The dissolution behaviour of titanium oxide phases in synthetic Bayer liquors at 90 °C

R. Chester#, F. Jones‡#, M. Loan*†, A. Oliveira#, W. R. Richmond#

AJ Parker Co-operative Research Centre for Integrated Hydrometallurgy Solutions. Nanochemistry Research Institute, Curtin University of Technology, GPO Box U1987, Perth WA 6845 Australia

‡Corresponding author: Phone: +61 8 9266 7677   Fax: +61 8 9266 4699   email: F.Jones@curtin.edu.au

*AJ Parker Co-operative Research Centre for Integrated Hydrometallurgy Solutions. CSIRO Division of Minerals, Waterford †current address: Alcoa World Alumina, Technology Delivery Group, PO Box 161, Kwinana, W.A. 6966 Australia

Abstract

Many of the bauxites currently being processed to alumina contain titanium minerals, yet little fundamental knowledge is available regarding their dissolution behaviour in Bayer liquors. In this paper the dissolution of various titanium oxide phases (anatase, rutile, sodium titanate and calcium titanate) are presented. It is shown that rutile, calcium titanate and sodium titanate have the expected dissolution behaviour, which increases with free caustic concentration. Anatase, too, generally increases in dissolution with free caustic concentration. However, anatase is shown to have an anomalous behaviour when gibbsite co-precipitates. In this case, the dissolution of anatase does not follow the expected free caustic trend. According to the data presented, the most probable cause is an impervious aluminium/sodium titanate surface layer hindering further dissolution.

Keywords: anatase, rutile, calcium titanate, sodium titanate, Bayer process, dissolution behaviour

1.0   Introduction

In the processing of bauxite ore to alumina (Al_2O_3) different conditions are used, depending on the main aluminium-bearing phases. A low temperature digest (~150 °C) is used when gibbsite is the main component while higher temperatures are required when boehmite (or diaspore) is present (~250 °C). Alumina production is essentially the same in both cases, being a dissolution-precipitation process where the

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aluminium bearing phases of the ore are dissolved in concentrated caustic solution, the waste then removed and aluminium trihydrate (gibbsite) precipitated in pure form before calcining to obtain alumina. Different challenges are encountered in high temperature processing when titanium is present in the bauxite, including the negative impacts of scale formation, titanium in the alumina product, and inhibition of boehmite extraction (Malts et al., 1985; Malts, 1992; Prakash & Horvath, 1979). TiO_2 dissolution/reactivity is believed to be minor at 'lower' temperatures, although data demonstrating this fact is noticeably lacking in the literature. There is also anecdotal evidence (from alumina plant operators) that the mineral form of the titanium phase is important. Recently, an *in-situ* XRD study demonstrated that anatase, and not rutile, inhibited boehmite dissolution (Loan et al., 2005), confirming this long-held belief that the presence of anatase in bauxite ores limits the extraction of Al in the high temperature process (Malts et al., 1985; Malts, 1992).

The literature on titanates in Bayer liquors has focussed almost exclusively on their impact on extraction and reaction with lime during digestion, or the final precipitation products. Studies have found that sodium titanates are formed at lower temperatures and higher caustic concentrations (Shultze-Rhonhof & Winkhaus, 1972) and that sodium titanate (all sodium titanate materials, regardless of composition) has a low solubility in aluminate liquors (Wefers, 1971). The solubility of anatase was found to be dependant on the free caustic concentration and the time allowed for dissolution to occur (Shultze-Rhonhof & Winkhaus, 1972). In the presence of calcium, both perovskite and tricalcium aluminate can form (Malts et al., 1985; Prakash & Horvath, 1979; Loan et al., 2005).

The interest in titanates is not limited to the alumina industry however, and titanate compounds are currently under investigation as a route to the formation of Ti-containing inorganic nanotubes (Wu et al., 2006; Morgado et al., 2007; Pradhan et al., 2007; Menzel et al., 2006). Results from this literature that are of relevance to the work described here include the observation that sodium titanates are formed at high caustic strengths and high temperatures (Wu et al., 2006; Morgado et al., 2007; Pradhan et al., 2007; Menzel et al., 2006). Furthermore, both rutile and anatase have been found to form sodium titanate nanotubes with the greater conversion of anatase to nanotubes related only to the higher surface area of the anatase starting material

(Menzel et al., 2006). Of more interest, perhaps, is the work of Wang et al. (2006) that shows that the form of titanium oxide can be important even when adsorbing organic titanates. The organic titanate was found to react with the corundum surface, strongly adsorb onto anatase and weakly adsorb onto rutile. This is further confirmed by the work of Hotta et al. (1991), where the organic titanate was coupled to a hematite surface, which is isostructural with corundum.

Missing from our current understanding is any fundamental information regarding the solubility of titanium (in various forms) in Bayer liquors. However, such data is difficult to obtain unambiguously when re-precipitation reactions can also occur. To this end we have begun to systematically measure the dissolution of anatase, rutile, sodium titanate and calcium titanate in synthetic Bayer liquors. Unfortunately, the measurement of dissolution under hydrothermal conditions is not a trivial exercise; the greatest challenge being to remove the excess solids without significant cooling, and subsequent re-precipitation, occurring. In the preliminary experiments we conducted, even at 90 °C we found that the measured [Ti] levels were lower when the filtered solution was left to stand undiluted or not sufficiently diluted. This highlights that re-precipitation can and does occur as the temperature drops towards ambient and the [Ti] level in solution reaches supersaturated levels, limiting experiments to lower temperatures. In what follows we present some preliminary dissolution data for anatase, rutile, sodium titanate and calcium titanate in synthetic Bayer liquors at 90 °C. Although this data can be used to extrapolate what can be expected under the hydrothermal conditions of the Bayer process, it is clearly well below even the low temperature Bayer process. However, collecting dissolution data at higher temperatures presents major technical difficulties which must first be overcome.

