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Effect of Partial Borate Autocausticizing on Causticizing Rate and Equilibrium

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**EFFECT OF PARTIAL BORATE AUTOCAUSTICIZING
ON CAUSTICIZING RATE AND EQUILIBRIUM**

by

Murugavel Anbalagan

**A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Paper Engineering, Chemical Engineering, and Imaging**

**Western Michigan University
Kalamazoo, Michigan
December 2003**

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Murugavel Anbalagan

EFFECT OF PARTIAL BORATE AUTOCAUSTICIZING ON CAUSTICIZING RATE AND EQUILIBRIUM

Murugavel Anbalagan, M.S.

Western Michigan University, 2003

Borate autocausticizing can replace – total autocausticizing, or supplement the kraft lime cycle- partial autocausticizing. Partial autocausticizing is undergoing trials in several mills and has been recently commercialized in one mill. One common observation in the on-going trials is that the causticizing efficiency increases. The primary objectives of this research are to study the effect of metaborate on the causticizing rate, equilibrium and rate controlling parameters such as the temperature, concentration and sulfidity. The aim is to define the conditions that resulted in the increase of the causticizing efficiency.

The major findings of the research are that when the causticizing reaction is rate limited, which is true in commercial operations, partial borate autocausticizing can increase causticizing efficiency due to the higher initial hydroxide content, temperature is a critical factor and has to be monitored and maintained to achieve good causticizing efficiencies, and the effect of sulfidity on the causticizing reaction rate and equilibrium is less pronounced with the presence of borate in the system.

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CHAPTER I

INTRODUCTION

Problem Statement

The existing Kraft recovery process has not changed much over the years. Though it has several advantages such as efficient chemical recovery, ability to meet emission requirements, and good thermal efficiency, it also has a certain drawbacks such as the need for large-scale equipments and the danger of smelt-water explosions. All these and the need to reduce heavy capital costs, which attribute 35% of the capital cost of a modern pulp and paper mill, have led to the search for alternatives to replace the existing conventional processes in pulping and chemical regeneration cycles.

A process that eliminates the causticizing and calcining operations by producing green liquor directly in the smelt can be a promising approach. This process is termed as autocausticizing. One well-known system is borate auto-causticizing, in which sodium metaborate reacts with sodium carbonate to eliminate CO_2 ; however, this is not used commercially.

Thus far, none of the new technologies offers sufficient benefits to justify the risk of implementation on a mill scale. According to Grace [1], four incentives that could induce mills try a new technology are:

1. Significantly lower capital cost
2. Elimination of causticizing/calcining
3. Improved energy values
4. Fully adaptable to changing pulping/bleaching technology

The presence of all four incentives could achieve much higher conversion than the conventional one.

Partial borate-autocausticizing appears to be technically feasible and may be attractive economically as predicted in recent studies. In the case of incremental capacity of the causticizing plant this serves as an attractive alternative. However, the effect of borate in various causticizing processes needs to be thoroughly examined before such a technology can be implemented.

Hence this research will deal with the effect of sodium-metaborate on the causticizing reaction rate and equilibrium.

CHAPTER II

LITERATURE REVIEW

Overview of Pulping Methodology

Any process, which reduces wood into a fibrous mass, is known as pulping. The main objective is to rupture the bonds within the wood structure. There are various kinds of pulping, which can be broadly classified as mechanical, thermal and chemical pulping. The general characteristics of these methods are explained below.

Mechanical Pulping

In mechanical pulping the wood is pressed lengthwise against a grinding stone revolving at peripheral speeds of 1000-1200 m/min. The fibers are washed away with water. The slurry of fiber and fiber particles are screened to remove any oversize particles and are thickened to form pulp stock suitable for papermaking. This process requires careful control of stone surface roughness, pressure and water temperature to obtain efficient and uniform production.

Even though the mechanical pulping converts 95% of the dry weight of the wood into pulp it consumes a lot of energy to do this. This pulp usually forms opaque paper with good printing properties.

Chemical Pulping

Chemical pulping is done by cooking wood chips with certain chemicals in an aqueous solution at elevated temperatures and pressure. This is done to dissolve the lignin and to retain most of the cellulose and hemicelluloses. The pulp yield is low when compared to mechanical pulping, usually in the range of 40% to 50% because the hemicelluloses and cellulose also get degraded in addition to the lignin by the chemicals.

The two main types of pulping processes are Kraft process (alkaline) and sulfite process (acidic). Of these two, Kraft process is the dominant one because of its advantages and pulp strength. The sulfite process is in the decline.

