

CHEMISTRY OF BAYER LIQUOR CAUSTICISATION

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High lime efficiencies and low alumina losses can be achieved when an unslaked slow slaking lime is charged as a causticisant to relatively high concentration green liquors.

Results obtained from laboratory batch tests indicate that this causticisation system requires a minimum reaction temperature of 95°C (203°F). At this temperature, maximum lime efficiencies and minimum alumina losses are obtained after two hours reaction; increasing reaction time results in reversion of residue calcium carbonate to tri calcium aluminate with a nett reduction in the overall efficiency.

At constant stoichiometric lime charges, lime efficiencies decrease and alumina losses increase with increasing liquor concentration. Similarly at constant liquor concentration, lime efficiencies decrease and alumina losses increase with increasing lime charge. Causticisation efficiencies increase to a maximum with increasing lime charge, this maximum being a function of liquor concentration.

Comparison of slaked and quicklime causticisation systems indicate substantial increase in lime efficiency for the quicklime system at liquor concentrations greater than 135 g/l T.A. Similar efficiencies are obtained for both systems at liquor concentrations below this level. Charging with a fast slaking quicklime results in efficiencies similar to those obtained with slaked lime.

The presence of fine mud in the causticisation system has no effect on the efficiencies obtained for the quicklime system.

X-ray diffraction and chemical analysis of causticiser residues suggest that the mechanism for both systems of causticisation is through a tri calcium aluminate intermediate.

Introduction

Carbonate levels in Bayer liquors are normally controlled by causticisation with lime, with alumina manufacturers employing one of two processes of causticisation.

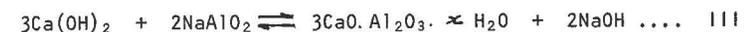
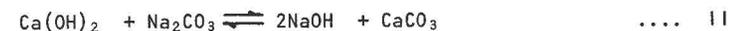
Firstly the process of "inside causticisation" initially developed by Hall around 1900, involves the addition of either pre slaked or dry lime to the bauxite slurry prior to digestion. Causticisation takes place in both the digestion and the residue washing systems. However, due to the high degree of reversibility of the causticisation reaction (equation II) in the initial contact liquor (high caustic, spent liquor), and the stability of the initial reaction products in subsequent liquors, the efficiencies obtained in this system are low. Therefore, to maintain an adequate plant carbonate removal rate, excessive lime usages are required and consequently high alumina losses are encountered.

In this system, lime also reacts competitively with other liquor impurities (e.g. phosphate, organics (oxalate) and fluoride) to form insoluble calcium compounds.

The alternative system of "outside causticisation" requires charging of lime to a dilute green liquor process side stream in a separate causticisation facility.

This process has the potential to maintain or increase the carbonate removal rate with high lime efficiencies and minimal alumina losses.

The chemical reactions involved in both systems include slaking of the lime (equation I) (this may be performed external to either system) to form calcium hydroxide. The hydroxide component then reacts competitively with carbonate (equation II) and aluminate (equation III) present in the liquor stream to form caustic, calcium carbonate and a series of hydrated tri calcium aluminates.



With both systems of causticisation the rate and extent of the reactions are controlled by the liquor parameters (i.e. caustic, carbonate and alumina concentrations), lime charge and temperature.

Bayer residue fine mud has also been quoted (Abboud (1), and Chaplin (2)) as having the potential to reduce the causticisation efficiency by depositing on the lime and/or calcium aluminate particles, effectively preventing them from entering into further reactions.

This presentation summarises the laboratory results obtained for the evaluation of an outside causticisation process. Parameters investigated include liquor concentration, reaction temperature, reaction period, lime charge and mode of addition, and liquor clarity. X-Ray diffraction and chemical analysis are presented to predict a mechanism of causticisation.

Materials and Methods

Causticiser residue analysis are based on the distribution of calcium components as a percentage of the total calcium, assuming the calcium phases formed are calcium carbonate (C) and tri calciumaluminate (A). The unreacted lime or calcium hydroxide (U) is calculated by difference. P is a measurement of liquor purity in terms of the total caustic to total alkali ratio (TC/TA).

All liquors employed in the experimentation were obtained from plant streams, any concentration adjustments were by either dilution or addition of analytical grade reagents.

Batch trials were conducted in sealed, mechanically agitated, baffled vessels. Temperature control was maintained by thermostatically controlled water jackets.

Physical and chemical properties of limes employed in all reactions are outlined in Table I, Slaking properties of fast and slow slaking limes are displayed in Figure I.

Table I. Quicklime Analysis

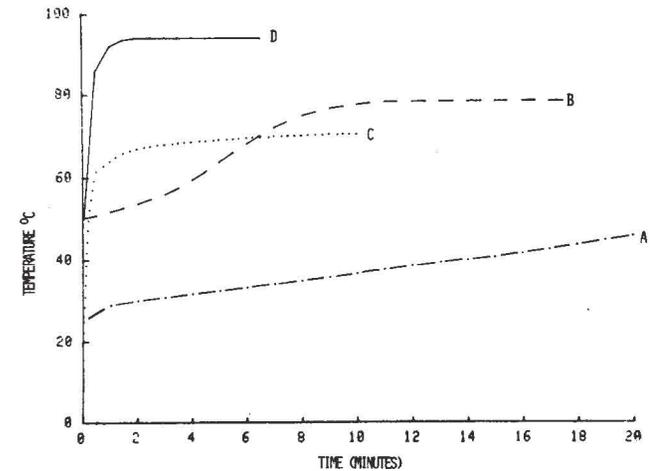
<u>Chemical Composition</u>	<u>Slow Slaking</u>	<u>Fast Slaking</u>
% CaO	82.4	95.1
% MgO	5.34	0.29
% Al ₂ O ₃	0.49	0.50
% Fe ₂ O ₃	0.44	0.28
% SiO ₂	10.2	ND
% CO ₂	0.73	1.04

<u>Particle Size Distribution</u>	<u>Slow Slaking</u>	<u>Fast Slaking</u>
+250 μm	45.2	41.8
+180	69.9	55.8
+150	79.5	63.0
+125	89.7	68.4
+ 90	95.4	76.6
+ 63	97.1	84.0
- 63	2.9	16.0

Figure I: Relative slaking rates of slow and fast slaking limes.

