DEVELOPMENTS IN CALCINATION TECHNOLOGY FOR SMELTER GRADE ALUMINA

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Abstract

Stationary Calciners of different design and technology have gradually replaced Rotary Kilns for production of Smelter Grade Alumina (SGA).

The Gas Suspension Calciner (GSC) Units now being build, incorporates about 75 years of technology experience from design, operation and maintenance of Stationary Calciners.

The features of the new generation of Gas Suspension Calciners will be presented with respect to Alumina Quality, Capex, Opex and Environmental Compliance.

1. Introduction

Stationary Calciners of different design and technology have gradually replaced Rotary Kilns for production of Smelter Grade Alumina (SGA).

Below is shown current Alcoa Fluid Flash Calciner technology with 3360 TPD peak capacity (Mk 6) and two (2) FFEM Gas Suspension Calciner (GSC) units equipped with Electrostatic Precipitators and hydrate filters with a peak capacity exceeding 2300 TPD each.

The new generation of Gas Suspension Calciners with 4500 TPD capacity is equipped with Baghouse.

While Alcoa calciners have been referred to as “fluid flash” calciners and the FFE Minerals (FFEM) calciners as Gas Suspension Calciners, they are both applying essentially the same technology.

The Gas Suspension Calciner is therefore a more accurate description of the technology employed by both Alcoa and FFEM. The only real difference is in the arrangement of the vessels and minor variations in how hydrate bypass is applied and how the SSA of the alumina is delivered and controlled.

2. Alumina Quality

2.1 *Alumina Quality Ranking*

Alcoa has published an internal investigation [Williams, 1992] comparing and ranking alumina smelting characteristics as defined in smelters with alumina characteristics as measured by refineries and ranked in a corresponding order. The resulting characterization is shown below.

Table 1 — Smelter Ranked Alumina Characteristics

Rank	Smelting Characteristics	Refinery Characteristics
1	Consistent Flowability	–20 Micron Content
2	Good Solubility	–325 Mesh content
3	Low Soda Level	Angle of Repose
4	Low dusting	Moisture Content (SSA related)
5	Won’t Segregate	Flow Funnel Reading
6	Robust Strength	Attrition Index
7	Consistent Bulk Density	LOI
8	Capture Fluorides (SSA related)	Trash
9	Other Parameters	Sodium Content
10		Surface Area (SSA)

The ranking suggest the following conclusions:

Consistency in flowability of alumina is the primary quality requirement, which requires good short and long term quality control in precipitation and calcinations.

Table 2 — Consistency of Alumina from Gas Suspension Calciner

Plant A Data	Unit	Year	Average	Std. Deviation
Specific Surface Area (BET)	m^2/g	1992 2000	73 76	NA 5 (= 3* Sigma)
Alpha Alumina Phase	%	1992 2000	6 4	1 —
LOI (300-1000C)	Wt-%	1992 2000	0.80 0.81	0.05 —
PSD — 45 Micron	Wt-%	1992 2000	6.0 3.0	0.9 —
Attrition Index	Wt-%	1992 2000	7 5	— —

The above plant data shows both short and long term quality control in calcination. Also an improvement in hydrate quality resulting in less particle breakdown and production of a more robust alumina particle is indicated.

Production of alumina in calcination with consistent flowability requires production of alumina with a reliable Particle Size Distribution (PSD). This can be influenced by a calciner design minimizing particle breakdown (<45 micron particles). Particle Breakdown on 45 micron screen in the pre-calcination zone correlates with Hydrate Properties [Raahauge, 1980, 1982, 1993] such as:

- Particle Structure,
- Contamination with occluded solid sodium oxalate, and
- Attrition Index of the Hydrate.

A change of crystal system from monoclinic to orthorhombic takes place, when Gibbsite is transformed into Boehmite [Raahauge, 1982] during pre-calcination. This change in crystal system can be clearly observed by dynamic thermal microscopy and may influence the hydrate dependent particle breakdown.

Particle Breakdown and Fines Generation (< 20 micron particles) beyond a hydrate dependent threshold gas velocity, depends on Fluid Dynamic Conditions [Raahaugr, 1982], such as:

- “Streamline” Geometry of Duct and Cyclone Inlets

KEY WORDS: calciners, quality, opex, environment, capex

- Maximum Critical Gas Velocity at different locations
- Minimum in-plant solids handling, i.e. minimum number of Cyclone Passes

The second ranked priority is to produce alumina with a good solubility, which apart from the requirements to the PSD of alumina requires production of alumina with a high degree of dis-order in the crystal structure [Allais, 1993].

