IMPACTS OF THE REFINERY PROCESS ON THE QUALITY OF SMELTER GRADE ALUMINA

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Abstract

Quality specifications for smelter grade alumina at Queensland Alumina Limited (QAL) are based on the requirements for its use in smelters (as feed to reduction cells and gas treatment centres), and on QAL's process capabilities. Although this may seem relatively simple, smelter requirements vary with respect to operating technologies and procedures, while QAL's capability is also impacted by many factors related to refinery technology, operation and raw material quality.

In general, smelters are requesting alumina that is low in impurities and dust content, and that gives increased dissolution rates. The expectation is continually for more consistent product.

This paper considers some of the alumina quality parameters that are important to smelters, and reviews how these parameters are controlled within the refinery. Impacts on the refinery process will also be considered.

While the paper gives broad comments based on external literature, it draws primarily from QAL experiences and in particular from observations during the commissioning of the Gas Suspension Calciners (GSC).

1 Introduction

Alumina quality is a threshold issue at Queensland Alumina Limited (QAL), which means that all possible actions are taken to ensure that alumina quality satisfies all internal quality aims and external specifications. These actions may result in shipment delays while better quality alumina is transferred from storage facilities, or in some cases, while better quality alumina is produced.

But what defines 'better quality'? Many papers have been written outlining the specific operating requirements for individual smelters, highlighting the related alumina properties. In addition, there have been a number of surveys completed that attempt to rank the importance of alumina properties. In general, smelters are requesting alumina that is low in impurities and dust content, and that gives increased dissolution rates. Consistency, particularly with respect to particle size, soda and flow properties, is important.

At QAL, the limits for internal quality aims and external specifications are based on feedback from smelters and on QAL's process capabilities. However, with five major smelters consistently using QAL alumina, it can be difficult to agree on a recommended level for each parameter. Prompted by the commissioning of the Gas Suspension Calciners (GSC), which commenced in July 2003, communication with each of the smelters has increased. Routine meetings have ensured regular and sometimes lively discussions.

This paper will review a number of the alumina quality parameters with respect to smelter requirements and how they are controlled within the refinery. The paper will give broad comments based on external literature, but will focus primarily on QAL experiences during commissioning of the GSC Calciners.

2 Defining 'better quality' alumina

The limits for internal quality aims and external specifications are based on feedback from smelters and QAL's process capabilities.

2.1 *Alumina quality from a smelter perspective*

Based on a number of externally published surveys outlining the specific operating requirements for individual smelters, yet another ranking of alumina properties has been attempted, as summarised in Table 1 (Williams 1992, Syltevik et al. 1996, Welch 1993, Hseih 1987, Raahauge 1993, Bakkerud et al. 1993, Cayoutte 1988, Wai-Poi & Welch 1984).

Table 1 – Ranking of Alumina Properties based on Smelter Requirements

	Smelter Preference	Associated Alumina Properties
1	Good solubility for rapid dissolution in bath	Alpha Alumina, SSA, LOI, PSD, Morphology
2	Low dusting during handling and cell feeding	%–20μm, Gibbsite
3	Consistency with respect to particle size, flow properties, SSA, Na_2O	PSD, Angle of Flow, Flow Time, Bulk Density, SSA, Na_2O
4	Desirable crust formation	Alpha Alumina, SSA, LOI
5	Ability to capture fluoride	SSA
6	No segregation with respect to particle size, density, impurities	PSD
7	Low moisture contamination	LOI (RT-300°C), LOI (300-1000°C), Gibbsite
8	Low impurities	All chemical impurities
9	Robust strength to minimise fines formation	Attrition Index, PSD
10	Good insulating properties to cover anodes	Alpha Alumina, SSA, LOI, PSD

It should be noted that :

- The surveys generally focus on more recent technology (eg. Soderberg technology is not well represented).
- The ranking may be distorted as feedback tends to be based on importance at the time of the survey (eg. although low impurities are important with respect to bath balance and metal purity, they are not ranked high on the list as they are generally not considered an issue with smelter grade alumina).
- The impurities cover a wide range of parameters from those that are important for current efficiency, bath chemistry or metal impurity to the minor impurities.
- A number of the properties are related (eg. low dusting, flow properties and segregation are all impacted by particle size distribution).

2.2 *QAL process capability*

Table 2 summarises the external specifications for QAL and typical values expected for 2005. In addition to the external specifications, there are a number of internal quality aims, including variability aims to ensure consistency in Na_2O and %–45μm to an individual smelter.

