

# GIBBSITE REVERSION TO BOEHMITE AS A CALCINER FEED

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## Abstract

Calcining boehmite instead of gibbsite to smelter grade alumina would result in significant energy savings. Until now attempts to produce boehmite from the Bayer process have concentrated on the direct crystallisation of boehmite from green Bayer liquors. These have not been adopted industrially due to the slow precipitation kinetics and the presumed unsuitability of the particle characteristics for subsequent calcination. We have investigated hydrothermally produced boehmite from product hydrate. It was found that although this product maintained good morphology and had low soda content, its overall lack of strength after calcination made it unsuitable as a smelter feed.

In this paper we present an alternative method for producing boehmite that maintains the physical characteristics of current smelter grade alumina, including strength. The method involves rapid reversion (dissolution and re-precipitation) of gibbsite in spent liquor at high volume fraction. Some issues remain to be addressed, especially those related to water balance and soda content in the product boehmite.

## Notation and units

Standard North American Bayer notation is employed: A= g/L Al<sub>2</sub>O<sub>3</sub>, C= g/L sodium hydroxide and sodium aluminate and S=C + sodium carbonate (C and S as equivalent g/L Na<sub>2</sub>CO<sub>3</sub>).

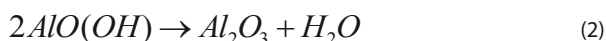
## 1. Introduction

In the Bayer process gibbsite, Al(OH)<sub>3</sub> is precipitated from sodium aluminate liquor and then calcined at ~1000°C to Smelter Grade Alumina (SGA), with the energy required to complete this transformation being approximately 3 GJ/t Al<sub>2</sub>O<sub>3</sub> (Filippou & Paspaliaris, 1993).



Over the years significant attention has been given to the production of alumina that not only has the correct chemical composition (e.g. not more than 5% α-Al<sub>2</sub>O<sub>3</sub>) but which has the correct physical properties suitable for the smelter e.g. particle size, strength, surface area and soda content (Lindsay, 2005).

It has long been recognised that boehmite would be an energy efficient calciner feed with an energy reduction of 1.8 GJ/t Al<sub>2</sub>O<sub>3</sub> during calcination stage, a saving of ~60% of the calcination energy and ~15% energy saving for the entire Bayer process (Panias et al, 2001). Other advantages include lower mass transport costs and lower impurities (Filippou & Paspaliaris, 1993 & Balomenos, Panias & Paspaliaris, 2011).



Attempts to produce boehmite directly by crystallisation from sodium aluminate solution have met with limited success, with studies ranging from various digestion temperatures/times, seed loadings to using organic additives to inhibit gibbsite formation (Dash et al., 2007 & Dash et al., 2009). However the main problems stem from the inherently slow crystallisation kinetics (Filippou & Paspaliaris, 1993) and the problems associated with the unsuitable physical properties of the material produced for subsequent calcination and use as a smelter grade alumina (Panias et al, 2001).

Boehmite can also be produced by the hydrothermal dehydration of gibbsite in water at temperatures around 190-200°C. Inui et al. (1983) studied the hydrothermal treatment of gibbsite to

boehmite and subsequent calcination. The study focused on the control of pore structures in the alumina product with the aim of producing an improved alumina support for catalysis. They showed that hydrothermal conversion of gibbsite to boehmite occurred at about 190°C, in agreement with Dash et al. (2007), Dash et al. (2009) and Skoufadis, Panias, & Paspaliaris (2003).

We have found that when gibbsite is digested in spent liquor at high volume fraction, reversion to boehmite occurs through dissolution and re-precipitation. Importantly, this appears to occur whilst maintaining the morphology of the parent gibbsite. We have produced boehmite by this method and calcined it to alumina. In this paper we compare this method of producing boehmite to the others mentioned above, and assess the boehmite's suitability as a calciner feed, particularly strength.

## 2. Aims and Methodology

In this paper we use a variety of methods to produce boehmite:

1. Hydrothermal transformation of gibbsite in water
2. Direct precipitation of boehmite from sodium aluminate solution
3. Reversion of gibbsite in sodium aluminate solution

We use Attrition Index (AI) and Scanning Electron Microscope (SEM) and Particle Size Distribution (PSD) to compare the strength and morphology of alumina produced from these boehmites and from gibbsite directly to meet the requirements of Smelter Grade Alumina (SGA).