Disorder in the crystal structure [Raahauge,1981] versus solids retention time is clearly indicated in Table 3, by the difference in alpha phase content between alumina from a GSC and alumina from a rotary kiln, while SSA and LOI are essentially the same.

Table 3 — Disorder in Alumina Crystal Structure versus Calcination Technology

Plant B Data	Unit	GSC	Rotary Kiln
Solids Retention Time		10–12 seconds	90–150 min.
Specific Surface Area (BET)	m^2/g	76	78
Alpha Alumina Phase	%	3	16
LOI(300–10000C)	wgt-%	0.76	0.84
Particle Size: –45 Micron	wgt-%	5.9	5.7
Attrition Index	wgt-%	15.1	21.0

Aluminium Pechiney has emphasized several times, that the correlations observed between crystal organization, moisture content and specific surface differ to a fair extent as between calcination technologies [Allais, 1993 and Homsi, 2001].

The attrition index (“or fragility”) of hydrate particles increases during pre-calcination above 250°C and subsequently decreases during final calcination to smelter grade alumina in both laboratory [Zwicker, 1985] and full scale calcination plants.

However, the fast heating in gas suspension systems have also indicated that an alumina with minimum attrition index is obtained [Zwicker, 1985] as can be supported from the above plant data. This benefit is obtained without generating significant additional particle breakdown owing to the “thermal shock” conditions in the gas phase.

The reason being, that the strongly endothermic calcination process is an efficient “heat sink/ brake” on the rate of the temperature rise of each particle.

Furthermore, the layer of calcined solid surrounding the un-calcined core of each particle is very porous preventing the build-up of excessive vapor pressures at the calcination front inside the particles.

In view of the above, and by referring to Figure 2B, the features of the GSC technology can be summarized as follows:

Uniform Calcination in One (1) Pass Only

- No Re-Circulation of Partially Calcined (“Weak”) Alumina

Low Particle Breakdown and Generation of Superfines owing to:

- Advanced Design of Cyclone Inlet Duct Geometry
- Seven (7) or less Cyclone Passes from Hydrate to Alumina
- Minimum solids handling without Re-Circulation of partially calcined (“Weak”) Alumina

Figure 1A — Alcoa Fluid Flash Calciner

Figure 1B — Gas Suspension Calciner (GSC)

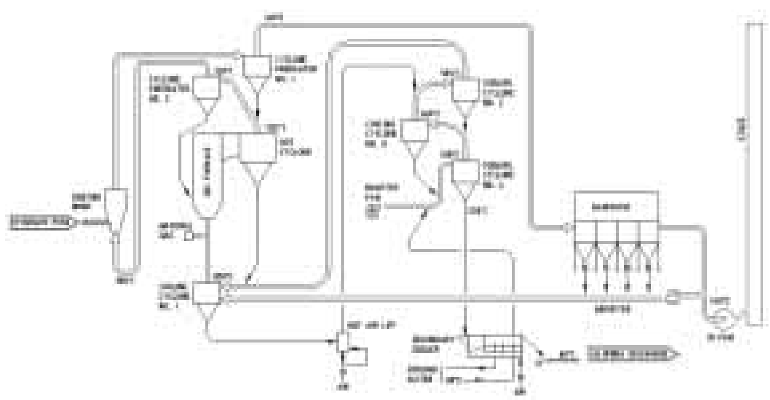

Figure 2A — Gas Suspension Calciner (GSC)

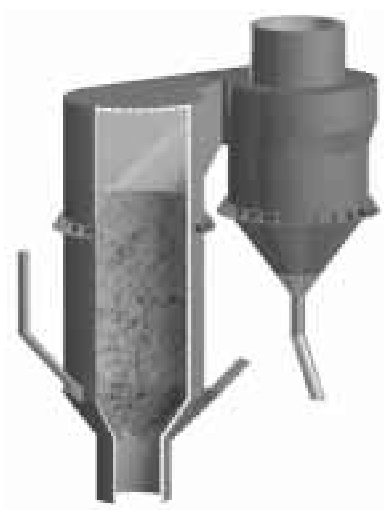

Figure 2B — Gas Suspension Calciner Furnace

Potential for Improved Solubility of Alumina owing to:
- High degree of crystal dis-order resulting from calcination at high temperture and short retention time