Table 2 – QAL Process Capability

Alumina Parameter	Max. QAL Specification	QAL Typical Value
%+150μm	5.0	2.0
%–45μm	10.0	8.0
%–20μm		1.2
SSA (m^2/g)	77±5	78.0
Alpha Alumina		10
%LOI (300–1000°C)	1.0	0.9
Attrition Index		23
%Na_2O	0.40	0.30
%Fe_2O_3	0.020	0.009
%SiO_2	0.020	0.014
%CaO	0.030	0.016
%TiO_2	0.005	0.004
%P_2O_5	0.002	<0.001

The capability in meeting these specification and internal quality aim requirements is closely monitored. It is based on the statistical process capability index, C_{pk}, which provides a measure of whether the process is capable of meeting the required specifications, taking into account the standard deviation and assuming that the process data is normally distributed.

Keeping these smelter requirements and QAL's process capabilities in mind, individual alumina quality parameters are discussed in more detail below. Not all parameters are discussed. This is not due to a lower priority, but rather because of a minimal impact on levels with the commissioning of the GSC Calciners.

3 Alumina Quality Parameters

3.1 *Particle Size Distribution*

Probably the most significant and on-going alumina quality issue as a result of the GSC commissioning has been increased particle breakdown and in particular, the alumina fines content (defined as %–20μm and %–45μm). As a result the levels that can be tolerated by smelters has been the topic of many discussions. These discussions have led to more than one study attempting to define the particle breakdown along the alumina supply chain from calcination to cell feeding.

Transport systems and handling facilities at smelters may include:

- pneumatic lifter or vacuum unloader for shipment unloading,
- belt conveyor and pneumatic lifter followed by multiple feeding points to plant silos,
- anti-segregation reclaiming devices from the silos to the dry scrubber with multiple feeding points,
- airslides to the dry scrubber system,
- hyperdense phase system.

Depending on operations at the individual smelter, these transport systems may result in significant breakdown between the refinery and smelter reduction line. Smelters using QAL alumina have reported significant breakage, with the extent depending on the systems used (eg. dense phase vs lean phase; belt conveyor vs truck). Figure 1 compares the breakdown between different smelters and technologies using the same baseline alumina. It should be noted that the sizing changes are not solely due to breakdown, and that other impacts may contribute (eg. recycling fines from scrubber).

In contrast, an externally published study of 6 smelters in Norway, concluded that transport and handling operations did not significantly alter the alumina, although some degradation was observed (de Silva & Enstad, 1990). However, there was considerable evidence to suggest that air induced segregation in poorly designed silos cause quality variations, leading to downstream handling issues and excessive dustiness. Similar evidence of segregation within the QAL system is not conclusive, and at times conflicting. However, increased fines can be observed during periods of low inventory. It is worth noting that as impurities are generally concentrated in the finer fractions, inconsistencies of these parameters can be a further impact of segregation.

Particle breakdown along the supply chain is also a function of the strength of the primary alumina. Alumina strength or attrition index, as measured by the Forsythe & Hertwig apparatus, has been the topic of many papers. There is general agreement that alumina strength is a function of hydrate strength and calcination conditions. For the same hydrate feed, alumina from stationary calciners generally has a lower attrition index compared with product from rotary kilns, as significant attrition has already occurred in the calcination process.

Hydrate strength is a function of precipitation conditions. These conditions will also impact the final particle size distribution and particle morphology. However, with no significant changes in the operation of the precipitation circuit at QAL since the commissioning of the GSC calciners, precipitation conditions will not be discussed in this paper. Although, it is worth noting that the conditions for lower attrition index are generally not ideal for low bound soda content in hydrate.

In more extreme cases, where excessive particle breakdown occurs during calcination, dust removal processes may be implemented. Such