Other issues considered include refinery water balance and product soda content.

### 3. Experimental

#### 3.1 Hydrothermal transformation

Hydrothermal experiments were undertaken using Industrial Gibbsite 1 (IG1), which was used without further treatment. XRD analysis indicated gibbsite to be the only crystalline phase present.

Gibbsite (IG1) was digested in deionised water (710 g/L slurry) using a small scale gas fired (Inconel) reaction vessel at 200°C for a holding time of 30 minutes. After digestion, the slurry was filtered through a pressure filter using a Supor 0.45 µm membrane. The filter cake was washed with deionised water and dried in an oven at 100°C overnight.

#### 3.2 Direct precipitation

Boehmite seed was initially formed by homogeneous nucleation from a supersaturated caustic aluminate solution (C = 165 g/L A/C = 0.800 prepared using AR grade reagents and deionised water). It was filtered, washed and dried and added at 6.73 g/L seed loading into a caustic aluminate solution (A = 135 g/L, C = 167.9 g/L A/C = 0.800 prepared using AR grade reagents and deionised water) in an Inconel Autoclave Vessel (PARR) at 140°C for 21 hours.

After digestion the slurry was filtered through a pressure filter using a Supor 0.45 µm membrane. Exit liquors were titrated for A, C and S (Connop, 1996). The filter cake was washed with deionised water and dried in an oven at 100°C overnight.

This procedure was repeated several times to produce sufficient material for experimental work.

#### 3.3 Reversion of gibbsite

Reversion experiments were undertaken using Industrial Gibbsite 2 (IG2). XRD analysis of IG2 indicated gibbsite to be the only crystalline phase present.

A synthetic caustic aluminate was prepared with an approximate liquor concentration of A = 60 g/L, C = 200 g/L, A/C = 0.300 and C/S = 0.920. IG2 was digested in this solution (710 g/L slurry) using the same small scale gas fired (Inconel) reaction vessel at 200°C for a holding time of 30 minutes. After digestion the slurry was filtered through a pressure filter using a Supor 0.45 µm membrane. Concentrated exit liquors were titrated for A, C and S (Connop, 1996). The filter cake was washed with deionised water and dried in an oven at 100°C overnight.

#### 3.4 Calcination

Around 90 g of material was weighed and placed into a steel tray. The kiln (Kiln West) was pre-heated to 1100°C and the sample was then placed inside (the over-temperature was to compensate for the temperature loss on loading the sample). The temperature was then re-set to 1000°C and timer started for 25 minutes. Once complete, the sample was removed, allowed to cool to a temperature suitable for handling, and stored in a desiccator until it cooled to room temperature. The sample was then reweighed.

#### 3.5 Attrition Index (AI)

Attrition Index (AI) is a number that quantifies the strength of a particulate material. It is normally measured by conducting breakage tests in a fluidized bed Attrition Index Column (Forsythe & Hertwig, 1949) over a range of times. The current tests were either conducted for breakage times of 3 minutes or 15 minutes using a CSIRO designed instrument. The index value is obtained by use of the following equation:

$$\text{Attrition Index (AI)} = 100x \frac{[\text{wt}\% + 45 \mu\text{m}_{(\text{pre-attrition})}] - \text{wt}\% + 45 \mu\text{m}_{(\text{post-attrition})}}{\text{wt}\% + 45 \mu\text{m}_{(\text{pre-attrition})}} \quad (3)$$

50 g of sample was weighed and placed in the column and the attrition test was run for a specified time. The flow of air through the unit was maintained at 6.5 L min<sup>-1</sup>. At the end of the run the column was left for at least 30 s to allow the particles in the column to settle. All material in the column was carefully collected. A long-handled brush was used to remove material adhering to the walls of the column and care was taken to ensure any particles stuck to the inside of the thimble were removed. The collected sample was re-weighed to ensure that >99% of the original mass was recovered, otherwise the run was repeated.

