"Experience with Commissioning New Generation Gas Suspension Calciner"

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Abstract

Gas Suspension Calciners (GSC) for Alumina have been designed, supplied and commissioned by FLSmidth since 1984 with a nameplate capacity from 820 to 4500 tpd of Smelter Grade Alumina (SGA). Several of these units have been supplied to China using Coal Gas as fuel, and the GSC technology is now used in almost all Chinese refineries build since 2005.

The first two (2) of seven (7) new generation GSC units with name plate capacity from 2500 to 3500 tpd SGA is now being commissioned at Rio Tinto Alcan's Yarwun Refinery in Australia. This paper describes design features of the new generation GSC units and reports the latest operating data with respect to alumina capacity and quality, environmental emissions and energy efficiency.

Introduction

The first oil fired GSC unit equipped with Electrostatic Precipitator was commissioned at Hindalco, India in 1986 [1], meeting all performance guarantees when replacing three (3) rotary kilns from 1954-56, (See figure 1).

Figure 1. 850 tpd GSC Unit, Hindalco, India.

In 1991, FLSmidth was the first to start-up GSC units using coal gas as fuel at the Shanxi Aluminium Plant in China utilizing a similar vertical arrangement as Hindalco.

Since then, many different Chinese companies have built many more GSC units [2] than the nine (9) GSC units, supplied by FLSmidth to China since 1987, with calcining capacities ranging from 820-1900 tpd.

Over time FLSmidth, has supplied and started up many GSC units, including the world largest stationary calciners with a capacity of 4500 tpd each, at Queensland Alumina Limited, Australia, where three (3) GSC units were replacing nine (9) 900 tpd Rotary Kilns equipped with Electrostatic Precipitators [3] in 2004-2005. These GSC units were Natural Gas fired and the first to be equipped with Fabric Filters (Bag House).

The latest GSC units under commissioning are two (2) 3200 tpd GSC units at Rio Tinto Alcan's (RTA) Yarwun Alumina Refinery in Queensland (Figure 2). These units are expandable to 3500 tpd to reach the nameplate capacity of the Worsley No. 6 GSC unit, also being commissioned presently.

Figure 2. Two (2) x 2300 tpd and Two (2) x 3200 tpd GSC Units at RTA Yarwun, Australia.

This paper describes some of the early commissioning experience with these GSC units, as well as some long term experience with other GSC units.

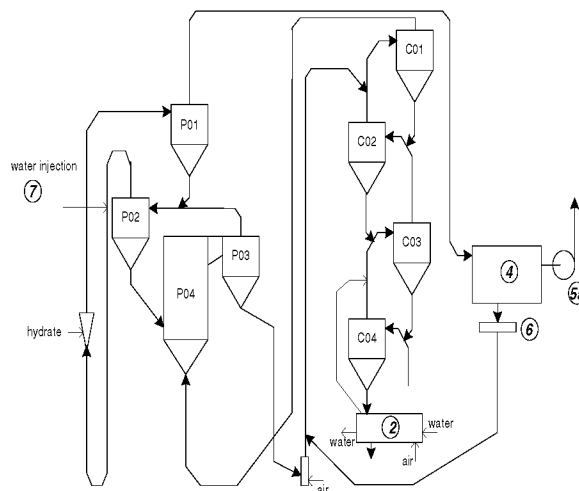### GSC Process – Arrangement and Flow Sheet

Figure 3. GSC flow sheet – Semi Vertical Arrangement without Holding Vessel.

FLS GSC Units comprises four main sections (Figure 3):

- Drying and Pre-heating/Pre-Calcination (P01,P02);
- Calcination Furnace (P04) and Furnace Cyclone (P03);
- 4 Stage Cyclone Cooler (C01-C04) for Heat Recovery from alumina by direct cooling with Air;
- Fluidized Bed Cooler (FBC) for Indirect alumina cooling with water.

Many physical-chemical processes are involved in the calcination of alumina hydrate.
When the moist hydrate enter the GSC system it is mixed with hot gases from both combustion of fuel and the calcination reactions.
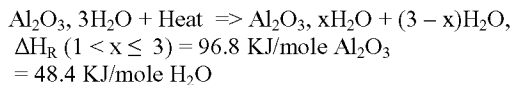
The purpose of the venturi and the first two cyclone stages is to utilize the heat for drying, pre-heating and pre-calcination of the hydrate. The foremost processes/ unit operations are suspension of the solids in the gas phase for proper heat- and mass-transfer and gas-solids separation.