2.0   Materials and Methods

The solids, TiO_2 (anatase, 99% and rutile, 99% pure) and calcium titanate ($CaTiO_3$), were obtained from Aldrich and used as received. Sodium titanate was obtained from Strem Chemicals (95% pure) and used as received. All were found to be single phases except the sodium titanate where the XRD found a combination of two sodium titanate phases; namely JCPDF# 37-951 Sodium Titanium Oxide ($Na_2Ti_6O_{13}$) and

JCPDF# 72-148 Sodium Titanium Oxide ($Na_2Ti_3O_7$). Table 1 and 2 give all the relevant physical characteristics of the solids used.
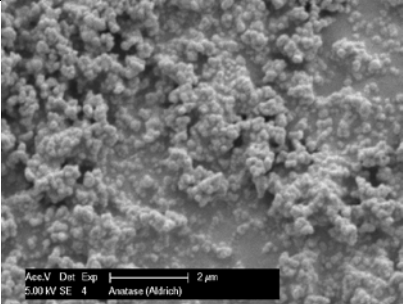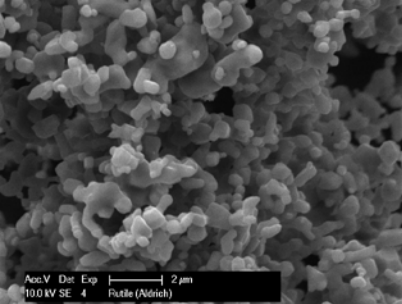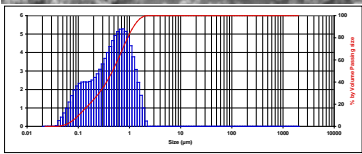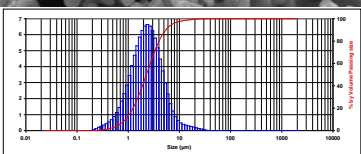
Table 1.
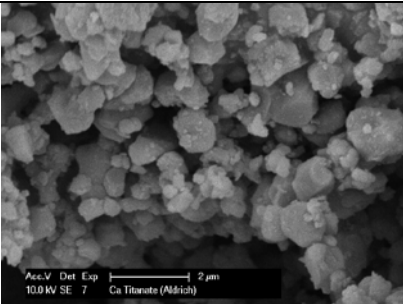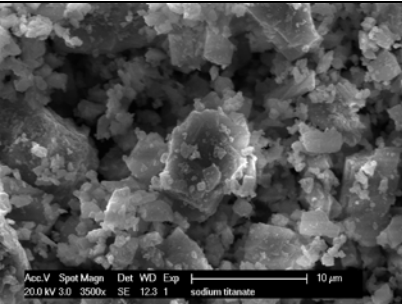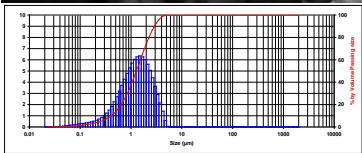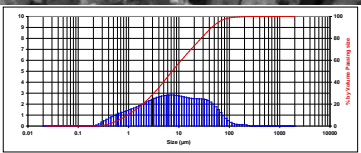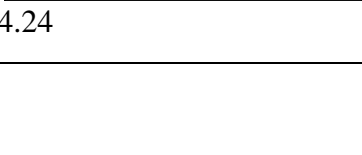
	Anatase	Rutile
SEM		
PSD		
Surface area (m^2/g)	8.89	2.13
	Calcium titanate	Sodium titanate
SEM		
EDX		
PSD		
Surface area (m^2/g)	4.24	2.06

Table 2.   XRD spectra of the phases investigated.
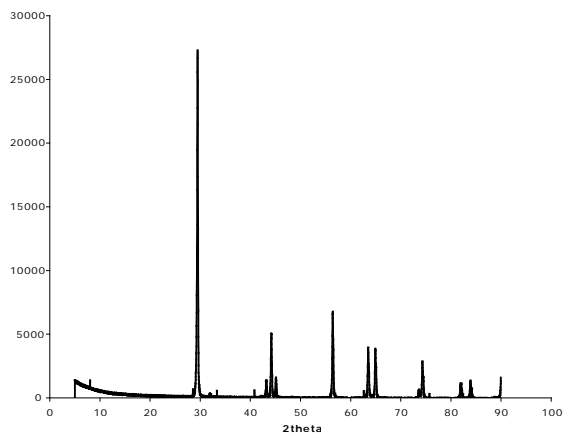
JCPD#21-1272 (anatase)
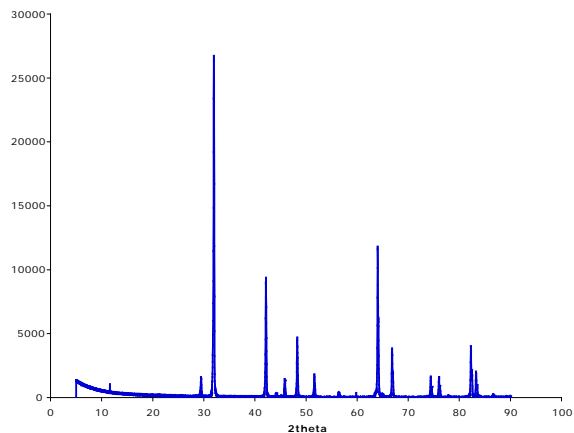
JCPD#21-1276 (rutile)

JCPD# 22-153 (calcium titanate)

JCPD# 72-148 and 37-951 (sodium titanate)