The AI obtained by use of Equation 3 is a number between 0 and 100. A small number indicates a strong material, while a larger number indicates a weaker material.

#### 3.6 Particle Size Distribution (PSD) and Surface Area

Pre-attrition and post-attrition samples were measured for size distribution by a Malvern (Mastersizer 2000) and surface area by the 5-point BET method (Micromeritics Tristar 3000).

#### 3.7 Scanning Electron Microscope (SEM)

Samples were imaged using a scanning electron microscope (JEOL JSM-5800LV). Samples were coated with carbon followed by gold before analysis.

### 4. Results

The overall results for all boehmite preparations, calcinations and strength tests are given in Table 1. Details of each method and interpretation of the results are given in the individual sections below.

**Table 1: Overall results for boehmite preparation, calcination and strength testing.**

Property	Industrial Gibbsite (IG1)	Al <sub>2</sub> O <sub>3</sub> from IG1	Boehmite (hydrothermal)	Al <sub>2</sub> O <sub>3</sub> from Boehmite (hydrothermal)	Direct Precip Boehmite	Al <sub>2</sub> O <sub>3</sub> from Direct Precip Boehmite
PSD (d <sub>50</sub> μm)	38.59	37.92	44.19	42.14	74.28	79.55
SSA (m <sup>2</sup> /g)	0.21	80.41	1.23	12.65	2.46	23.21
LOI (%)	34.8	2.71	17.9	0.3	17.5	--
Al (3 minutes)	6.96	4.40	87.17	96.44	1.74	~0

Property	Industrial Gibbsite (IG2)	Al <sub>2</sub> O <sub>3</sub> from IG2	Boehmite (reverted from IG2)	Al <sub>2</sub> O <sub>3</sub> from Boehmite (IG2)
PSD (d <sub>50</sub> μm)	76.40	72.12	102.51	110.61
SSA (m <sup>2</sup> /g)	0.09	58.04	5.38	24.70
LOI (%)	34.7	2.1	18.0	0.9
Al (15 minutes)	5.35	26.73	11.83	17.86

#### 4.1 Hydrothermal transformation of gibbsite in water

The LOI of the boehmite formed after 30 minutes of hydrothermal treatment was 17.9. Increasing the holding time (up to 120 minutes) did not change this value. The value differs significantly to that reported by Dahl et al. (2009) who produced a boehmite with an LOI of 23% by hydrothermal transformation. Using LOI as a measure of transformation indicates a theoretical conversion of 88% of the gibbsite to boehmite. However XRD analysis indicated negligible crystalline gibbsite remaining with boehmite being the only identified crystalline phase.

SEM images (Figure 1) illustrates the morphological changes in transforming the gibbsite (IG1) (a) to boehmite (b) and after calcination to alumina (c).

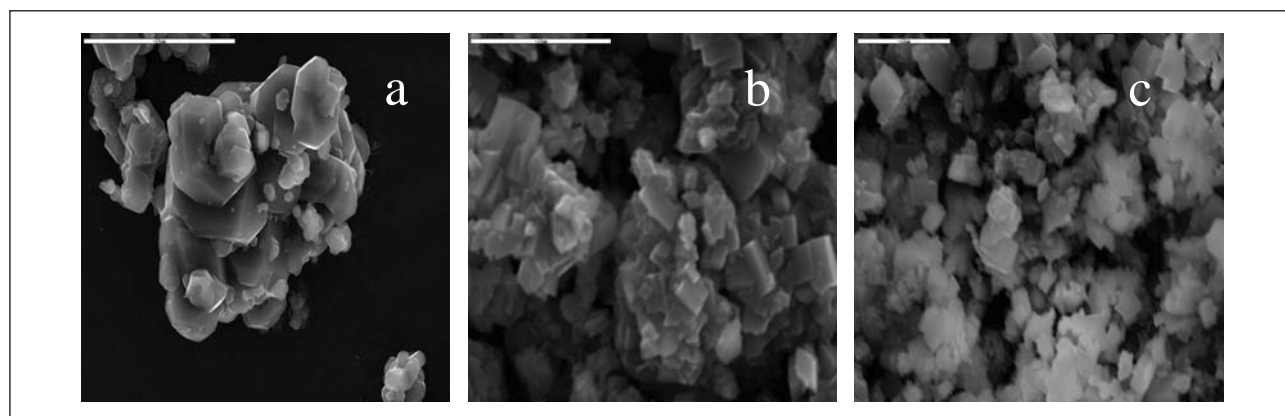


Figure 1: (a) Industrial Gibbsite – 1 (b) Boehmite from hydrothermal transformation; (c) Calcined boehmite (scale bar 20 μm (a) and 10 μm (b & c)).

