High lime efficiencies and low alumina losses can be achieved when unslaked slow slaking lime is charged as a causticisingant 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 changes, 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.

\[
\begin{align*}
\text{CaO} + \text{H}_2\text{O} & \rightleftharpoons \text{Ca(OH)}_2 + \text{heat} \quad \text{(I)} \\
\text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 & \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3 \quad \text{(II)} \\
3\text{Ca(OH)}_2 + 2\text{NaAlO}_2 & \rightleftharpoons 3\text{CaO}.\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{NaOH} \quad \text{(III)}
\end{align*}
\]

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 calcium aluminate (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 1. Slaking properties of fast and slow slaking limes are displayed in Figure 1.

Table 1. Quicklime Analysis

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Slow Slaking</th>
<th>Fast Slaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CaO</td>
<td>82.4</td>
<td>95.1</td>
</tr>
<tr>
<td>% MgO</td>
<td>5.34</td>
<td>0.29</td>
</tr>
<tr>
<td>% Al₂O₃</td>
<td>0.49</td>
<td>0.50</td>
</tr>
<tr>
<td>% Fe₂O₃</td>
<td>0.44</td>
<td>0.28</td>
</tr>
<tr>
<td>% SiO₂</td>
<td>10.2</td>
<td>ND</td>
</tr>
<tr>
<td>% CO₂</td>
<td>0.73</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Particle Size Distribution

| +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 1: 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