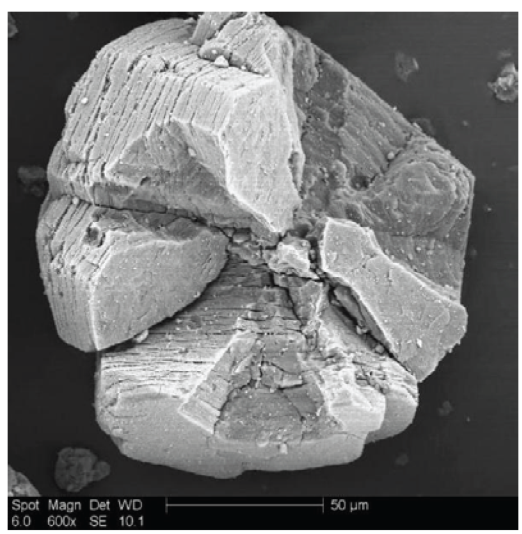

Figure 1. 600X magnification of a calcined alumina particle.

Calcined smelter grade alumina, SGA, has a large amount of surface area available for alumina adsorption. Typically this falls in the range of 70 to 80 square meters of surface per gram of SGA for most commercial suppliers world wide. Only a small fraction of this total surface area is located on the periphery of the alumina particles. The vast majority of SGA surface area results from internal porosity between the crystalline layers or platelets of calcined crystals of alumina as illustrated in Figure 1.

The stratified and fractured morphology of SGA allows readily accessible surface sites to adsorb fluorides contained in pot off-gases by rapid exchange reactions with surface hydroxyls. [3, 4] Access to the surface area between crystalline layers is driven by diffusion after reaction with easily available surface sites nears completion. Continued mass-transfer limited reactions occur with bridging and subsurface aluminum sites once surface hydroxyls have exchanged with adsorbed fluoride. [4] In both of these latter cases the reaction mechanisms are relatively slow compared to surface hydroxyl exchange, as implied by the breakthrough curve behavior shown in Figure 2.

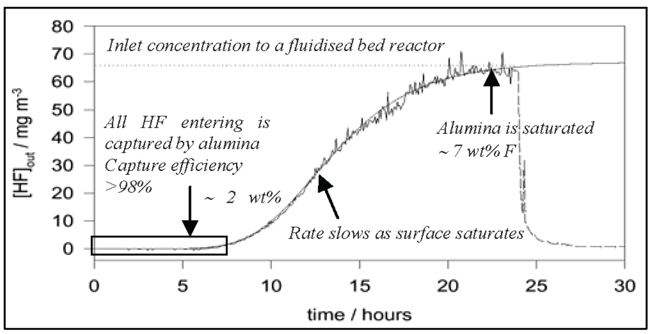

Figure 2. Break-through curve for HF to a fluidized bed. [3]

The significance of this reaction behavior is that commercial dry scrubber manufacturers typically recognize that alumina is "spent" as a fast reacting scrubbing agent once 0.28 mg F has been loaded per each square meter of BET [Brunauer-Emmett-Teller] surface area. Most manufacturers will not guarantee optimal dry scrubbing performance once 85% or more of this loading rate has been realized. It is important for reduction operations to recognize that there is a practical limit as to how much fluoride can be rapidly and efficiently scrubbed per unit of alumina consumed, particularly since the available alumina is limited to the production rate of the potroom. The important concept here is that changes in fluoride evolution rate (per ton Al) will impact the capture performance of a given SGA feed rate.

In practical terms this limit may be expressed as 1.9% to 2.2% F on secondary alumina depending upon the BET surface area of the fresh SGA. The lower value of 1.9% F corresponds to the lower end of surface area produced by most refineries, at 70 m2/gm BET and 2.2% F corresponds to 80 m2/gm surface area SGA. Figure 3 shows typical BET surface areas for SGA from a variety of different alumina refineries.