Calcination in Theory and Practice

The overall basic and simplified thermo chemical reactions taken place, when converting alumina hydrate to smelter grade alumina by calcination is:
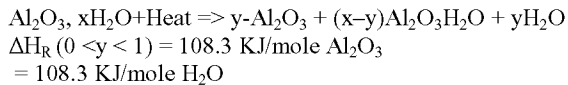
(1) Pre-calcination (P01-P02):
$$250 - 380^{\circ}C$$
$Al_2O_3, 3H_2O + Heat \Rightarrow Al_2O_3, xH_2O + (3 - x)H_2O,$
$\Delta H_R\ (1 < x \leq 3) = 96.8$ KJ/mole Al_2O_3
$= 48.4$ KJ/mole H_2O

(2) Calcination (P04-P03):
$$380 - 1075^{\circ}C$$
$Al_2O_3, xH_2O + Heat \Rightarrow y\text{-}Al_2O_3 + (x\text{--}y)Al_2O_3H_2O + yH_2O$
$\Delta H_R\ (0 < y < 1) = 108.3$ KJ/mole Al_2O_3
$= 108.3$ KJ/mole H_2O

(3) Alpha Alumina formation (P04-P03)
$$900 - 1075^{\circ}C$$
$y\text{-}Al_2O_3 \Rightarrow \alpha\text{-}Al_2O_3 + Heat$
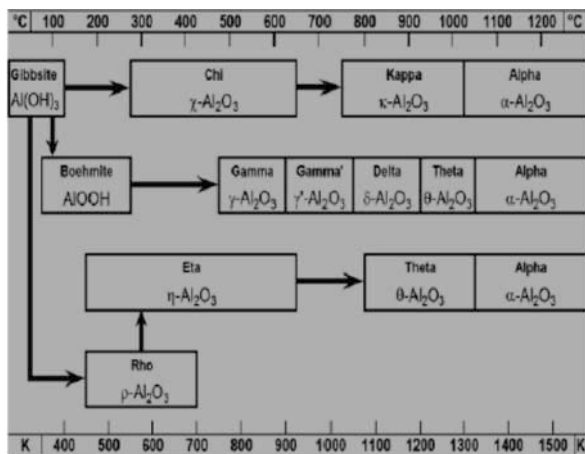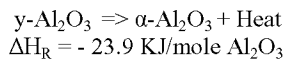$\Delta H_R = - 23.9$ KJ/mole Al_2O_3

Figure 4. Phase changes during Calcination [19].

In the above reactions 0 and (2) the calcination reactions remove water by the rate of heat-transfer to the reaction front of the solid particles. The final reaction 0 is the formation of α–alumina phase, which takes place through several intermediate solid state phase changes as illustrated in Figure 4, adapted from Wefers and Misra, Alcoa technical Paper No. 19. The phase changes taking place during calcinations of Gibbsite in the Gas Suspension Calcination process, is mainly via the path Gibbsite to Rho-, to Gamma/Alpha – phase [5], as only 3-8% Boehmite phase has been detected in material samples of cyclone P02 under flow to the Furnace/Reactor:

(4) Gibbsite => Rho => Gamma => Gamma' => Delta => Theta => Alpha Conversion

The Gas Suspension Furnace/Reactor is at the heart of the GSC process:
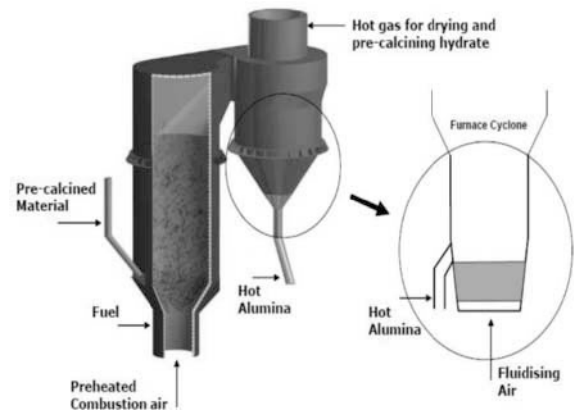

Figure 5: Gas Suspension Furnace/Reactor without Fluidized Holding Vessel and With.