2.2 *Flexibility in Calciner Design Options*

Consistency in Calcination Control with a targeted SSA of 3*Sigma <5 m^2/g is achievable from the following Calciner Design Options from FFE Minerals:

2.2.1 *GSC with Standard Cyclone Design for Pull or Push/Pull Operation (Figure 1B)*

- Capacity range: 750–2800 TPD
- Easy to Operate and Maintain
- High Availability

2.2.2 *GSC Hybrid with New Cyclone Design for Pull or Push/Pull Operation (Figure 2A)*

- Capacity Range: 1000–4500 TPD
- Easy to Operate & Maintain
- Low Capex

2.2.3 *Standard Alcoa Mk VI Unit for Pull or Push Operation (Figure 1A)*

- Capacity Range: 2500–3360 TPD
- Equipped with Holding Vessels and Hydrate By-Pass
- Short Downtime
- Low Opex and Refractory Lifecycle Cost

2.2.4 *Control Strategies versus Calciner Design*

In GSC units, the Alumina Quality (Degree of Calcination) is controlled through Calcination Temperature by adjustment of the Fuel Rate, independent of Calciner Production Rate.

In Alcoa Mk VI units the Alumina Quality is controlled through Calcination Temperature by adjustment of the Calciner Feed Rate maintaining a fixed Fuel Rate.

3. Operating Cost Expenditures (Opex)

3.1 *Operating Stability*

The major factors impacting on the operating cost of calciners are the cost of energy and maintenance costs. Apart from the basic cost of fuel, energy cost as a function of specific heat consumption expressed in GJ/tonne of alumina, is significantly impacted by the consistency of the operation. The greater the variation in throughput and the number of planned and unplanned outages the higher will be the energy consumption. Older style gas suspension calciners (with hydrate bypass and internal surge vessels built in the late 1970s), operating reasonably consistently can achieve a net energy consumption of around 3.1 GJ/tonne of alumina (based on the HHV), whereas the same design calciners operating with a number of unplanned outages will consume energy in the order of 3.4 to 3.6 GJ/tonne of alumina.

3.2 *Maintenance Costs*

Maintenance costs are generally divided into two categories, Planned and Unplanned. Clearly to reduce operating costs the unplanned outages must be reduced but so too must be the planned outages. In the past Alcoa calciners were overhauled every 12 months, driven mainly by the refractory requirements. Over the past 10 years calciner capacity has increased and the period between refractory overhauls has increased to 2 to 3 years in most cases, with a reduction in the scope of refractory work. With major refractory overhauls costing in the order of AU$ 1M to 2M there is a clear driver to extend the period between major refractory overhauls.

There are many areas in calciners where the refractory survives well in excess of 20 yrs and there is clear evidence that with attention to detail in the design of refractory systems, selection, installation, heating and cooling schedules, refractories can survive in excess of 10 yrs in all areas. But at a cost that must be balanced against the advantages of longer campaigns between major refractory overhauls.

3.3 *Fuel Types*

For gas suspension calciners, where all the combustion air is used for cooling the alumina, the air flow through a calciner has little impact on the energy requirements. If more air enters the cooling section then more energy will be recovered from the alumina. This energy recovery is mostly offset by an increase in the losses to the stack. However, the losses to the stack will be higher for coal gas than for heavy fuel oil and natural gas, owing to the fact that coal gas produces relatively more products of combustion per unit heat released by combustion.

Coal gas has the added disadvantage that due to it's low calorific value, large volumes of coal gas are required and this large volume of gas must itself be heated to calcining temperature, further reducing the energy efficiency of coal gas. Furthermore the relatively low requirement of air for combustion, results in a relatively higher amount of sensitive heat lost to the cooling water when using coal gas as fuel (less recovery of heat from the alumina).

Fuel oil has the disadvantage of requiring a significant investment in storage and oil heating equipment. This along with the potential future issues regarding sulfur emissions makes heavy fuel oil less attractive than natural gas as a fuel for alumina calciners, despite its lower higher heating value per unit heat released by combustion.