Once the practical scrubbing limit of SGA has been reached, the primary reaction mechanism begins to shift from fast surface reactions to slower reactions limited by diffusion and/or mass transfer. There still remains a large capacity for alumina particles to react with fluoride, but at slower rates. As suggested by the data shown in Figure 2, the fluoride loading on SGA may increase to more than 7% F by weight, but at fluoride capture efficiencies that are not acceptable for assuring compliance with the operating permit for the plant.

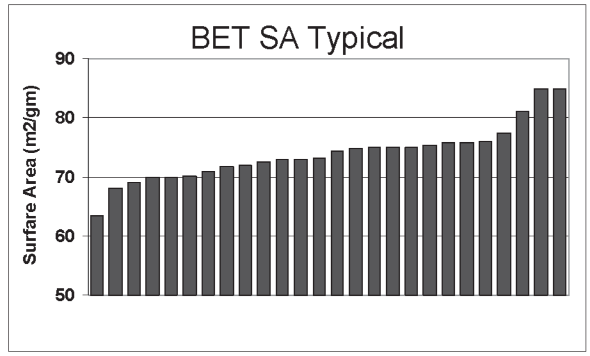

Figure 3. A continuum of BET S.A. for various refineries.

As noted above, the shift from fast to slow reaction mechanisms impacts the concentration of HF in the dry scrubber exhaust. This is illustrated by field measurements taken at various locations, as shown in Figure 4.

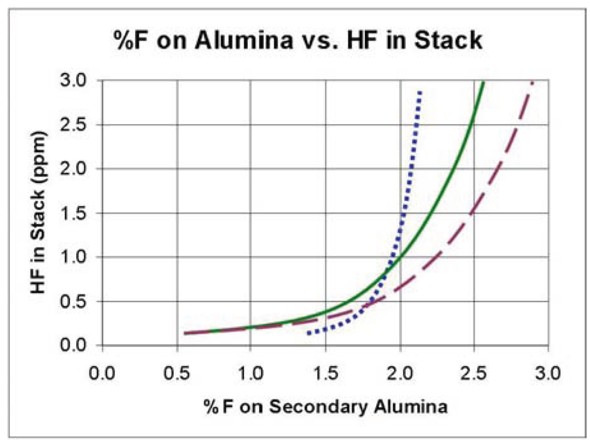

Figure 4. %F on secondary alumina vs. HF concentrations in dry scrubber stacks at 70 to 75 m2/gm BET S.A.

Assuming 1.9% total fluoride on secondary alumina to be an approximation of the practical limit for efficient scrubbing, and using 1.92 kg Al_2O_3 consumed per kg Al produced, this translates to 38.5 kg TF/t Al as a maximum sustainable total fluoride evolution rate. However, this is the maximum fluoride evolution that may be tolerated when 100% of alumina consumed actually passes through the dry scrubbers. In most smelter configurations this is not the case. Note that 1.9% TF is based on multiple sets of field data. It is not based solely upon reaction with gaseous fluoride. Thus it serves as an approximation of the saturation limit that none-the-less is also used by most GTC manufacturers.

Dry Scrubbing

To efficiently remove fluoride, reactor designs strive to attain intimate contact between a dispersion of SGA particles in the process gas stream or fluid bed, and gas/solids contact as the process gas passes through the particulate cake on filtration media.

Primary fluoride removal is achieved through a variety of methods used to inject, disperse or circulate alumina into the process gas stream. Primary contact may also be made with the use of a fluidized bed of alumina where the process exhaust gas is the fluidizing agent.

Secondary contact in what is often the final, or polishing, step for fluoride removal happens on the filter cake and varies with the thickness and composition of the cake. Recently cleaned filter media will not have much filter cake, nor the ability to effectively remove residual HF.

When existing hardware is pushed to accommodate higher gas flows during process activities such as anode change or to support larger motors, fans, or add-ons such as hot anode butt fume treatment, the fundamentals of the reactor design may also shift.