The hydrate is partly calcined in the riser duct to the second pre-heater cyclone (P02), but will continue to react in the next section, which is the calciner furnace/reactor followed by a fluidized holding vessel. The fuel is injected into the furnace and combusted at a rate necessary to achieve and control the furnace temperature.

The hot combustion gases entrain the partially calcined alumina from the furnace/reactor (P04) into the Holding vessel (HV03), where sufficient retention time is provided to reach the final degree of calcination (LOI, SSA and alpha phase), and thus smelter grade alumina quality.

The Furnace/Reactor has the multiple functions of:

- Providing sufficient gas retention time for combustion of the fuel at the prevailing temperature;
- Provide dispersion of the pre-calcined alumina particles entering at about 320°C;
- Provide fluid dynamic condition for effective heat transfer between the burning fuel gas and the surface of the pre-calcined alumina particles.
- Provide sufficient solids retention time for calcination of the pre-calcined alumina particles entering with an LOI (0 – 1000°C) of 7 – 25%, subject to particle size (see

Figure 8 below), without generating excessive particle breakdown.

➢ Provide fluid dynamic condition for effective mass transfer of water vapor from the surface of the alumina particles and into the bulk gas phase leaving the Furnace/Reactor at an elevated temperature.

In the above context, calcination of the pre-calcined alumina particles means the four (4) process steps comprising:

(1) Conduction of heat from the particle surface through the porous transition alumina phase to the reaction front, where reaction (2) needs heat to take place.
(2) Release of solid state "crystal water" as water vapor at the reaction front, when close hydroxyls react through a proton capture mechanism [4].
(3) Diffusion of water vapor from the reaction front in the particle to the surface of the particles.
(4) Phase transformation and partial formation of Alpha phase according to reaction (3) in that part of the particle where crystal water has been removed.

As a result of the above endothermic calcination processes (1) and (2), the calcined part of each solid particle becomes very porous with a large surface area as seen in Figure 6 below.
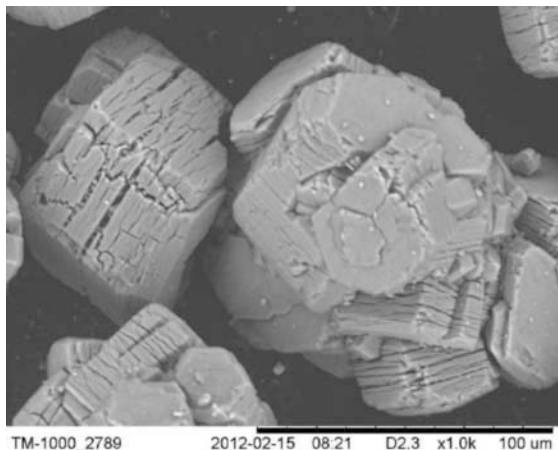

Figure 6: Alumina from GSC plant.

The internal porosity of the calcined particle makes it relatively easy for water vapour to escape from the reaction front, in the interior of the particle, and diffuse to the surface of the particle.
Therefore no excessive water vapour pressure is formed that causes particle breakage contrary to what has been reported elsewhere [4].
On the other hand, Alpha – phase formation tends to start at the outer surface of the particles owing to the relatively low rate of heat conduction through the porous calcined layer of intermediate alumina phases.

New GSC Process Flow Sheet

The latest design of GSC plant incorporates a fluidized holding vessel, HV03, with several minutes of solids retention time (Figure 7).
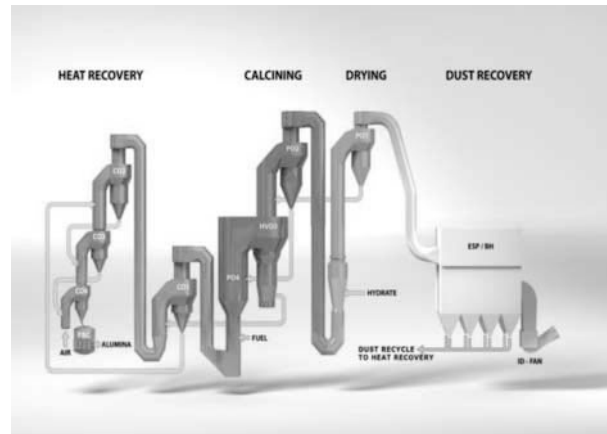

Figure 7. FLS GSC flow sheet with Fluidized Holding Vessel.

