ABSTRACT

This paper collates existing information from the literature on the reactions of lime added directly to high temperature Bayer digestions. It examines the reaction of calcium in lime with liquor components to form reaction products. Reactions are considered individually and in competition with each other. Because of the scarcity of information about competing reactions involving calcium / lime, the paper contains some speculation, drawing on different pieces of evidence from the literature to suggest possible reaction pathways. Three lime types have been considered – slaked lime (Ca(OH)$_2$) calcite (CaCO$_3$) and tri-calcium aluminate (TCA, $\text{Ca}_3\text{Al}_2(\text{OH})_1_{2}^\text{2}$).

Individual reactions of calcium in lime have been considered with - alumina and carbonate, fluorine, vanadium, phosphorus, silica, titanium and iron. Consideration has also been given to the “catalytic” actions of lime in transforming goethite to hematite and enhancing boehmite dissolution.

1. REACTIONS OF LIME WITH INDIVIDUAL LIQUOR COMPONENTS

1.1 Alumina and Caustic

When quicklime or slaked lime contacts Bayer liquor, the slaking process will involve reaction with both aluminate and carbonate ions. There is general agreement that the mechanism by which either calcite or TCA (the main causticisation products) forms from quick lime (CaO), or slaked lime (Ca(OH)$_2$), is through the formation of an intermediate product. This intermediate is a layered double hydroxide (LDH) of the hydrotalcite type with a carbonate ion inclusion. The main discrepancy in the descriptions of the LDH appears to be the level of carbonate incorporation (Roach, 2000; Rosenberg et al. 2001). Alcoa identifies the mono-carbonate $\text{[Ca}_2\text{Al(OH)}_{6}\text{.CO}_3\text{.5H}_2\text{O}}$, whereas Worsley describes the hemi-carbonate $\text{[Ca}_2\text{Al(OH)}_{6}.\text{½CO}_3\text{.OH.5½H}_2\text{O}}$ (also called hydrocalumite). The decomposition of the LDH to either TCA or calcite defines the causticisation equilibrium.

$$\text{Ca}_3\text{Al}_2(\text{OH})_{12} + 3\text{Na}_2\text{CO}_3 \Leftrightarrow 3\text{CaCO}_3 + 2\text{NaAl(OH)}_4 + 4\text{NaOH} \quad (1)$$

The experimentally measured $[\text{OH}]/[\text{CO}_3]$ equilibrium for calcium has been given by Zambo and Orbán-Keleman (1976) (reproduced by Whittington and Cardile (1996)). Neither Zambo nor Whittington report the alumina concentration for this data.

![Figure 1 Phase diagram for the system CaO-Na$_2$O-Al$_2$O$_3$-H$_2$O after Whittington (1996)](image)

1.2 Fluorine, vanadium and phosphorus

TCA, once formed, can incorporate other anions by the substitution for some of its hydroxyl groups. The most well known of these is silicate, and these substituted TCA’s are considered in some detail below. There are other anions in the liquor that can substitute, in some cases directly into TCA, and others into the already silica substituted versions. The incorporation of fluoride into TCA has been examined by Wilson et al. (2002). They point out that incorporation of F into TCA is one of the major (and at the time unrecognised) sinks for fluorine in liquor. The mechanism they postulate is that the strong association of the fluoride ion with aluminate ion to form Al(OH)$_3$F carries through to the incorporation of aluminate into the TCA. The paper essentially dismisses the concept that
fluoride exists as CaF$_2$ co-precipitated with TCA.

The knowledge gained from Wilson’s investigation resulted in the application for a patent which is claimed to apply to the removal of, not just fluoride, but a variety of anionic impurities (Rosenberg et al. 2000). The incorporation of vanadium, titanium and phosphorus is also postulated through the formation of substituted aluminates ions (Al(OH)$_3$X) and into TCA. However there is little evidence to suggest that the mechanism (which is plausible for fluoride) extends to the other ions. In particular, the form of precipitated calcium phosphate as carbonateapatite is well documented, and there appears to be no evidence to suggest that phosphorus substitutes into TCA. Vanadium is significantly scavenged from solution using lime, and despite a recent paper (Zhao et al. 2012), the current author believes there is no experimental evidence for the precipitation of a simple calcium vanadate from Bayer solutions, and so the formation of vanadium substituted TCA is possible or even likely. The incorporation of V into TCA is assumed to be the primary vanadium scavenging mechanism for the rest of this document.

