



## Investigating the impact of anatase on the dissolution of boehmite



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### ABSTRACT

The dissolution of boehmite in synthetic Bayer liquors is inhibited in the presence of anatase. It has been suggested both by us and others (e.g. Loan et al., 2005) that dissolved titanate adsorbs onto the surface of the boehmite limiting its dissolution. This manuscript reports on digestion, X-ray diffraction (XRD) and transmission electron microscopy (TEM) investigations of boehmite solids partially dissolved in synthetic Bayer liquor in the presence of anatase. Energy filtered transmission electron microscopy (EFTEM) is used to obtain elemental distribution maps, which support the adsorption hypothesis and show enrichment of titanium on the boehmite crystals. Interestingly, the aluminium also becomes associated with some of the Ti-rich particles.

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### 1. Introduction

The Bayer process used to extract alumina from bauxite involves leaching the bauxite with sodium hydroxide solutions at elevated temperatures and pressures (Authier-Martin et al., 2001; Pearson, 1955) followed by separating the insoluble solid impurities from the pregnant liquor, re-precipitating pure gibbsite, and removing water by calcination to produce alumina. The alumina bearing minerals most commonly found in bauxite are gibbsite ( $\text{Al}(\text{OH})_3$  also called alumina tri-hydrate) and boehmite ( $\gamma\text{AlOOH}$ , also called alumina mono-hydrate), while diaspore (an alternative alumina mono-hydrate,  $\alpha\text{AlOOH}$ ) is less common (Hudson et al., 2000; Gow and Lozej, 1993). The temperature used in the digestion stage of alumina refining varies according to the main aluminium bearing phase; gibbsite can be digested at 140–150 °C, while boehmite requires temperatures above ~220 °C (typically 250 °C). Ti-bearing minerals have been found to slow the extraction of boehmite at high temperatures (Authier-Martin et al., 2001; Malts et al., 1985; Prakash and Horvath, 1979); with the phase being important – anatase has a significant impact on dissolution, while rutile showed no effect. It has been suggested that at high temperatures, the titanium reacts with NaOH to form sodium titanates forming a gelatinous film that coats the boehmite particles and impedes their digestion (Loan et al., 2005; Whittington, 1996). Whittington (1996) found that the effect of sodium titanate on extraction is not seen at low temperature digestions (~180 °C) and stated that anatase does not react in caustic until ~180 °C, thereby suggesting why gibbsite extraction is unaffected.

However, as Dudek et al. (2009) found, anatase can have a non-trivial impact on boehmite dissolution even at temperatures as low as 90 °C. Lime ( $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$ ), added to Bayer liquor, is proposed to minimise the formation of sodium titanate by reacting with titanate in solution to form perovskite ( $\text{CaTiO}_3$ ) which is highly insoluble and is removed with the red mud (Loan et al., 2005; Shultze-Rhonhof and Winkhaus, 1972).

A previous study (Chester et al., 2009) found that the extent of dissolution for anatase and rutile is similar at 90 °C (after 24 h) while sodium titanate dissolved least of the three minerals when aluminate ions are present. For all three Ti-bearing solids the amount dissolved is generally related to the free caustic (FC, defined below). Only at higher aluminate concentrations (lower FC values) was anatase dissolution found not to be related to the FC and it was suggested that this was due to the precipitation of an amorphous and impervious layer (possibly of sodium titanate). Another study (Dudek et al., 2009) on the effect of anatase, rutile and sodium titanate on the dissolution of boehmite and gibbsite at 90 °C found that Ti-bearing minerals had no effect on the digestion of gibbsite at 90 °C. Ti-bearing minerals were found to affect boehmite dissolution even at 90 °C, with anatase reducing extraction significantly, followed by sodium titanate and rutile.

In this work, the solids remaining after the partial dissolution of boehmite in the presence of anatase at 250 °C are investigated. This temperature is characteristic of boehmitic bauxite digestion and, therefore, the results in this study are relevant to current industrial practice. The aim was to investigate the hypothesis that titanates could adsorb onto the surface of the boehmite and limit extraction. In order to achieve this, solids were collected, ultramicrotomed and energy-filtered transmission electron microscopy (EFTEM) was used to image the elemental

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distributions within and on the surface of particles at sub-micron scale spatial resolution. This technique has been successfully used previously to investigate the nickel distribution in natural goethite crystals (Landers et al., 2011) and goethite–silica cementation structure in Western Australian nickel laterite ores (Wang et al., 2014).

### 1.1. Terminology

North American Bayer industry nomenclature is used to describe the various concentrations in solution.

- alumina (A) is expressed as g/L  $\text{Al}_2\text{O}_3$ ,
- free Caustic (FC) is defined as g/L free sodium hydroxide,
- caustic (C) is defined as the FC plus sodium aluminate,
- soda (S) is C plus sodium carbonate

where FC, C and S are all expressed as equivalent g/L  $\text{Na}_2\text{CO}_3$ .