- Curve A - slow slaking lime, start temperature 25°C
- B - slow slaking lime, start temperature 50°C
- C - fast slaking lime, start temperature 25°C
- D - fast slaking lime, start temperature 50°C

Test conditions - 60g quicklime - 270ml, 7.5 g/l sodium hydroxide



Outside Causticisation

Conventionally, alumina plants employing the outside causticisation system select their stream from the overflows in the mud washing circuits. These streams generally provide the necessary liquor requirements for successful causticisation i.e. dilute green liquor, with caustic to alkali ratios ranging between 0.700 and 0.850 (Abboud (1)). The selected stream should contain sufficient carbonate such that the removal rate in comparison to an inside system can be maintained or increased.

Causticisation Parameters

(1) Liquor Concentration

The extent to which liquor concentration influences the resultant lime efficiency and alumina loss then becomes the criteria in terms of which washer overflow is selected.

Figures II (a) and (b) and III (a) and (b) graphically outline results obtained from causticisation of a range of liquor concentrations, with pre slaked (in process lake water at 95°C) and quicklime as a function of residence time at 95°C.

(a) Slaked Lime Causticisation. Analysis of the residues immediately after addition to the causticiser indicate that the calcium carbonate concentrations are essentially constant at approximately 25%. The tri calcium aluminate component of these residues on the other hand, are significantly higher, with values ranging between 50-57%, the amount tending to decrease with increasing liquor concentration.

With time the reaction to form calcium carbonate (figure IIa) increases in rate and magnitude with decreasing liquor concentration. The maximum calcium carbonate concentrations and causticisation efficiencies are, at all concentrations, achieved after 120 minutes. Increasing residence time results in reversion of calcium carbonate to tri calcium aluminate, the extent and rate increasing with increasing liquor concentration.

For the tri calcium aluminate distributions (figure IIb), the general trend is for the concentration to decrease from the initial level, the rate of reaction increasing with decreasing liquor concentration. At higher liquor concentrations the trend is for tri calcium aluminate to be formed continuously, to the extent that calcium carbonate formed initially reverts to the tri calcium aluminate.

(b) Quicklime Causticisation. A similar treatment of the distributions (figures III a and b) for quicklime causticisation, show that residues obtained initially have their calcium carbonate concentrations increasing (12-42%) with decreasing liquor concentration. The tri calcium aluminate concentrations, unlike those obtained with slaked lime, are reduced and average approximately 20% for all liquor concentrations.

With time, the rates of carbonate formation increase with decreasing liquor concentration. The maximum efficiencies are obtained after a similar residence period of 120 minutes, and again, product reversion is apparent with increased residence time. For tri calcium aluminate in this system (figure IIb), there is a trend for the residues at the higher liquor concentrations to increase in the tri calcium aluminate component,

Figure II (a): Effect of liquor concentration on the rate of calcium carbonate formation - Slaked Lime Addition. Temperature 95°C, Stoichiometric Lime Charge 53%, Start P 0.786

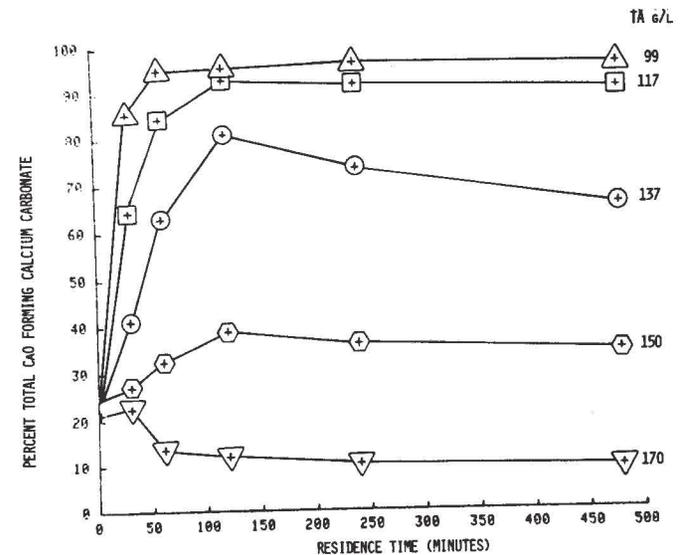


Figure II (b): Effect of liquor concentration on the rate of tri calcium aluminate formation - Slaked Lime Addition.

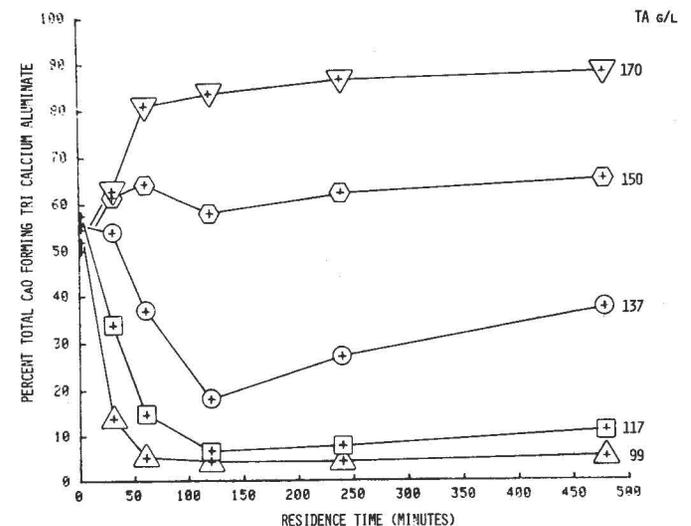


Figure III (a): Effect of liquor concentration on the rate of calcium carbonate formation - Quicklime Addition. Temperature 95°C, Stoichiometric Lime Charge 50%, Start P 0.780

