

SOME ASPECTS OF CALCIUM CHEMISTRY IN THE BAYER PROCESS

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Lime is used in vast quantities in alumina refineries throughout the world and is often regarded as something of a universal cure for many of the ills of the Bayer process. However, like many popular remedies, information as to how it actually works is quite sparse, and often contradictory. Fortunately, this situation is now changing. A few recent studies have begun to reveal some of the complex solution and solid-phase chemistry that exists between calcium and the many species present in Bayer refinery liquor streams. Worsley Alumina's research in this field has led to several innovations, including the Improved Causticisation Process, which allows very high liquor causticity to be achieved at nearly 100% lime efficiency. In this paper, aspects of Worsley's studies as they relate to this and other new processes are discussed, and some explanations are offered for the sometimes confusing behaviour of lime in the Bayer process.

Introduction

Lime is one of the major raw materials of the Bayer process, primarily for its application in recausticising the refinery's liquor streams. However, it is also one of the most useful processing aids available to alumina refinery operators, indeed in some refineries it would be impossible to operate without it. In some cases this utility arises directly from reactions of the lime itself; in others it is more likely to be through the actions of some soluble form of the calcium cation. For example, the direct reaction of slaked lime with Bayer process liquors under the appropriate conditions results in the formation of highly stable calcium aluminate crystals, which are useful as a filter aid in the polishing (or security) filtration operation in most alumina refineries. On the other hand, it is likely that the presence of dissolved calcium species in the liquor stream assist the action of polyacrylate flocculants in the mud clarification circuits, presumably by binding to both the flocculant molecule and to the goethite or haematite particles (1).

Add to this the use of lime for oxalate removal and disposal (2), as an aid in the digestion of boehmitic or diasporic bauxites (3),

for the recovery of soda from desilication products (4), for phosphate control in some bauxites (5) and as a means of preventing autoprecipitation in settlers and mud washers. Given this, it is not difficult to see why it is common practice in many refineries, faced with a disturbance in the operation of the digestion or clarification areas, to add lime almost automatically as the first approach to overcoming the problem.

Given the very important role that lime plays in the refinery, it is surprising how few in-depth studies have been published in the open literature of the alumina industry. This is despite the significant cost of inefficient lime use: low liquor causticity, high lime consumption and high alumina losses. Prompted by these considerations, some time ago Worsley Alumina's Process Chemistry group embarked on a programme to investigate, in detail, the chemistry of calcium in the Bayer process. This work culminated in a series of patent applications we have filed over the past several years (6-8), in which we outlined some of the major reactions of lime in Bayer liquors, and described several means of controlling these reactions to give dramatic improvements in the performance of many of the applications mentioned earlier. For example, in our causticisation patent (6) we describe a process that allows even concentrated liquors to be causticised, to very high causticity (C/S) ratios, and with almost 100% lime efficiency.

In a recent paper that describes studies similar to our own, Roach (9) discusses some of the consequences of this chemistry as it relates to causticisation, dispelling some of "myths" surrounding this process and emphasising the importance of an unstable intermediate calcium aluminate species in the causticisation mechanism. Many of the conclusions we have drawn from our own work agree with those of Roach, although there are some important differences, particularly in the detail of the reaction pathway. Our own work identifies a number of reaction intermediates, and useful outcomes can be derived by understanding the pathways by which these species form, and blocking some of them. In this paper we describe some of this work, and describe a reaction "map" that can be used to explain the behaviour of lime in almost all of its common applications.

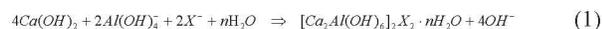
Terminology

In this paper, the word ‘lime’ will be used to describe slaked lime, Ca(OH)₂, rather than quicklime. In aqueous solution, quicklime will give similar results, but must first react with water to form calcium hydroxide. Other terminology includes ‘A’ to describe the concentration of sodium aluminate in solution, expressed as equivalent g/L of Al₂O₃. ‘C’ is used to describe the sum of the free sodium hydroxide and sodium aluminate, expressed as the equivalent concentration of sodium carbonate in g/L. ‘S’ refers to the sum of ‘C’ plus the actual sodium carbonate concentration, again expressed as g/L of sodium carbonate. From this one can see that a liquor with a C/S (or causticity) ratio of 1.0 will contain no sodium carbonate.