The PSD of the boehmite formed was not significantly different to the starting gibbsite. However the particle strength of the boehmite is significantly decreased compared to the parent gibbsite, and the SGA from boehmite is similarly weak compared to the direct calcination of the starting gibbsite (Figure 2 & Table 1).

In addition, alumina produced by calcination of boehmite has a lower surface area than alumina produced by calcination of gibbsite.

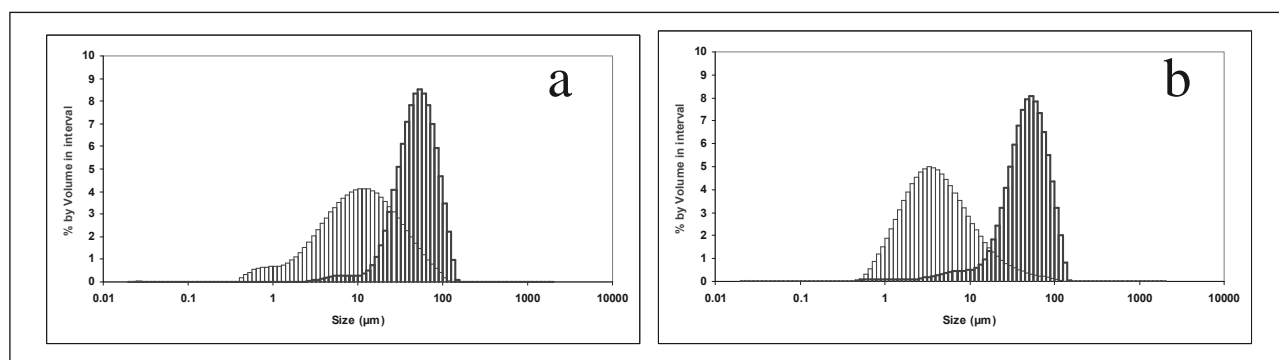


Figure 2: Particle Size Distribution of (a) Hydrothermally transformed boehmite before (bold) and after attrition tests (b) Calcined boehmite before (bold) and after attrition tests. Attrition is indicated by an increase in amount of fines.

#### 4.2 Direct precipitation

The yield of boehmite produced from the seeded precipitation at 140°C for 21 hours was low when compared to a typical gibbsite precipitation. This is consistent with previous findings (Skoufadis et al. 2003).

SEM images (Figure 3) indicate that the boehmite produced is composed of agglomerates of platy crystallites. The agglomerate structure appears to be preserved through calcination with a possible decrease in the platelet size.