Normally the first area of concern is the velocity of process gas at the surface of the filter media that may otherwise be expressed as the air-to-cloth ratio in English units. This measure primarily addresses negative pressure maximums, bag house structural concerns, and blinding of fabric media.

Higher gas flow rates through the same system ducts and reactor tubes directly translate into higher linear flow velocities and greater attrition of alumina particles. [5]

Without proportionately increasing the total mass of injected alumina to compensate for an increase in gas flow, the density of SGA particles per unit volume of process gas is reduced. This in turn reduces the effectiveness of the primary contact mechanism. If alumina recirculation is then increased to improve scrubbing efficiency, the median number of passes of alumina particles increases. This amplifies the net attrition of alumina particles, increasing the amount of fines sent back to the pots. It also increases the likelihood of hard gray scale formation. [2]

Normally an increase in system gas flow translates into higher velocities and no change in alumina recirculation rates. This often results in a reduction in dry scrubbing removal efficiency and increases in HF emissions from the dry scrubber.

In either case higher exhaust flows place a toll upon attrition and its negative impacts on downstream operations in the pot rooms, or upon dry scrubber removal efficiency, or both.

<u>Alumina Flow Path</u>

<u>Anode Cover</u>

In most smelter configurations between 3% and 12% of the alumina consumed arrives to the pots without having passed through the GTC units that service the pot rooms.

The most common alumina by-pass mode is via the bath crushing system. Anode cover typically falls into the pot during process activities and additional crust cover dissolves in the bath between tending operations. This requires that some make-up material must be added to have sufficient quantity of anode covering material for covering newly set anodes. Normally the recipe for new anode cover material will include 20% or more by weight of fresh alumina to arrive at about 50% total alumina by weight in the anode cover material itself. In some cases the fresh alumina added may be well above these values increasing crust-feeding.

The crust-feed rate to the pot typically varies from as low as 3% to as high as 12% of total alumina consumption. The root causes behind this wide range depend on pot technology and operating practices. The surface area of fresh alumina that is used to produce anode cover is not available for scrubbing HF at the GTC. Instead this new alumina is mixed with reclaimed material from previous anode sets and is consumed by the pots.

Some might argue that this fresh alumina helps the anode crust to scrub out fluorides that never reach the GTC. This in part is true, but much of the HF that escapes the pots passes through open holes or cracks in the crust rather than percolating through the crust itself. Alumina on the crust achieves a high loading of fluoride via a range of reaction mechanisms [4] that allow HF to access the internal porosity, sub-surface and bulk aluminum sites of the SGA particles over the days and weeks that the anode crust is in place at elevated temperatures and at high HF concentrations near the bath surface.

<u>Anode Baking Fume Treatment</u>

The Fume Treatment Center, or FTC, that serves to collect hydrocarbons and fluorides from the anode baking furnace exhaust is a location at which 4% to 8% of the total alumina flow for a smelter may pass depending upon operating and design factors. Typically the fluoride content on the alumina discharged from these systems is very low, often at less than 0.4% by weight. Some additional alumina surface area is occupied by adsorbed organics

Under these conditions most of the surface area that is available for the fast HF reaction mechanism has not been utilized. Unless this alumina is widely dispersed and used as feedstock to the pot line dry scrubbing systems, its full scrubbing potential may be significantly underutilized.

<u>Other Flow Path Issues</u>

There are other plant design issues that can cause significant fractions of the total surface area that might pass through the dry scrubbers to be under-utilized.

These may trace their roots to previous plant expansions. A bath crushing facility may use secondary alumina to make anode cover, but may draw this from GTCs in an original pot line near the bath crusher to serve the anode cover needs of newer pot lines. The GTCs that service the bath crusher will have higher average alumina flow rates that vary substantially depending upon anode cover demand rates. The secondary alumina from these GTCs will tend to be under-saturated. The secondary alumina from the GTCs on the newer pot line will have a higher %F on secondary alumina and be at greater risk of higher stack emissions.