For the purposes of this discussion, we will use the common terminology of the cement industry to describe the various calcium aluminate species we have encountered. For example, C₃AH₆ is equivalent to the alumina industry term TCA6, where C represents CaO, A represents Al₂O₃ and H denotes H₂O. We have elected to adopt this terminology because it is more descriptive and comprehensive than the alumina industry terminology. Also, there is a long history of research in the chemistry of these species in the cement industry, and consequently most of the relevant information is available in the cement industry literature. For example, the discussion by Turriziani (10) provides an excellent overview of the calcium aluminate species, while the study by Fischer and Kuzel (11) is of particular relevance to this discussion.

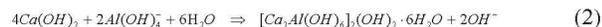
Reactions of Lime in Aluminate Solutions

Strictly speaking, the only solid phase calcium species that is stable in contact with an aluminate solution is C₃AH₆ (i.e. TCA). However, it is the metastable species and their pseudo-equilibria that are of most interest in the Bayer process. Calcium hydroxide is very unstable in sodium aluminate solutions, and reacts rapidly to form one or more members of a family of metastable layered double hydroxide (LDH) compounds of the general form C₄AH_x. The crystal structures of these quaternary compounds are still in some doubt, although it is generally agreed (11) that the layers have repeating units with composition [Ca₂Al(OH)₆]⁺. The cavities between the layers are occupied by water and charge-balancing anions (usually monovalent, divalent, or a mixture of both). The general equation for the formation of the C₄A species in aluminate solutions is as follows:



where X⁻ represents the charge balancing anion that is intercalated between the layers.

The identity of the charge-balancing anion(s) is dependent upon the solution composition, however in pure sodium aluminate / sodium hydroxide solutions, we believe that the following reaction occurs, producing a C₄AH_x species, in this case C₄AH₁₃:



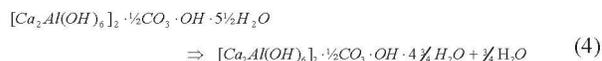
In Bayer liquors, other anions are always present, and some will be intercalated into the structure. The identity and amount of intercalated anions is dependent upon the concentration in

solution, but by far the most preferred anion is carbonate. The amount of carbonate incorporated into the structure is often variable, but two distinct forms are known, the hemicarboxylate [Ca₂Al(OH)₆]₂·½CO₃·OH·nH₂O and the monocarbonate [Ca₂Al(OH)₆]₂·CO₃·nH₂O. In Bayer liquors, both of these species can form, as well as dehydrated polymorphs that are produced upon ageing. Our own findings disagree with those of Roach on this point, in that he describes only the monocarbonate, C₄A·CO₂·H_x. In our work, we find that it is the hemicarboxylate that is the first product to form:



This is a critical reaction in the chemistry of lime in the Bayer process, and there are several points of interest to note. First, during the reaction, aluminate ions are removed from solution. Second, the reaction is causticising: that is, for each formula unit one half of a carbonate anion is removed from solution and replaced with an hydroxyl ion. Third, the formation of the LDH is favoured by high aluminate and carbonate concentrations and inhibited by high free hydroxyl concentrations. We will return to this aspect later.