This design allows the calcination temperature in the Gas Suspension Furnace/Reactor to be reduced from about 1050°C to less than 950°C, without sacrificing insufficient gas retention time to achieve complete combustion of the fuel used.

However, the approximately 100°C lower temperature of the gas out of the Furnace/Reactor and into the holding vessel (furnace cyclone), HV03, contain less energy available for the pre-calcination. This means that some of the pre-calcination according to reaction (1) is moved from P02 cyclone riser into the Furnace/Reactor.

This is confirmed by analysing the underflow from the second preheating cyclone, P02, which reveals higher amounts of gibbsite/LOI in calcinations systems with holding vessels compared to calcinations systems without. This has no effect on the final alumina quality as the material is fully calcined in the Furnace/Reactor and Holding Vessel, HV03, anyway as seen from Figure 8 below.
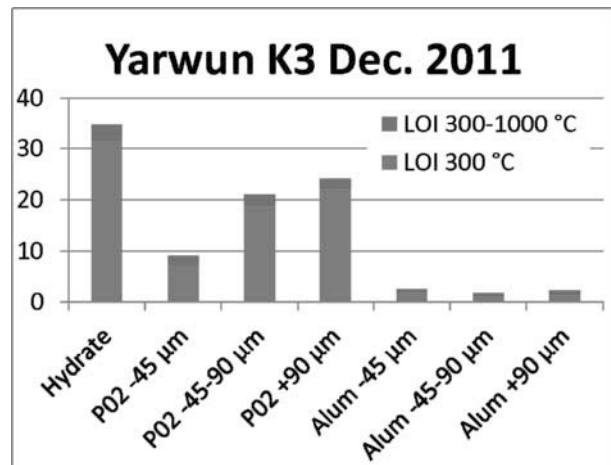

Figure 8. Size Fraction LOI (0-1000°C) from PO2 versus GSC Produced Alumina.

The introduction of a proven Fluidized Holding Vessel with overflow discharge, into the new GSC process flow sheet in a Semi - Vertical arrangement (see Figure 7 above), do not in

any way reduce the easy, responsive and stable operating characteristics of the GSC process.

The advantages and disadvantages of installing a holding vessel is:

- ✓ Reduced calcination temperature => Smaller vessel size => Lower Capex;
- ✓ Lower Alumina temperature to Fluid Bed => Smaller quantity of cooling water => Lower Opex;
- ✓ Less refractory thickness installed to reach the same shell temperature => Less Capex;
- ✓ Lower thermal stress on the refractory lining => Longer service life => Lower Opex;
- ✓ Installation of High Temperature Fluid Bed => Higher Capex;
- ✓ Blowing and Heating fluidization air to stack temperature => Higher Opex; (insignificant)

Overall, the installation of the fluidized Holding Vessel resulted in lower Capex and Opex. Several other new design features have been introduced into the new generation GSC units in order to reduce the dust circulation around the Fabric Filter, so that all dust is re-cycled completely without the need of any additional process equipment such as a dust lift calciner [3], or the necessity of bleeding dust to the Fluid Bed cooler.

The Hydrate Drying and Pre-Heating/Pre-Calcination (P01 & P02) comprise two stages that are very similar in all calcination flow sheets. This is dictated by the drying requirement of hydrate with typically 6 – 9% surface moisture and the thermo chemistry of the calcination process. However, the dust collected from cyclone P01 contains both gibbsite and a fraction of α-alumina phase and constitutes a small Hydrate By-pass.

In the FLS and Alcoa calciner flow sheets, dust from cyclone P01 enters an ESP (4) or Bag House [4], from where it can be either fully or partially recycled back (dust management) to the calcination process. No gibbsite is detected in the alumina from the FBC (Figure 9) due to all the dust being re-entered into the main alumina stream. This is because the dust enters a cooling cyclone with high enough temperature for complete pre-calcination to take place in accordance with reaction (1). The below TGA DTA curve for alumina shows no presence of Gibbsite.