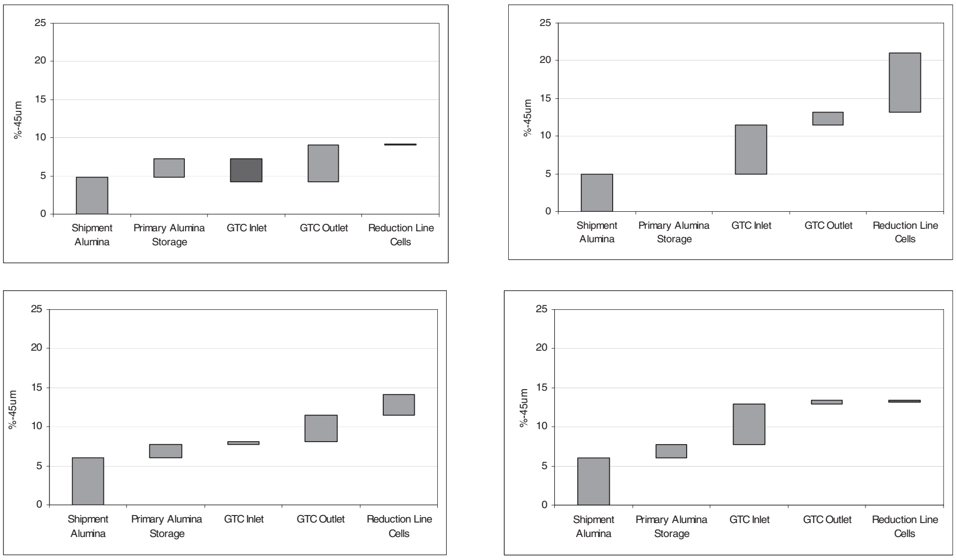

Figure 1 – Alumina Breakdown

processes can range from recycling the dust within the Bayer circuit to the dumping of dust with the red mud. Alternatively speciality products can be produced for ceramic, abrasive or refractory applications. These options have been considered as not suitable as long term solutions to increased particle breakdown at QAL.

3.2 *Flow Properties*

Fines content tends to impact the flow properties of alumina. From a smelter perspective, the inconsistencies in flow can lead to a greater proportion of sludge within the reduction cell, which can ultimately result in reduced cell control and current efficiency.

The traditional measurement for flow properties is the Angle of Repose, where the slope of a pile of alumina of a fixed height is measured. The method has the disadvantages that it represents the alumina under static equilibrium rather than dynamic conditions, and that the analysis lacks sensitivity. A more recent method, the Angle of Flow, is defined as the angle described by the base of a flat bottomed funnel and the slope of the residual material in the funnel after the flow of powder has ceased (Raahauge, 1993, Smith, 1990).

Despite the obvious impacts on the smelter with respect to cell feeding, these flow properties are not routinely measured at QAL. However, samples taken during the commissioning of the GSC calciners have shown the expected relationship between angle of flow and %-45μm for secondary alumina (Figure 2). Surprisingly, analyses of primary alumina have not shown a similar trend (Figure 3).

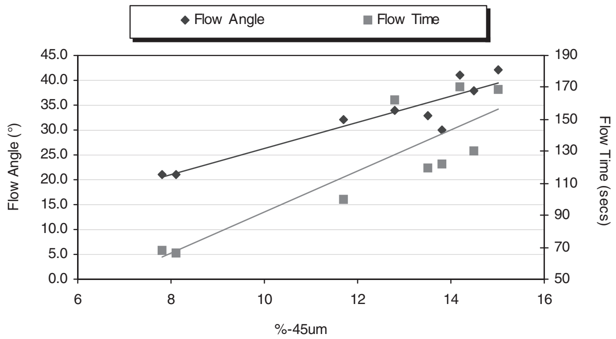

Figure 2 – Flow Properties of Secondary Alumina

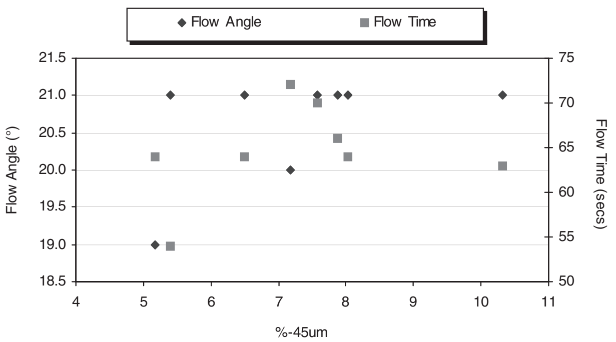

Figure 3 – Flow Properties of Primary Alumina

3.3 *SSA / LOI / Alpha Alumina*

Specific surface area, LOI and alpha alumina are all related to each other via calcination conditions, as indicated by Figure 4, which shows the relationships between SSA and alpha alumina for different calcination technologies. As such, it can be difficult meeting aims. This is compounded by the often differing requirements within a smelter.

Good solubility is a key requirement for any smelter. When alumina is added to a cell, rapid dispersion and dissolution as the alumina sinks into the electrolyte is preferable. However, depending on the alumina properties and cell operation the alumina may clump and freeze around its mass without dispersion, or it may sink through the electrolyte again without dispersion.