The hemicarboxylate (which is denoted as C₄A·½CO₂·H₁₂ and has an interlayer distance of 8.2Å) is also the least stable of the calcium aluminate carbonate species, and will usually convert to other forms at a rate that rises with temperature. Under causticisation conditions, this conversion can be quite rapid, and this may explain why the hemicarboxylate is not always observed. The species is quite stable below 20°C, but above this it can convert into another species with a smaller interlayer distance. Since this conversion does not seem to involve the gain or loss of any of the structural species or intercalated anions, we believe that this conversion is a dehydration reaction. Fischer and Kuzel describe such a reaction in dry solids under controlled humidity, and the d-spacing of the compound they describe closely matches that in our work. We believe that the following equation describes the dehydration reaction and the compound that forms:



This species (denoted as C₄A·½CO₂·H_{11.25}) has a d-spacing of approximately 7.6 Å, very close to that of the monocarbonate [Ca₂Al(OH)₆]₂·CO₃·nH₂O, and for some time we misidentified the dehydrated species as the monocarbonate. In our studies we have rarely found the formation of the monocarbonate in plant Bayer liquors, although it appears to be the major species formed in synthetic Bayer liquors. The reasons for this disparity are not altogether clear, although we suspect that the presence of certain organic anions present in the plant liquors available to us may stabilise the hemicarboxylate. Studies in this area are continuing.

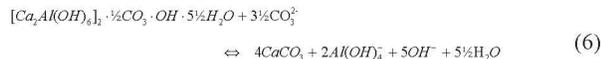
The equation for the formation of the monocarbonate species is



For obvious reasons, this is a more efficient causticising reaction than that of the hemicarboxylate. However, in our studies, we find

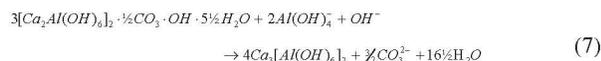
that it is the hemicarbonates reaction that accurately describes the stoichiometry of the reaction in plant Bayer liquors.

Above about 80°C the quaternary calcium aluminates become progressively more unstable, reacting with carbonate ions to form calcium carbonate. This is the main causticisation reaction, and its rate is under chemical control, rising rapidly with temperature.



Note that the equation is written in the form of an equilibrium. If a calcium carbonate slurry in causticised liquor is cooled sufficiently, the hemicarbonates will re-form, as we will demonstrate later. This has implications for the so-called reversion reaction.

Studies of the quaternary calcium aluminates are usually complicated by the formation of C₃AH₆. The mechanism of its formation has not been conclusively resolved, however our studies lead us to believe that the formation of C₃AH₆ also occurs via the hemicarbonates species:



The rate of formation of C₃AH₆ is diffusion controlled, increasing with agitation, and also with increasing concentrations of aluminate and hydroxide. It is inhibited by high carbonate concentrations.

Calcium Solubility

Any description of calcium reactions in Bayer solutions is incomplete without knowledge of the soluble species. The issue of calcium solubility in Bayer liquors has provoked considerable discussion over the years, and of course is of importance because of its effect on calcium incorporation into alumina. The and Sivakumar (12) investigated the effect of solution composition on the solubility of calcium in Bayer liquors, and found that certain organic species such as humic acid and sodium gluconate appreciably increased the solubility of calcium. They suggested that calcium formed soluble complexes with these organics. In addition they found that low C/S ratios (or high carbonate concentrations) also increased the concentration of calcium in solution, while phosphate decreased solubility at low carbonate concentrations, but had little effect at low C/S ratios. They tentatively ascribed this behaviour to the higher solubility of calcium carbonate relative to tricalcium aluminate. However, if one assumes that calcium is entering solution as the expected hexaquo calcium cation, then by Le Chatelier's principle, the calcium concentration should *decrease* with rising carbonate concentration. Furthermore, the change in behaviour of the phosphate ion cannot be explained in this way. Clearly some other factor is at work.

However, all of the above observations can be quite simply explained, if it is considered that the least stable species will also be the most soluble. In other words, we believe that the major soluble species in Bayer liquors is a calcium aluminate monomer, in equilibrium with the solid hemicarbonates C₄A species.

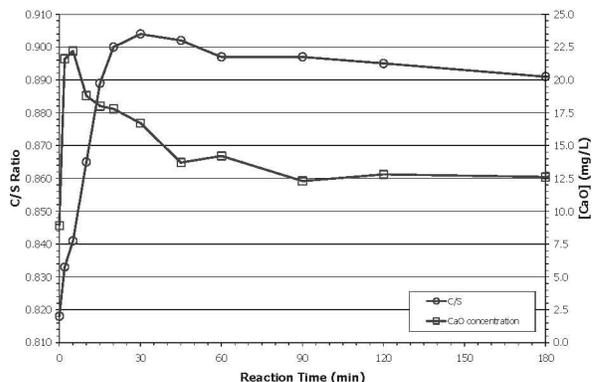


Figure 1: Plot of calcium concentration and C/S ratio with time, during a typical causticisation reaction.