A very common design factor that can cause even more serious imbalance of alumina flow is found in many smelters that use overhead buckets to fill pot feed bins. When there is more than one bucket fill station available and each fill station is tied to a different GTC variations in alumina flow can be driven by a variety of factors that are difficult to control. Proximity of a fill station to the pots requiring alumina, and other work or maintenance activity that blocks the pathway to the normal fill station can cause one GTC to have high alumina flow rates and another to have low flow rates. This leads to some tons of alumina not having its surface area effectively utilized and other tons over-utilized risking high emission rates in the stacks. See

Figure 5 for an example of an actual alumina flow path that is susceptible to under-utilization of fresh alumina surface area and its availability for fluoride scrubbing.

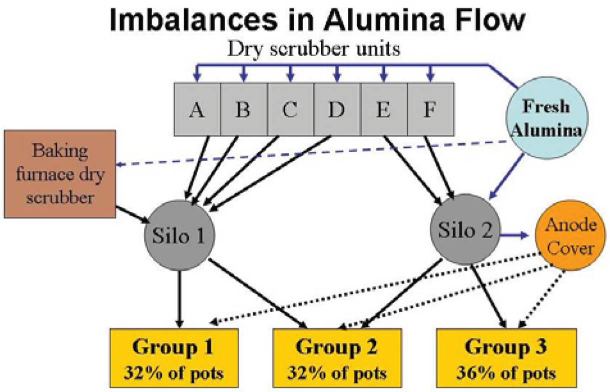

Figure 5. Example of an alumina flow path.

Even miscellaneous losses of alumina such as that which spills between pots and into the basement can have some temporary effect on dry scrubber effectiveness. This alumina typically is harvested during certain periods of the year when the weather permits. The basement material goes to the bath crushing area into anode cover. The alumina content may then displace other tons of alumina that would have been able to pass through a GTC and be more effectively utilized for scrubbing HF. In addition, this material may have elevated chemically adsorbed moisture levels, thereby increasing net fluoride evolution to the scrubber.

Our calculated maximum for fluoride evolution was 38.5 kg of total fluoride evolution per ton Al produced. But, this estimated value over-states realistic limits for most smelters which in some cases may be well below 35 kg TF/t Al as a practical maximum after all deviations in the alumina flow path have been considered.

In all situations dry scrubber operation is most robust when fresh alumina flow through the GTC approaches 100% of pot line consumption. This implies uniform flow through all GTC reactors over time as well as minimal side stream flows for fresh alumina. The importance of sustaining this objective grows as fluoride evolution approaches the approximate saturation point of the alumina of 1.9% to 2.2% F by weight.

Fluoride Evolution

There are a number of factors that drive fluoride evolution. In 1993 Haupin and Kvande [6] put forth a model that identified key drivers of evolution including; bath temperature, and %LOI on alumina. Later, in 2003, Slaughenhaupt, Bruggeman, Tarcy and Dando [7] more clearly defined the role that open holes in the pot crust play in fluoride evolution.

As existing technology is boosted to higher pot line loads the factors that increase fluoride evolution and the effective use of alumina and its available surface area must be considered. If additional line load is not counter-balanced with equivalent heat sinks then bath temperature and delta T, or superheat, will tend to rise. Open holes in the crust will tend to increase to release excess heat and fluoride evolution through these open holes will also increase.

This is all quite fundamental. However these basics may be over-looked during trials of increased line load. Testing conducted on boost rectifier sections seldom includes pot-specific, or test group-specific evaluation of fluoride evolution. General indicators such as changes in exhaust duct temperature,[8] the sum of open holes in crust, increased bath tapping rates, or higher AlF_3 consumption may be missed as well.