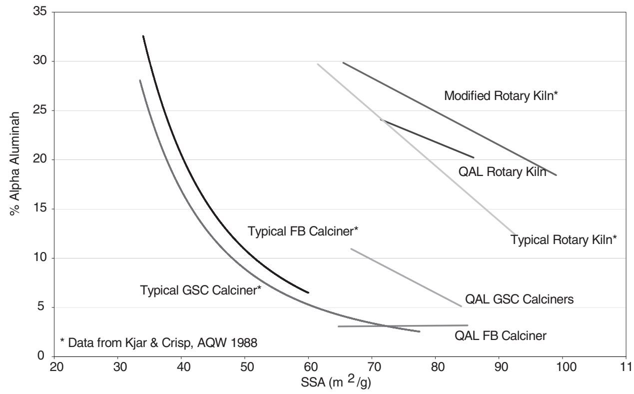

Figure 4 – SSA vs Alpha Alumina

The alumina properties that may impact the rate of alumina dissolution include:

- Flow Properties (with respect to feeder design).
- Particle Size Distribution (coarser fractions are preferred, as there are problems with the solubility of finer particle linked with freezing and aggregation).
- Moisture (high moisture gives turbulence upon addition and this may prevent the formation of aggregates).
- SSA (to give increased surface area in contact with the bath).
- Alpha Alumina (dissolution is slower with high alpha alumina, as it tends to settle more readily).
- Morphology.

In addition to assisting in the dissolution process, there is evidence to suggest that the release of adsorbed moisture aids gaseous fluoride absorption. Conversely, the disadvantages of moisture include:

- hydrogen in metal,
- the 'geyser' effect, contributing to generation of dust in the cells,
- inconsistent feeding and flow properties as a result of the dust generation,
- source of gaseous fluoride emissions.

Similarly, in addition to assisting in the dissolution process, SSA also has a direct impact on the ability of alumina to absorb HF, with a higher SSA giving lower fluoride emissions.

It is expected that this correlation is indicative of crystal structure, although this is not always the case. Generally, low SSA aluminas (less than 30 m^2/g) tend to be predominately alpha alumina. Higher SSA levels (greater than 50 m^2/g) are preferred for both HF scrubbing efficiency and crust formation in the reduction cell. With the increasing emphasis on emissions control, high surface area is therefore favourable. However, other impacts need to be considered due to the links between SSA, alpha alumina and moisture. Generally an SSA no greater than 80 m^2/g is preferred.

To add further complexity, alpha alumina content also impacts crust formation. Desirable crust formation is of a stable crust that can support a thermal insulating layer of alumina and minimise ingress of air to anodes, while still being relatively easily broken prior to alumina feeding. Low alpha alumina will form a stronger crust due to the reinforcement by the gamma phase to alpha crystal transformation. The question of what is the optimum alpha alumina level for a smelter can result in significant discussion.

It is worth noting that cell technology and operation will also impact the cell performance. For example, with respect to cell technology, centre worked cells tend to be more sensitive to dissolution phenomena than side worked cells. With respect to cell operation, preheating the alumina prior to addition decreases the dissolution time.

The complexity in controlling these parameters within the refinery, has increased with the commissioning of the GSC calciners. With the rotary kilns, control of SSA, LOI and alpha alumina was relatively simple with calcination temperature the primary impact. Given the comparative ease in measuring %LOI by a thermogravimetric analyser, these parameters were generally controlled by adjusting temperatures bases on regular LOI analyses.

However, for the GSC calciners other factors impact the relationship, including burner configurations and production rates. As a result, as our experience develops, more detailed relationships are being incorporated in the LOI / SSA control strategy.

3.4 *Gibbsite*

For the same hydrate feed, the level of gibbsite in alumina can vary significantly based on the calcination technology.

Prior to the commissioning of the GSC calciners, gibbsite in QAL alumina was only detected occasionally. However, from the start of commissioning the shipment levels of gibbsite in alumina steadily increased as the percentage of calcination production through the GSC calciners increased.

It is expected that gibbsite will increase dust emissions from the reduction cells as a result of the formation of geysers or volcano effects. However, feedback from smelters regularly using QAL alumina has indicated that the impacts from the higher gibbsite are dependent on the smelter technology for cell feeding, with impacts ranging from minimal to significantly increased anode effects as a result of increased geyser formations.

Gibbsite levels from the GSC calciners are now maintained consistently below 0.3%. However, it took considerable effort to reach this, with solutions ranging in difficulty from the relatively simple control of increasing back end temperatures (Figure 5) to more complex solutions.