Figure 1 depicts the change in calcium concentration and C/S in a Bayer liquor during batch causticisation at 100°C. It can be seen that upon adding lime to the solution, the calcium concentration rises sharply and then decreases gradually over some time.

The reason for these changes in calcium concentration can be deduced from Figure 2, which shows the corresponding XRD spectra for samples taken throughout the reaction. Upon addition of calcium hydroxide, there is an immediate reaction with the aluminate ion to produce the hemicarbonates (2θ=10.8°) and its dehydrated polymorph (2θ=11.2°). The amount of the hemicarbonates decreases rapidly, and is virtually absent at 30 minutes, this corresponding to the maximum C/S. The dehydrated polymorph is slightly more stable, and persists for longer, slowly converting to C₃AH₆. Eventually, the species remaining are mainly calcium carbonate and tricalcium aluminate, with a trace of residual calcium hydroxide. The change in calcium concentration mirrors the increase and decrease in the amount of the two C₄A hemicarbonates species.

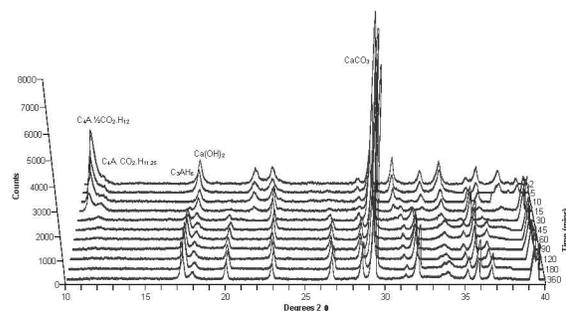


Figure 2: Chart of XRD spectra as a function of time.

Organics influence the solubility of calcium by chelation of the monomeric calcium aluminate. In our studies, we have used the gluconate ion, amongst others, as it is commonly used as a model organic carbon compound in Bayer studies. Calcium gluconate is also known to be appreciably soluble in water. A large number of

experiments were conducted, but for brevity, the results of only a few tests that illustrate the concepts are presented.

When either calcium hydroxide or calcium chloride was added to a sodium hydroxide solution (C=130 g/L), the steady state calcium concentration was found to be approximately 4.5 mg/L (expressed as CaO). Addition of sodium gluconate had little effect on the solubility until quite high concentrations were achieved: even at 1 g/L sodium gluconate, the calcium concentration was only 18 mg/L. Subsequent tests showed that at low doses the gluconate anion is removed from solution by adsorption at the calcium hydroxide surface.

By contrast, similar mixtures containing sodium aluminate (C=130 g/L, A/C = 0.230) showed a linear increase in calcium concentration with rising sodium gluconate, with a 1:1 molar ratio of calcium to gluconate. With no gluconate present, the aluminate ion had no effect on the calcium solubility, this being almost identical to the pure sodium hydroxide solution (4.5 mg/L). In other words, complexation with the gluconate ion has little effect on calcium solubility, but has a direct effect on the solubility of a calcium aluminate species. It is interesting to note that borate, the solution chemistry of which is very similar to that of aluminate, is used to greatly increase the solubility of calcium gluconate for pharmaceutical purposes (13) by formation of a calcium borogluconate complex.