Smelter Grade Alumina Quality

The primary quality requirements from Smelters are to receive a consistent Smelter Grade Alumina (SGA) quality with each shipment. This is especially so with respect to bulk density and Particle Size Distribution (PSD) for modern cells with point feeders. Ideally this should be possible to a large extent given well known and accepted international specifications [6].This is however not always easy, when considering the many chemical and physical parameters to fulfil [7] owing to the dual application of the smelter grade alumina for (1) removal of HF from the smelter gasses in Dry Scrubbers, before it is used as (2) feed stock for production of primary aluminium in the electrolytic pot/cells. So what can the real impact from Calcination be?
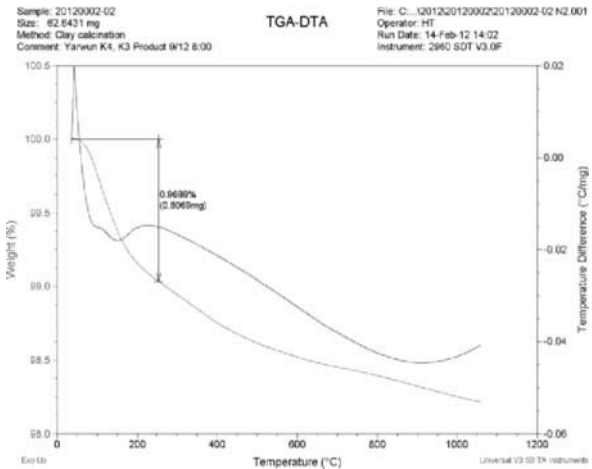

Figure 9. GSC Produced Alumina with no Gibbsite.

Alumina for Removal of HF in Dry Scrubbers

The Specific Surface Area (SSA) is the primary physical property of the alumina specified, for capturing HF gas emitted from the smelting pots, in the Dry Scrubbing, Gas Treatment Centres. However, during calcination, the pore size distribution in alumina has recently been of interest [8].The development of pore size during Gas Suspension Calcination is shown in Table 1 below.

Physical Parameter / GSC Design	Pore size (nm)	Pore volume (cm³/g)	BET (m²/g)
GSC with HV P02 material	4.2	0.07	109.2
GSC with HV alumina	6.6	0.14	80.6
GSC without HV Alumina 1	8.8	0.3	75.5

Table 1. Pore Size Distribution of GSC Alumina.

The pore size distribution of alumina from GSC units, is mono dispersed with an average pore size of 6 – 9 nm. The range 6-8 nm is believed to be optimal [7], though still not proven to be of importance [7, 8] for the HF adsorption capacity of alumina. Here it is worthwhile to remember that the size of HF and H_2O molecules respectively, is of the order of 0.092 and 0.096 - 0.152 nm, only.
According to earlier work [9], there is no apparent correlation between alumina phase composition, pore size, pore volume, surface acidity, MOI or LOI (300-1000°C), and adsorption of HF on alumina plant samples. HF adsorption on plant samples is correlated with SSA, though not totally linear like for laboratory calcined samples from the same hydrate source [9].

Alumina Degree of Calcination

The Degree of Calcination parameters comprises Gibbsite, LOI (300-1000 C), SSA and Alpha phase content, in Alumina from GSC units equipped with and without Fluidized Holding Vessel, and having different calcining capacities as well.

The below Table 2 shows typical values of Degree of Calcination in Alumina from GSC Units:

Degree of Calcination	Gibbsite wt %	LOI 300 - 1000°C wt %	BET m^2/g	Alpha %
No Holding Vessel 2100/2300 tpd	<0.1	0.69	73-74	4-6
No Holding Vessel 4500 tpd	<0.1-0.2	< 1.0	75-78	4-6
Holding Vessel 3200/3500 tpd	<0.1	0.8	74-81	3-5

Table 2. Degree of Calcination of GSC Alumina.

Alumina Strength and Particle Size

Dry Scrubbers and alumina handling in general requires a strong alumina particle [10], as measured by the Attrition Index (AI), in addition to sufficient Specific Surface Area (SSA) to meet the guaranteed scrubbing efficiency and PSD of the alumina as pot feed.
The strength, or rather friability of alumina particles (AI) from any stationary calciner is mainly determined by the hydrate particle morphology (be it mosaic or radial) established in the precipitation circuit of the Alumina Refinery [11].
However, increasing the heating rates decreases the AI [12], as seen when comparing AI values of alumina from a rotary kiln with AI values of alumina from a GSC [11].
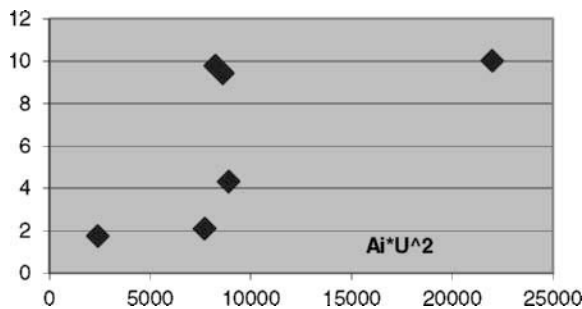