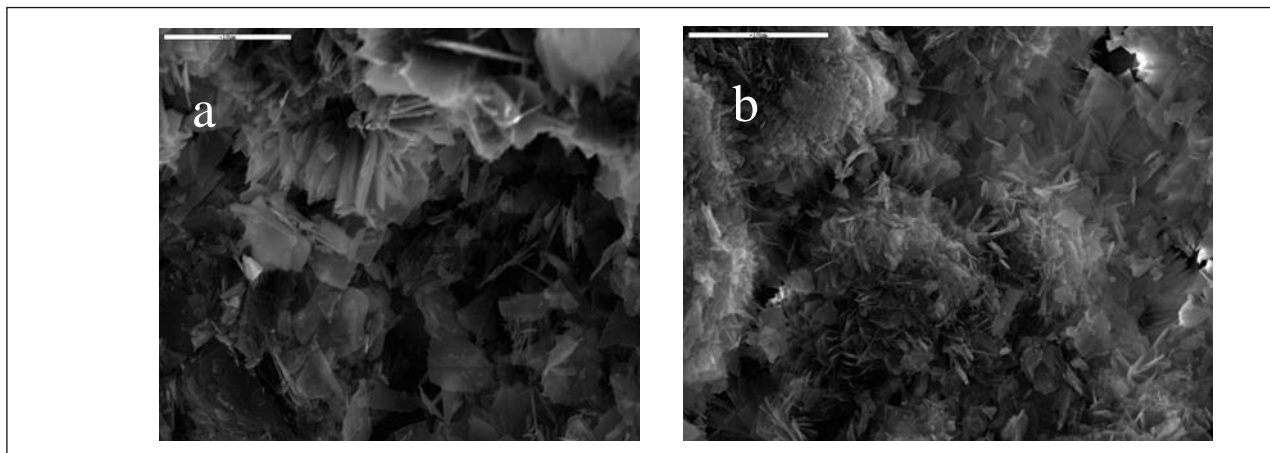


Figure 3: (a) Boehmite from direct precipitation; (b) Calcined boehmite. Scale bar for both 10 µm.

The PSD graphs of the boehmite and the calcined boehmite are given in Figure 4. There is surprisingly little difference between the attrited and non-attrited boehmite (or the calcined boehmite).

This is reflected in the AI values which indicate a product which does not appear to break down easily (Table 1).

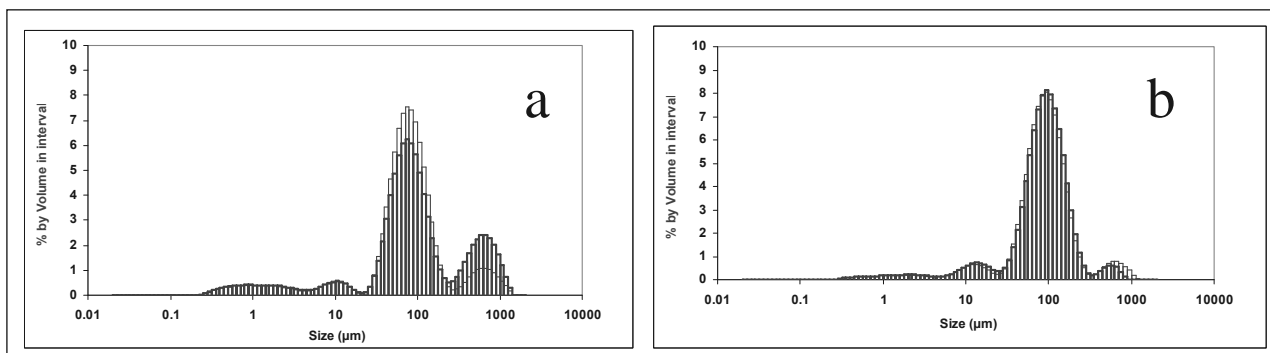


Figure 4: Particle Size Distribution of (a) Directly precipitated boehmite before (bold) and after attrition tests (b) Calcined boehmite before (bold) and after attrition tests.

#### 4.3 Reversion of gibbsite in sodium aluminate solution

Reversion of IG2 in synthetic spent liquor at 710 g/L produced a boehmite with the same platelet surface structures as the direct precipitation but which maintained the bulk morphology of the parent gibbsite. XRD confirmed that boehmite was the

only crystalline phase after reversion and its LOI was similar to the boehmite produced by hydrothermal transformation. SEM images (Figure 5) illustrate the change in morphology for the gibbsite (a) reverted boehmite (b); and the calcined alumina (c).

