

The effect of anatase, rutile and sodium titanate on the dissolution of boehmite and gibbsite at 90 °C

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Abstract

Industrial plants that refine bauxite to alumina using the high temperature process have always held the belief that anatase was detrimental to the extraction of boehmite while rutile was not. This study shows that this effect is real and that it is observable at temperatures as low as 90 °C. The extraction of gibbsite is shown to be unaffected which leads us to believe that the kinetics of both the Ti-bearing mineral and the Al-bearing mineral is important in this phenomena. In addition, it is shown that not only is the presence of anatase an issue in boehmite extraction but so too is the presence of sodium titanate. Rutile was found to have the least impact of the three mineral phases.

Keywords: Bayer process, high temperature process, dissolution, boehmite, gibbsite, anatase, rutile, sodium titanate

1. Introduction

The Bayer process of refining bauxite ore to alumina (Al_2O_3) operates under different conditions depending on the main aluminium bearing phases. Gibbsite, $\text{Al}(\text{OH})_3$, only requires a relatively low temperature for digest (~150 °C) while higher temperatures are required when boehmite, AlOOH , (or diaspore) is present (~250 °C). The subsequent stages are essentially the same in both cases, the waste is removed and aluminium trihydrate (gibbsite) is precipitated before, finally, the solids are calcined to obtain alumina.

In the high temperature process the presence of titanium minerals can have significant impacts. These include the negative impacts of scale formation, titanium in the alumina product, and inhibition of boehmite extraction (Malts et al., 1985; Malts, 1992; Prakash and Horvath, 1979). There is also evidence that the phase of the titanium mineral is important; that is, that rutile has little impact while anatase has a significantly negative impact (Authier-Martin et al., 2001). Recently, an *in-situ* XRD study demonstrated that anatase (and not rutile) inhibited boehmite dissolution (Loan et al., 2005) confirming a long held belief that the presence of anatase in bauxite ores limits the extraction of Al in the high temperature process (Shultze-Rhonhof & Winkhaus, 1972; Wefers, 1971). An excellent overview of the effect of titanates in Bayer liquors can be found in Croker et al. (2006).

The formation of titanates is also currently an area of interest as precursors to the formation of Ti-containing inorganic nanotubes (Wu et al., 2006; Morgado Jnr et al., 2007; Pradhan et al., 2007; Menzel et al., 2006). From this literature it is observed that sodium titanates are formed at high caustic strengths and high temperatures (Wu et al., 2006; Morgado Jnr et al., 2007; Pradhan et al., 2007; Menzel et al., 2006). Both rutile and anatase form similar structures while the greater conversion of anatase to nanotubes is related only to the higher surface area of the anatase starting material (Menzel et al., 2006).

In relation to a Bayer system, a previous study (Chester et al., 2009) found that the extent of dissolution for anatase and rutile are similar at 90 °C while sodium titanate dissolved to a lesser extent when aluminate ions are present. For all these phases the amount dissolved is generally related to the free caustic (FC). Only at higher alumina loadings (lower FC values) was anatase dissolution found to not be related to the FC and it was suggested that this was perhaps due to the precipitation of an amorphous and impervious layer on the anatase surface. In this manuscript we investigate the dissolution process of gibbsite and boehmite rather than the titanium phases at 90 °C. The greatest challenge for this work is to sample at a relevant temperature, remove residual solids and

avoid subsequent re-precipitation. This continues to be our long term aim, however, we begin with a temperature that is readily accessible.

North American liquor terminology is used throughout this paper. Free Caustic (FC) content of a liquor is defined as g/L of sodium hydroxide, Caustic (C) is defined as Free Caustic plus sodium aluminate, and Soda (S) is defined as caustic plus sodium carbonate - all expressed as g/L of equivalent sodium carbonate. Aluminium in solution is expressed as g/L Al_2O_3 . A/C is the alumina to caustic ratio and is related to the level of alumina (super)saturation in the caustic solution.