The nature of the soluble species and the relationship to gluconate concentration can be deduced from data such as that shown in Figure 3. In the test from which this data is drawn, the sodium aluminate concentration in a 130 g/L 'C' caustic solution was progressively increased. This solution was carbonate-free, but contained 1g/L calcium chloride and 1 g/L sodium gluconate. Initially, the calcium concentration was 19 mg/L, slightly elevated due to complexation with gluconate (the remainder of the calcium chloride had of course precipitated as calcium hydroxide). As aluminate is added, the CaO concentration rises linearly with a slope of 3.0, reaching a plateau at about 0.0042 mol/L due to depletion of the gluconate ion. This data, together with the gluconate response data described earlier, suggests that the complex species is of the form $[Ca_3Al(OH)_3L_3]^{3+}$, where L represents the complexing ligand (in this case the gluconate anion, but could equally be some other organic anion or the hydroxyl ion). The similarity between this monomer and the repeating unit in the C_4A species is obvious.

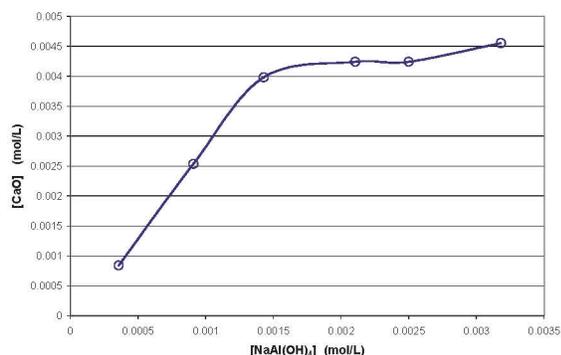


Figure 3: Variation of calcium concentration with sodium aluminate concentration, in the presence of sodium gluconate.

From the above discussion, it is reasonable to expect that the presence of one of the C_4A solid phase species in contact with a Bayer liquor would inevitably result in high calcium concentrations, unless the liquor is free of complexing agents. However, it is important to note that growth of the C_4A solid will occur via incorporation of the monomer, removing some of the organic anion from solution. If the initial concentration of the organic species is already low, it is possible that the concentration may decrease sufficiently that it no longer has an appreciable effect on calcium solubility.

Tests similar to those already described in which sodium carbonate was added suggest that the carbonate ion itself plays little part in the solubilisation of calcium in Bayer liquors. While this appears to contradict the observed behaviour in the plant, a plausible explanation of the role of carbonate in this environment can be deduced from equation 7. In highly caustic liquors, the quaternary calcium aluminate species are very unstable and convert rapidly to the highly insoluble C_3AH_6 . In liquors with lower caustic concentrations and higher carbonate concentrations, the C_4A species are quasi-stable, and can persist in contact with Bayer liquors for extended periods. This results in higher calcium concentrations in solution, aided by chelating anions such as certain organics.

The Calcium Reaction map

The preceding discussion leads us to propose a schematic "map" of the reactions of calcium in Bayer liquors, which can be used to describe the behaviour of calcium in virtually all of its common applications. Such a map is shown in Figure 4.

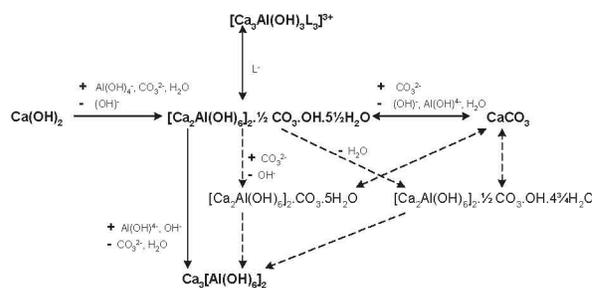


Figure 4: "Map" of the reactions of calcium in Bayer liquors.

Since the map is primarily intended to show the relationships between the various species, the reactions depicted are not chemically balanced. The relevant equations are described earlier in this paper.

Causticisation

The calcium reaction map emphasises the critical role of the C_4A species in the causticisation reaction, and the competing reactions that it undergoes to produce either $CaCO_3$ or C_3AH_6 . Thermodynamic equilibrium between these two latter species occurs via the C_4A intermediate, but in a practical Bayer causticisation process, true equilibrium between $CaCO_3$ and C_3AH_6 is not only unlikely to be achieved (because residence

times in typical causticiser tanks are too short), but is also undesirable, as it limits the maximum C/S that can be achieved. Rather than targeting true thermodynamic equilibrium in the causticiser, a better approach is to tailor the reaction conditions such that the reaction described by equation 6 occurs as rapidly as possible, whilst inhibiting reaction 7. If this is done well, reaction 7 can be almost completely stifled, and a pseudo-equilibrium between the hemihydroxide C_4A species and $CaCO_3$ is established, as defined by equation 6.