Kraft Process

In the kraft process, the wood chips are cooked using NaOH and Na₂S. The alkaline nature of the chemicals fragments the lignin molecules into smaller one, which are soluble in the cooking liquor. Kraft process produces strong pulps but the unbleached pulp is characterized by a dark color. In German, kraft means strong and hence the name. The kraft process uses organic sulfides, which causes environmental concerns.

The Kraft process uses sulfate as the makeup chemical. Since the traditional makeup chemical was sulfate it was sometimes called the sulfate process.

The Kraft process produces a number of different pulp grades. Unbleached pulp used for packaging applications contains more lignin than the bleached ones, which are made into white papers.

Sulfite Process

The sulfite process uses a mixture of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-) to attack and solubilize the lignin. The lignin sulfate compound lignosulfonic acid is soluble in the cooking liquor. Sulfite pulps are lighter in color than kraft pulps and can be bleached more easily, but the paper sheets are weaker than kraft sheets. Sulfite process can be carried out at different pH levels. Acidic sulfite denotes cooking at pH 1-2 and bisulfite denotes less acidic conditions of pH 3-5. The sulfite process generally produces pulps, which are lighter in color when compared to the kraft process, but the sheets are not as strong as the Kraft ones.

Kraft Chemical Recovery

Some of the primary objectives of the kraft chemical recovery process are:

1. Recovery of the chemicals used from the spent liquor
2. Reconverting them into fresh liquor
3. Incineration of the residuals
4. Reducing the environmental pollution caused by the chemicals used

According to Smook [2] the various steps involved in the chemical recovery are as follows:

1. Concentration of the residual liquor in multiple-effect evaporators to form “strong black liquor”.
2. Black liquor oxidation.
3. Further concentration of the residual liquor to form “heavy black liquor”.
4. Incineration of liquor in the recovery furnace.
5. Dissolving smelt from the furnace to form green liquor.

6. Causticizing green liquor with lime to form white liquor.
7. Burning of lime mud to recover lime.

Figure1 shows the general flow sheet of a chemical recovery process.