Sodium hydroxide (analytical grade from BDH), MilliQ water, sodium carbonate (analytical grade from BDH) and aluminium wire (from BDH, 99.9% pure) were used for synthetic Bayer liquor preparation. XRD patterns were collected on a Philips Xpert diffractometer using Co K_α radiation. Scanning electron microscopy was performed on a Philips XL30 SEM and surface area was determined using the BET isotherm with N_2 as the carrier gas.
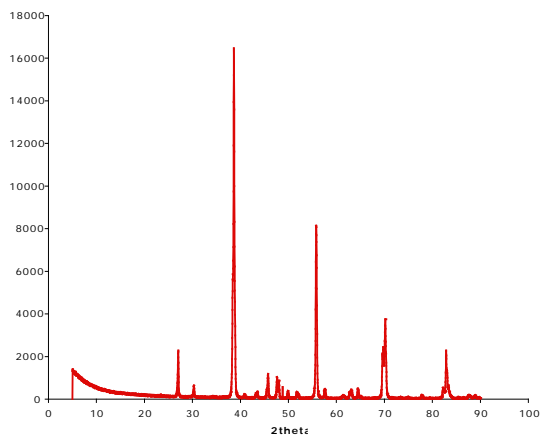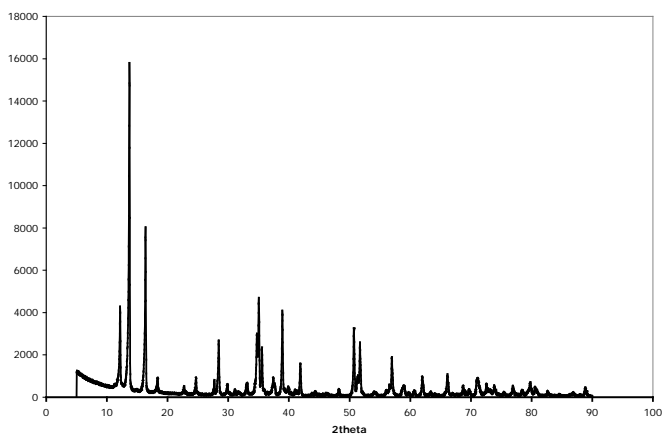
The following conventions used in the alumina industry have been followed for this study:

A= aluminium in solution expressed as g/L Al_2O_3

C= total caustic, expressed as g/L Na_2CO_3

S= total alkalinity, expressed as g/L Na_2CO_3 , (=sodium carbonate+C)

A/C = alumina to total caustic ratio (is related to the supersaturation of aluminium in solution)

FC = Free Caustic = C – (106*A/102) (in g/L Na_2CO_3)

$\quad$ = $[OH^-]_{total}$ – $[Al^{3+}]$ (in moles OH^-); the free caustic takes into consideration the caustic consumed in forming the aluminate ion

The subsequent graphs shown in this manuscript show the data as a function of C as well as FC. This is because in plant situations, C is often the measure used.

Bayer liquor preparation

Concentrated sodium hydroxide (16M, corrosive) solution was prepared and placed in a refrigerator for 3 days in order to precipitate carbonate before pressure filtering (and produce low carbonate Bayer liquors). The filtered hydroxide solution was then diluted with Milli-Q water to the desired C value in a stainless steel vessel containing a magnetic stirrer. Heat was applied and aluminium wire was dissolved (slowly adding Al wire and avoiding excessive boiling) to achieve the desired 'A' value. When all of the Al wire had dissolved the liquor was filtered and allowed to cool before making up to volume. The resulting liquor was then ready for use.

Dissolution experiments

Synthetic Bayer liquor (30 mL) was equilibrated to 90 °C (± 1°C) in a Teflon® centrifuge tube with magnetic stirring at 1000 rpm. Solids were added such that the solids loading was not excessive and were easily stirred (0.5 g), to obtain solubility data by reaching the temperature from below. This was left for 24 hours to equilibrate before filtration through a 0.2 µm caustic resistant membrane. An aliquot was subsequently diluted (10x) into pure sodium hydroxide (at the equivalent C value) before analysis by ICP(-AES) for Ti and Al. Dilution was necessary in order to avoid re-precipitation of Ti due to temperature changes. The synthetic liquor was analysed prior to the run for C, S and A/C using a standard titration method (Connop, 1996). This method uses gluconate to stop aluminate precipitating during carbonate and hydroxide analysis by titration with a standard HCl solution. A preliminary study was performed to find the optimal dilution factor (0 to 20x investigated) and time to equilibrate (up to 2 weeks). The optimal dilution was found to be ≥10x and 24 hours was observed to be the time required for maximum dissolution to be reached. The dissolution versus time runs were performed in the same manner, but an aliquot was removed at the desired time rather than 24 hours.

3.0   Results

Dissolution behaviour in pure caustic and low A/C liquors at 90°C

As can be seen in Figure 1a), anatase and rutile are very sparingly soluble at 90°C. For all of the solids used in this study, the level of dissolved [Ti] was related to the free caustic concentration and was found to be independent of the carbonate concentration up to 30 g/L, which was the upper limit of this study. The dissolution behaviour for the two oxides was also equivalent at low A/C values (up to 0.3). The slopes of the curves in caustic liquors are very similar and the minor variation may simply reflect measurement errors. Since these are diluted samples, the errors become multiplied, so an error of 0.05 mg/L [Ti] in the measured sample becomes 0.5 mg/L error in final concentration. This suggests that the dissolution behaviour for rutile and anatase is equivalent at these FC values. However, the difference in dissolved [Ti] in pure caustic for anatase and rutile becomes more significant with increasing free caustic (up to ~1 mg/L) suggesting there might be a difference between the two phases.