3.4 *Specific Heat Consumption.*

3.4.1 *Gas — Solid contacting to maximize efficiency using "spreader boxes"*

Heat transfer in a GSC results from several stages of mixing gas and solids prior to separating them again to move to the next heat exchange stage. If the mixing of the gas and solids is not sufficient there will be a significant difference between the exit temperatures of both streams leading to lower thermal efficiency. Attention to detail in this area through the design and application of appropriate "spreader boxes", enables effective mixing and low temperature differentials. The spreader boxes as used by FFEM have a proven track record through the cement industry as well as in alumina calcination.

Table 4 — Typical Fuel Data impacts Calciner Operating Cost

Fuel Type	Typical Lower Heating Value (LHV)	Combustion Air Theoretical Volume Nm^3/ GJ	Combustion Gas Theoretical Volume Nm^3/ GJ	HHV/LHV
Heavy Fuel Oil	40.485 MJ/Kg	264	279	1.061
Natural gas	37.345 MJ/Nm^3	253	281	1.107
Coal Gas	6.530 MJ/Nm^3	208	326	1.058

3.4.2 *Effect of Holding Vessel.*

Because SSA is time and temperature dependent, the use of holding vessels as in Alcoa calciners allows the alumina to reach target SSA with lower temperatures in the furnace.

The operational benefit therefore of a holding vessel is that there is less heat to recover from the alumina and there is therefore a slightly lower energy requirement.

3.4.3 *Hydrate By-Pass (HB-P) Options*

Hydrate By-Pass applied to Gas Suspension Calciners was patented by FFE Minerals in 1979 [Raahauge, 1979] and later practiced by Alcoa, Alcan and others [Schmidt, 1996] in various ways.

In GSC units, dust containing hydrate is recycled from the ESP/Baghouse catch to the top cooling cyclone operating at about 700°C, to ensure sufficient calcination. Subject to the collection efficiency of the top cyclone and the amount of dry hydrate particles in the dust, a 2–5% hydrate by-pass of fine particles only, is realized this way.

Mathematical calciner plant modeling, allows the theoretical calculation of the effect of hydrate by-pass on the degree of calcination of the resulting alumina quality with corresponding values for SSA, LOI and Alpha phase content.

In the below table, it is noteworthy, that the Alpha phase content can be "designed" to different levels suiting a particular smelter technology, without violating the smelter requirements to SSA and LOI.

Table 5 — Theoretical Hydrate By-Pass (HB-P) in GSC units

HB-P (%)	SSA (m^2/g)	LOI (wt-%)	Alpha (%)	Temperature (°C)
0	77	0,76	3,8	1072
4	77	0,75	3,9	945
8	77	0,70	4,7	843
16	77	0,72	12,2	703

The savings in fuel consumption from the lower temperature of alumina discharged from the HB-P into the cooling system, depends on the plant design with respect to efficiency of heat recovery from the hot alumina in the cooling system. The amount of HB-P possible depends on the operating conditions with respect to calcining temperature level and retention time in the calcining furnace.

Practical experience in Alcoa plants equipped with holding vessel and HB-P suggest a fuel saving amounting to about 3%. A simultaneous increase in calcining capacity is also possible owing to the lower air temperature and gas velocities in the cooling system.

Needless to say, the plant design and operation of a calciner incorporating a HB-P is more complex, though fully automated and as reliable as a plant design without HB-P.

3.5 *Power Consumption*

3.5.1 *Pressure Drop*

Calciners are designed with a typical operating pressure drop of 11–12 kPa to be overcome by the primary gas/air moving fan/blower. The above pressure drop reflects the "streamlining" design geometry of the calciners and the air/gas velocities specified in designing the calciners. The air/gas velocities are selected to avoid refractory wear and minimize particle breakdown and fines generation. Smaller capacity secondary centrifugal or positive displacement blowers, are selected to supply air at 35–45 kPa(g) for fluidized bed coolers, hot air lift and dust pump applications.

3.5.2 *Pressure profiles versus plant design*

Pressure Above Ambient (Push): A centrifugal blower is used in positive pressure (push) units, like the Alcoa Mk VI calciner.

Pressure Below Ambient (Pull): An ID-fan is used in fully negative pressure units, like in the FFE Minerals standard design of Gas Suspension Calciners.

Pressure Partially Below Ambient (Push/Pull): An FD-fan on the air side is used in combination with an ID-fan in partially negative pressure units like in the newly designed Gas Suspension Calciner units by FFE Minerals incorporating Alcoa technology.

3.5.3 *Specific Power Consumption*

Typical specific power consumption of the different plant designs is shown below.