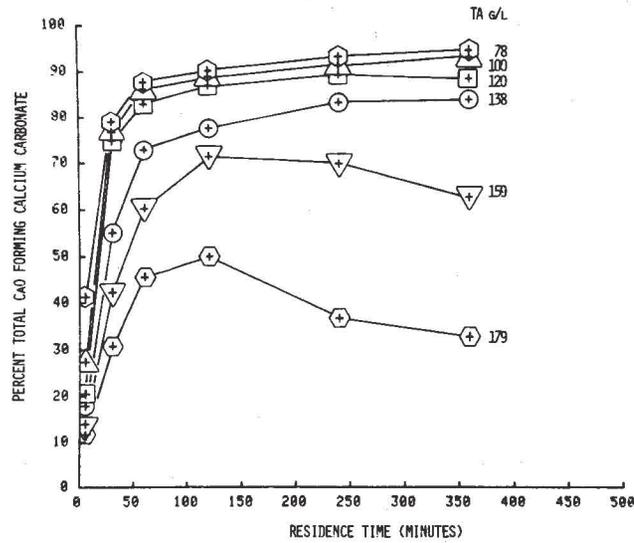
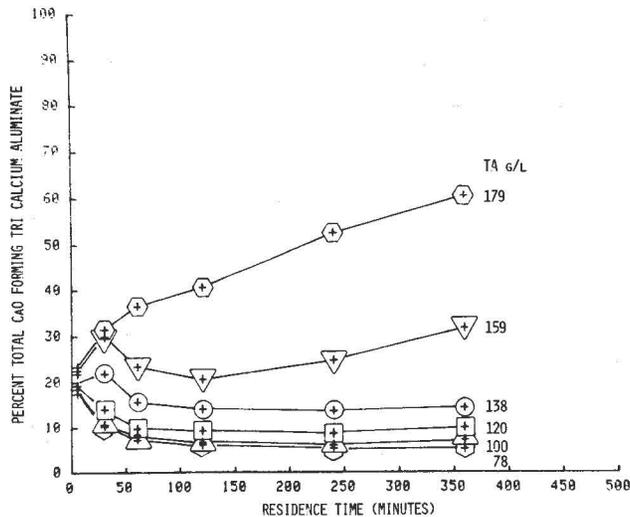


Figure III (b): Effect of liquor concentration on the rate of tri calcium aluminate formation - Quicklime Addition.



the magnitude increasing with increasing liquor concentration. At lower concentrations, the tri calcium aluminate concentrations decrease from their initial level by reaction with sodium carbonate to form calcium carbonate (similar mechanism to that observed with slaked lime). At all liquor concentrations the proportion of unreacted lime is less than 10% after 120 minutes reaction.

In summary, with respect to increasing liquor concentration, causticisation with either slaked or dry lime results in:

- (i) slower reaction rates for calcium carbonate and tri calcium aluminate formation
- (ii) reduced lime efficiencies and increased alumina losses at an optimum residence time of 120 minutes
- (iii) increasing rates and magnitudes of carbonate reversion to aluminate

Comparisons of the lime efficiencies and aluminate losses for both modes of lime addition as a function of liquor concentration are represented in figure IV (a) and (b). These curves illustrate that a substantial increase in lime efficiency and decreased alumina loss can be achieved for quicklime causticisation of liquors greater than approximately 135 g/l T.A. This phenomenon illustrates the peculiar advantage of employing a slow slaking lime for causticisation. Comparative efficiencies and alumina losses obtained for quicklime causticisation with fast and slow slaking limes are graphically outlined in figures V (a) and (b).

After a residence time of 120 minutes, the lime efficiencies are significantly different at 54 and 34% for the slow and fast slaking limes respectively. Increased residence time does not reduce the difference in efficiency. Tri calcium aluminate losses are similarly comparable at 29% and 44% respectively.

(2) Temperature

The minimum reaction temperature for causticisation is 95°C (203°F) (Chaplin). (2) Trials conducted at 75°C, 85°C and 95°C confirm this observation.

For all liquors and lime charges examined, decreasing the reaction temperature below 95°C resulted in reduced lime efficiencies (figure VI (a)) and increased alumina losses (figure VI (b)). Extended residence times do not compensate for reduced reaction temperatures.

(3) Lime Charge

To quantify the effects of increasing lime charge on causticisation efficiency, trials were conducted with slaked and quick limes as a function of reaction time at 95°C.

The carbonate distribution curves (figures VII (a) and VIII (a)) for the two lime addition systems, although representing different liquor concentrations, are similar in construction. In both cases, the percentage lime forming the carbonate decreases with increasing charge. Causticisation efficiencies increase with increasing charge to a maximum, which is dependent on the concentration of the liquor components.

Figure IV (a): Comparison of calcium carbonate formation rates for Slaked and Quicklime causticisation.
Temperature 95°C, Residence Time - 120 minutes

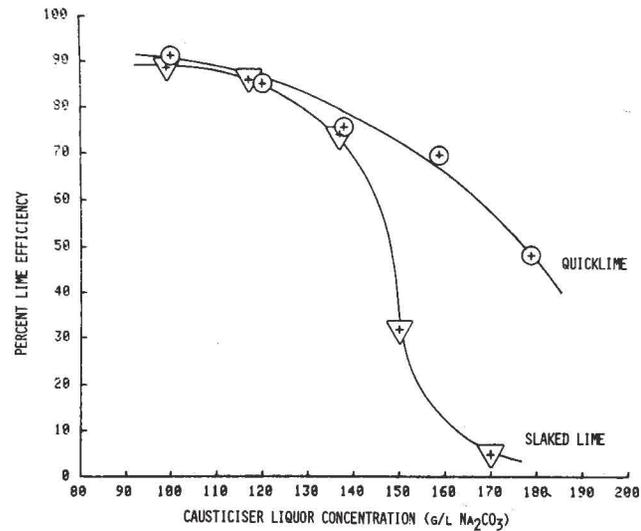


Figure V (a): Comparison of calcium carbonate formation rates for Quicklime causticisation with fast and slow slaking limes.
Liquor concentration 162g/l T.A., Start P 0.790, Temperature 95°C, Stoichiometric Lime Charge 50%