The dissolution behaviour of sodium titanate and calcium titanate are presented in Figure 1b), and it can be seen that sodium titanate has a similar dissolution behaviour to rutile and anatase in pure caustic, but marginally lower when the A/C is 0.3. This difference becomes more evident at the higher free caustic concentrations where the sodium titanate dissolves at ~4 mg/L [Ti] at 3 M free caustic (A/C=0.3) and >5 mg/L [Ti] for rutile and anatase at 3 M free caustic (A/C=0.3). In essence, we may conclude that adding aluminate to the solution does not impact on the dissolution behaviour of sodium titanate to the extent that it does for rutile and anatase. In fact, the dissolution behaviour of sodium titanate appears to depend only on the free caustic concentration and can be considered independent of the A/C.

Of the 4 solid phases, calcium titanate has the lowest solubility. The concentration of calcium titanate dissolved (at A/C = 0.3), is ~0.5 mg/L, and is equivalent to a concentration of 3.68×10^{-6} M Ca^{2+} (or only ~0.15 ppm Ca^{2+}) at 90 ^{o}C.
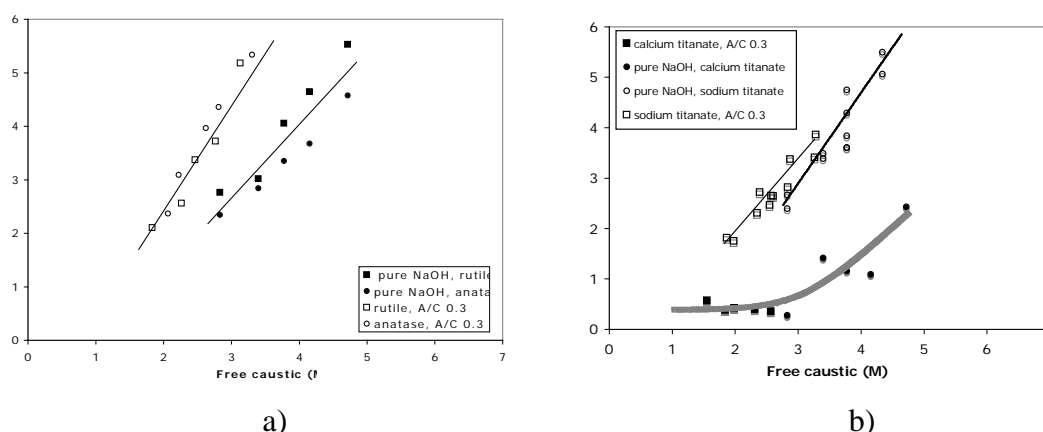
Figure 1. Dissolution behaviour (mg/L) of a) anatase, rutile, b) sodium titanate and calcium titanate in pure caustic and at low A/C levels versus the FC concentration

For anatase and rutile, the dissolution increased significantly at the equivalent free caustic level when aluminate was also present. Sodium titanate did not show such behaviour. Calcium titanate showed a decrease in dissolution as the free caustic concentration decreased, however, the value in pure caustic at a free caustic concentration of ~2.8 is also quite low and this appears to be a direct effect of the variation in free caustic rather than being due to the presence of aluminate.

The dissolution behaviour in synthetic Bayer liquors at 90 °C

It should be noted that, depending on the A/C value, the liquors can be unstable. Gibbsite will precipitate at 90 °C and an A/C 0.7 for all the solids investigated. At A/C = 0.5 no gibbsite precipitation was observable either by the presence of gibbsite particles or by EDX.

In the case of rutile, when viewed from a free caustic perspective, the dissolved [Ti] is seen to increase with increasing A/C (Figure 2a&b). That is, as the aluminate increases at a fixed FC, the dissolution of rutile also increases. It has been observed for many compounds that an increase in ionic strength will increase the solubility of that compound (Hausler, 1978; Christov et al., 2007), so it is tempting to suggest that this is the cause of the solubility increase in the present case. However, if this were true, the addition of carbonate should also have increased the solubility of either rutile or anatase – which was not observed for any of the solids investigated in this work. More importantly, this increase is most pronounced in the case where the liquor is unstable and gibbsite precipitation occurs. In order to determine the real cause of this observed increase in solubility, we performed an experiment in which we monitored both the Al and the Ti levels with time.

a)   b)
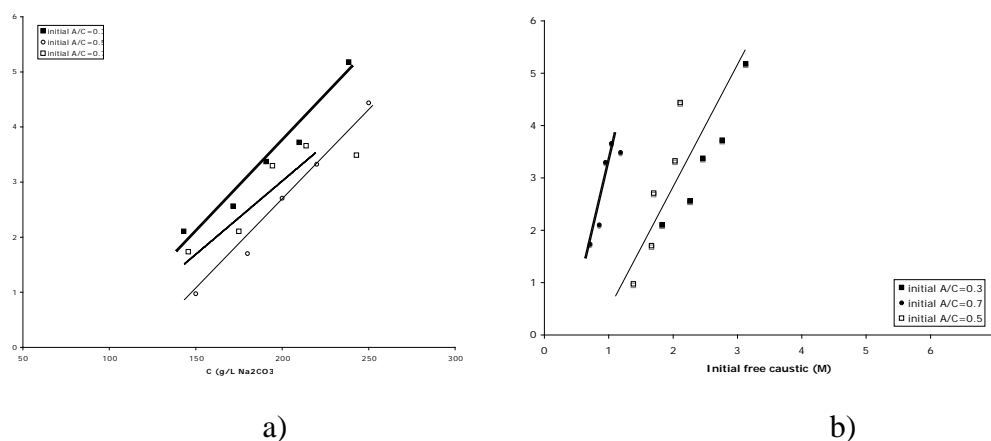
Figure 2.   Dissolution behaviour of rutile in synthetic Bayer liquor versus caustic concentration - expressed as either a) C or b) Initial FC