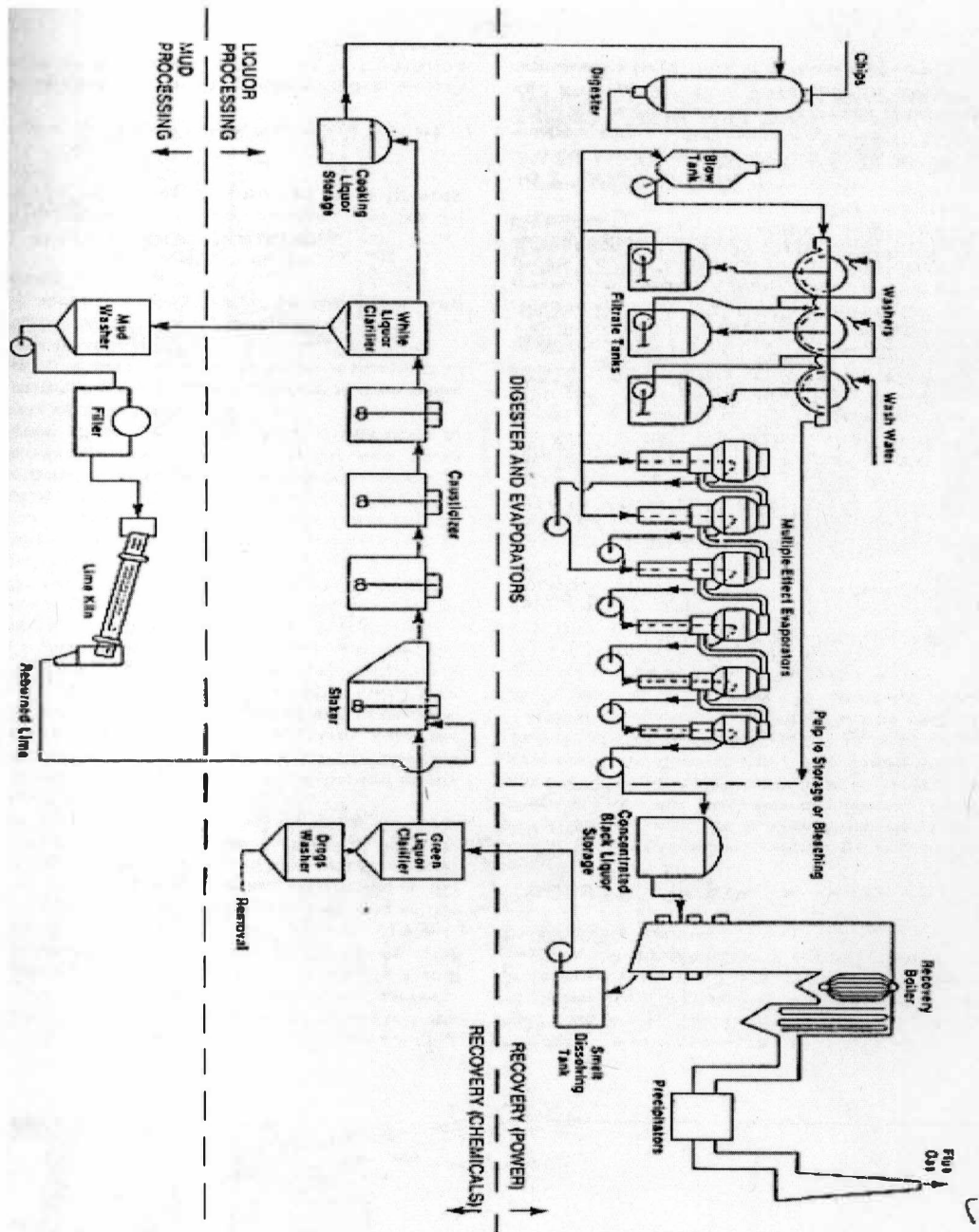


Figure 1. Kraft Chemical Recovery Process [2]

Process Description

The Kraft pulping recovery cycle consists of the following steps:

1. Pulping
2. Washing
3. Evaporation
4. Combustion
5. Recausticizing
6. Calcining

Recausticizing

The recausticizing system constitutes two separate cycles:

1. Sodium cycle, which is the liquor system.
2. Calcium cycle, which is the solid system.

According to Grace [3], the Sodium cycle and the Calcium cycle contain the following major steps:

Sodium Cycle

1. Treatment of the aqueous solution from the dissolving tank (called green liquor) to remove solid impurities (dregs) that would otherwise enter the lime loop.
2. Chemical reaction between the sodium carbonate in the green liquor and lime to form sodium hydroxide (caustic) and solid calcium carbonate (lime mud). This is the slaking/causticizing reaction.

3. Separation of the solid phase lime mud from the aqueous caustic solution (white liquor).

Calcium Cycle

1. Chemical reaction of the solid calcium oxide (lime) with aqueous sodium carbonate to form solid calcium carbonate (lime mud).
2. Separation of the solid lime mud from the aqueous caustic white liquor.
3. Calcination of the lime mud to reform lime (CaO).

Figure 2 illustrates a typical recausticizing cycle.

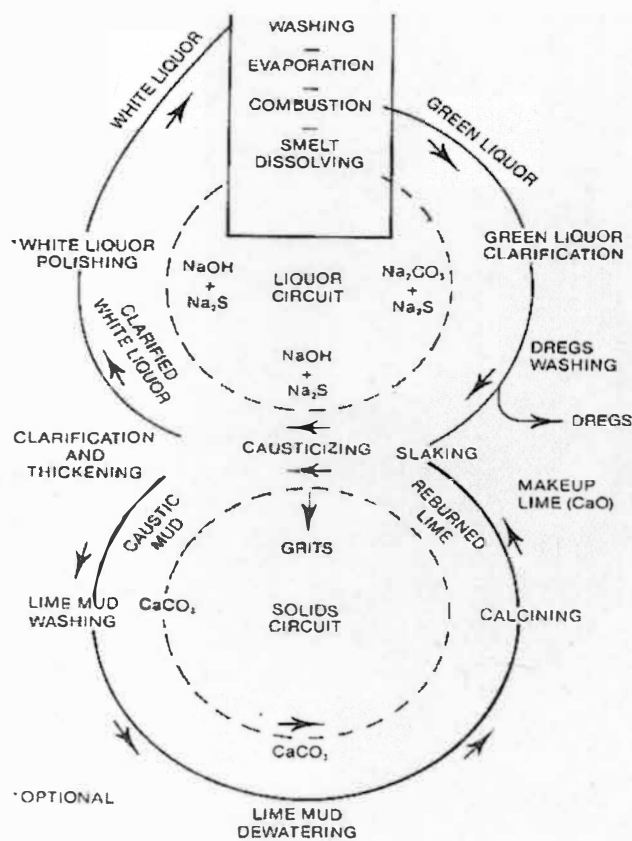


Figure 2. Typical Recausticizing Cycle [1]

