

**THE EQUILIBRIUM APPROACH TO CAUSTICISATION FOR OPTIMISING LIQUOR CAUSTICISITY.**

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Abstract

The causticisation reaction using lime to convert sodium carbonate to sodium hydroxide, with the formation of calcium carbonate, has a thermodynamic equilibrium that depends upon liquor composition. The causticisation reaction has been studied from both a theoretical and practical standpoint. The reaction involves an intermediate that is formed almost instantaneously with the approximate composition  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$  (commonly called monocarbonate or hydrocalumite). The kinetics of decomposition of the monocarbonate species to either calcium carbonate or tricalcium aluminate were studied. The equilibrium data have been used in carbonate balance models to help optimise causticisation in Alcoa World Alumina Refineries. Opportunities to increase plant causticity were identified, especially for Western Australian Refineries, where the majority of the carbonate added to the liquor circuit is in the bauxite and the causticity of the liquor is relatively low. This basic understanding indicated the potential use of the monocarbonate to achieve higher than equilibrium ratios and ways to achieve higher lime efficiencies.

Introduction

The conversion of sodium carbonate back to caustic soda using lime (causticisation) is an integral part of most Bayer refineries. For many refineries the efficiency of this process determines the causticity of the main liquor circuit and hence productivity. After energy, bauxite and caustic, lime is normally the next major raw material cost. Hence efficient causticisation is critical for running an efficient Bayer refinery. The causticisation process is not unique to the Bayer process being used by several industries, most notably within the Kraft process used by the pulp and paper industry. Causticisation is also an old process having been the major process for producing caustic soda from soda ash for many years.

Historically Bayer refineries produced caustic by causticisation of soda ash through digestion using what is termed internal causticisation. When liquid caustic became both plentiful and economically attractive, that became the source of caustic soda. Causticisation was then used to counteract the carbonate build up in the Bayer liquor from the bauxite and the carbon dioxide adsorbed at the residue lakes, rather than replenish the caustic loss to desilication product. Because less conversion was required this could then be achieved in the washer circuit, a process known as external causticisation. The specific benefit was that both higher causticity of the liquor and improved lime efficiency (ie the relative proportion of lime converted to the desired calcium carbonate rather than calcium aluminate) could be achieved.

For maximum productivity of a Bayer process, the plant causticity must be maximised. To achieve this the causticity of the causticisers must be maximised and other liquor streams amenable to causticisation must be targeted. Such an approach is commonplace within the industry. To assess which streams can potentially be causticised requires knowledge of the thermodynamics of the system. Also, in order to predict the final effect on the plant liquor stream, such information must be used within a steady state carbonate balance model as the recyclic nature of the Bayer liquor streams means that gains in some areas of the process can be negated in other areas.

Several years ago Alcoa World Alumina (Alcoa) initiated studies of the causticisation process to maximise the causticity of the refinery liquor streams. A fundamental approach was undertaken which looked at the thermodynamics of the system to determine what was possible and assessing how that could be achieved. A key ingredient of the ultimate success was a steady state carbonate model containing no empirical (or “fudge”) factors and that could be used to predict the causticity of the liquor circuit.

This paper will focus on the fundamental approach used in the causticisation studies, how that was incorporated into a carbonate balance model and examples of how such an approach can lead to significant causticity gains. Also, from understanding the kinetics, the potential to achieve higher than equilibrium causticity and high lime efficiency were recognised.

The Causticisation Reaction

The causticisation reaction is:



(In this paper the form of the lime is assumed to be calcium hydroxide; dry lime reacts similarly although there are some subtle differences (1).)

The thermodynamics and kinetics of this reaction have been studied extensively. There is a chemical equilibrium between the two solid species as defined by Equation 1. Lindberg and Ulmgren (2,3), in their two excellent articles on the thermodynamics and kinetics of the causticisation of Kraft pulping liquor, describe this equilibrium and give relevant experimental data.

From Equation 1 the equilibrium constant (which is essentially where the solubility of the two species are equivalent) is given by:

$$K_i = \{\text{OH}^-\}^2 / \{\text{CO}_3^{2-}\} \quad (2)$$

where {} represents the activity of the various species in solution.

By assuming that the activity is proportional to the concentration of the components in the liquor, this expression can be rearranged in more familiar terms (to the Bayer industry) such that the causticity of the liquor is given by:

$$TC/TA = 1/(1+TC/K_i) \quad (3)$$

where TC is the caustic concentration of the liquor and TA the total alkalinity (both in terms of g/l sodium carbonate, Alcoa terminology). Other terminology would have C for TC and S for TA.