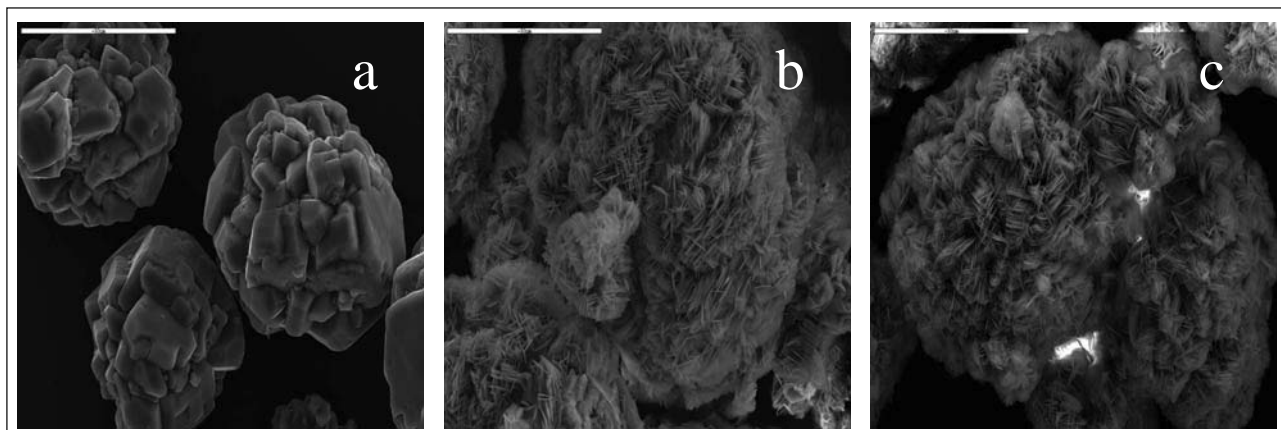


Figure 5 : (a) Gibbsite - IG2 (b) Boehmite from reversion (c) Calcined boehmite. Scale bar = 10 µm.

The PSD of the boehmite and the calcined boehmite before and after attrition (Figure 6) indicates a slight shift of the median particle size (~100  $\mu\text{m}$ ) on attrition. The AI results (Table 1) suggest a product that is comparable in strength to that produced by direct calcination of the gibbsite.

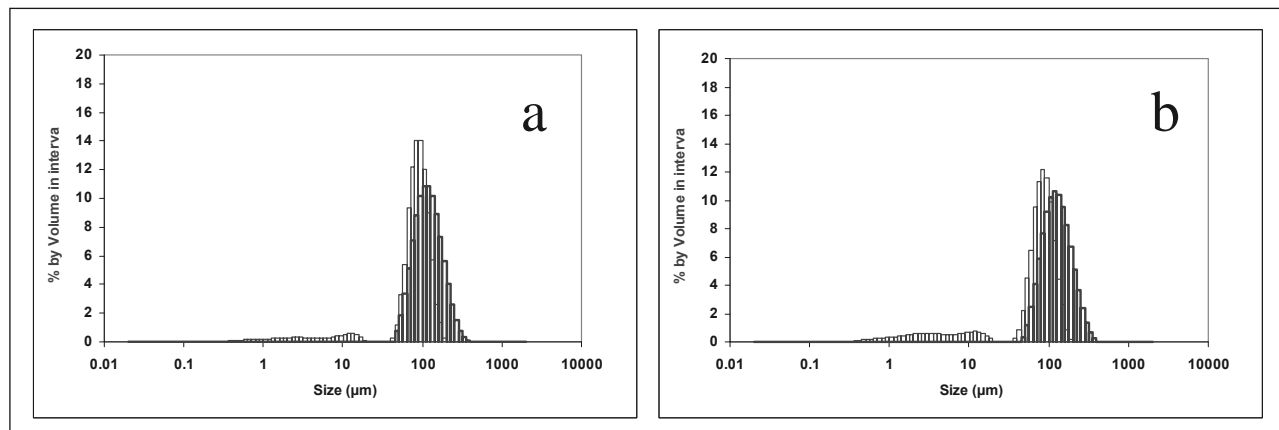


Figure 6: Particle Size Distribution of (a) Reverted boehmite before (bold) and after attrition tests (b) Calcined boehmite before (bold) and after attrition tests.

Figure 7 illustrates the effect of attrition on particle shape/morphology for the reverted and calcined product. The Reverted boehmite (b), when calcined and attrited has a surface dominated by collapsed platelets but maintains a solid core which is probably the source of its strength. It compares well to the attrited gibbsite (a).