2. Materials and Methods

Gibbsite, C33, was obtained from Alcoa World Alumina. Boehmite was produced via the hydrothermal dehydration of gibbsite method (Asimidis et al., 2001). The samples were characterised by X-ray Diffraction (XRD), Scanning electron microscopy (SEM) and Particle size distribution (PSD). XRD showed the solids consisted of only the expected phase (gibbsite or boehmite) while the PSD showed a much fine size distribution for boehmite than gibbsite and this was confirmed by SEM.

The anatase, sodium titanate and rutile have been previously characterised, the details of which can be found in Chester et al. (2009).

Figure 1 near here

The equilibrium solubility of gibbsite is greater than boehmite at 90 °C. For a caustic strength of 250 g/L (4.72M NaOH), a target A/C of 0.4 and 0.2 for gibbsite and boehmite respectively are achievable (this is equivalent to 100 and 50 g/L Al_2O_3). Thus, it is expected that boehmite will only dissolve at most to 50% of the level possible for gibbsite. We did however, observe noticeable dissolution of the particles even at 90 °C, although as expected more so for gibbsite than boehmite.

Caustic solutions were prepared by dissolving sodium hydroxide pellets (188.7g) and sodium carbonate powder (30g) with deionised water and brought to volume in a volumetric flask (1L). The resulting caustic concentration (C) and soda (S) was 250 g/L and 280 g/L Na₂CO₃, respectively.

When Al was required (for titanium mineral dissolution), aluminium wire was slowly dissolved into the hot caustic solution with care to the desired level before filtration and cooling.

Caustic liquors were checked for their C and S values by using an automatic titrator to accurately determine the caustic, alumina and soda concentrations. This method is based on an acid-base titration described by Connop (1996).

2.1 Dissolution experiments

The dissolution of boehmite and gibbsite was performed using a thermostatted bottle roller (Thornton Engineering, Perth). The synthetic caustic liquor (200mL, C = 250 g/L, S = 280 g/L) was added to a plastic nalgene® bottle (250mL). Once the samples equilibrated at the required temperature (90°C), an aliquot of 1.5mL was taken (t=0) and diluted 10 fold in the initial caustic solution. Sufficient gibbsite/boehmite was added to achieve a target A/C for the control runs and then the slurry sampled at the desired times. When titanium mineral solids were added, they were added at 0.1 g with the boehmite or gibbsite (i.e. at the start of the run). For the pre-saturated liquors, gibbsite or boehmite was added as per the control but the pre-saturated liquor was used (i.e. no other solids were added). The aliquot samples taken during the run were vacuum filtered and the solids collected for gravimetric determination of residual solids. The liquor samples were diluted (1 in 10) in the initial caustic solution (to be absolutely sure no Al was lost due to re-precipitation and for consistency with other experiments) then analysed for Al and Na using ICP-OES.

2.2 *Pre-saturation of liquor*

A caustic solution (200mL, C = 250 g/L, S = 280 g/L) was placed in a plastic nalgene® bottle with 100 mg of the desired titanium mineral and equilibrated to 90 °C for 24 hours. After this time had elapsed, the liquor was filtered through a 0.2 µm caustic resistant membrane and the liquor was then re-equilibrated to 90 °C for use in a dissolution experiment with either gibbsite or boehmite.

2.3 *Kinetic titanium mineral dissolution experiments*

A orbital action rotating water bath (model TWBS-20 from Thermoline Scientific) was used to equilibrate 30 mL liquor (C = 250, S = 280 A/C = 0.3) to 90 °C. On achieving the temperature, 100 mg of the titanium mineral was added and left to dissolve. At the desired sampling time, 2mL of the liquor was filtered through a 0.2µm caustic resistant membrane and 1 mL of this was diluted (1 in 10) in caustic of the same liquor strength (to avoid known re-precipitation losses as found by Chester et al., 2009). The diluted liquor samples were then analysed for Ti using ICP-OES.

The results from ICP were Na and either Ti or Al values in mg/L. The Na values were used to calculate the C value by converting the moles of Na to moles of Na₂CO₃ (this gives the S value) and subtracting the sodium carbonate (30 g) added to the liquors. The Ti values were only adjusted for dilution while the Al values were converted to moles Al and then mass Al₂O₃.