Bonnel et al. cited by Kirwan et al. (2009), gives a revised stoichiometry for a “Bayer” carbonate-apatite which has a higher carbonate content than the literature version and includes some soda – Ca$_{10-x}$Na$_{2x/3}$[(PO$_4$)$_6$$(CO$_3$)$_x$$(H$_2$O)$_{12-x/3}$] where x=2.5 or 2.7 depending on the lime source (calcite or slaked lime respectively).

1.3 Silica

The most common product of reactive silica transformation is Bayer sodalite. The formation of this product starts in predesilication and is completed (along with liquor desilication) in digestion and the flash train.

However lime can act to reduce the soda loss associated with sodalite formation by including silica into the structure of TCA. In mineral terms there is a continuous solid solution series of compounds from TCA (mineral name hydrogrossular - Ca$_3$Al$_2$(OH)$_{12}$) to grossular (Ca$_3$Al$_2$[(SiO)$_4$]). The silica substituted TCA is generally known by the less specific term “hydrogarnet - HG” - Ca$_3$Al$_2$[(SiO)$_4$]$_n$[(OH)$_{12-4n}$]. It is accepted that Bayer hydrogarnets have relatively low silica substitution in predesilication (n~0.1) rising to n~0.6 during digestion to 250°C (Whittington, 1996b) and perhaps as high as 1.0 at 280°C (Mal'its, 1992) – see Figure 2.

One of the factors influencing “n” is almost certainly the molar OH/SiO$_2$ ratio in the liquor. Assuming ~constant silica in solution, this decreases from ~330 in spent liquor to ~150 in green liquor, i.e. a higher “n” could be expected under digestion liquor compositions.

Whittington’s experimental findings are consistent with the phase diagram (Figure 3) constructed by Whittington and Cardile (1996) using data from earlier Russian papers. This shows that incorporation of silica into TCA effectively extends the stability region (TCA/HG) at the expense of calcite.

It is interesting to speculate on the ultimate products formed by lime addition at different temperatures. If added at predesilication under conditions where TCA forms and subsequently digested to ~250°C in the presence of silica it is likely that the TCA will transform into HG. However if lime is added directly to digestion, its dissolution releases calcium ions that may be consumed in a variety of reactions and in that case the formation of HG is less likely. Featherston et al. (1976) was amongst the first published authors to suggest that lime addition directly to digestion promoted additional activity and a variety of reaction products.

It is more than likely that kinetics plays an important, even dominant consideration in the different reaction pathways at different temperatures. Rosenberg (2000) indicated a

![Figure 2. Silica substitution into TCA.](image)

![Figure 3. Influence of silica incorporation into TCA (HG) on the stability field (calcite/HG).](image)

References are given in Whittington and Cardile (1996).
significant influence that temperature has on the fate of the reaction of lime to TCA or calcite over a wider range of liquor compositions than could be expected from Figure 1.

Under high temperature digestion conditions an alternative zeolite type desilication product forms (cancrinite). It is not known whether cancrinite forms directly from reactive silica in the bauxite, but it is certain that some sodalite (including that formed at lower temperatures) re-dissolves and re-precipitates as cancrinite (Barnes et al. 1999, Crocker et al. 2008). Bayer cancrinite containing no calcium can form under high temperature conditions, but its transformation from sodalite is very slow (Xu et al. 2009). The presence of calcium (and carbonate) in liquor dramatically increase cancrinite formation rate (Xu et al. 2009; Smith et al. 2001; Croker et al. 2008).