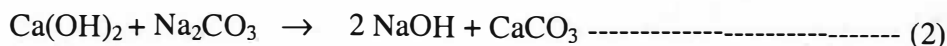
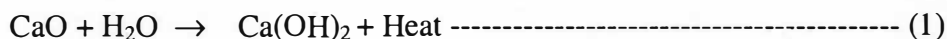
Process Steps

1. Dregs Removal and Washing

The insoluble impurities in the green liquor that arise from the unburned carbon in the smelt are called as dregs. The dregs may cause some problems if they enter the solids circuit. Dregs are removed using sedimentation type clarifiers. The dregs are generally washed and land filled.

2. Slaking and Causticizing

The two relevant chemical reactions are:



About 80-95% of the causticizing reaction gets completed in the agitator section of the slaker and the remaining 5-20% conversion takes place in the causticizers.

In the slaker it is important to control the amount of lime that is added. Addition of excess lime will lead to poor lime mud separation and less amount of lime will cause poor conversion of carbonate to caustic.

1. White Liquor Clarification

The slurry from the causticizers is passed through sedimentation-type clarifiers or filters to separate white liquor and lime mud.

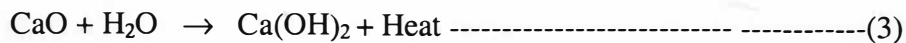
2. Lime Mud Washing and Dewatering

The soda content of the lime mud from the white liquor clarifier is reduced from 16-20% to 3% by washing before it is fed to the calciner. Washing normally takes place in sedimentation units and dewatering is carried out in a rotary drum vacuum filter. The final range of the discharged solids is from 60-90%.

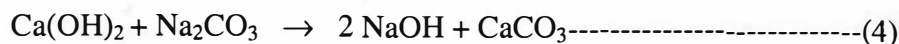
Slaking/Causticizing Chemistry

The conversion of green liquor to white liquor takes place in the slaking, causticizing and calcining reactions.

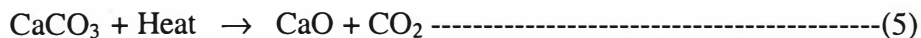
Slaking



Causticizing



Calcining



Nomenclature

In recent days the alkali concentrations in white and green liquors are expressed as Na_2O equivalent. Thus according to Grace [1],

$$1 \text{ lb NaOH} = 0.775 \text{ lb Na}_2\text{O}$$

$$1 \text{ lb Na}_2\text{S} = 0.795 \text{ lb Na}_2\text{O}$$

$$1 \text{ lb Na}_2\text{CO}_3 = 0.585 \text{ lb Na}_2\text{O}$$

Concentrations are usually expressed in terms of g- $\text{Na}_2\text{O}/\text{l}$ or lb- $\text{Na}_2\text{O}/\text{ft}^3$.

The following are some important terms that are encountered

		Units
Active Alkali:	AA = NaOH + Na_2S	g/l as Na_2O
Effective Alkali:	EA = NaOH + $\frac{1}{2} \text{Na}_2\text{S}$	g/l as Na_2O
Total Titratable Alkali:	TTA = NaOH + Na_2S + Na_2CO_3	g/l as Na_2O
Sulfidity	= $\frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{NaOH}}$	% (on Na_2O basis)
	or sometimes	

$$= \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{NaOH} + \text{Na}_2\text{CO}_3} \quad \%(\text{ on Na}_2\text{O basis})$$

$$\text{Causticizing Efficiency:} = \frac{\text{NaOH}}{\text{Na}_2\text{CO}_3 + \text{NaOH}} \quad \%(\text{ on Na}_2\text{O basis})$$

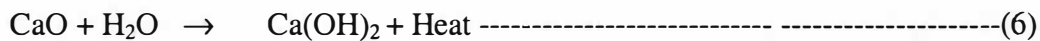
$$\text{Activity:} = \frac{\text{NaOH} + \text{Na}_2\text{S}}{\text{TTA}} \quad \text{expressed as } \%$$

$$\text{Causticity:} = \frac{\text{NaOH}}{\text{TTA}} \quad \%(\text{ on Na}_2\text{O basis})$$

The advantage of the Na_2O convention is that the TTA remains constant throughout the causticizing process. Causticizing then results in an increase in the active alkali content of the liquor. The advantage of basing the sulfidity on the TTA rather than the AA is that the sulfidity will remain constant through the causticizing process except for loss due to oxidation.