3. **Results**

Firstly, in order to determine an impact on dissolution, a baseline must be obtained. To this end several runs using gibbsite or boehmite were performed at different target A/C values in order to determine an appropriate solids content required for a suitable dissolution curve. The dissolution curve of gibbsite to a target A/C=0.4 is shown in Figure 2.

Figure 2 near here

Figure 2 shows that the reproducibility of the measured A/C for the 0.4 target case was at worst $\pm 10\%$. This error is not the error in Al determination since the instrumental ICP-EAS method has a better reproducibility than this ($\sim 2\text{-}5\%$ accuracy) but is the total error in reproducing the experimental conditions as well as sampling conditions.

It is clear from Figure 3 that at times < 15 min there is little difference in the amount of gibbsite dissolution between the various solids loading. Only after this time do we see distinct differences due to changes in solids loading. We chose to investigate the gibbsite dissolution at a target $A/C=0.2$ since at this A/C, dissolution occurred over the time period of ~ 2 hours and almost reached its target value (~ 0.17 compared to 0.2).

Figure 3 near here

Although, boehmite dissolution was expected to be lower than gibbsite at this temperature, it is also much slower as confirmed by the low A/C measured compared to the target A/C value (see Figure 4). Clearly, very little boehmite goes into solution at 90°C .

Figure 4 near here

After 4 hours, at a target A/C of 0.1, an A/C of 0.007 is achieved (only 7% of desired target). The differences between target A/C values were, however, measurable and each target A/C curve had distinct rates of dissolution. From this data it was decided that boehmite would be investigated at a target A/C solids loading of 0.1 .

3.1 Dissolution in the presence of solids (anatase, rutile or sodium titanate)

When gibbsite dissolves in the presence of one of the titanium mineral solids the curve shown in Figure 5 is obtained. As can be observed no noticeable difference to the control is apparent.

Figure 5 near here

Clearly, the presence of titanium mineral solids at this target A/C has no impact on gibbsite dissolution. The anecdotal evidence that gibbsite extraction is unaltered in the presence of such solids has been verified experimentally at least at 90 °C and at this solids loading.

The case is quite different for boehmite (Figure 6) where the presence of all three titanium mineral solids appears to impact on boehmite dissolution, with rutile having the least impact and anatase the greatest. The effect of sodium titanate appears to be intermediate between the two.

Figure 6 near here

In this case, the addition of anatase results in the boehmite dissolution rate being ~20% of the control value (% inhibition = 76.7%). Sodium titanate also impacts (% inhibition = 67%) on the dissolution of boehmite but less so than anatase while the presence of rutile solids only inhibits the dissolution rate by 33%. All results are well outside the errors of the method and are significant. The change in FC during the experiment (over the time period of 300 minutes), even in the absence of titanium mineral solids, has dropped only slightly (from 250 to 248 g/L Na₂CO₃ equivalent). Although there are differences in the dissolution of the three solids in aluminate (as opposed to caustic) solution, at these low A/Cs, the Ti in solution is expected to be roughly equivalent for all titanium mineral solids since the dissolution of these solids is equivalent in caustic (Chester et al., 2009). The lowered number of moles of boehmite dissolved gives the following molar ratios of Ti/Al,

	molar ratios of Ti/Al
when rutile is present	0.0064

when sodium titanate is present	0.0128
when anatase is present	0.0255

We assume, due to the low values of these ratios, that the molar ratios of Ti/Al is not a significant parameter in the dissolution process.

3.2 *Pre-saturation of the Bayer liquor with solids*

When the liquor is pre-saturated with the relevant solids (anatase, rutile or sodium titanate) for 24 hours the solubility of gibbsite remains unaltered (data not shown). When the liquor is pre-saturated with the solids and this liquor used for the dissolution of boehmite, the dissolution is reduced but by the same amount, regardless of the original solids used to pre-saturate the liquor (Figure 7).

Figure 7 near here

In this case all the data show a ~50% reduction in dissolution rate, in between the situation where rutile and sodium titanate solids are added.