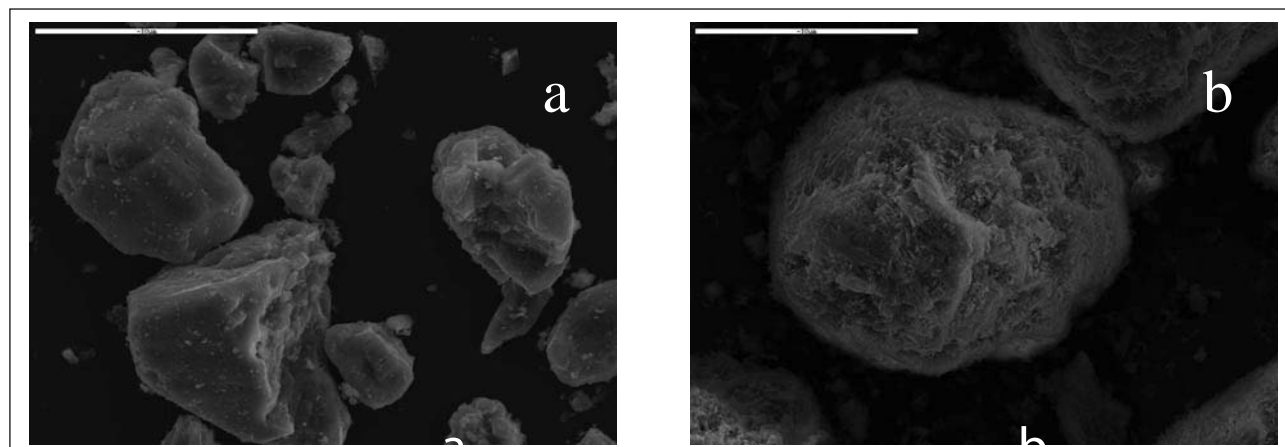


Figure 7: Particle morphology after calcination and attrition (a) IG2 - (b) Boehmite from reversion. Scale bar = 50  $\mu\text{m}$ .

## 5. Discussion

It is clear from the results above that hydrothermally produced boehmite has a strength that would immediately exclude it from consideration as a calciner feed. The reverted boehmite on the other hand produces a much stronger product that may be of suitable strength as a calciner feed. However there are other issues and/or requirements that need be considered.

**Specific surface area.** The surface areas of aluminas calcined directly from gibbsite are in the range generally considered to be suitable for SGA (60-80  $\text{m}^2/\text{g}$ , Lindsay (2005)). Those formed from boehmite appear to have SSA's approximately one third of this value. It is not known whether this related to the respective water contents of boehmite and gibbsite.

**Soda content** The soda content of gibbsite has some relationship to the speed (flux) at which it forms (Grocott and Rosenberg 1988). It might be expected that since the reversion is rapid, the boehmite has a high soda content. Table 2 shows the soda content for the reverted boehmite compared to that produced hydrothermally.

Table 2 Alumina and soda contents of boehmites and aluminas.

Source	Method	$\text{Al}_2\text{O}_3$ (%)	$\text{Na}_2\text{O}$ (%)
Boehmite	Hydrothermal	81.9	0.1
Boehmite	Reversion	79.9	2.1
Alumina	Hydrothermal	99.5	0.1
Alumina	Reversion	99.2	2.9

The soda value of reverted boehmite and the alumina produced from it would be unacceptable as a calciner feed, and therefore soda removal techniques would be required. Removal techniques include  $\text{CO}_2$  leaching or a more costly acetic acid treatment - Park et al (2006).

**Water balance** If gibbsite is the main source of alumina from the bauxite and boehmite is the main product (whether through direct precipitation or reversion) then excess water remains in the liquor which needs to be removed.

## 6. Conclusions

The main conclusions of this work are:

1. Boehmite can be formed through reversion (dissolution and rapid re-precipitation) of product gibbsite in spent liquor.
2. This reverted boehmite is likely to meet the strength requirements of smelter grade alumina and may be of similar strength to that produced by direct calcination of the gibbsite.
3. Other issues and requirements of SGA (including water balance and soda content of the boehmite) need to be solved before this technique could be used to produce boehmite as a calciner feed.

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