Figure 10: Particle Breakdown 45 Micron (Y-axis) for Industrial Calciners [2100 − 4500 tpd] versus the parameter AI*U^2 (X-axis),[11].

The Particle Breakdown seems to increase significantly when the parameter AI*U^2 exceeds 7,500 - 8,000, regardless of the plant considered has a Holding Vessel or not.

Since the parameter AI*U^2 is a measure of the friability (AI) and kinetic energy (U^2) of the particles, when passing the cyclones in the calcinations plant, it seems the particles will break when they exceed a certain threshold value of impact energy or strength.
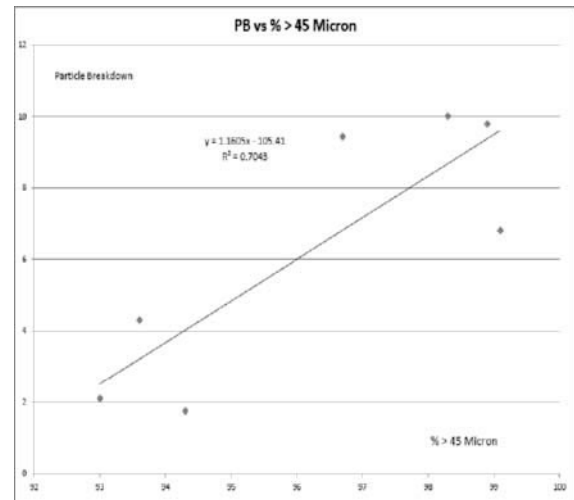

Figure 11: Particle Breakdown 45 Micron (Y-axis) with increasing fraction of hydrate > 45 Micron (X-axis).

It is the coarse particles that break the most [11], when their threshold value is exceeded, as can be seen from the increase in particle breakdown with increasing size fraction exceeding 45 micron in the hydrate to the calcinations plant.

This is not new or surprising information, as it has been shown previously [13], that over coarsening the hydrate particles to meet the requirement of maximum 10% < 45 micron in the alumina shipped [6], results in the precipitation of less strong hydrate particles, which upon calcinations results in increased particle breakdown, and not a coarser alumina.

Alumina as Primary Aluminium feed stock

The dissolution rate of alumina is of major importance in smelters using point feeder technology [14], while crust formation, properties and its subsequent breakage and slow dissolution rate [15] are of major importance in cells with side feeding.

However, the dissolution process is improved by good dispersion and wetting of the alumina, by the molten electrolyte bath, when fed to the pot where the following reaction is taken place [14]:

(5) $2Na_3AlF_6(l) + 2Al_2O_3 (s) + HEAT =>$

$$3Na_2AlO_2F_4 (l)$$
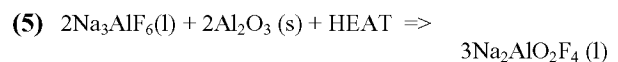
In the above reaction (5), wetting is promoted by the volatiles content on the alumina as expressed by the LOI of the alumina. The LOI (300-1000C), on the other hand, shall be less than 1.0% in order to limit the generation of HF to less than can be efficiently adsorbed in the Dry Scrubber system [4].
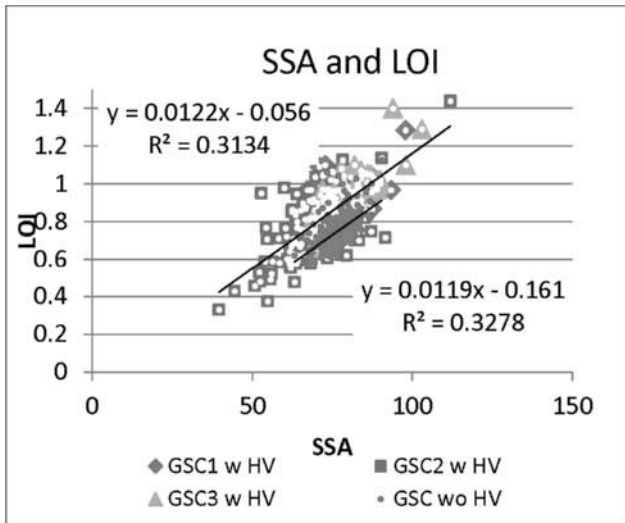
Figure 12. LOI (300-1000°C) versus SSA in GSC Alumina.