4. Discussion

As previously noted, the results presented here confirm the anecdotal evidence from alumina plants that operate at high temperature with boehmite; that is, that anatase affects the dissolution of boehmite in Bayer liquors (Authier-Martin et al., 2001). The results here suggest that rutile might also affect the dissolution but to a much lesser extent; anatase is found to inhibit the extraction of boehmite almost twice as much (although the data presented here is at 90 °C and the behaviour might be different at 250 °C). The question remains, what is the mechanism that causes anatase and sodium titanate to severely impact boehmite dissolution while rutile does so to a much lesser extent and why are they equivalent when the liquor is pre-saturated?

Let us hypothesise that the mechanism by which boehmite dissolution is inhibited is by way of re-precipitation onto a surface, blocking further dissolution as suggested by Chester et al. (2009). In that manuscript, the dissolution of these three minerals is

equivalent in pure caustic for the same FC value but differ when aluminate is present. Thus all three would dissolve to the same extent over the 24 hour period used to pre-saturate the liquor and have an equivalent titanate concentration in solution. If the titanate were to re-precipitate on the boehmite, this would explain why pre-saturating the liquor with either of the three minerals affects dissolution to the same extent (because the driving force for re-precipitation would be equivalent for the three minerals). Thus, this result supports the hypothesis.

The observation that titanium mineral solids can inhibit the dissolution of boehmite is interesting. It would be expected that the solids will only dissolve to their equilibrium value and a supersaturated solution cannot result. However, the solubility is actually changing as the aluminate concentration increases with increasing boehmite (or gibbsite) dissolution. Sodium titanate has its highest solubility in pure caustic (Chester et al., 2009) and as the boehmite dissolves (and the FC decreases) the 'equilibrium' solubility of sodium titanate is constantly decreasing. In Figure 8 the solid straight line would represent the equilibrium Ti concentration for the initial caustic solution. The thick black curve thus would represent the dissolution of a solid to the equilibrium value over time. As boehmite dissolves the equilibrium Ti concentration will be changing according to the dotted line. In this case, the dissolution of the solid is constantly having to adjust to the new equilibrium level. A situation such as the dashed curve may now result. Thus, supersaturation can be achieved due to the constantly changing equilibrium solubility. Unfortunately, the change in FC value is rather small over the course of the 300 minutes, which the experiment runs. Even in the absence of other solids the FC only changes from 250 to 248. This change in Ti dissolution would, therefore, result in a small supersaturation ratio being created over this time. In addition, while this mechanism can explain how the supersaturation state can be achieved, it does not explain why differences in the three solids are observed (since the Ti dissolved into solution would be expected to be the same at this very low A/C, according to Chester et al., 2009).

Figure 8 near here

There is also the matter of these titanium mineral solids inhibiting boehmite but not gibbsite dissolution. If re-precipitation of a solid phase from solution were driven solely by the titanate concentration in solution (which is directly related to the FC) then as the gibbsite dissolved this would lead to a greater drop in free caustic than the small dissolution of boehmite and this should lead to greater re-precipitation of a solid phase on gibbsite – inhibiting its further dissolution. This is not observed. Thus, other factors must also be at play. One possibility is; if the degree of supersaturation is not above the metastable limit, then the surface present can have a significant impact. This is because, in this regime, heterogenous primary nucleation is possible and this is dependant on the affinity of the substrate to the crystallizing unit (Mullin, 1997). Thus, this would suggest that gibbsite has less affinity and boehmite greater affinity with the sodium titanate crystallizing from solution. In this scenario, it is important to state that surface area effects may also be operating. Re-crystallization onto boehmite may also be promoted due to the higher surface area present than in the case of gibbsite.

It is also interesting to note that the effect of the Ti-containing solids is greatest on the slowest of the Al-dissolving species. It suggests that in addition to the amount of titanium mineral dissolved, other non-equilibrium effects are also important. At 10 minutes, about 50% of the gibbsite solids have dissolved while only 0.3% of the boehmite (even under optimal conditions) solids have dissolved at this stage. Thus, the re-precipitation may be driven by kinetic as well as thermodynamic effects. This would correlate with preliminary data obtained at 250 °C. At this temperature all of the solids show a decreased impact on boehmite dissolution compared to 90 °C (Dudek, 2008). Thus, another possibility is that the slower the dissolution process, the more ‘affected’ the Al-containing solids will be by the Ti-mineral phases. This implies that the rate of adsorption of titanate on the surface of the aluminium-containing mineral and/or on the desorption/diffusion of aluminate from the surface might be important.