1.4 Titanium

Early work by the Hungarians and the Russians on the behaviour of titanium minerals are reported by Zambo and Orbán-Keleman (1976). In particular authors cited in that paper found that anatase reacts with Bayer liquor more quickly than rutile, and that the reaction with liquor often produced amorphous sodium titanate (tentatively identified as having a stoichiometry Na$_2$O.3TiO$_2$.2.5H$_2$O). These precipitates can coat the surface of dissolving boehmite inhibiting its extraction (Ma’lts et al. 1985). Stability diagrams for various sodium titanates in caustic and aluminate solutions have also been given by Wefers (1967, 1971). The most authoritative description of the inhibition of boehmite dissolution by a hard-to-characterise sodium titanate is given by Croker et al. (2006). Xu et al. (2010) found that a similar mechanism was responsible for inhibiting the transformation of sodalite to cancrinite under high temperature Bayer digestion conditions (in the absence of lime). Gu et al. (1989) identified reaction products of lime with titanium in liquor. In particular he gave a comprehensive description of calcium hydroxy-titanate (CTH) and its relationship to both perovskite (CaTiO$_3$) and another compound he described as a titanium substituted TCA. They found that all three compounds formed during the digestion of a diasporic bauxite, nominated CTH as an intermediate product that ultimately reverts to perovskite, and that high levels of lime are likely to increase the proportion of Ca reporting as titanium substituted TCA. Ma’lts (1992) confirmed the identity of CTH. Seif et al. (1991) described the structure of the mineral kassite, which may be a good model CTH. Gu (1989) did not give a stoichiometry for CTH but the following (based on kassite) is a reasonable equation for its formation from the dissolution of anatase

$$\text{Ca}(OH)_2 + 2\text{TiO}_2 \rightarrow \text{CaTi}_2\text{O}_4(OH)_2$$

(2)

Unpublished work by CSIRO suggests that, under some conditions, CTH may be structurally closer to caffetite – CaFe$_2$Ti$_2$O$_{12}$.4H$_2$O than to kassite, where, in the absence of significant dissolved iron, aluminium substitutes into the trivalent ion position – i.e. CaAl$_2$Ti$_2$O$_{12}$.4H$_2$O. Notice that the Ca/Ti ratio will be the same for either caffetite or kassite but different for perovskite.

Suss et al. (2002) considered the formation of CTH, perovskite and the titanium substituted TCA from Indian bauxites. He also showed the relationship of titanium in liquor to temperature and lime charge, showing minimum level at ~210°C (the corresponding solid phase is not identified). Gu et al. (1989) does not indicate the nature of the titanium substituted TCA, but Suss (2002), who identified it in scale, gives its stoichiometry as Ca$_3$(Al,Fe)$_2$[Si,TiO$_3$]$_n$(OH)$_{12-4n}$, suggesting that it has some iron for alumina substitution as well as titanium for silica substitution. Whether titanium only substitutes into silica substituted, or silica and iron substituted TCA is not known. However Rosenberg et al. (2002) claim that titanium in liquor can be scavenged by lime addition under very mild conditions (~97°C). These are conditions unlikely to see significant silica and iron incorporation into TCA.

Although there is evidence to suggest that perovskite can form from CTH (Gu et al. 1989), Croker et al. (2008) showed that lime (calcite) can concurrently react with silica from sodalite to form cancrinite, and with titanium from TiO$_2$ to form perovskite (no intermediate CTH was observed). In a subsequent paper Croker et al. (2009) reported the formation of CTH (kassite) from hydrogarnet rather than calcite. Simultaneous formation of cancrinite and perovskite was also reported by Smith et al. (2011) again from calcite.

1.5 Iron

Many of the reactions of lime with iron in solution are as a consequence of, or depend on, the form and concentration of the iron in liquor itself. Iron in liquor is in turn related to the solubility and the reactions of the iron minerals in the bauxite. It is generally accepted that the true iron solubility for
hematite in Bayer liquor is only a few ppm and possibly only slightly higher for goethite (Roach and Jamieson, 2002) but that the apparent solubility increases markedly with temperature (Basu et al. 1986). Ostap (1984) discusses the nature of this iron and suggests that much of it is in fact ultra-fine iron oxide-hydroxide “fractions” which are not separable from liquor by normal filtration techniques. He called this “colloidal” iron.

The dissolution / transformation of goethite is a likely source of colloidal iron, and bauxites with high goethite contents (or bauxites with high goethite to hematite ratios like those from Jamaica) are most at risk from iron in liquor problems (residue settling, product quality issues). Colloidal iron could also arise from the reaction of pyrite (FeS₂) with Bayer liquor liberating potentially harmful sulphide (Grachev and Kuznetsov, 1974). A third source for some bauxites could be iron incorporated in the gibbsite which is liberated during digestion (Roach and Jamieson, 2002).

The importance of lime reactions with iron therefore stem not only from the true reactions and products of calcium, iron and other liquor components, but also, and quite crucially, what lime can do in controlling residual colloidal iron in liquor, especially liquor to precipitation.