It is more convenient to describe Equation 3 in terms of TA as it is constant in the causticising reaction. Multiplying top and bottom by (1-TC/ K<sub>i</sub>), and for values of TC/TA > 0.8, the expression can be approximated to:

$$TC/TA = 1 - zTA \quad (4)$$

$$\text{and } z = 1/K_i$$

Hence at increasing TA the equilibrium TC/TA is lower, a well-known outcome.

The alumina in Bayer liquors affects the reaction in two ways. First, at a constant TC the alumina ties up free hydroxide and

$$TC = [OH^-] + [Al(OH)_4^-] \quad (5)$$

all expressed as sodium carbonate. Secondly, the solubility of calcium hydroxide is much higher than calcium aluminate hexahydrate (3CaOAl<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O), commonly referred to as TCA6. Consequently TCA6 is the other stable phase in the system. (Calcium hydroxide is not stable in Bayer liquor; the reason for the detection of calcium hydroxide in causticiser products will be discussed later).

The equilibrium causticisation reaction in Bayer liquor becomes:  
 $3Ca(OH)_2 \cdot 2Al(OH)_3 + 3Na_2CO_3 = 3CaCO_3 + 2NaAl(OH)_4 + 4NaOH$  (6)

(The TCA6 formula is written in the hydroxide form as that better reflects its structure and the reaction.)

This reaction has been successfully used at Alcoa to causticise sodium carbonate solutions (a product from burning sodium oxalate) with the press mud (which is predominantly TCA6) from the Kelly security filters.

The equilibrium constant for this reaction is:

$$K_t = \frac{[OH^-]^4 \cdot [Al(OH)_4^-]^2}{[CO_3^{2-}]^3} \quad (7)$$

Or,

$$K_t^{0.5} = \frac{[OH^-]^2 [CO_3^{2-}]}{[Al(OH)_4^-] [CO_3^{2-}]^{0.5}} \quad (8)$$

At a fixed alumina to TA ratio (A/TA) - the second term of this equation - the equation is equivalent to that for the sodium carbonate scenario such that:

$$TC/TA = 1 - yTA \quad (9)$$

where y is now dependent on the A/TA ratio and is lower at higher alumina content - ie the equilibrium TC/TA is higher at higher alumina /TA ratios (another well known outcome).

Equilibrium data for an A/TA ratio of 0.65 are plotted in this way in Figure 1 and demonstrate the relationship; the equilibrium line separates the two phase fields for calcium carbonate and TCA6, the two species involved in Bayer liquor causticisation. For comparison the equilibrium line for the alumina free causticisation reaction is also given. The similarity in values is of interest especially considering that the free hydroxide concentration of the Bayer liquors is so much lower.

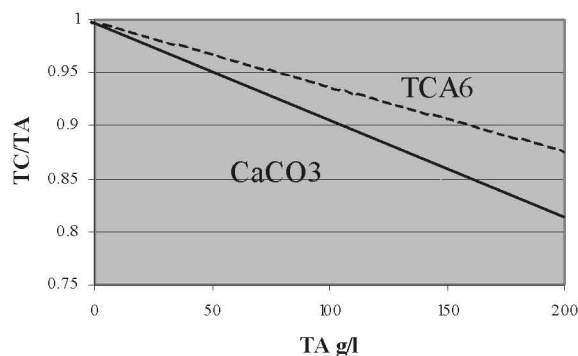


Figure 1. A schematic of the equilibrium phase fields for the causticisation of Bayer liquor (solid line). The broken line is that for an alumina free liquor (2).

The equilibrium relationship is relatively insensitive to temperature both from theoretical considerations (the solubilities have a low temperature coefficient) and from experimental evidence (3,4).

The success of this approach will depend on whether the appropriate speciation of calcium and other ions in solution have been adopted. Unfortunately there is little data on such speciation in Bayer liquors. Also the TCA6 is not a pure compound but contains silica. There is a complete solid solution between TCA6 and calcium alumino-silicate with the silica replacing the water. The level of silica substitution depends on the liquor composition but is approximated by 3CaOAl<sub>2</sub>O<sub>3</sub>·0.25SiO<sub>2</sub>·5.5H<sub>2</sub>O. The silica substitution can be determined from the shift in the XRD pattern. For this discussion the product will be assumed to be pure TCA6 as the silica substitution generally has little effect on the thermodynamics or kinetics at low silica substitutions (unlike that at high levels (5)). Where the silica can have a large effect is that it consumes lime forming the calcium alumino-silicate (TCAS) such that there is insufficient lime for causticisation.