Table 6 — Specific Power Consumption versus Air/Gas Moving Equipment Design

Plant Design	Push	Pull	Push/Pull
Primary Fan/Blower	Centrifugal Blower	ID — Fan	FD and ID — Fan
Air/Gas Flow	100% Air	100% Gas	85% Air/ 100% Gas
Secondary Blower	15% Air	15% Air	15% Air
Total * Spec. Power	8,3 kWh/ton	17,4 kWh/ton	14,8 kWh/ton

4. Environmental Compliance

4.1 *Particulate Emission*

Until recently all calciners have been equipped with Electrostatic Precipitators owing to their cost effectiveness and flexibility towards accepting temperature excursions up to 400°C. However, recently Baghouses have been preferred owing to their ability to functioning under operating conditions where the power to Electrostatic Precipitators have to be cut to prevent explosion risk of gas mixtures containing un-burnt fuel and/or CO.

Below typical properties of alumina dust is from a GSC unit.

Table 7 — Typical properties of Alumina Dust from GSC Unit

Electrostatic Precipitator Catch	Unit	Typical Range
Na_2O (Soluble)	Wt-%	0.2–0.5
LOI(300-1000°C)	Wt-%	4–5
SSA	m^2/g	190–235
Alpha Phase (by X-Ray)	%	4–12
+ 45 micron (by Alpine)	%	3–9
– 45 micron (by Laser)	%	91–97
– 20 micron (by laser)	%	65–79

Fines Generation in the precipitation circuit or calciner, will to a large extent report to the dust catch. Increased dust load will increase the build-up of inter cyclone stage circulations and should as such be minimized, in order not to overload the dust handling capacity of the cyclones and cause unnecessary wear on the refractory lining.

ESP's or Baghouses are designed for the alumina dust to be fully recycled, or partially separated from the final alumina product, subject to compliance with the targeted alumina quality for shipment.

4.2 *Sources of Gaseous Emissions SOx, NOx, CO and VOC's*

4.2.1 *Fuel Types*

- A mixture of SO_2/SO_3 is formed from burning of heavy fuel oil resulting in a stack gas dew point in the 130–145°C range subject to sulfur content of the oil. In a GSC unit about 20% of the fuel sulfur reports to the alumina.
- A mixture of NO_2/NO_3 (NO_x) is formed from combustion of all the above mentioned fuel types as thermal NOx. Fuel NOx may also be formed when combustion of heavy fuel oil or coal gas containing nitrogen compounds is used. In GSC units using Natural Gas as fuel, less than 20 ppm NOx emission have been experienced.
- CO can be formed during sub-stoichiometric combustion of all fuels, but this is rarely a problem in Gas Suspension Calciners at prevailing calcination temperatures, with a proper functioning burner management system and pre-mixing of all combustion air and fuel.

4.2.2 *Liquor/Solid Impurities*

- Hydrate containing organic material from the precipitation stage and filter aids, liberates CO as a decomposition product of solid sodium oxalate and VOC's when heated in the pre-calcination stage to above 200–250°C. In GSC units about 70 ppm CO have been experienced from these impurities.
- VOC's are liberated in the pre-calcination stage from hydrates containing organic material from the precipitation stage. This may decompose to odours and CO emitted through the calcination stack. Less than 20 ppm VOC have been experienced in GSC units operating on non-Australian hydrate.

4.3 *In-situ VOC Destruction*

The Gas Suspension Calciners equipped with baghouses and operating with full recycle of the alumina dust to the hottest alumina cooling cyclone, offers the possibility of in-situ destruction of VOC's (patent pending).

The VOC's are adsorbed onto the alumina dust with high SSA in the baghouse (see table 7), owing to the increased gas — solid contact time provided between each cleaning cycle.

When the alumina dust is recycled back into the hottest alumina cooling cyclone, the adsorbed VOC's are thermally stripped-off into the hot combustion air flowing into the GSC furnace and then ultimately combusted,

5. Capital Expenditures (Capex)

5.1 *Plant Lay-Out Options*

Through combining of the Alcoa and FFEM technology there is the potential to design calciners with a number of configurations. These configurations range from the typical Alcoa, basically horizontal design with pneumatic solids air lifts and internal surge capacity to FFEM's original vertical design optimizing the use of gravity.