If shifts in fluoride evolution are not realized until load has been increased, emission rates may climb substantially at the exhaust points of the dry scrubbing systems much to the dismay of operating personnel.

In situations when higher fluoride evolution is combined with any factors of diminished fresh alumina flow substantial problems can emerge. Once the practical scrubbing capacity of the alumina is exceeded emission performance will be compromised. For an example of such a case see Figure 6.

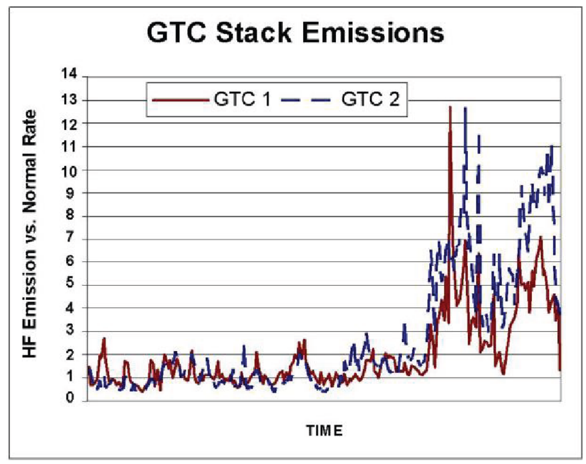

Figure 6. GTC emissions following a 5% increase in line load.

Higher fluoride evolution and stack emissions may be countered, in part, with an increase in surface area target. However, as Homsi [9] described, increases in surface area will generally have proportional increases in %LOI in the range of 70 to 80 m^2/gm BET, S.A. as shown in Figure 7.

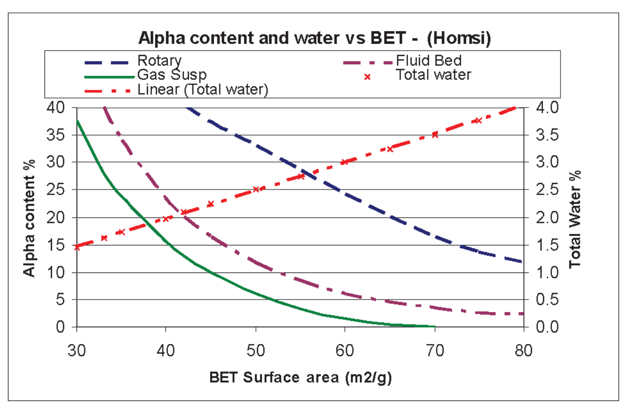

Figure 7. BET S.A. vs. Total Water. [7]

The tradeoff of %LOI vs. surface area can result in a cycle in which higher fluoride evolution demands greater surface area on alumina. Increases in %LOI will drive fluoride evolution rates to higher levels, creating something of a vicious circle.

The fluoride evolution factors described by Haupin and Kvande [4] also indicate that by increasing the specific exhaust rate on a pot that localized barometric pressure will decrease, resulting in a possible net increase in fluoride evolution. While the net effect upon average fluoride evolution has been small in cases where higher exhaust rates are limited to specific process activities, this may become a factor of concern with technologies that rely upon inordinately high pot evacuation rates. These would correspond to average evacuation rates greater than 60 acfm [250 F] per linear foot of pot hooding enclosure perimeter, or >0.0644 $Nm^3/sec/m$. These dimensions are schematically illustrated in Figure 8. While increased flow rates pull more air from the pot rooms to reduce roof line emissions, increased fluoride evolution may compromise the scrubbing efficiency of the GTC.

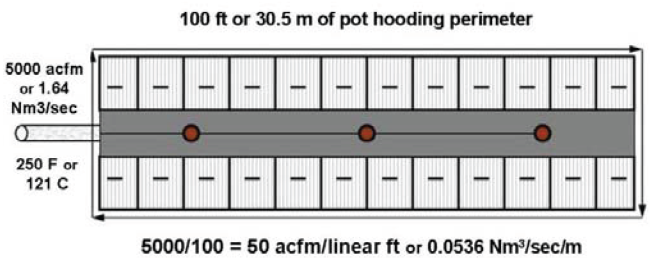

Figure 8. Illustration of hooding perimeter & exhaust flow.