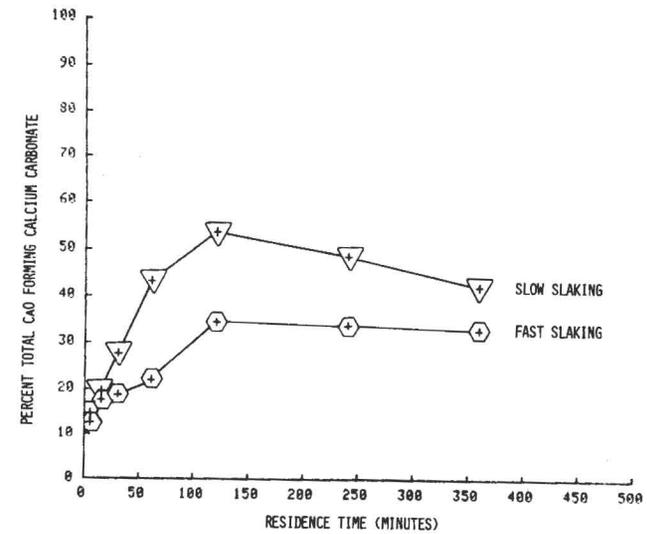


Figure IV (b): Comparison of tri calcium aluminate formation rates for Slaked and Quicklime causticisation.

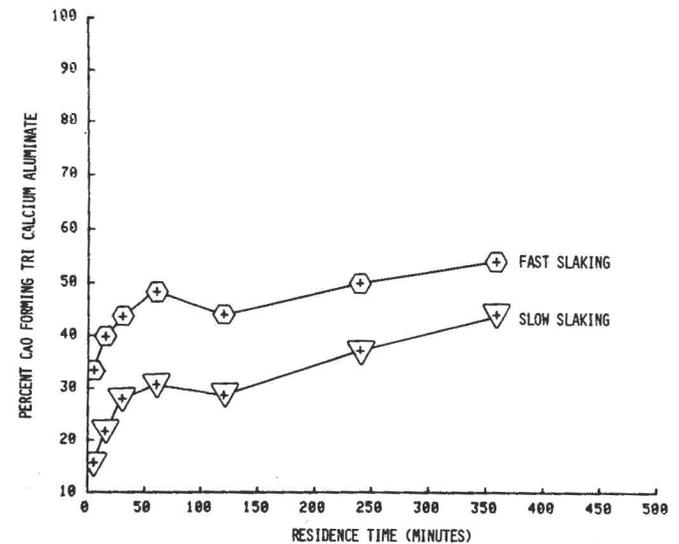
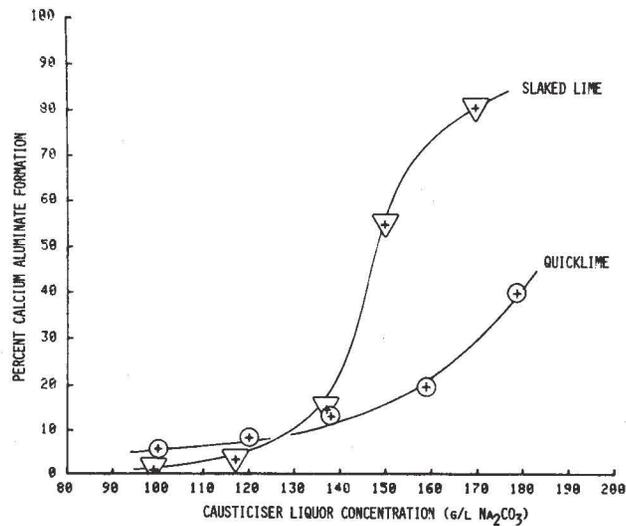


Figure VI (a): Effect of temperature on the rate of calcium carbonate formation - Slaked Lime Addition.
Liquor Concentration 124g/l T.A., Start P 0.780, Stoichiometric Lime Charge 50%

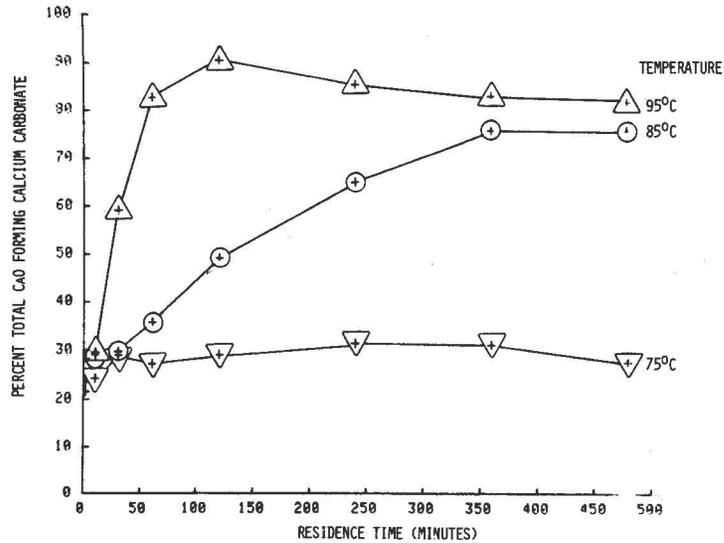


Figure VII (a): Effect of Quicklime charge on the rate of Calcium Carbonate formation.
Liquor concentration 116g/l T.A., Start P 0.760, Temperature 95°C