#### Causticisation studies.

The data presented in this paper is a combination of that of Young (1) and some from the studies initiated in 1992. Young's data was of such good quality that it readily lent itself to re-interpretation and it consequently reduced the amount of subsequent work required on the kinetics and thermodynamics. The procedures and analyses in this subsequent work were similar to those used by Young and, for brevity, will not be described. The laboratory studies from 1992 onwards were primarily undertaken by Glenn Reid, Sylvia Scally, John Cornell and Winnie Kwok and are reported in several internal Alcoa reports. The reports describe equilibrium stability fields for the various phases, calcia solubilities and other relevant information.

The experimental work determined the equilibrium phases at different liquor compositions, and the calcia solubility of those phases at a wide range of liquor composition and temperatures. The simplest speciations of the components were assumed. The



work was complicated by the kinetic issues involved and that gibbsite was prone to precipitate in many of the liquors of interest. That work, completed very successfully by W. Kwok, gave a very good picture of the stability fields and the many interactions involved in calcium solubility. The data confirmed the type of phase fields given in Figure 1, but gave more accurate predictive tools, with valid and precise relationships being obtained, that could be used in assessing plant performance and modeling.

Carbonate and species such as phosphate and organics affect calcium solubility (6). The current work highlighted further the importance of such factors (as well as a few others). It is even possible that some form of carbonate type complex exists within the system. Although such level of detail is not required in considering the use of the equilibrium approach, it is needed when assessing application of the results to the refinery. In particular the study gave information related to calcia in liquor values and their relevant interaction with solids. The information was critical in assisting application of the findings without causing calcia in product issues.

Reaction pathway

When slaked lime is added to Bayer liquor the thermodynamics readily indicate that either calcium carbonate or calcium aluminate should be formed. This is not the case. On adding lime to a typical causticising liquor there is an immediate reaction in which a poorly crystalline intercalate phase is formed which has the approximate formula  $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$ . This phase is often referred to as monocarbonate or hydrocalumite

The formation of this compound is readily apparent in Young's data; the data for the change in TC/TA and lime efficiency with time at different TA's are plotted in Figures 2 and 3. The first sample, taken as rapidly as possible (<1 minute), showed a rapid increase in TC/TA at all TA's and with 20 to 25% lime efficiency. The aluminate content of the corresponding products are shown in Figure 4 with all containing 50 to 60% alumina in the original reaction phase. A 25%:75% ratio of lime to carbonate and aluminate would have been expected if there had been one hundred percent conversion of the calcium hydroxide. The initial TC/TA achieved at one minute was similar for all liquors, irrespective of TA.

After the initial TC/TA increase because of the monocarbonate formation, the TC/TA slowly approaches the equilibrium value either increasing or decreasing. The initial 25% lime efficiency from monocarbonate formation correspondingly decreases or increases.

This initial phase was misidentified as a hydrated calcium aluminate (a point that has been questioned in many subsequent paper on causticisation (4). XRD or thermal analysis is required to indicate the presence of the monocarbonate phase (Samples should not be dried above 60°C to avoid decomposition.) Chemical analysis by itself is not adequate to determine if monocarbonate is present as that would also be consistent with both calcium carbonate and TCA6. Reliance on solely chemical analysis has led to a myriad of false information and folklore about the "back reaction" or "reversion" of calcium carbonate

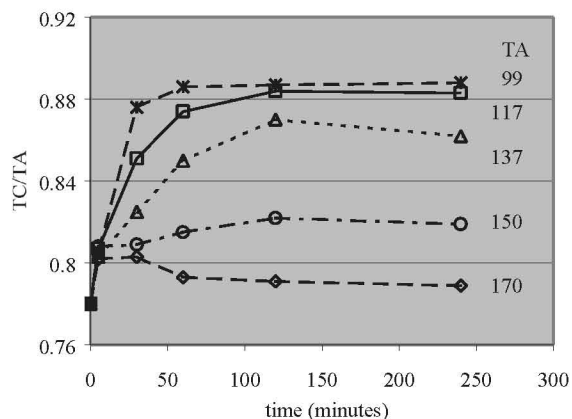


Figure 2. Effect of TA on TC/TA (2).