Optimization of the SSA versus LOI (300-1000°C) to the 0.8 – 1.0% range benefits the dissolution process. Gibbsite shall be minimized in the alumina in order to avoid "Vulcano-Effects" causing excessive HF and dust emissions.

The above LOI versus SSA (Figure 12) shows how the GSC operator can optimize the alumina in response to smelter demands for GSC units with and without Holding Vessel by adjusting the calcinations temperature.

The smelter requirements have led to the general specification of max 10% Alpha phase in SGA [6]. However, to further improve dissolution in modern smelters with point feeders, the Gamma-to- Alpha ratio shall be optimized, and the Alpha phase is specified to be less than or equal to 5%. This requirement is easily achievable in the new generation GSC with Holding Vessel as seen from Figure 13 below.
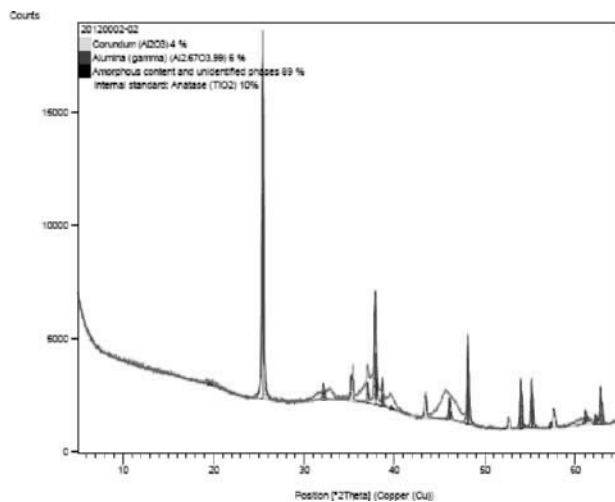
Figure 13. TGA DTA of GSC Alumina with XRD of alumina showing 6% Gamma and 4% Alpha Phase.

Also GSC units without Holding Vessel can produce alumina with Alpha phase < 5%, if so desired, by adjustment of the fuel distribution into the Furnace/ Reactor (Figure 14).
It is however, questionable if it is at all possible to prove a significant difference in smelter operation or performance from a change in alpha phase from, say 4 to say 7 % [4, 7].

Figure 14. Fuel Distribution by Burner Nozzle Allocation.

Chemical Purity and Contamination

There will be no impact on the chemical purity of alumina from a new GSC process, when using natural gas as fuel, provided a good and durable refractory lining is installed. Except for a very short period of time right after the start up of a new GSC unit, it has not been possible to detect an increase in contamination from Iron and Silica Oxides. Contamination of the alumina with Na_2O and CaO, that changes the bath chemistry [16], must be addressed in the Bayer process itself.

Energy Efficiency and Specific Heat Consumption

The cooling section (C01, C02, C03 and C04) is used for recuperating heat from the hot calcined alumina. This is efficiently done by using four cyclone cooler stages. The stage wise counter-current flow of air and alumina obtained with four (4) cyclone stages of inherent co-current flow, is providing a high thermal efficiency with respect to cooling the alumina and simultaneously pre-heating the combustion air as discussed elsewhere [17].

The last section of the GSC system comprises a water cooled fluid bed cooler, which reduces the alumina temperature from 180-200 °C to a temperature low enough for the alumina to be transported with a belt conveyor.

The reporting and comparison of the specific heat consumption for different calcination plants is difficult because the number reported depends on several variables beyond control of the calcination process, such as:

➢ Moisture content of the production hydrate, typically varying from 5 – 9%, subject to the content of wt -% of particles < 20 and 45 micron in the production hydrate fed to calcinations?
➢ Use or not of dewatering surfactants?
➢ Use or not of installed Hydrate By-Pass?

➤ Battery limits of the calcinations process including or excluding the water cooled Fluid Bed Cooler?