Because reaction 7 is under diffusion control, certain surfactants can have a profound effect on the rate of this reaction. The use of these C_3AH_6 "inhibitors" is part of the strategy within Worsley Alumina's improved causticisation process (6), but can also be applied to an existing causticisation process with very good effect. The Worsley refinery has been using a surfactant mixture (developed in-house) in this way since March 2000. Since there are no undesirable side-products, causticisation efficiency can approach 100%, and the achievable C/S is much higher than can be achieved through conventional means. Furthermore, performance is far less dependent upon the 'S' concentration of the liquor: indeed liquors may be causticised to C/S ratios that are even higher than can be achieved in pure sodium hydroxide/sodium carbonate mixtures.

The factors limiting conventional causticisation performance, and the effect of inhibiting the C_3AH_6 reaction are illustrated in Figure 5.

In this experiment, two samples of a typical refinery mud washer overflow liquor were causticised with excess lime (target C/S of 0.950) in 2 litre agitated Parr reactors at 103°C. To one of these, the inhibitor we developed for the Worsley refinery was added. The 'S' concentration of the liquor was approximately 140 g/L.

The causticisation curve for the conventional process is very typical, and displays aspects of all of the reactions we described earlier. The C/S initially rises rapidly due to formation of the hemihydroxide, indicated by the inflection at a C/S of about 0.835. The C/S at which the inflection occurs can be calculated from the amount of lime added and equation 4. This reaction is accompanied by a fall in the aluminate content of the liquor.

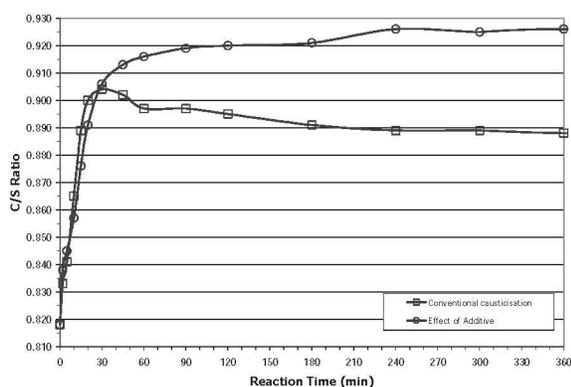


Figure 5: Causticisation curves for a 140 g/L 'S' solution, with and without TCA inhibiting additives.

As the reaction proceeds, the hemihydroxide reacts with carbonate ions in solution, forming calcium carbonate and releasing aluminate ions. As the aluminate and hydroxide content of the liquor rises, and the carbonate concentration falls, the reaction of the intermediate to form C_3AH_6 becomes increasingly favourable, while the rate of the calcium carbonate reaction falls. Maximum C/S (and maximum lime efficiency) will be achieved at the point where the rate of these two reactions just balances. In this experiment, this occurs at a C/S of approximately 0.90. From this point on, the C_3AH_6 formation reaction (equation 7) outstrips the calcium carbonate reaction (equation 6) and the C/S begins to fall: given sufficient time, the C/S would stabilise at the thermodynamic equilibrium. Obviously, there is no point in permitting the reaction to proceed beyond the maximum C/S, so operation of the causticiser should be tailored such that the residence time coincides with the maximum C/S point of the reaction (in this test, this occurs at a residence time of approximately 30 minutes).