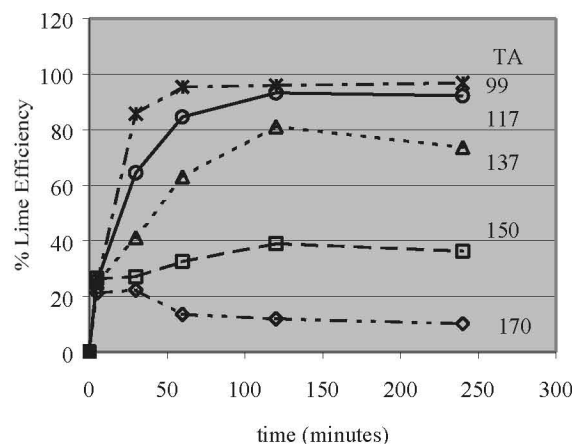


Figure 3. Effect of TA on Lime Efficiency (2)

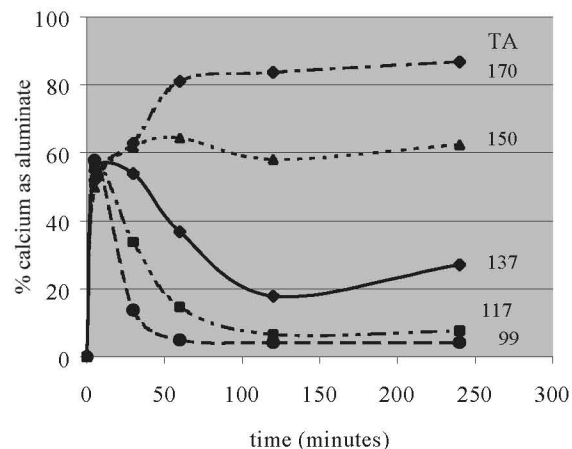
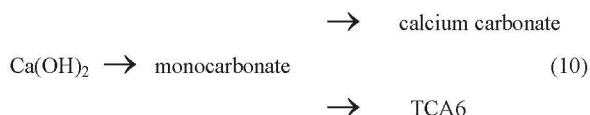


Figure 4. Effect of TA on aluminate content of causticiser residue (2)

to calcium aluminate under what would be thermodynamically appropriate conditions. In the author's knowledge such reversion rarely occurs (and then only slowly) and normally any further reaction in washer systems has been because of the presence of monocarbonate which is still transforming. The transformation of TCA6 to calcium carbonate (or the reverse) is slow unless there is a high driving force.

The overall reaction sequence can be summarised as follows:



The monocarbonate converts either to calcium carbonate or TCA6 depending on the TA and TC/TA of the liquor. Formation of the monocarbonate results in the removal of carbonate irrespective of the thermodynamics – the potential use of this effect is discussed later.

The monocarbonate transforms because its solubility is high compared to calcium carbonate or TCA6. The solubility of monocarbonate can be in excess of 50ppm calcia compared to 10 to 15ppm for TCA6. In the preparation of filter aid for the security filters it is important that the conditions and reaction times are chosen such that the monocarbonate has fully converted to the stable TCA6 otherwise high calcia in liquor values result when filter aid is added to green liquor. This is normally achieved by 'aging' the filter aid.

Stoichiometric versus equilibrium lime charge

The lime charge has often been expressed in terms of the stoichiometric ratio (1). This is confusing as it is based on a TC/TA ratio of one that is unachievable. A lime charge based on that required for equilibrium, as proposed by Lindberg and Ulmgren (3), is the preferred approach as it is then clear why either low or high lime efficiencies are obtained. For example the effect of lime charge on the causticicity achieved and lime efficiency is shown in Table 1; the lime charge is expressed as both stoichiometric and equilibrium charges. The equilibrium charge readily indicates whether causticisation of the liquor is possible and gives an indication of the lime efficiency that might be expected.