In the absence of lime, goethite to hematite transformation is thought to proceed by the dissolution of goethite, the formation of an intermediate sodium ferrite which then decomposes to hematite (Basu, 1983, King, 1971).

\[
2\text{FeO(OH)} + 2\text{NaOH} \rightarrow \text{Na}_2\text{Fe}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{NaOH} + \text{H}_2\text{O} \quad (3)
\]

This transformation is significantly speeded by the catalytic action of lime by the formation of intermediate iron hydrogarnets Ma’lts et al. (1985) which then decompose to hematite (equations modified from Whittington, 1996a).

\[
3\text{Ca(OH)}_2 + 2\text{FeO(OH)} \rightarrow 3[\text{CaO}.\text{Fe}_2\text{O}_3].2\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow 3\text{Ca(OH)}_2 + \text{Fe}_2\text{O}_3 \quad (4)
\]

Given the composition of Bayer digestion liquor, the formation of a iron hydrogarnet of this stoichiometry would almost certainly not occur in solution and so it may be inferred that the mechanism described by Ma’lts is intended to be one mediated at the goethite surface.

Lime reactivity with iron in liquor, in a similar way to that with silicates, appears to improve when lime is added directly to digestion – O’Donnell and Martin (1976) and also Orban et al. (1977) patented direct injection of lime to digestion to speed goethite to hematite transformation. This is almost certainly due to the increased reactivity of lime added to digestion, and in particular the supply of significant calcium to liquor from non-equilibrium reactants. Murray et al. (2009) used synchrotron techniques to follow the goethite to hematite transformation and applied a kinetic model to characterise its mechanism. They showed that the rate determining step in the transformation is the availability of hematite seed surface sites. They also note that the presence of anatase (and presumably the formation of sodium titanate) was enough to completely halt the transformation under their experimental conditions. This indicates a preference for reaction of calcium ions with titanium over the corresponding reactions with iron.

There is a substantial body of work concerning the substitution of iron (for aluminium) into hydrogarnets. These are the so-called iron hydrogarnets (IHG), of stoichiometry \((\text{Ca}_3[\text{Al},\text{Fe}]_{12-n} \text{SiO}_{12-4n})(\text{OH})_{12-4n}\). The first reference we can find of these compounds relevant to the Bayer process is by Ni et al. (1968), but it is the work of Solymar and co-workers at Hungalu (later, Aluterv) that championed their use as “catalytic additives” (Zoldi et al. 1987; Solymar and Zoldi, 1993). The initial use of these compounds was as a form of lime to aid goethite to hematite transformations (Boros et al. 1980) but they were later touted as additives to promote a low soda form of desilication product (Solymar et al. 1983). Most authors agree that the formation of these IHG’s is more favourable in liquors / solutions of low alumina content (low A/C) where the molar ratio of Al/Fe is as low as possible. However Zoldi et al. (1987) have used Mossbauer spectroscopy to show that iron hydrogarnets do form under high temperature conditions (temperatures in excess of 270°C) even though the molar Al/Fe ratio in the digestion liquor could be as high as ~3,800.

Despite the weight of material in the literature on the formation of these compounds at high temperatures within the Bayer process, the difficulty in proving conclusively that iron hydrogarnets form under high temperature digestion conditions (particularly at high A/C) may leave the reader open to the possibility that they do not form under these conditions. The following descriptions are from the
literature and the reader is advised to draw their own conclusions.

The efficiency of the iron hydrogarnet as a desilication product is crucially dependent on the value of “n”. In the preparation of hydrogarnets and iron hydrogarnets Zoldi et al. (1987) noted that “n” substantially increased from ~0.8 for HG to ~2.0 for IHG (although Zoldi implies that this “n” value may only be achieved for full substitution of iron for aluminium). The conditions needed to maximise iron substitution into IHG’s are not those necessarily present under high temperature Bayer digestion (e.g. low A/C (~0.1)), and in regular high temperature digestion conditions perhaps only 25% iron for aluminium substitution may be achieved. Zoldi does not say what the corresponding “n” would be, but it is clear that the greater the iron substitution, the greater “n” is expected to be.