Slaking

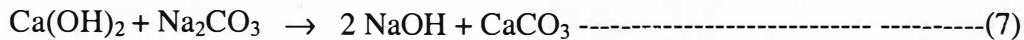
The reaction between calcium oxide and water to produce calcium hydroxide is termed as slaking and is highly exothermic. The addition of lime increases the temperature of the green liquor by 30-40° F.



The recommended temperature for slaking is 200-220° F. The slaking process will not be fast enough if the lime used is not very reactive.

Causticizing

The causticizing reaction begins in the slaker and is completed in the causticizers. The reaction can be written as



Na_2CO_3 and NaOH take part in the reaction as liquid phases and Ca(OH)_2 and CaCO_3 take part as solid phases. The fact that CaCO_3 is more insoluble than Ca(OH)_2 is the reason for the reaction to shift to the right. The heat of reaction for the causticizing reaction is quite small. The temperature rise that occurs in slaking and causticizing is from the slaking reaction and not the causticizing reaction.

Equilibrium Behavior

According to Grace [1] the causticizing reaction does not go to completion, but instead approaches equilibrium and this equilibrium can be described by the following equation:

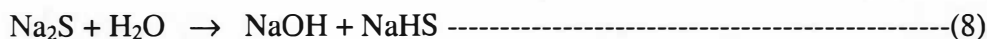
$$K = \frac{[\text{OH}]^2}{[\text{CO}_3^{2-}]} = \frac{[\text{Ca}^{++}] [\text{OH}]^2}{[\text{Ca}^{++}] [\text{CO}_3^{2-}]}$$

$$= \frac{K_{\text{Ca(OH)}_2}}{K_{\text{CaCO}_3}}$$

Where, $K_{\text{Ca(OH)}_2}$ = Solubility product of Ca(OH)_2
 K_{CaCO_3} = Solubility product of CaCO_3

Grace [4] predicted that the equilibrium conversion efficiencies are in the order of 90% and the value of the equilibrium constant decreased with increasing sodium ion concentrations. The equilibrium conversion limit is reached at lower percent conversions as the initial green liquor concentration is increased because the hydroxide concentration is squared while the carbonate enters to the first power.

The sodium sulfide in the green liquor tends to hydrolyze according to the following reaction:



The hydroxide ions hence produced suppress the causticization. The equilibrium causticizing efficiency is lowered if the sulfidity is high.

Excess lime will not cause the causticizing reaction to proceed beyond the equilibrium conversion and increase in concentration of both green liquor and sulfidity will decrease the conversion of carbonate to caustic.

Equilibrium causticities as a function of TTA at two different sulfidities are shown in Figure 3 taken from Grace [4]. In the mill range of TTA concentrations (110 – 135 g/L) the equilibrium causticity decreases by about 5% as the concentration is increased.

There are no benefits in adding excess lime because the conversion efficiency is not affected but the lime settling quality will be severely hindered. According to Van't Hoff equation, the equilibrium will not be influenced by temperature since the heat of reaction for causticizing is negligible.

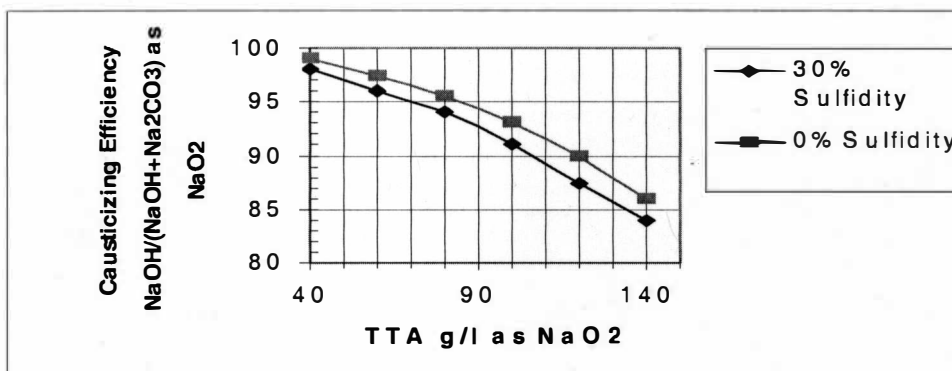


Figure 3. Effect of Increasing Concentration of Liquor and Sulfidity on Causticizing Efficiency

$$dK / dT = \Delta H / RT^2 \text{ -----(9)}$$

Causticizing Rates

The mill conversion is controlled by rate processes rather than by the equilibrium. Data on slaking/causticizing rates from Rydin et al. [5] are shown in Figure. 4. The initial period shows a very rapid rate, during which most of the conversion occurs; followed by a much longer period with a very low rate as the equilibrium conversion is approached. It looks as if the equilibrium limit is increased because the conversion rates are very slow in the low rate region. This effect is on the rate and not on the equilibrium. Works done by Lindberg and Ulmgren [6] indicates that the reaction rate increases by 2 to 3 times for a 20° C increase in temperature.