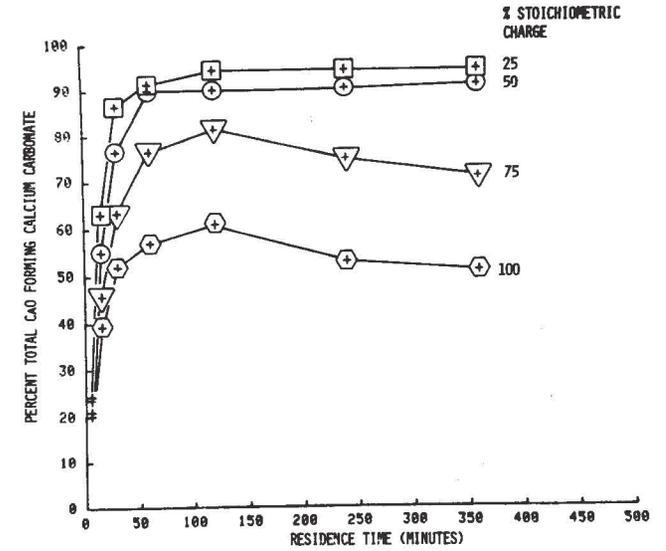


Figure VI (b): Effect of temperature on the rate of tri calcium aluminate formation - Slaked Lime Addition.

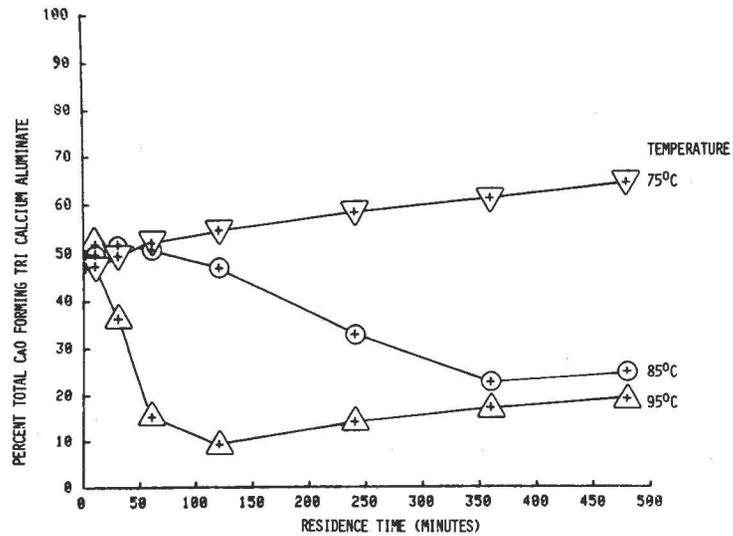


Figure VII (b): Effect of Quicklime charge on the rate of tri calcium aluminate formation.

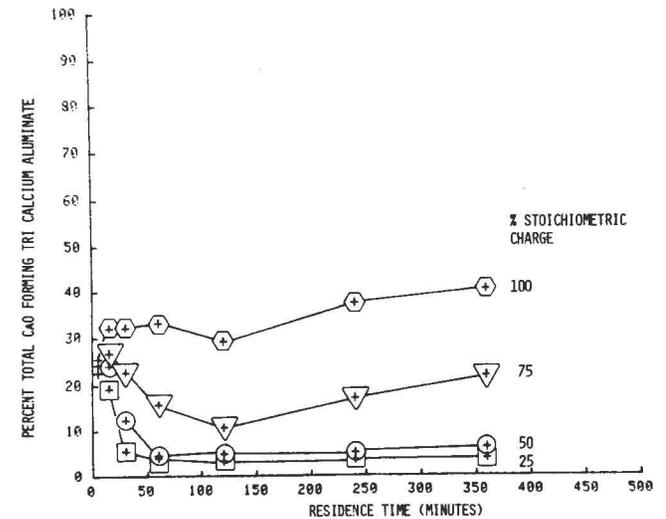


Figure VIII (a): Effect of Slaked lime charge on the rate of calcium carbonate formation.
Liquor concentration 135g/l T.A., Start P 0.780, Temperature 95°C

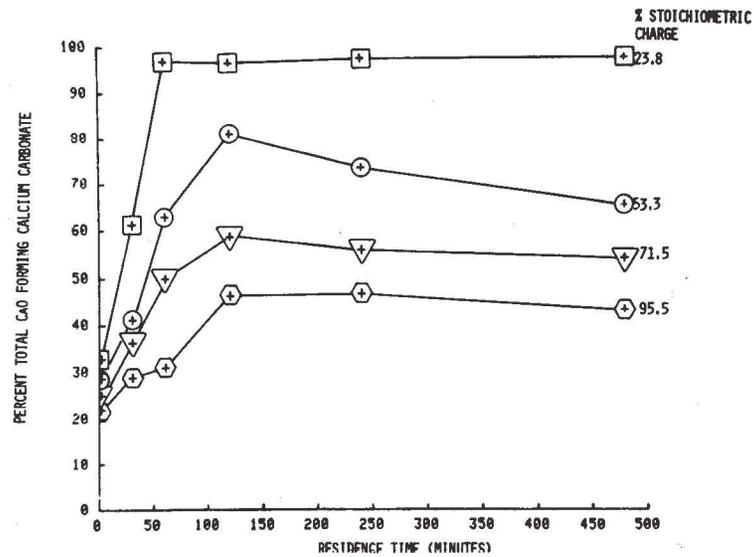


Figure VIII (b): Effect of Slaked lime charge on the rate of tri calcium aluminate formation.