Recent studies have shown that the most cost effective layout appears to be a combination of the above

5.2 *External Feed Bins versus In-plant Surge Capacity*

Alcoa have traditionally used internal surge capacity to smooth out variations in hydrate feed whereas FFEM have used external damp hydrate storage bins. The advantage of the external damp hydrate storage bin is that it is cost effective to have a significantly larger storage capacity and variations or short interruptions to the filter operation have no impact on the calciner operation. This issue is critical to maintaining consistent operation and maintaining product quality and low energy consumption. This arrangement also allows for the process steps of filtration and calcination to be separated both physically and operationally, which has benefits in some applications.

5.3 *Optional Compact Arrangement with different Pressure profiles.*

GSC units can be designed for either positive or negative pressure or both.

A calciner designed for negative pressure will be physically larger for a given velocity profile but has the potential to be significantly increased in throughput by the addition of an FD blower, without significantly increasing the velocity profile through the calciner.

A calciner having negative pressure, requires larger gas cleaning equipment due to the increase in gas volume at the lower absolute gas pressure. However, there are no safety issues from potential leaks and some plant permits opening of vessels on-line.

5.4 *Holding Vessel*

If a holding vessel is used to provide some residence time for alumina then the maximum operating temperature of the furnace can be reduced. Reducing the furnace temperature reduces the thickness of the refractory and size of the furnace, and hence the capital cost.

The cost reduction of the smaller furnace is offset by the inclusion of the holding vessel. However, the optimization with respect to operating temperature, retention time and size of the furnace with the location and subsequent height of the building needs to be considered here.

5.5 *Hydrate bypass*

Hydrate bypass can be used to control SSA and to recover energy from hot alumina. If hydrate bypass is to be used then higher furnace temperature is required to offset the impact on SSA of the hydrate bypass (re. Table 4). The net impact of hydrate bypass on capital cost is therefore quite small.

5.6 *Refractory design, Surface Heat losses and Life Cycle Cost*

With the combination of current refractory technology and low velocities in calciners it is possible to design calciners with refractory that will last well in excess of 10 yrs between major overhauls. There is of course a premium to pay for these refractories which needs to be balanced with the cost of maintenance and the associated extended outages required to repair/replace refractories.

Part of achieving the above success is achieving a balance between the surface heat losses and the type of refractory used. Calciner refractory linings are typically two component linings (insulation and wear resisting). It is possible to design the insulation layer such that design shell temperatures can be achieved with very thin layers, however these materials are typically very low density and are easily eroded through any cracks in the wear resisting lining and/or crushed due to the differential thermal expansion. The compromise is to design thicker, stronger and more dense insulation layers. The result is a more expensive installation but with increased reliability.

6. Looking Ahead

The major cost drivers can be confined to construction and operating cost as well as environmental compliance.

6.1 *Construction Cost*

Construction cost factors from engineering to supply of equipment and bill of materials including field labor etc., increases with number, complexity and size of vessels needed for the calcination process. Consequently, the development work currently undertaken by FFEM and Alcoa is driven by the target of reducing the number, complexity and size of vessels needed.

6.2 *Operating Cost*

Operating cost is impacted by external price factors that are market economy driven in the short term. In the long term, the specific utility factors are driven by new process technology development such as the Alcoa pressure calcination process [Sucech, 1986].

However, the size of the global calcination market for alumina and the likely achievable reduction in specific utility factor(s), is not sufficient to economically justify a systematic and planned development of breakthrough technology. Therefore, this will most likely come from outside the alumina industry like in the past, unless it happens by sheer luck.

Consequently FFEM and Alcoa focuses the technology development towards improving availability, up-time between refractory overhauls, as well as operational stability and reliability of the calciners.

6.3 *Environmental Compliance*

Environmental requirements are externally driven by the globalization of the issue, as well as the local/regional urbanization process taking place simultaneously with the industrial development.

As the allowed particulate emission is gradually reduced from, typically 50 mg/Nm^3 (wet) to 25 mg/Nm^3 (wet) [~ 50 mg/Nm^3 (dry)], the cost efficiency of baghouses will tend to be comparable with electrostatic precipitators [Pedersen, 2002].

The short term development path with respect to environmental compliance followed by FFEM and Alcoa, will be to optimize the bag selection and in-situ VOC destruction capability of baghouses in full scale operation.

Acknowledgements

The authors are grateful to the many people among our customers and colleagues who have made this work possible.

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