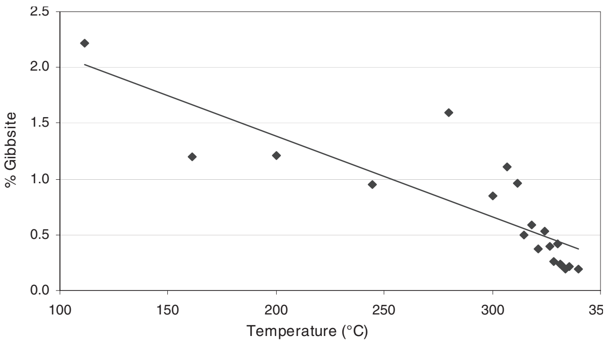

Figure 5 – Temperature vs %Gibbsite (clustered data)

3.5 *Na_2O*

Na_2O, CaO and other elements from the alkali and alkali earth metal groups, are not electrochemically reduced within the smelter and very small amounts are co-deposited in the metal. Therefore, most of them end up us permanent contributors to the electrolyte, impacting the chemical balance in the reduction cell. Consistency is therefore important. As a result, Na_2O ship-to-ship limitations apply for the major smelters using QAL alumina. For consecutive shipments to the same smelter within a three month period, Na_2O levels must not differ by more than a given value.

Na_2O in product alumina is a combination of bound soda and leachable soda. Bound soda is incorporated into the hydrate structure during precipitation. Many papers have been written with respect to the mechanism for soda incorporation and to the control of bound soda within the refinery. As such, this paper will not discuss bound soda, other than to comment that during the commissioning of the GSC calciners, bound soda levels of QAL alumina have been relatively stable.

Leachable soda consists of entrained liquor or solid sodium oxalate that is removed through washing prior to calcination. It is therefore impacted by the calcination filter table performance. Factors contributing to high leachable soda include:

- Media Blinding (insufficient repulping results in the concentration of fines at the bottom of the cake, giving areas of low permeability).
- Holes in Media (holes can result in soda levels up to 10-20 times higher).
- Uneven Cake Thickness (cake thickness is determined by feed concentration, feed distribution, feed rate, vacuum level, filter speed).
- Wash Water Flow Rates and Distribution.

With 11 filter tables at QAL, constant process monitoring is required to ensure consistent product. For the rotary kilns early detection of problems was relatively simple with each table linked to an individual kiln. Control is more complex with the GSC calciners, as hydrate from a number of tables is combined to a single GSC unit. Regular visual inspections of the table are useful, however at times increased Na_2O in product alumina cannot be easily attributed to problems with a specific table.

On-line soda measurement is being considered which will assist in process control. However, there are no easy solutions, with the application of any technology new to the alumina industry.

3.5 *SiO_2*

Impurities that are easily reduced within the smelter, such as SiO_2 and Fe_2O_3, can contaminate the metal. The alumina does not account for the major proportion of the contamination of these impurities in the metal. For example, SiO_2 in alumina accounts for approximately 30% of the total Si in metal. The remaining 70% primarily comes from bath components and anode carbon (Kvande, 1988).

At the refinery, SiO_2 in product alumina is impacted and controlled by a number of factors, including:

- Bauxite Grade Properties.
- Pre-Desilication Performance (the formation of DSP is the main mechanism for removing silica from plant liquor).
- Flash Train Desilication Conditions (liquor silica levels can be controlled by adjusting the addition of trihydrate bauxite to the digestion circuit).
- Precipitation Conditions (silica co-precipitates under certain conditions).
- Calcination Refractory.

Of these, all but the last are prior to calcination and therefore not impacted by the GSC calciner commissioning.

Historically, silica pick-up in calcination at QAL has averaged 0.003% and is primarily a result of refractory degradation. More recently with the aging rotary kilns, this has increased, at times requiring significant product blending to ensure overall product quality is maintained.

Preliminary data indicates that SiO_2 pick-up with the GSC calciners will be similar to the historical levels.

4 Conclusions

- Transport systems and handling facilities along the alumina supply chain may result in significant particle breakdown between the refinery and smelter reduction line.
- Alumina fines content impacts the flow properties of alumina.
- SSA, LOI and alpha alumina content are related via calcination conditions. The complexity of the relationship has increased with the commissioning of the GSC calciners.
- Gibbsite levels can vary significantly based on calcination technology, with levels from the GSC calciners now maintained consistently below 0.3%.
- Control of leachable soda by monitoring performance of the calcination filter tables is more complex with the GSC calciners, as hydrate from a number of tables is combined to a single GSC unit.
- SiO_2 pick-up with the GSC calciners is expected to be similar to historical levels of 0.003%.

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