Efficient and Effective Approaches

The best path forward in situations that challenge dry scrubber design fundamentals generally requires an efficient and effective use of resources as opposed to brute force. As indicated above, larger, more powerful systems may only amplify problems.

Pot superstructure designs are seldom efficient at capturing fluorides at low evacuation rates. Unless the design incorporates the vertical rise of convective evolution losses into the approach for fume capture, additional flow and energy will be required. Passive efficiency improvements can be accomplished with tapered profiles that guide pot fumes to well-balanced evacuation points. However, this may require a re-design of the pot superstructures.

A more pragmatic approach is to work with the thermal balance of the pots to assure that proper crust integrity can be sustained at higher line loads. This may require changes in anode size, stub diameter, and/or elements to spill more heat from the side or top of the cell. If the net result is an increase in fluoride evolution it is important to then understand how close this may move the pot line to saturation of the alumina. Some allowances must also be made for periods of minor upset condition during which fluoride evolution would be expected to rise temporarily.

In all cases a well-sealed pot crust is the best primary defense against high fluoride evolution rates. [7]

Lower overall pot exhaust flow rates may be enabled by uniform pot crust cover practices as well. Many modern cell technologies have been able to operate at reduced exhaust rates during periods of little activity to counter-balance the effects of exhaust rates that may be 2X to 3X normal exhaust during process activities such as anode changing. This approach works to minimize emissions, evolution, and alumina particle attrition, but a stable pot crust cover practice is an essential pre-condition for success.

Optimization of alumina flow through the dry scrubber is another approach that must be considered for modern smelting technology at boosted line load. There can be many approaches to redirect alumina flow to come closer to the ideal state where 100% of ore consumption actually passed through the dry scrubbers. In any case, the principles of equal parts of air to equal parts of alumina must still remain in effect.

The greatest area of opportunity for alumina flow optimization is often accomplished by eliminating the use of fresh alumina in the anode cover material recipe. This is often followed in importance by reducing the flow of reacted alumina through the anode baking furnace dry scrubber, if it is not widely dispersed as feed to pot room dry scrubbing systems. The third area with significant opportunity often has to do with reducing the crust ore feed rate to the pots, especially in circumstances where fresh alumina is used in the anode cover mix.

Conclusions

Modern pre-bake cell designs operating at higher line loads tend to increase fluoride evolution rates unless additional heat sinks are added to counter-balance increased energy input.

There are limits to how far this may go before fluoride emissions from gas treatment centers begin to rise sharply. These limits are a function of SGA surface area and scrubber technology and generally fall between 1.9% and 2.2% F on secondary alumina.

At times other system changes are made to support higher line loads that increase the net process gas flow from the pot lines. While many of these may be aimed at lower rates of fluoride emission via better capture of fume during process activities or add-on systems, there can be negative effects from higher flow rates. Increased attrition of alumina particles can be driven by higher system flows and velocities as well as by increases in alumina recirculation rates to avoid reductions in dry scrubber removal efficiency.

Answers are available in various forms. These include:

- Increased fractions of fresh alumina that pass through the dry scrubbing systems,
- Better utilization of the total SGA surface area available,
- Stable feed rates that support equal parts of process gas flow to equal parts of alumina,
- Proper thermal balancing and management of heat sinks,
- More efficient superstructure designs to capture fumes and
- Optimization of exhaust flow rates matched to process activities.

Finally, it is essential to include monitoring activities on test sections of pot at boosted line load to understand the impact of higher amperage on fluoride evolution rates. This may then be translated to estimates of the resultant percentage of fluoride on secondary alumina and the likelihood of approaching practical saturation conditions.

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