Table 1. The effect of lime charge on lime efficiency  
Initial liquor concentration, 135g/l TA, TC/TA 0.780  
Data of Young (1)

% stoichiometric charge	24	53	72	96
% equilibrium charge	57	129	173	230
Final TC/TA	0.825	0.865	0.860	0.862
Equilibrium TC/TA	0.865	0.865	0.865	0.865
Lime efficiency, %	98	74	56	47

Kinetics

Based on the above understanding, the reaction of interest is the decomposition of the monocarbonate phase to form the equilibrium end members, calcium aluminate or calcite. The kinetics will determine the lime efficiency. The instantaneous reaction of calcium hydroxide with the liquor suggests that if calcium hydroxide is detected in a causticiser product, it is a result of an impervious layer of one of the reaction products coating the calcium hydroxide, i.e. calcium hydroxide cannot exist in contact with the liquor. The rapid formation of such impervious layers was well demonstrated in the slaking work of Xu (7) using rotating disc studies. Calcium hydroxide cannot exist in contact with Bayer liquor and its presence in causticiser products (or filter aid) indicates the potential for improved efficiency through changing reaction conditions, the form of the lime or the addition/mixing system.

The effect of temperature on the conversion of monocarbonate is demonstrated in Figure 5. Higher temperatures speed up the conversion. At temperatures lower than 60°C, the monocarbonate conversion virtually stops (8).

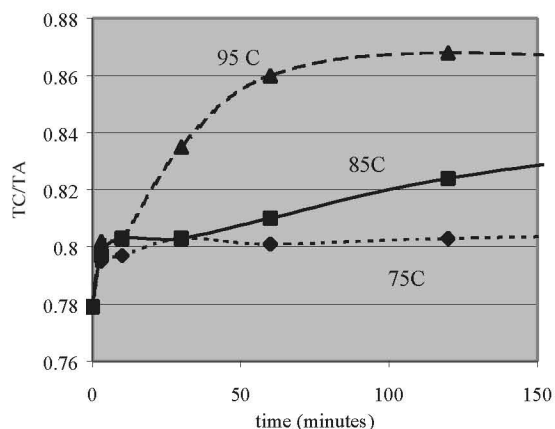


Figure 5. Effect of temperature on the monocarbonate conversion.

The effect of TA for the conversion at 95°C is shown in Figure 6. Sufficient monocarbonate was added to achieve the equilibrium TC/TA. (The data in Figures 3 and 4 similarly represent the conversion of the monocarbonate, however in that work the data are compromised by some unreacted lime being present in the early stage.)

The conversion becomes progressively slower the closer one approaches the equilibrium, a well known kinetic effect. Higher lime charges increase the rate of approach to equilibrium. To reach equilibrium in a reasonable time (to limit capital expenditure) requires lime additions in excess of the equilibrium charge and thus results in less than optimum lime efficiency.

From a practical standpoint, analysis of the causticiser product for the various phases will indicate whether the reaction conditions have been sufficient for the reaction to have reached completion (no monocarbonate present). If monocarbonate is



present then either longer holding time, higher temperature, lower lime charge or finer particle size of lime is required.

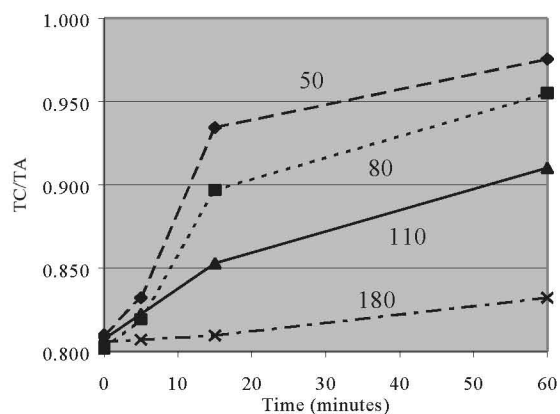


Figure 6. The effect of TA on the conversion of monocarbonate at 95°C. (The numbers represent the TA in g/l)

Use of the equilibrium approach.

The thermodynamics give a relationship between the total alkalinity, TA, and the causticity TC/TA. The amount of carbonate removed by the causticisers is a function of the flow, the TA and the inlet TC/TA. The carbonate removal is shown in Figure 7 for different initial TC/TA concentrations and TA assuming that equilibrium is achieved. There is a maximum carbonate removal for each inlet TC/TA. For a refinery, which will operate at steady state, the input and exit carbonates must match. As carbonate is removed from the liquor the inlet TC/TA will increase thus reducing the carbonate removal potential. The TA must then be adjusted to again ensure sufficient carbonate removal. To determine the optimum TA, and thus location, for causticisation requires a steady state carbonate balance model.