From much of the literature on iron hydrogarnets it is clear that the extent of iron substitution into IHG’s follows the true or apparent iron solubility in liquor, and thus it increases with temperature. It may be that the extent of formation and degree of substitution is controlled by the supply of this crucial ingredient. This is the concept behind a process described by Medvedev (2002, 2003) in which sodium ferrite is added as an “active” source of iron which allows the formation of IHG at digestion temperatures below those normally required ~250°C instead of ~280°C. The process (to reduce fixed soda losses to desilication) also requires low A/C digestion liquor which is consistent with the formation conditions described by Zoldi et al. (1987). This process appears to have little exposure in the Western literature since its description has only appeared in the Russian language. A recent paper has validated these concepts (Xu and Smith, 2012). The ideal stoichiometry for the formation of these iron hydrogarnets from (hydroxy)-sodalite is given below:

\[
\text{Na}_3(\text{AlSiO}_4)_2 \cdot 2\text{NaOH} + 9\text{Ca(OH)}_2 + 3\text{Na}_3\text{Fe}_2\text{O}_4 + 12\text{H}_2\text{O} \rightarrow 3\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_2(\text{OH})_4 + 6\text{NaAl(OH)}_2 + 8\text{NaOH}
\]

(5)

The problem of colloidal iron in liquor (and consequent issues of product quality) are usually associated with low iron ores (i.e. those without enough hematite surface area to scavenge the dispersed iron, Roach and Jamieson, 2002). Yamada et al. (1974) were one of the first authors to recognise this and suggested the addition of calcined red mud to the digestion slurry (calcining mud transformed all iron compounds to hematite).

Another method for scavenging (colloidal) iron in liquor has been patented by Deville and Lamerant (1996) assigned to Pechiney. The novel step appears to be the introduction of lime or a calcium salt into the flash train of a high temperature bauxite digestion. The temperature of addition is preferably in the range 170-220°C but definitely more than 140°C. The mechanism of how the lime compounds scavenge the iron is not disclosed.

Other methods for scavenging colloidal iron from solution are given by Fulford (1989). Amongst these he suggests that the addition of lime to digestion could result in the formation of iron hydrogarnets. He also suggests that competing lime reactions with titanium species remove sodium titanates that might otherwise coat iron particles, leaving them more likely to act as scavengers.

The use of sodium ferrite as “active iron” (Medvedev 2003) is an example of the use of non equilibrium reactants to supply high levels of the corresponding ions at a time when other reactions are occurring, to promote or drive the reaction path in a desired direction. Other examples given in previous sections relate to the supply of calcium ions from non-equilibrium reactants (lime added at digestion) during the transformation of sodalite to cancrinite or the transformation of goethite to hematite. It is therefore clear that the mechanisms and reaction pathways are not always determined by thermodynamic considerations, and that kinetic factors (including when, where and how reactants are brought together) are crucial in determining the final products.

2. COMPETING REACTIONS UNDER HIGH TEMPERATURE DIGESTION

In this section we consider the reactions of lime, added as slaked lime (Ca(OH)\(_2\)), TCA (Ca\(_3\)Al\(_2\)(OH)\(_12\)) or calcite (CaCO\(_3\)) to high temperature digestion (200°C and above) under conditions whereby many of the reactions described above can occur simultaneously and are therefore in “competition” for the calcium ions liberated.

From Figure 1 it may be assumed that there are digestion conditions in which either TCA or calcite is the stable causticisation product. However it must be remembered that these phases have been identified as possible “stable” digestion phases in the absence of other liquor components (particularly Si, V, F, Fe, Ti and carbonate).
For all three types of lime added to digestion, possible reactions are:

- No change
- Dissolution and re-precipitation to a stable (or meta-stable) product
- Slow incorporation of species into the solid (solid state transformation), e.g. TCA to HG.

It is expected that if transformation occurs, one compound will be the most stable under the digestion conditions (thermodynamic product) but this will not stop the formation of other products which may include those that are kinetically favoured on the timescale of the digestion or those that form through exhaustion or limited supply of the favoured anion.

2.1 When TCA is the starting material

Examining the range of liquor compositions in Figure 1 it is clear that in most modern, high caustic, high temperature digestions (temperature >200°C, TC ≥250, A/C~0.7) TCA is the favoured causticisation product. Under these conditions TC/TA would have to be less than ~0.735 in order to favour calcite and so TCA added to digestion will not react to calcite. There will however be competition for Ca from P (carbonate-apatite), Si (HG, cancrinite) V or F (substituted TCA) and Ti (CTH). There will also be secondary reactions to other products from these initial compounds, e.g. CTH to perovskite and iron, titanium substitution into HG’s.