In the test in which inhibitor was added, the behaviour is similar up to the point where the conventional process achieves maximum C/S. However, since the C_3AH_6 reaction has been stifled, there is no corresponding decrease in C/S, and the causticisation reaction continues until the hemihydroxide/calcium carbonate pseudo-equilibrium is approached at a C/S of approximately 0.926. Since the reaction rate is similar to that of conventional causticisation, additional residence time will be required, unless the temperature can be increased. The final C/S ratio achieved is 0.025 higher than the maximum C/S of the conventional causticisation process, and more than 0.050 higher than the thermodynamic equilibrium C/S (0.875). Moreover, lime efficiency was 82%, compared with 45% for the conventional process. Lime efficiencies of well in excess of 95% have been achieved routinely in full-scale refinery operation by controlling lime addition such that just enough is available to achieve the pseudo-equilibrium C/S.

A second aspect of the Worsley causticisation process involves making use of the causticising nature of the C_4A hemihydroxide formation reaction. Since the equilibrium for reaction 1 lies overwhelmingly to the right, it will proceed to completion virtually independent of the liquor 'S' concentration or the initial C/S. This creates the possibility of preparing the C_4A hemihydroxide in one liquor stream (thereby partially causticising it), separating the hemihydroxide and then using it to causticise a second liquor stream. Alternatively, the process could be used in a countercurrent configuration, such that the hemihydroxide formation reaction boosts the C/S of liquors that have already been causticised. In this way, it is possible to achieve very high causticity ratios (C/S up to 1.0 can be achieved), while still achieving maximum lime efficiency.

While the use of C_3AH_6 inhibitors is not essential in this approach, it does make the process much simpler and more stable. This is not only because the C_4A hemihydroxide is prevented from undergoing an undesirable conversion to C_3AH_6 during preparation in high causticity liquors, but because the higher C/S afforded in the main causticisation reaction makes balancing the amount of lime required for the two reactions straightforward. In addition, the inhibitor assists in producing a much more crystalline C_4A hemihydroxide which has superior settling and filtration characteristics. This process has been piloted, but has currently not been implemented on a plant scale. A comparison of the performance of the full Worsley causticisation process, the use

of the inhibitor only and conventional causticisation are shown in Table 1.

Table 1: Comparison of causticisation processes.

Process	'S' (g/L)	C/S	Lime efficiency (%)
Full Worsley process	154	0.932	91%
Conventional causticiser + Worsley inhibitor	152	0.906	95%
Conventional causticiser	152	0.882	55%

Note that in these tests we have deliberately used a very high 'S' liquor, to emphasise the flexibility of the Worsley process. Operation at more typical 'S' concentrations (110 – 130 g/L) results in even higher C/S and lime efficiency being achieved.

The Reversion Reaction

If calcium carbonate is added to a typical causticiser overflow liquor, and the temperature maintained at 100°C, there is no observable change in either the solution or the solid for quite extended periods of time. After several days, if the solids are examined by XRD it is usually possible to detect a trace of poorly crystalline C₄A hemicarbonate, as evidenced by a shallow hump in the XRD spectrum at about 11° 2-theta. After an even longer period, some of this will slowly convert to C₃AH₆, especially if the system is vigorously agitated. Experiments such as these confirm that there is no direct reversion of calcium carbonate to tricalcium aluminate, but it can proceed via the C₄A intermediate, as suggested by the calcium reaction map.

However, if the temperature is reduced, both the rate of formation and quantity of hemicarbonate increase, as the equilibrium with CaCO₃ shifts in favour of the hemicarbonate. This creates the potential for reversion to occur, if the causticiser sludge is not separated from the liquor prior to cooling.

In one experiment, a sample of mud washer overflow liquor was causticised with lime in the conventional way at 103°C. The causticised liquor was then quickly cooled to 80°C without removal of the solids, and allowed to equilibrate for up to 30 minutes. Results of this test are shown in table 2 below.