Figure 4 illustrates the effect of temperature on the causticizing reaction rates.

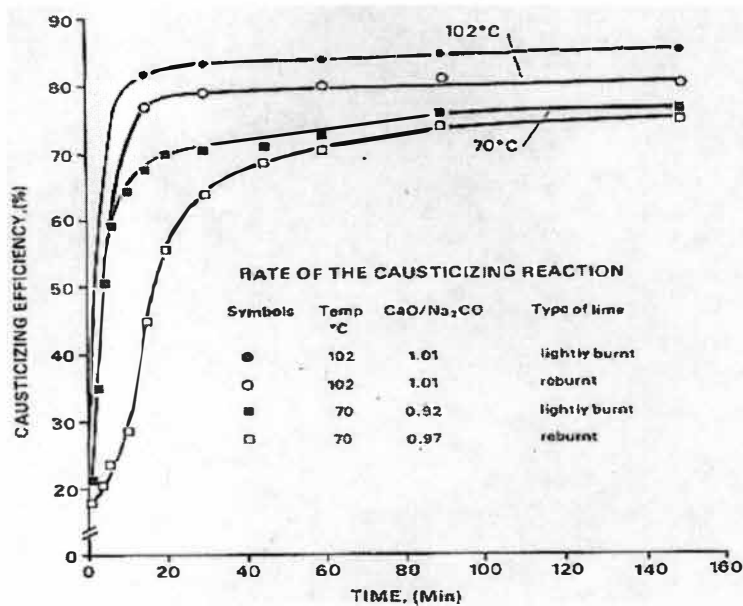


Figure 4. Effect of Temperature on Causticizing Reaction Rates [5]

It is found that the causticizing rates are strongly influenced by lime quality and lime charge as well as by temperature. An increase in lime charge will result in “poor-settling” lime mud downstream in the process.

Sulfate Effects

The sulfate ion present in the green and white liquor undergoes the following reaction:



Grace [4] has predicted that CaSO_4 can only exist in the equilibrium in the white liquor if the concentration of sulfate was 10,000 times the concentration of carbonate. Thus CaSO_4 should be soluble in white liquor. The dissolved CaSO_4 in the green/white liquor would be removed with the grits at the slaker.

The chemical composition of green and white liquors can be determined with the procedures given in TAPPI Standard Method T624 os-68. A simpler approach commonly used in the mill is a series of titrations known as the ABC test [1].

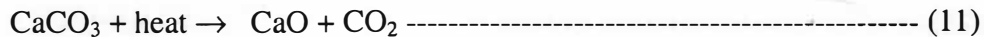
Calcining

The conversion of CaCO_3 back into CaO for reuse in the causticizing process is termed as calcining. This usually takes place in a lime kiln. Calcinations usually yield a product of 90-94% CaO which reacts rapidly with the green liquor.

A typical calcining operation consists of the following operations [2]:

1. Drying the lime mud
2. Raising the temperature of the lime mud to the level (about 800°C) required for the calcinations reaction
3. Maintaining a high temperature for sufficient time to complete the endothermic reaction.

Calcium carbonate is broken down into CaO and CO_2 as follows:



CHAPTER III

ALTERNATIVE KRAFT RECOVERY

The existing Kraft recovery process has not changed much over the years. Though it has several advantages such as efficient chemical recovery, ability to meet emission requirements, and good thermal efficiency, it also has a certain drawbacks such as heavy capital cost, the need for large-scale equipments and the danger of smelt-water explosions. All these and the need to reduce costs have led to the search for alternatives to replace the existing conventional processes in pulping and chemical regeneration cycles.

A process that eliminates the causticizing and calcining operations by producing green liquor directly in the smelt can be a promising approach. This process is termed as autocausticizing. One well-known system is borate autocausticizing, in which sodium metaborate reacts with sodium carbonate to eliminate CO_2 .