The results are presented in Figure 3 and clearly show that the initial A/C is not equivalent to the final one after 24 hours. Thus, a simpler explanation is possible for the observed solubility of rutile at high A/C: as gibbsite precipitates over the 24 hours to

equilibration, the free caustic level is increasing (as the A/C is decreasing). When plotted on a final FC scale the originally A/C=0.7 liquor has an A/C ~0.4 at 24 hours and now shows the solubility as given in Figure 3b. This highlights only one of the many difficulties with measuring solubilities of species in Bayer liquors.

a)   b)
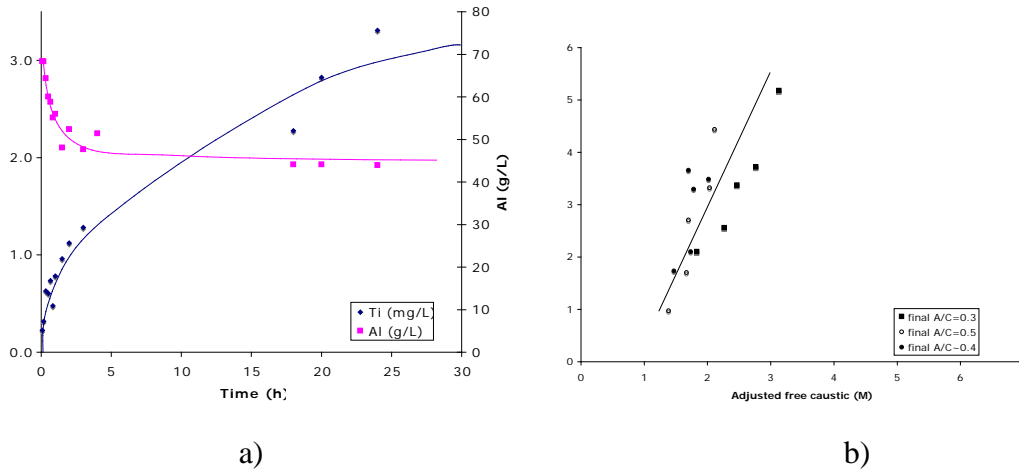
Figure 3.   a) [Ti] and [Al] versus time for a synthetic liquor having an initial A/C = 0.7 with rutile solids dissolving and b) the rutile dissolution results adjusted for the final free caustic levels

The dissolution behaviour of calcium titanate, plotted against the final free caustic level, is shown in Figure 4 a). The solubility of calcium titanate shows little dependence on A/C values remaining quite low. Given the similarities in free caustic levels this is not surprising. As in the case of rutile, gibbsite precipitation occurred at the high A/C levels but this did not impact on the solubility other than to change the FC level. Similarly, for sodium titanate at high A/C values, (Figure 4 b) the dissolved [Ti] levels reflected the increased free caustic on gibbsite precipitation. Overall, for all of these solids the results support the work of Wefers (1971) and Rhonhof & Winkhaus (1972) who both found that solubility was dependant on the free caustic level.

a)   b)
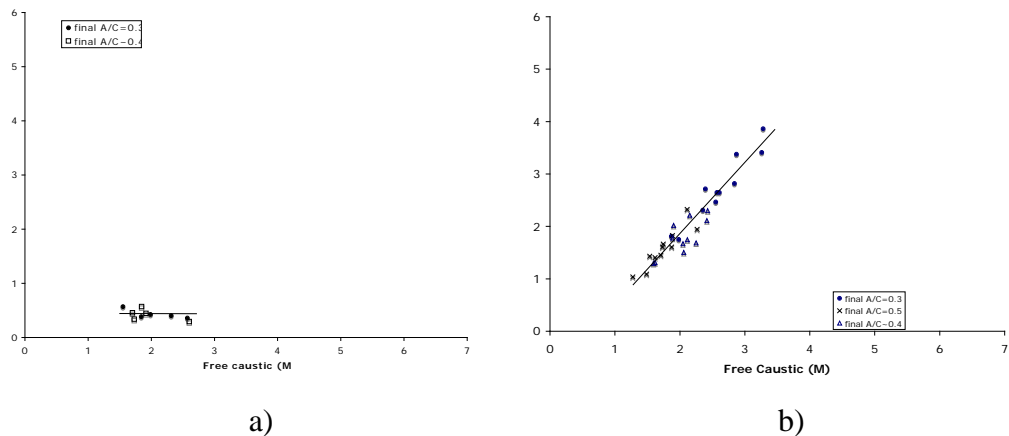
Figure 4. Dissolution behaviour of a) calcium titanate and b) sodium titanate in synthetic liquors having a variable A/C level but where the liquor having an initial A/C = 0.7 was plotted using the final free caustic levels

The situation is quite different for anatase where the dissolution behaviour of the TiO$_2$ follows a trend in *initial* free caustic (Figure 5).