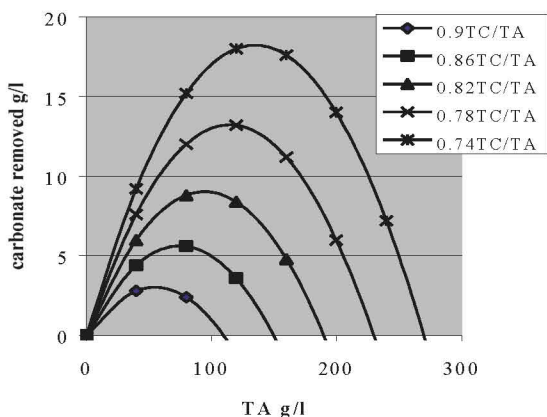


Figure 7. Carbonate removal for liquors of varying TA and start TC/TA assuming equilibrium TC/TA is reached.

Such a carbonate model using a simplified flowsheet was originally put together by Z. Olszewski at Alcoa and has now been further extended and includes other liquor impurities (9). The carbonate model has been successfully used at all Alcoa refineries.

The model requires input of both the carbonate from the bauxite and at the lake. The former requires some relatively subtle analyses to obtain the correct input value (complicated by carbonate removal via desilication product and phosphate phases, and further complicated for Jamaican bauxites with the presence of calcite in the bauxite). The carbonate input at the lake can be determined from the lake area and the rate of carbon dioxide adsorption, a function of free caustic. Factors such as roughening of the lake surface can affect the carbon dioxide pick up. (For more information see the many papers on CO<sub>2</sub> adsorption in oceans used in global warming simulations.)

With such a model the various liquor streams can be assessed to determine if their causticisation would significantly increase the main liquor circuit causticity. In the model there are up to five causticisers available with causticisation of most liquor streams being possible. The maximum causticity in the main plant liquor stream can be predicted assuming that the causticisers can achieve the equilibrium causticity.

An example of the potential gain is that the causticity of one particular refinery was consistently around 0.81TC/TA. The model indicated that if the causticisers were achieving the equilibrium TC/TA of 0.90TC/TA, rather than the 0.84TC/TA obtained, the plant causticity could be increased to 0.855. Work was undertaken to improve the causticiser performance using the knowledge gained on the kinetics of the reaction and from relevant analyses of the causticiser products. Following some changes the refinery attained the equilibrium TC/TA levels at the causticisers and the predicted new level of causticity in the main liquor circuit. Further, some of the carbonate inputs were reduced via changes to some of the return liquor streams from the lake such that the TC/TA has been increased to 0.885.

Another example was where a refinery had dropped in causticity from 0.81TC/TA to 0.76TC/TA because of a major return of caustic (as sodium carbonate) from the lake. The causticisers were not operating at their ultimate capacity, however any improvement there would only increase the causticity to 0.78TC/TA. In this plant the main carbonate input was with the bauxite. The pre-desilication slurry storage tanks in that refinery operate at close to 100°C and about 1000g/l density. The majority of the carbonate in the bauxite is dissolved in those tanks and the TA of the liquor is reduced because of dilution from moisture in the bauxite and formation of DSP that removes caustic. Consequently the liquor in such tanks has a relatively low TA and a low causticity. Indeed, the causticity is below the equilibrium value for that TA. As a result it is possible to causticise the liquor simply by adding sufficient lime as the temperature and residence time are ideal for causticisation. This was undertaken and the effect on the plant causticity is shown in Figure 8, increasing from 0.76 up to 0.83. In this instance a new stream was causticised. (The challenge to increasing the causticity became how to quickly get sufficient lime into the slurry storage tanks, a problem that plant engineers, technical and operational personnel were up to through some excellent and innovative thinking.)

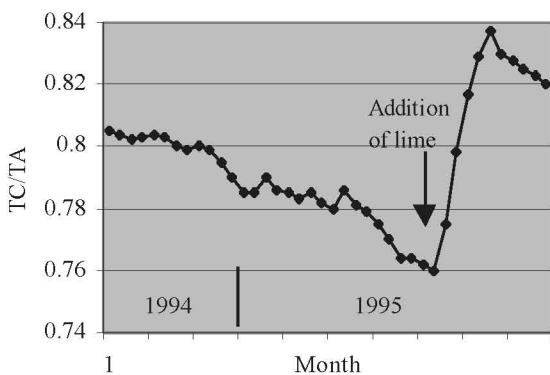


Figure 8. Increased causticisation via addition of lime to the slurry storage tanks.