Table 2: Effect of cooling on causticised slurry composition

Sample	A (g/L)	C (g/L)	'S' (g/L)	C/S
Starting liquor	76.7	115	140.3	0.819
After causticisation at 100°C	74.5	123	135.6	0.907
2 min after cooling to 80°C	73.5	122.2	135.8	0.899
30 min after cooling to 80°C.	73.4	122.1	135.9	0.898

As can be seen, establishment of equilibrium at the new temperature is achieved very rapidly, and is accompanied by a loss of alumina and an increase in carbonate. Examination of the XRD spectra of the solids shows a decrease in the CaCO₃ peak intensity, and a hump in the XRD base line at about 10 to 11° 2-theta, indicating the formation of poorly crystalline C₄A compounds. After further time, some of this poorly crystalline material began to convert into tricalcium aluminate.

Our perception of the so-called reversion reaction, then, is that it is the re-formation of the C₄A hemicarbonate that is primarily responsible for the effects that are ascribed to reversion. Analysis of the "reverted" solids by XRF will not distinguish between this species and C₃AH₆, leading to the widespread perception that reversion involves the conversion of calcium carbonate to tricalcium aluminate.

In practice, though, reversion of causticiser sludges in typical mud washing circuits is unlikely to be significant. While the temperature profile across the mud washers may be conducive to calcium carbonate conversion to C₄A hemicarbonate, the comparatively low A/C and C/S of mud washer liquors is not. In addition, conversion of the hemicarbonate to C₃AH₆ will be slow for similar reasons, and because mass transfer characteristics in washer beds are invariably poor.

Calcium Oxalate formation

In some alumina refineries, lime is used to recover soda from sodium oxalate solutions, such as seed wash liquors. The reaction is conducted at relatively low temperature (rarely any hotter than 60°C) and ostensibly involves formation of the highly insoluble calcium oxalate monohydrate. It is found that the 'S' concentration of the oxalate-rich liquor must be kept low or both oxalate removal and lime efficiency are poor.

In our experience, insoluble calcium salts such as calcium oxalate do not form to any appreciable extent in the presence of the aluminate ion, despite very favourable thermodynamics. Essentially, this arises because any calcium ions entering solution are rapidly sequestered as the calcium aluminate monomer discussed earlier. Direct precipitation of insoluble salts such as calcium oxalate does not occur until the aluminate ion has been almost completely removed from solution. Given these considerations, the reasons for the poor performance of the calcium oxalate process are apparent.

Upon addition of lime to a seed wash liquor, it is immediately converted to C₄A hemicarbonate. Since these liquors generally contain some sodium carbonate, this LDH will initially contain almost no intercalated oxalate, because carbonate is the preferred anion for intercalation. This process will continue until either the aluminate or carbonate in solution is almost completely removed, or all of the lime is consumed.

If any aluminate remains at this point, some oxalate may be intercalated into the C₄A layered double hydroxide that forms next. If not, then calcium carbonate and calcium oxalate will start to form. Clearly, if the seed wash liquor is high in both aluminate and carbonate, a considerable amount of lime will be consumed (at 12.5% efficiency) before any oxalate is removed.

This behaviour can be put to advantage and the efficiency of the process greatly improved if it is broken into two parts (7). In the first part, lime is added to form the hemicarbonate and strip aluminate ions from solution. These solids may then be separated and used efficiently in the refinery's causticisation circuit, with recovery of the alumina. The clarified liquor that remains will be essentially free of aluminate, so that addition of further lime results in the direct precipitation of calcium oxalate.

Conclusions

Our research has revealed a number of aspects of the complicated behaviour of calcium in Bayer liquors, some of which has been presented here. In our work, we find that the chemistry of calcium in aluminate solutions centres around the formation of a range of quaternary calcium aluminate compounds, of which the hemicarbonatate is predominant. This species, being the least thermodynamically stable, is also responsible for most of the soluble calcium, in the form of a complex calcium aluminate monomer. Ligands such as certain organics enhance the stability, and hence the solubility, of this monomer.

These data have been used to develop a map of calcium reactions in aluminate solutions, and this has been useful in interpreting the behaviour of lime in many of its common applications and in suggesting ways of avoiding some of the undesirable side-effects of lime use.

Moreover, a fundamental understanding of the reaction mechanisms has permitted us to “reconstruct” some of the traditional lime-based processes in new ways that allow higher performance, higher lime efficiency, or both.

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