a)   b)
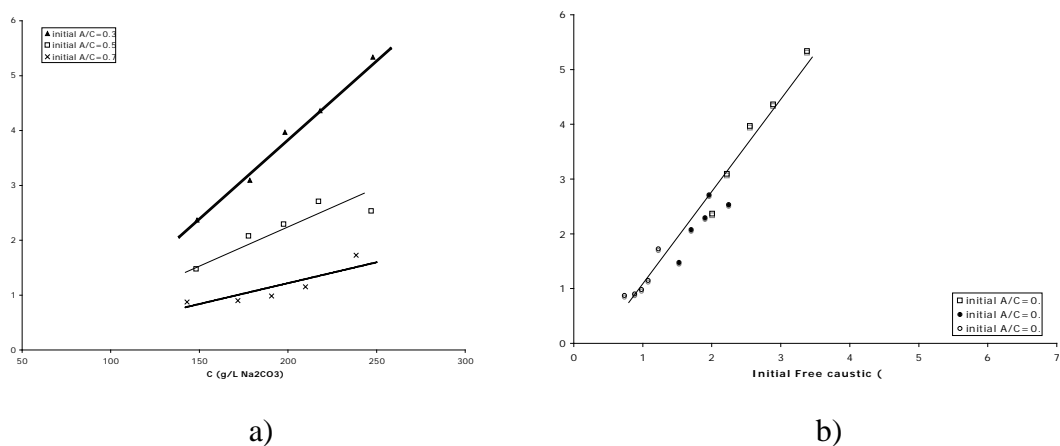
Figure 5. Dissolution behaviour of anatase in synthetic Bayer liquor versus caustic concentration - expressed as either a) C or b) initial FC

If we take into consideration the final free caustic concentration of these solutions the resulting trend shown in Figure 6a would follow. A time dependant analysis of the dissolution behaviour was undertaken as per rutile in order to understand what was occurring in the presence of anatase, and the results of these measurements are presented in Figure 6 b).

a)	b)
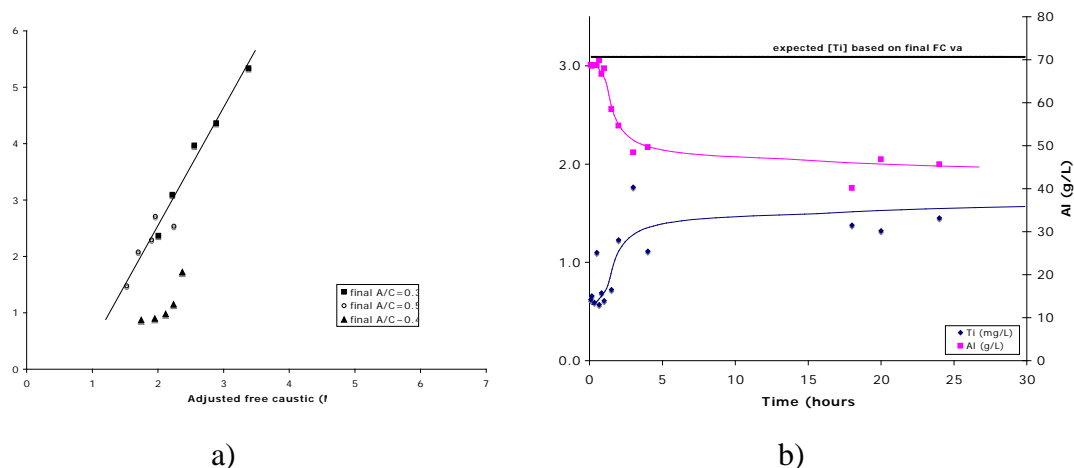
Figure 6.   a) the anatase dissolution behaviour adjusted for the final free caustic levels of the 0.7 A/C liquor and b) [Ti] and [Al] versus time for a synthetic liquor having an initial A/C = 0.7 with anatase solids dissolving

Comparing this graph with that shown in Figure 3 a), we can see that in contrast to the case of rutile dissolution, the precipitation of gibbsite now mirrors the dissolution of anatase. Also of interest is that the gibbsite precipitation shows an induction time while in the presence of rutile no induction time was observed, and the initial dissolution of anatase appears higher than that of rutile until the precipitation of gibbsite commences. Gibbsite precipitation seems to be inhibiting the further dissolution expected at higher free caustic concentrations.

SEM images of this sample (Figure 7) show that there are sufficient free surface anatase solids exposed to the liquor for it to reach equilibrium according to the new FC value. However, based on the final FC, we can see that the anatase is clearly not equilibrating to this value. Despite being decorated with anatase particles, the surface area of this sample was only 1.23 m^2/g (i.e. dominated by the gibbsite particles). This is surprising since, as shown in Table 1, the surface area of the original anatase was ~8 m^2/g. Since surface area should be dominated by the smaller particles it would seem that some form of cementation of the anatase has occurred, lowering its contribution to the surface area.
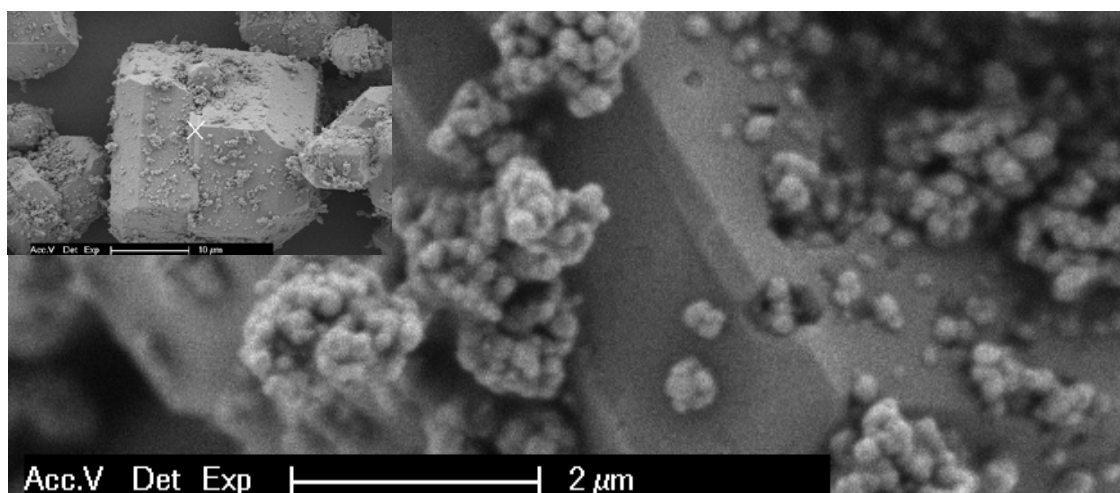
Figure 7.   SEM images taken from a synthetic liquor with initial A/C = 0.7 with anatase solids dissolving. Small (~250nm), fluffy aggregates of particles are anatase, larger crystals (≥10μm) are gibbsite. Inset shows lower magnification image where gibbsite crystals are clearly seen.