Such lime addition to the slurry storage tanks prior to digestion not only affects causticisation: the phosphate in the liquor is depleted, the silica can be affected and the resultant caustic liquor can be high resulting in product quality issues. The challenge is to manage the lime addition whilst maintaining these other parameters under control. Some novel methods to obtain the benefits of such causticisation whilst minimising the downsides have been introduced at the Kwinana, Western Australian refinery and has resulted from excellent collaborative work between the technical, production and research personnel. That has enabled causticity in that plant to be increased close to its optimum.

#### Further Improvements in Causticity.

The reaction sequence given in equation 10 indicates that with the formation of monocarbonate, carbonate is removed from the liquor *independent of the causticity of the liquor*. Indeed, liquors which are at, or higher than, the equilibrium causticity can be causticised through the formation of the monocarbonate albeit at only 25% lime efficiency. Such an increase above the equilibrium value can be seen in Figure 2 at the highest TA in which the TC/TA first increases and then decreases. A further example is given in Figure 9 for spent and green liquors of approximately 250g/l TA and greater than equilibrium causticity. The liquors have been further causticised by formation of the monocarbonate to exceedingly high causticity levels through successive lime additions. To achieve this the reaction is undertaken at either low temperatures or short reaction times to ensure that the monocarbonate does not convert to TCA6, thus putting the carbonate back into solution. This monocarbonate can be separated and then used in the causticisers to be converted through to calcite and recovering much of the alumina. The process was named Spent Liquor Causticisation.

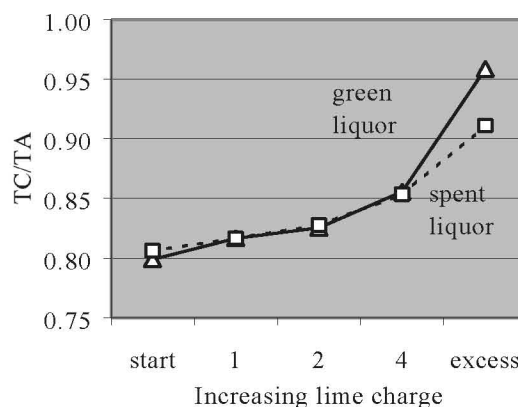


Figure 9. Spent liquor causticisation.  
Reaction conditions: 75°C and 180 seconds.

The process has many attractions in that it causticises the main liquor stream on the spent liquor side. Unfortunately there are also many practical issues:

- a solids liquid separation is required,
- the separation will result in spent liquor/green liquor mixing,
- sufficient carbonate is required at the causticisers to convert all the monocarbonate; i.e. the process will be sensitive to the balance between the carbonate input with the bauxite and from the lakes.

These and a host of other considerations have meant that to date this potential method of increasing the causticity above that attainable via the equilibrium approach has not been progressed.

#### Improvements in lime efficiency

To achieve both the equilibrium TC/TA and high lime efficiency within reasonable residence times (and thus capital) is not readily possible. One potential method to achieve this ideal is to use a relatively short reaction time in the causticiser to produce monocarbonate and some calcite. The residue is then separated and reacted in lower TA liquor to convert the monocarbonate to calcite. This process was termed Two Stage Causticisation. To a certain extent this can happen through the washer train if the causticiser residence time is short and there is still monocarbonate present. The causticiser products enter the washer where the TC/TA will be close to (and often slightly above) equilibrium and then will relatively quickly be transferred to the next washer where the TC/TA will be below equilibrium (being the causticiser feed). The monocarbonate can potentially causticise in that liquor. The causticiser residue could alternatively be separated and used for causticising much further down the washer train or lake water. For any such alternative it is necessary to have the liquor hot.

### Conclusions

A fundamental understanding of the causticisation process has assisted in determining the potential causticity that can be achieved in the causticisers.

Inclusion of this information within a steady state carbonate balance model has enabled meaningful predictions on causticity of the refinery liquor circuit to be made. That has assisted in optimising causticity in the refinery liquor circuit.

With the improved understanding of the basic mechanisms, potential methods to increase both causticity and lime efficiency have been identified. However, the practicalities have, to date, prevented their implementation.

### Acknowledgments

Many Alcoans within and external to R&D have made valuable contributions to this understanding of causticisation over the years. A special acknowledgment to Laurie Stonehouse who has championed the equilibrium approach at Alcoa and who has always provided useful ideas. Also to the Technical and production people, especially at the WA Refineries, who have been so helpful and contributed in so many ways.

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