The following [modified] text is an extract from Whittington and Cardile (1996): Sizyakov and Smirnov (1969) report it is possible to prepare HG with n~0.5 at ~100°C from CaO and a sodium aluminate solution containing dissolved silica, but that reaction of TCA [in the same solution] results in the formation of HG with n<0.2. This implies that reaction of TCA to HG is either slower or occurs by a different mechanism to that via CaO. One possible explanation is that CaO (or Ca(OH)₂) reacts directly with liquor components to produce HG, whereas TCA reacts slowly to HG, perhaps by a solid state incorporation mechanism. O’Donnell and Martin (1976) note that the presence of phosphorus in bauxite inhibits the transformation of goethite to hematite and speculate that it could be from the preferential reaction of lime (Ca) with P to form apatite. This also points to the reaction with P having high precedence.

Zambo and Orban-Keleman (1976) claim that CTH forms from sodium titanate whereas perovskite forms directly from the dissolution of anatase. This observation is supported by the thermodynamic calculations of Li et al. (2010) – apparently unaware of Zambo’s work. These pathways are consistent with the slow reaction of TCA with titanium (which may have already formed sodium titanate) whereas in a high rate mechanism, calcium from calcite or slaked lime reacts directly with titanium ions to form perovskite.

\[
3\text{TiO}_2 + 2\text{NaOH} + 1.5\text{H}_2\text{O} \rightarrow \text{Na}_3\text{O}.3\text{TiO}_2.2.5\text{H}_2\text{O}
\]

\[
2[\text{Na}_2\text{O}.3\text{TiO}_2.2.5\text{H}_2\text{O}] + \text{Ca}_3\text{Al}_2(\text{OH})_12 \rightarrow 3[\text{CaTi}_2\text{O}_4(\text{OH})_2] + 2\text{NaOH} + 2\text{NaAl}(\text{OH})_4 + 3\text{H}_2\text{O}
\]

\[
\text{CaTi}_2\text{O}_4(\text{OH})_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaTiO}_3 + 2\text{H}_2\text{O}
\]

\[
\text{Ca}(\text{OH})_2 + \text{TiO}_2 \rightarrow \text{CaTiO}_3 + \text{H}_2\text{O}
\]

Iron and titanium substituted TCAs (HG) form under more extreme temperatures (270-280°C and above (Zoldi et al., 1987). Although iron hydrogarnets (IHGs) form best under liquor conditions of low alumina, high iron in liquor and high free caustic, IHGs will form as iron solubility increases with temperature, or as demonstrated by Medvedev (2003) and Xu and Smith (2012), with a source of active (soluble) iron e.g. ferrite. Suss et al. (2002) identified titanium substituted TCAs (in scales) as compounds containing iron as well. It isn’t clear whether titanium substitutes into IHGs or whether the titanium and iron substitute together. It appears from Suss (and also earlier work by Zoldi et al. (1987) and Solymar and Zoldi (1993)) that these high temperature substitution products have higher degrees of silica and iron substitution when all three substitutions occur together. This makes them more efficient desilication products.

2.2 When calcite / slaked lime is the starting material

The general consensus from many studies is that the reactions of lime added at digestion are faster with calcite or slaked lime as the lime source than for TCA. This is probably related to the fact that for most high temperature digestions, TCA is the stable causticisation product, and therefore calcite (or slaked lime) will be inherently unstable and dissolve, liberating calcium for a variety of reactions. Calcite is not often used in digestion because of the potential adverse effect on liquor causticity (C/S). However it does have some specific uses (and advantages) compared to slaked lime (e.g. calcite supplies carbonate as well as calcium both of which speed the formation of cancrinite). To avoid the problems associated with reducing causticity, most examples of the
addition of non-TCA lime directly to digestion involve the use of quicklime (CaO) or slaked lime (Ca(OH)$_2$).

The preceding arguments could be taken to imply that there is no difference in the fate of lime added to digestion either as calcite or slaked lime. However it should be remembered that the dissolution of calcite is expected to be much slower than that of slaked lime and this may well have consequences for the distribution of reaction products. For instance, the transformation of sodalite to cancrinite which, in the absence of lime is a very slow process even at digestion temperatures above 200°C, is greatly enhanced when calcite dissolves and supplies calcium for cancrinite formation at the appropriate rate (Xu et al. 2009). The opposite is also probably true, i.e. compared to calcite, the addition of slaked lime to digestion results in a distribution of products favouring those formed more quickly.