Thus far, none of the new technologies offers sufficient benefits to justify the risk of implementation on a mill scale. According to Grace [1], four incentives that could induce mills try a new technology are:

1. Significantly lower capital cost
2. Elimination of causticizing/calcining
3. Improved energy values
4. Fully adaptable to changing pulping/bleaching technology

The presence of all four incentives could achieve much higher conversion than the conventional one.

To eliminate the causticizing and the whole lime cycle in soda and kraft mills the green liquor should be used as white liquor. Since sodium carbonate is not sufficiently alkaline the cooking alkali should be based on a system other than sodium hydroxide – sodium carbonate.

Janson [10] from the Finnish Pulp and Paper Research Institute, Helsinki proposed that disodium borate and some other compounds provide the necessary alkalinity during cooking and the desired reactions during regeneration.

When the causticizing, that is the removal of carbon dioxide, occurs in the recovery furnace by the action of the cooking agent itself, which is by the borate, that phenomenon is called autocausticizing.

Pulping with Disodium Borate

Janson [7] predicted that without essentially changing any other conditions, one mole of sodium hydroxide could be replaced by one mole of disodium borate. He assumed that in borate pulping there are two effects operating in different directions: one increasing the pulping rate by keeping the alkalinity high with the aid of the buffer capacity of borate, and the other decreasing the rate by enhancing the ionic strength [7].

He also found out that there is very little difference in the pulp yields from hydroxide and borate based pulping, nor are there any differences in pulp properties. The borate liquor can be washed out completely, leaving only traces of borate in the pulp.

Janson [12] predicted no difficulties at all during cooking and washing. According to him, also from the energetic point of view the borate pulping seemed advantageous, the main saving being the consumption of oil used for firing the lime sludge kiln. The total gain amounted to about 6 USD/ton of pulp. Janson [12] thus regarded the results of the mill trial as very promising.

The Finnish Pulp and Paper Research Institute (FPPRI) and at the Institute of Paper Chemistry in Appleton, USA, declared that the environmental impact of using borate for pulping gave no cause for alarm. The contribution of borate to toxicity of effluent seemed to be negligible.

Preliminary calculations made on the changes in investment costs and operation costs of a new kraft mill revealed that the borate alternative would be still more advantageous [7], if the savings in capital costs are also incorporated.

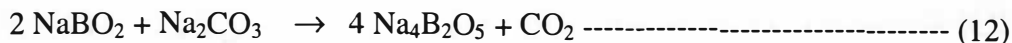
To summarize, Janson [7] concluded that replacing sodium hydroxide by disodium borate in kraft pulping is feasible.

Grace suggested that full scale implementation of the borate process is technically difficult and economically unattractive, due primarily to the large amount of borate “deadload” in the liquor cycle, and to the low heating value and the high viscosity of the resulting borate-containing black liquor [1].

Partial Autocausticizing

As per Janson’s suggestion, the autocausticizing process is attained by reacting sodium carbonate (Na_2CO_3) in the molten smelt with sodium-metaborate (NaBO_2) to

form disodium borate ($\text{Na}_4\text{B}_2\text{O}_5$), which subsequently is hydrolyzed to form sodium hydroxide (NaOH) and to regenerate NaBO_2 in the dissolving tank.



Partial autocausticizing seems to be an attractive alternative for mills that require incremental causticizing and lime kiln capacities since it requires a proportionately smaller borate load [8]. But Janson [7] predicted that Reaction 12 would be severely hindered if the Na:B molar ratio (or Na/B) of the reactants is greater than 1.5:1 (or 1.5); and that it would not even occur if Na/B is greater than 3. This means that partial autocausticizing is technically not feasible because Na/B is likely to be much greater than 3. The development work involving borates became dormant by the end of 1980s.

According to H.Tran, X.Mao, J. Cameron and C.M.Bair [8], in 1990 US Borax Inc., in search of new applications for borate products began to re-examine technologies that involve the use of borates in the pulp and paper industry. This led to the review of previous research work on borate-autocausticizing and performance of numerous in-house experiments. A large research program started examining the effects of borates on various processes in kraft pulping and chemical recovery. The program involved several independent research groups such as Econotech Services Inc., Vancouver, BC, Western Michigan University, Kalamazoo, MI, Institute of Paper Science and Technology, Atlanta, GA, Oregon State University, Corvallis, OR, and the University of Toronto.

Work by Econotech Services suggested that the use of borate might produce better quality pulp and pulp which shrinks less during bleaching. The study at the University of Toronto shows that in air, sodium borates can react with molten Na_2CO_3 at any Na/B value, and that the reaction product is likely to be trisodium borate, $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ (or Na_3BO_3). These findings implied that partial autocausticizing with borate was now

technically feasible [8].