When the liquor is not pre-saturated and dissolution of boehmite occurs in the presence of one of the titanium mineral solids, we would expect that the trend in inhibition should be anatase = rutile > sodium titanate according to the dissolution of

these minerals in aluminate solutions (Chester et al., 2009). Yet, the trend in dissolution inhibition is anatase > sodium titanate > rutile. This is an important point; why does rutile have a lesser effect than predicted from dissolution experiments? This leaves two possibilities:

- i) the dissolution values for rutile found previously are too high, or
- ii) the presence of rutile somehow impacts less on the boehmite dissolution process.

The possibility of i) is actually low, given that as stated previously there is a great deal of literature showing that regardless of whether anatase and rutile is used as the Ti source, sodium titanates are formed (Wu et al., 2006; Morgado Jnr et al., 2007; Pradhan et al., 2007; Menzel et al., 2006) – suggesting that they indeed have a lower solubility than rutile. This leaves possibility ii) whereby the presence of rutile somehow limits the formation of a new phase on boehmite.

It must be noted that data from Chester et al. (2009) were collected at 24 hours. If rutile dissolution is slow, the addition of rutile solids should have the least impact. To test this hypothesis experiments were run to determine the effect of time on the titanate concentration more closely. In this way an idea of the kinetics could be gained.

Figure 9 near here

Firstly, all solids dissolve quickly to an initial level ranging from ~3-4 mg/L (see Figure 9). It is interesting to note that the amount of sodium titanate and anatase dissolved is higher at 1 hour than that of rutile. If we look at the Ti levels in solution at the 5 hour stage (boehmite dissolution runs were 4 hours), we note that the solubility of the minerals is anatase > sodium titanate > rutile. This continues to be the case up until ~15 hours. At this point, the amount of rutile and sodium titanate dissolved is similar while that of anatase clearly is still increasing. The sodium titanate dissolution has actually decreased slightly over this time and this could be due to other titanate phases having different solubility equilibria. At 24 hours, the amount of rutile and anatase dissolved is similar while that of sodium titanate is slightly lower. Values obtained

previously (using a different piece of equipment as Chester et al., 2009 but similar method) are also superimposed and are consistent. Thus, anatase has the greatest impact because it dissolves quickly and continues to dissolve significantly over time. Sodium titanate has the next most significant impact because the initial amount dissolved is high but then very little happens over time. Rutile has the least impact because it has the lowest initial dissolution rate and only after a very long period of time begins to significantly dissolve. In addition, surface specific effects as mentioned for heterogenous nucleation may also be occurring.

5. Conclusions

The presence of anatase, sodium titanate and rutile is shown to impact on the dissolution of boehmite, confirming a long held belief by plant operators that Ti-minerals can limit boehmite 'extraction'. This was not the case for gibbsite dissolution suggesting that the kinetics of dissolution for the Al-species is an important factor in determining whether the ore will be impacted on by the titanium containing minerals. It is also possible that boehmite promotes sodium titanate precipitation onto itself.

Anatase was found to impact boehmite dissolution the most, with sodium titanate having an intermediate effect and rutile impacting the least.

Pre-saturation of the liquors with the Ti-containing phases had no impact on gibbsite (confirming the previous result) and an intermediate effect on boehmite dissolution. The results tend to suggest that boehmite is inhibited by way of an impervious surface layer formed by dissolved titanate species, the most likely form of which is a sodium titanate.

From the present results sodium titanate would be expected to inhibit boehmite dissolution as well as anatase. However, sodium titanate is unlikely to be present in ores and as such is not expected to significantly contribute to plant operations.

The phase with the least impact on boehmite dissolution was rutile, although at 90 °C it was shown to have a non-zero effect. Analysis at 24 hours showed that rutile and

anatase dissolve similar Ti concentrations into solution at 90 °C and this suggests that the kinetics of dissolution of the Ti-containing mineral is also important. This was confirmed by timed runs showing that rutile dissolution does not significantly change until >15 hours has elapsed. Thus, rutile impacts the least because it is the slowest to dissolve.

6. Acknowledgements

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