➤ Credits received for extracting heat in the Fluid Bed Cooler from the hot alumina, to be used elsewhere, i.e. for heating the condensate used to wash the production hydrate before it is fed to calcinations?

➤ Types of fuel used, and whether reporting and comparison of the specific heat consumption of the calcinations process is based on the High Heating Value (HHV) or Lower Heating Value (LHV) of the fuel?

Unfortunately, the HHV is used as basis for paying the fuel consumption bill. But, only the LHV of the fuel can be used in the calcination process itself. The use of the HHV of the fuel would require that the water vapour from the combustion process is condensed, and that is not taken place within any of today's proven stationary calcination technologies. In the case of Natural Gas, the LHV is only approximately 90% of the HHV, while the LHV is approximately 95% of the HHV for Heavy Fuel Oil.

The battery limits for reporting or guaranteeing the specific heat consumption of GSC units by FLS do not include the Fluid Bed Cooler, and any credits for utilizing the hot alumina/water from the Fluid Bed Cooler for other heating purposes. The specific energy consumption for a standard GSC unit with good performing hydrate filters is typically about 2795 kJ/kg based on LHV of the fuel. When decreasing the moisture content in the hydrate the specific heat consumption will decrease about 25 kJ/kg/ % decrease in hydrate moisture.

When introducing the holding vessel one would intuitively think that the specific heat consumption would decrease due to the lower calcining temperature, and this is also the FLS experience. Understanding specific numbers for comparison is not possible without a clear definition of hydrate filtration pre-conditions, measurement and reporting conditions, and in addition hereto, reporting is commercially sensible.

Environmental Compliance

All the latest GSC units now under commissioning are installed with Fabric Filters. Earlier on [3] the selection of a Fabric Filters with 6 m long bags, instead of Electrostatic Precipitators, was often dictated by Fabric Filters absolute filter characteristics minimizing the sensitivity of emission towards process upsets and power failure, rather than from an economic point of view.

Figure 15. Fabric Filter with 6 m long bags.

With the advent of 10 m long bags Fabric Filters will most likely be the economic choice of the future as well [18]. Bag life experienced by FLS exceeds 2 year with dust emissions significantly below 50 mg/Nm^3 (dry).

Operational Reliability and Availability

The ID–Fan is the prime gas mover in the GSC plant, creating a pressure below ambient throughout the flow sheet, when no Forced Draft Fan is installed.
This makes it very easy and reliable to control the pressure profile, and thus the gas flow and calcining capacity of the calcination plant throughout its capacity range, varying from its design capacity to less than 50% of its design capacity.

Availability

Availability of GSC units depends to a large extent upon the quality of the refractory installed and subsequent quality of the refractory maintenance work performed.
Replacement quantity of refractory may range from less than 1% to 20% of original installed refractory per major overhaul for different GSC units without Holding Vessel. In some GSC units, with 36 month between each major refractory repair, availability has exceeded 98.5% in the interim period between major refractory repairs. Still other GSC units have only reached an average of 94%, when including the GSC commissioning period.
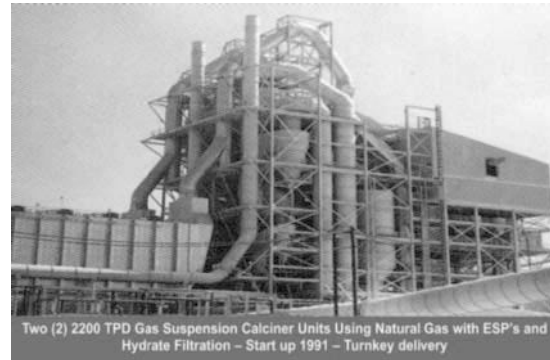

Two (2) 2200 TPD Gas Suspension Calciner Units Using Natural Gas with ESP's and Hydrate Filtration – Start up 1991 – Turnkey delivery

Figure 16. GSC units with availability > 98.0%.

It is expected that GSC units with Holding Vessel has the potential to match and even surpass the best experience reported above. Provided, however, good quality refractory work is performed in the first place and recommended operating practice is followed, including the use of the Hot Stand-By facility of the GSC unit control system.

Conclusion

The recent commissioning experiences with GSC units including several new design features improving specific heat consumption and flexible dust management, shows that the GSC producing SGA at specifications, is as flexible and easy to operate as ever, and at the same time living up to the expectation from the design stage.

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