Surface blocking is the most likely explanation for the dissolution behaviour results at high A/C. EDX and XRD on the sample confirmed the presence of Al and bulk gibbsite precipitation but this bulk precipitation (which also occurred for all the other solids at high A/C) cannot be the mechanism of inhibition. It must be stressed that since gibbsite precipitation did not lower rutile dissolution that any mechanism proposed must be peculiar to anatase. Thin sections of the gibbsite precipitated in the presence of anatase were thus prepared for analysis of the interface between anatase and gibbsite solids in order to determine whether a surface coating could be the cause of the difference. The results from TEM analysis on the thin sections showed that the anatase solids were incorporated into the gibbsite crystals (see Figure 8), and confirmed the existence of a strong attraction between gibbsite and anatase. It is possible that the association of anatase and gibbsite may also involve the formation of a surface coating, such as an amorphous phase, for example at the anatase/gibbsite interface, but a boundary layer of this nature could not be definitively identified in our TEM experiments.
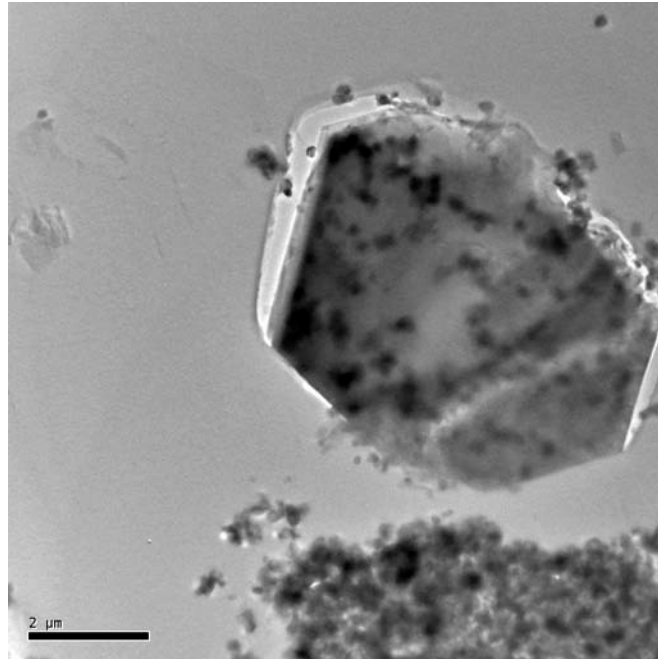
Figure 8.   TEM image of a gibbsite particle after embedding in resin and microtoming, showing anatase particles within the gibbsite particle