Xu et al. (2009) examined the fate of lime added before digestion (either as CaO or as calcite) on the phase distribution of reaction products at 250°C. Results indicate that TCA forms during heat-up times even when calcite is the favoured thermodynamic phase at this temperature. Zambo and Orban-Kelemen (1976) found that the reactions of quicklime with silica and titanium containing aluminate liquor were identical to those of calcite. However in this digestion system, the lime was added before a slow period of heating to 210°C (1.5h) with a 1 hour residence time at that temperature. In this case, it is almost certain that TCA will have formed from either lime source during the heat-up stage, and therefore no differences would be expected.

If calcite or slaked lime is added directly to digestion in which TCA is the stable causticisation product, then one pathway is the reaction through hydrocalumite to TCA. Thereafter, the range of pathways described in the previous section comes into play. However the reaction to TCA (even if it is the stable causticisation product) will be in competition with other reactions. A good example is the patent by Featherston et al. (1976) in which quicklime, water slaked lime or calcite (but not TCA) is added directly to promote a variety of beneficial outcomes. The brief description of the digestion and liquor conditions in the patent suggest that under these conditions, TCA would be the favoured causticisation product. Without describing the mechanism whereby these outcomes are achieved, the claimed benefits of adding lime directly to digestion are claimed to include increased boehmite extraction (reaction with titanates), reduced caustic loss (cancrinite formation?) and reduced flocculant consumption (better settling due to increased goethite to hematite conversion?). All of these outcomes are consistent with the liberation of calcium ions from unstable starting materials and their consumption in reactions other than those to form TCA.

Featherston goes further in saying that the presence of TCA (he calls it calcium aluminate) in residue is an indication of lime added in excess (i.e. lime that is above that required to complete reactions with Ti, Si, P etc). This does not indicate that TCA is not initially formed from the initial reaction of slaked lime or calcite with liquor, only that there should not be TCA present at the end of digestion when there is still Ti, Si, P to be reacted. But if TCA is an initial reaction product of slaked lime or calcite with spent liquor, it would be hard to understand why this TCA would not react in a manner similar to TCA added directly to digestion.

The study by Kirwan et al. (2009) indicated that even at 90°C, the reaction of slaked lime with rapidly dissolving phosphorus minerals was fast, such that unreacted lime remained encapsulated within the formed hydroxyapatite (or carbonate-apatite). It is thus probable that reaction of lime with phosphorus to apatite / carbonate-apatite will be at least faster (and likely more favourable) than the reaction to TCA.

Xu et al. (2010) digested quicklime (CaO), soda lime and anatase at 250°C in a liquor of composition close to the phase border between TCA and calcite (Figure 1). Figure 8 in Xu’s paper showed that TCA (formed during the heat-up period) gradually transformed to calcite, indicating that the system was probably in the calcite stability region. A fraction of the anatase transformed to perovskite quickly, which remained stable with increasing time at temperature. Further dissolution of anatase resulted in CTH rather than more perovskite formation, and cancrinite formed at a rate similar to that of CTH formation.

Xu et al. (2010) also showed that when calcite is added to the same liquor with sodalite and anatase, both CAN and perovskite formed. Interestingly perovskite formation reduced titanium in liquor more than when CTH formed, supporting the speculation by Gu et al. (1989) that CTH is probably an intermediate product. Unpublished work from
the CSIRO laboratory showed that injection of calcite at different temperatures showed that cancrinite and perovskite appeared to start forming at the same temperature but that the preference was for perovskite formation before cancrinite formation. Suss (2002) noted that the titanate formed (CTH or perovskite) is a function of the bauxite processed. He also notes that titanate scales that form from the dissolution of rutile are different to those from anatase. It is not clear whether these two observations are related. Some of the suggestions for phase formation are summarised in Figure 4.

Figure 4  Map of possible products of the reaction of lime with approximate temperature at which they start to form. HC=hydrocalumite, SOD=sodalite. Dotted line indicates direct pathway is uncertain.

3. ACKNOWLEDGEMENT

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4. REFERENCES