The A/C ratio is a rough guide to supersaturation – spent refinery liquors have A/C ~ 0.35 and pregnant (green) liquors have A/C ~ 0.7. The “causticisation” of the liquor is expressed by the ratio C/S. When this ratio is equal to 1 the liquor contains pure hydroxide; lower values indicate the presence of carbonate, which reduces the potential of the liquor to dissolve aluminium (oxy)hydroxides present.

## 2. Materials and methods

Boehmite was produced via the hydrothermal dehydration of gibbsite (Asimidis et al., 2001; Panias et al., 2003) and was assessed as a pure phase using laboratory X-ray diffraction (XRD). The anatase powder from Sigma Aldrich (99 wt.%) and the sodium titanate solids from STREM Chemicals have been previously characterised, with details given in Chester et al. (2009).

### 2.1. XRF analysis of boehmite and anatase

The “grab” weight method was used, whereby approximately 0.3 g of accurately weighed and oven dried samples was placed into 95% Pt/Au crucibles with 0.6 g of 12:22 lithium metaborate/tetraborate flux. The mixture was fused into a homogeneous glass over an oxy-propane flame at a temperature of approximately 1050 °C and the molten material was poured into a 32 mm diameter 95% Pt/Au mould heated to a similar temperature. Air jets then cooled the melt for approximately 300 s. Samples were analysed on a PANalytical PW2404 4 kW wavelength dispersive XRF system for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$ .



### 2.2. Liquor preparation

Caustic solutions were prepared by dissolving sodium hydroxide pellets (188.67 g) and sodium carbonate powder (30 g) with deionised water, and brought to volume in a volumetric flask (1 L). The resulting nominal caustic concentration (C) and soda (S) were 250 g/L and 280 g/L  $\text{Na}_2\text{CO}_3$  respectively. The caustic liquors were then titrated using the Connop method (Connop, 1996) to accurately determine the caustic (C) and soda (S) concentrations.

### 2.3. Caustic digestion of boehmite and anatase mixture at 250 °C

A Gas Fired Reactor (GFR), Fig. 1, was used in the digestion of boehmite in caustic liquor. The caustic liquor (C = 250, 150 mL), boehmite ( $30 \pm 1$  g) and titanium mineral ( $0.45 \pm 0.01$  g anatase or  $0.56 \pm 0.01$  g sodium titanate) were added to a 250 mL stainless steel bomb (a control without titanium mineral was also run). The mass of boehmite was chosen such that if all the boehmite was to dissolve an A/C ratio of ~0.7 would be achieved. This was related to the volume of liquor that could be safely placed into the bomb that would allow for expansion on heating. Finally, the mass of anatase and rutile was determined by using slightly higher ratios to the initial boehmite solids than used in the previous work at 90 °C (Dudek et al., 2009) and matching the number of moles Ti present in both anatase and sodium titanate. The bomb was loaded into the GFR and the appropriate time–temperature profile was selected. The GFR heated the bomb to 250 °C at 35 °C/min. It was kept at 250 °C for the allocated time and then cooled down rapidly to 30 °C by immersing in a continuous shower. When the program was completed, the bomb was removed from the GFR. The sample was filtered using a 2 L pressure filtration vessel, and then was subsequently washed with three sequential washings of 800 mL deionised water. The residue was dried in an oven overnight at 100 °C, and then cooled and weighed. This process was repeated for 2, 5, 10, 30 and 60 min.

### 2.4. Titration and ICP-OES analysis of liquors

After filtration, the A, C and S of exit liquors were determined by a standard titration method (Connop, 1996). Exit liquors were also diluted 10 times with caustic solution containing mannitol (to stabilise aluminium) and analysed for Na, Al, and Ti by Inductively Coupled Plasma (ICP) with relevant standards.

### 2.5. XRD analysis of solid samples

X-ray diffraction patterns were collected for the initial boehmite and residue samples using a PANalytical® X'pert X-ray APD diffractometer

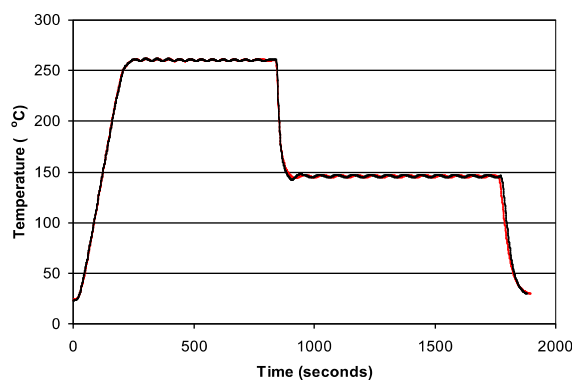


Fig. 1. Gas Fired Reactor (LHS, stainless steel bomb mounted horizontally) and an example of a time–temperature profile (not indicative of actual profiles used in the present work – shows heat-up and cool down rates and temperature stability).

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