What is not completely known at this point is whether the dissolution behaviour we have measured are the actual solubilities of each mineral phase or the equilibrium solubilities for a lesser soluble phase. That is, as anatase and rutile are dissolving, is there a re-precipitation reaction based on an equilibrium phase having a lower solubility? As an example, if we compare Figures 3a and 6b, anatase shows an initially higher dissolution level than rutile but then is lower once gibbsite begins to precipitate. Is anatase dissolving at a higher level but then precipitating as rutile or sodium titanate? In Figure 9, the dissolution behaviour of anatase, rutile and sodium titanate are overlaid for the various A/C and FC values. At high FC values, there is a large difference between the rutile/anatase dissolution values and the sodium titanate values. We can be confident in this regime that after 24 hours equilibration sodium titanate is not re-precipitating. At low FCs (and high A/C values) the sodium titanate dissolution behaviour is remarkably similar to the dissolution behaviour of rutile and anatase. This suggests that we are, in fact, measuring the sodium titanate solubility in this regime. Figure 10 is a schematic showing how this might be represented in terms of the metastable zone and the solubilities of the various solids.
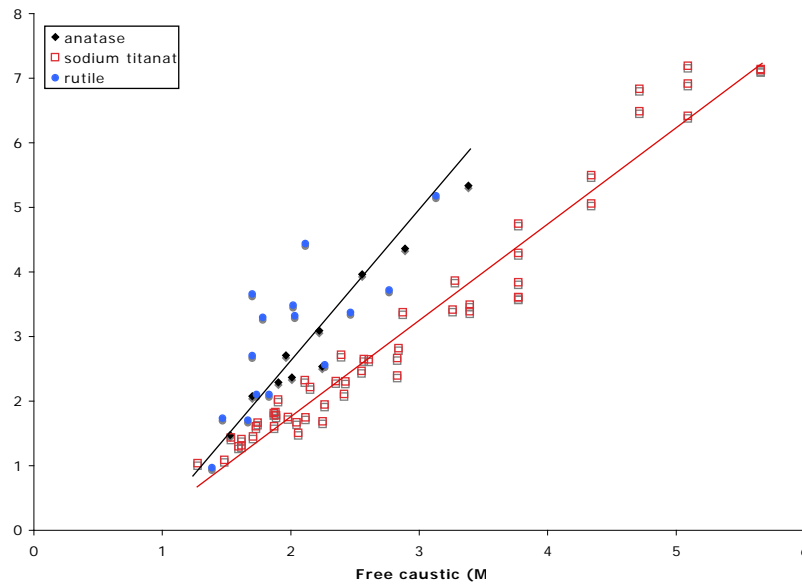
Figure 9. Rutile, anatase and sodium titanate dissolution behaviour as a function of FC
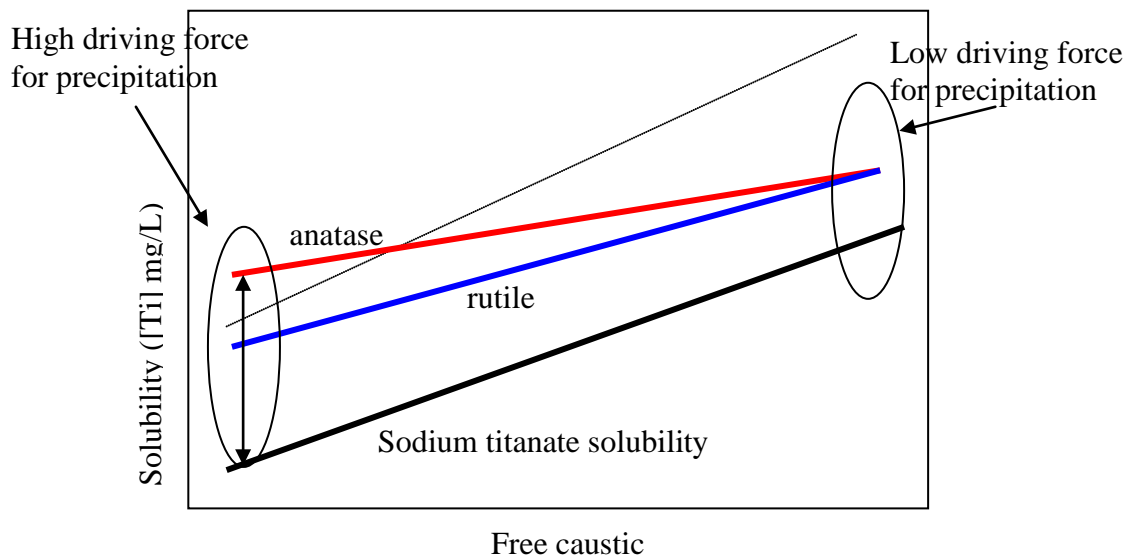
Figure 10. Schematic showing a possible mechanism in which anatase (red line) will dissolve but then re-precipitate as sodium titanate (black line) while rutile (blue line) will not (dashed line represents sodium titanate metastable limit)

If the sodium titanate solubility is given by the black line and its metastable zone limit by the dotted line, then as FC decreases, the solubility of anatase (red line) is higher than the metastable zone limit and sodium titanate can precipitate. The solubility

of rutile on the other hand,(blue line) does not lie above the metastable zone limit and thus sodium titanate does not precipitate, or at least not to the same extent. It is also feasible that less sodium titanate forms on rutile than on anatase as a result of surface area differences and so rutile is less affected than anatase overall.

Sodium titanate has a low dissolution level at low FCs and by inference also at high A/Cs. Thus, in the experiment with initial A/C = 0.7 and sodium titanate little dissolution should occur, and as gibbsite precipitates the sodium titanate dissolution increases but only to its equilibrium level. Thus, the initial presence of sodium titanate will *never* create a situation where sodium titanate re-precipitation will occur. In the case of an industrial Bayer process liquor however, the process will be reversed. In this case, as gibbsite or boehmite is dissolving the FC is decreasing, while the A/C is increasing. Over time, as extraction of aluminium is increasing, the solubility of sodium titanate is decreasing and this could lead to re-precipitation reactions.

The results presented here support the results of Wang et al. (2006) who showed that the titanate moiety is attracted to the anatase surface through chemisorption. It remains to be shown that aluminate is also attracted to titanate. In this regard, the work of Yamada (1981) report that sodium titanate is able to seed gibbsite precipitation. However, it would also be desirable to obtain some chemical modelling data to ascertain the interaction of aluminate with sodium titanate, rutile, calcium titanate and anatase.

4.0   Conclusions

Rutile, calcium titanate and sodium titanate dissolution behaviour in synthetic Bayer liquors is proportional to the free caustic concentration. Gibbsite precipitation in the liquors did not affect the dissolution behaviour determined for rutile, calcium titanate or sodium titanate, other than to change the free caustic levels and therefore cause the system to re-equilibrate to the new free caustic level. Sodium titanate and calcium titanate showed no change in dissolution behaviour when the aluminate ion was present, while rutile and anatase showed a slight increase in dissolution in aluminate solutions when compared with pure caustic solutions.

Anatase dissolution behaviour is generally proportional to free caustic levels but at high A/Cs it is lowered by the precipitation of gibbsite; a behaviour that is quite different from the other mineral phases studied here. This means that after gibbsite precipitation the anatase does not equilibrate to the expected level based on the free caustic concentration. Aluminate and/or sodium titanate may adsorb or precipitate on anatase surfaces forming an impervious layer that prevents further dissolution and the re-establishment of equilibrium with the new free caustic concentration. The mineral phase most likely to make up this impervious layer is some form of re-precipitated sodium titanate.

Calcium titanate (perovskite) has the lowest solubility of all the phases studied at $90^{o}C$ and the equilibrium solubility at a FC of 3 M corresponds to only ~0.15 ppm calcium ions. In an alumina refinery, the temperature drop from digestion ($250°C$) to clarification ($107°C$) conditions would be expected to result in precipitation of titanium containing phases, in particular sodium titanate.

5.0   Acknowledgements

6.0   References

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