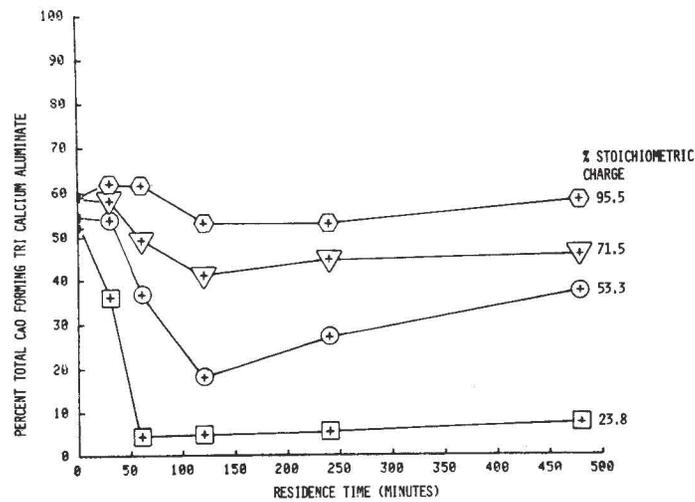


Figure IX (a): Extent of Causticisation efficiency for Quicklime causticisation.

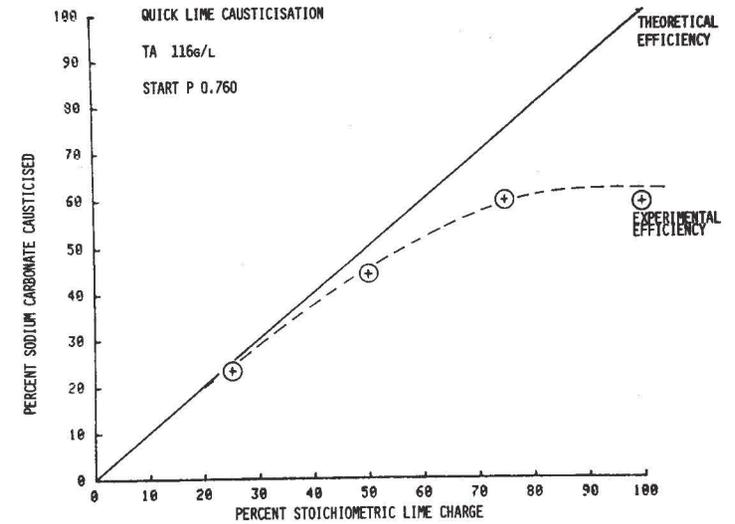
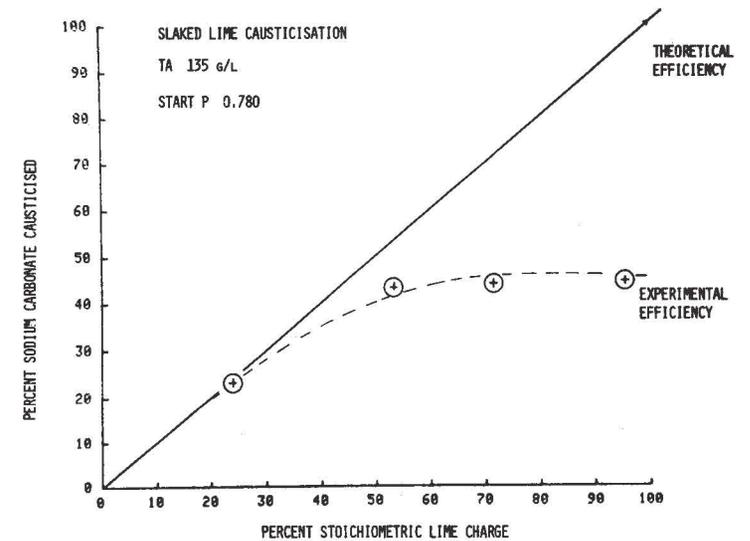


Figure IX (b): Extent of Causticisation efficiency for Slaked lime causticisation.



Graphical representations of the percentage sodium carbonate causticised after 120 minutes versus percent stoichiometric lime charge are shown in figures IX (a) and (b). Maximum P values obtained for each system are comparable to those calculated by the method of Adamson, Bloore and Carr (3) (i.e. lower concentration liquors can be causticised to a greater P value, although greater amounts of carbonate can be removed from higher concentration liquors per unit flow).

For the calcium aluminate formation, the percentage reporting to the residue increases with increasing lime charge (figures VII (b) and VIII (b)).

(4) Liquor Clarity

Causticisation trials with identical liquors containing zero and up to 30 g/l fine mud (Table II) indicate that fine mud has no effect on causticisation. It has been surmised that the effects of fine mud observed by other alumina plants are due to the properties of their fine mud i.e. fine mud produced from Darling Range bauxite differs from those of other bauxite sources, notably in that it contains little material less than 1µm.

Table 2. Causticisation in the Presence of Fine Mud

Mud Concentration g/l	0				30*				
	%C	P	%C	P	%C	P	%C	P	
Residence Time (Minutes)									
5	25.5	.792	40.5	.809					
15	64.7	.845	66.5	.850					
30	84.6	.870	80.5	.869					
60	90.1	.877	85.5	.876					
120	91.3	.880	86.0	.880					

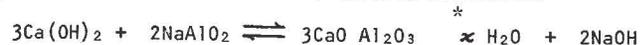
* CaO present in find mud, reduces lime efficiency.

Liquor TA 107 g/l

Quicklime Charge 50%

Mechanism of Causticisation

All causticisation trials with slaked lime have shown that there is a rapid initial formation of tri calcium aluminate.



where * represents the initial hydrated tri calcium aluminate phase; with time this component reacts with sodium carbonate to form calcium carbonate and sodium hydroxide.



X-Ray diffraction patterns and residue component distributions obtained from a slaked lime trial (100% stoichiometric charge) are recorded in figures X (a) and (d).

Initially, (5 minutes after charging) the components of the residue are shown to include calciumaluminiumhydrate $3CaO \cdot Al_2O_3 \cdot 8-12H_2O$ which can be identified by major characteristic reflections at 7.65Å and 2.86Å, calcium hydroxide (4.90Å, 2.63Å) and calcium carbonate (3.04Å). With time, the calciumaluminiumhydrate phase decreases in intensity and is supplemented by the development and growth of reflections at 5.13Å, 4.44Å, 3.36Å and 2.81Å. These reflections are associated with a phase identified as calcium aluminium hydroxide $3CaO \cdot Al_2O_3 \cdot 6H_2O$.

Treatment of residues obtained for a dry lime trial (100% lime charge) result in a similar series of diffraction patterns (figure X (b) and (e)).

For both systems, with time, the calcium carbonate reflections increase in intensity (as do analytical values), and calcium hydroxide reflections decrease, this phase being detectable in residues from both systems after 240 minutes reaction.

For causticisation with slaked lime at reduced charges (33%), the calcium aluminium hydrate reflection at 7.65Å (figures X (c) and (f)) is resolved into two components at 7.4 and 7.9Å, these probably suggest that this phase is composed of a range of tri calcium aluminate hydration states. In all patterns the reflections associated with this phase are broad, indicative of very fine grain material. Reflections from the calcite and tri calcium aluminate hexa hydrate components are sharp, suggesting larger more crystalline particles.

A simplified interpretation of the X-ray diffraction and analytical results provides a mechanism whereby the initial tri calcium aluminate phase may either form the tri calcium aluminate hexahydrates through a transition or ageing process (although no reflections associated with a transition phase are present in the X.R.D. patterns) or react with sodium carbonate (which residue analysis suggests), the tri calcium aluminate hexahydrate is then formed by reaction of calcium carbonate with sodium aluminate i.e. the mechanism of reversion.



Graphically a reaction mechanism for slaked lime causticisation can be represented by:

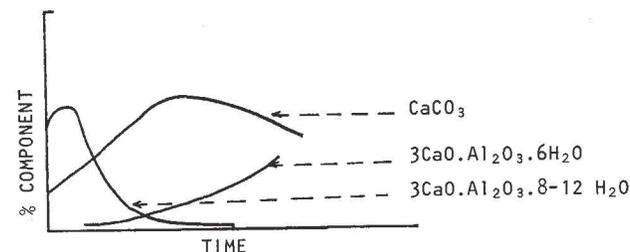


Figure X (a): X.R.D. patterns for residues produced from slaked lime causticisation.

Liquor concentration:
114g/l T.A.
Temperature 95°C
Stoichiometric Lime Charge
100%

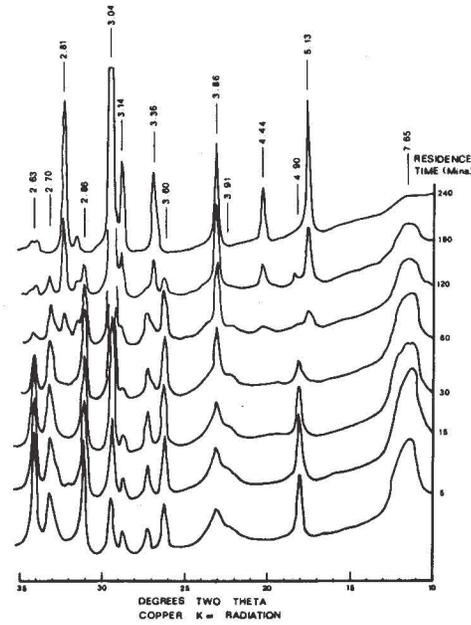


Figure X (b):

X.R.D. patterns from residues produced from Quicklime causticisation.

Liquor Concentration -
137g/l T.A.
Temperature - 95°C
Stoichiometric Lime Charge
- 100%

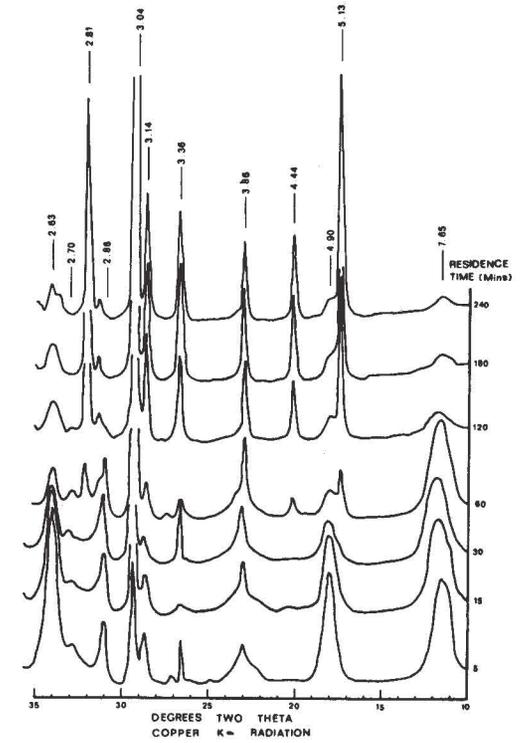


Figure X (d): Distribution of CaO products from Slaked Lime causticisation.

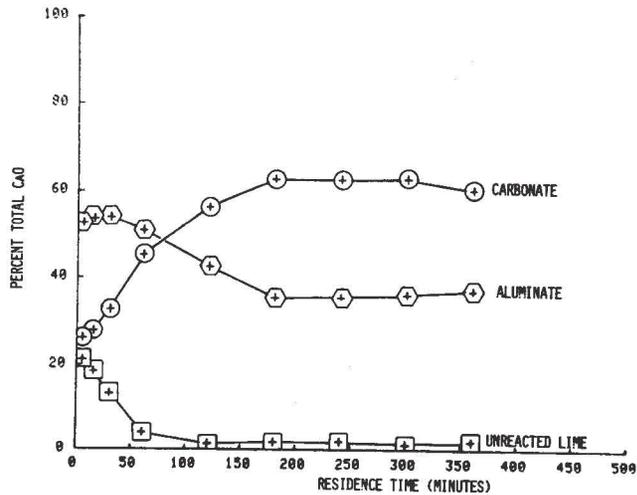


Figure X (e):

Distribution of CaO products from Quicklime causticisation.

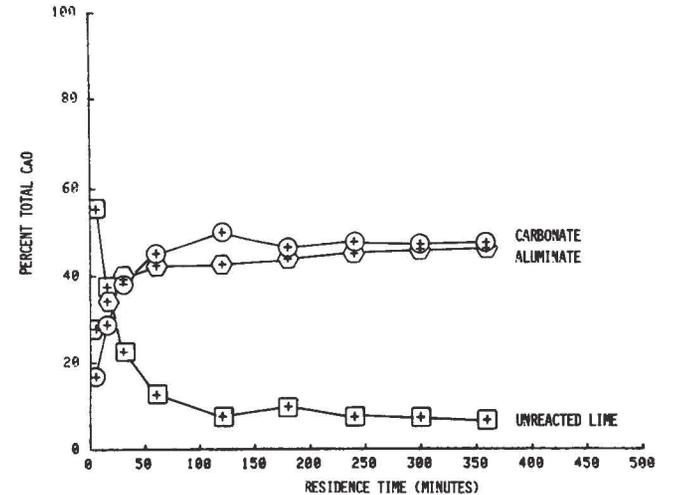
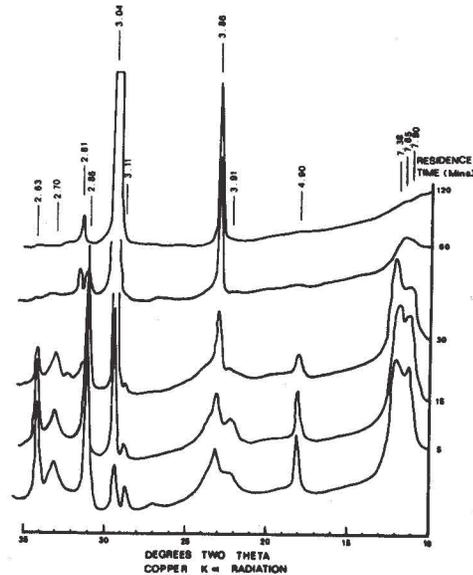
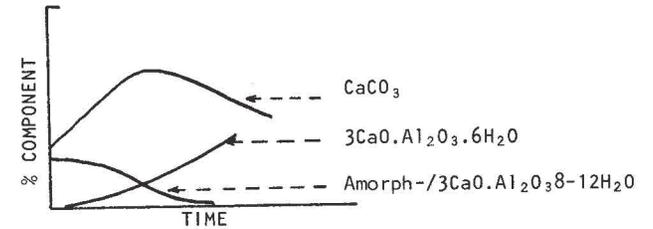


Figure X (c): X.R.D. patterns from residues produced from Slaked Lime causticisation.
Liquor concentration 136g/l T.A., Temperature 95°C, Stoichiometric Lime Charge 33%.



For quicklime causticisation, a slightly more complex interpretation is required. X.R.D. data obtained from initial residues produced at high liquor concentrations (>150g/l T.A.), indicate no crystalline aluminates phases for a residue containing 19% tri calcium aluminate. This suggests that the initial calcium aluminium hydrate phase is developed from growth of an amorphous or very fine crystalline phase. The reactions then proceed as per the mechanism outlined for slaked lime causticisation.

Schematically this can be represented by:



In this case unreacted lime is present in the residue for a greater part of the reaction period. This infers a mechanism of causticisation through a shrinking core model i.e. the mechanism assumes complete initial slaking (no lime detected by X.R.D. after 5 minutes reaction) and a reaction front through the lime particle of tri calcium aluminate. Notably, the particle size distribution of quicklime residue is only marginally reduced over a 120 minute reaction period.

Conclusions

Conditions which favour causticisation of relatively high concentration green liquors are:

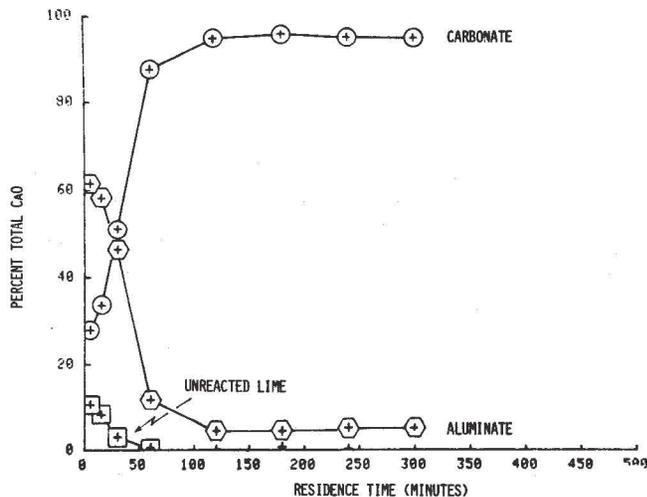
- (a) Quicklime causticisation with a slow slaking lime; higher efficiencies and lower alumina losses are achieved in comparison to fast slaking and pre slaked limes.
- (b) A reaction temperature of 95°C, decreasing the temperature below this level results in reduced efficiencies and increased alumina loss; increased reaction times do not compensate for the reduction.
- (c) A minimum residence time of 120 minutes.

The extent of the causticisation reaction is limited by concentration of caustic, carbonate and aluminate in the causticising liquor; increasing the lime charge increases the causticisation efficiency to a maximum level; further charging results in reduced lime efficiencies and increased alumina losses.

The presence of fine mud has no effect on causticisation with quicklime.

Causticisation of sodium aluminate liquors proceeds through a calcium aluminate intermediate; the rate of sodium carbonate reaction with the calcium aluminate governs the magnitude of alumina loss and lime efficiency.

Figure X (f): Distribution of CaO products from Slaked Lime causticisation.



References

1. Abboud H.I., "Successful Side Stream Causticisation in an Alumina Plant," Extractive Metallurgy of Alumina, A.I.M.E. 1963, Vol. 1 pp 265-270.
2. Chaplin, N.T., "Reaction of Lime in Sodium Aluminate Liquors," Light Metals, 1971 A.I.M.E., Proceedings of 100th Annual Meeting.
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