Autocausticizing Reactions

At the University of Toronto, researchers used dehydrated borax ($\text{Na}_2\text{B}_4\text{O}_7$) and dehydrated sodium metaborate (NaBO_2) as a source of borate. They prepared mixtures of Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ (or NaBO_2) with various Na/B values and the reaction was examined by means of simultaneous differential and thermogravimetric analysis (DTA/TGA). The researchers found that the decarbonization of Na_2CO_3 occurs according to Reaction 14 [8].



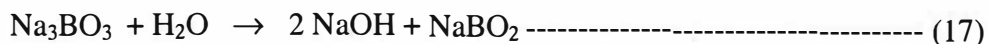
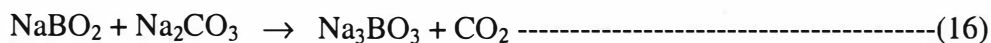
Na_3BO_3 was assumed to be the reaction product, Reaction 4, than $\text{Na}_4\text{B}_2\text{O}_5$ as was assumed by Janson, Reaction 12.



These studies implied that Reactions 14 and 15 can occur at any Na:B molar ratio, and the reaction product is Na_3BO_3 . These conclusions contradicted the original findings by Janson [7], which suggested that reaction product is $\text{Na}_4\text{B}_2\text{O}_5$ (Reaction 12); that the reaction will be severely hindered if the Na/B value of the reactants is greater than 1.5; and that it will not even occur if Na/B is greater than 3 [8].

Implications

The overall autocausticizing reactions can therefore be summarized as follows:



This reaction sequence suggests that only half a mole of borate is needed to produce one mole of NaOH in the liquor system. This is important because the amount of borate required would be half of that needed for the reaction sequence suggested by Janson, Reactions 12 and 13. Therefore if Reactions 16 and 17 can be fully attained, the amount of borate deadload in the system would be reduced by half. This, in turn, would significantly lower the black liquor viscosity and reduce other potential effects caused by borate [8].

The fact that Reaction 16 can occur at any Na:B molar ratio implies that partial autocausticizing is technically feasible and it requires less borate. For mills that require incremental causticizing capacity this seems to be an attractive alternative. However before this technology could be implemented the effect of borate in various causticizing process should be examined thoroughly.

Conventional Causticizing after Partial Borate Autocausticizing

With partial borate autocausticizing, only part of the sodium carbonate reacts with sodium metaborate to produce sodium hydroxide as per Reactions (16) and (17), in the recovery furnace and the rest of the conversion takes place through the conventional lime cycle. Mill trials report an increase in the causticizing efficiency through partial borate autocausticizing. One of the objectives of this research would be to determine those reaction conditions where an increase in causticizing efficiency through partial borate autocausticizing is observed.

CHAPTER IV

OBJECTIVES

The primary objectives of this research are as follows:

1. To measure the activity of commercial burnt lime (CaO).
2. To conduct the conventional causticizing reactions at different temperatures, concentrations, lime additions and borate levels, to gain confidence in running the causticizing reactions by comparing the results with previously published ones.
3. To study the effect of metaborate addition on causticizing rate and equilibrium of conventional causticizing reactions without simulating autocausticizing.
4. To simulate borate autocausticizing and to study its effect on the causticizing reaction rate and equilibrium at mill conditions of concentration, sulfidity, and temperature.
5. To vary the extent of autocausticizing, to study its effect on the causticizing reaction rate and equilibrium following borate autocausticizing.

CHAPTER V

EXPERIMENTAL

Experimental Reagents

Synthetic green liquor was prepared using reagent grade sodium sulfide, sodium metaborate, industrial burnt lime, sodium hydroxide, and de-ionized water. The commercial burnt lime was obtained from one of the pulp mills and reactivity of the lime was measured according to TAPPI test method T617 cm-84. The burnt lime was crushed finely in a mortar before it was introduced in the system. The grounded lime was stored in air tight containers to prevent any oxidation.

Experimental System

The experimental system used for the study was as shown in Figure 5. It consisted of a reaction vessel, a temperature probe, thermocouples, vapor condenser, heater with variable temperature and variable magnetic stirring and a custom made needle/filter attachment to obtain samples from the reaction system.

Figure 5 shows the experimental system used for the study. The reaction vessel used for the causticizing reactions as shown in Figure 5 was a 1L three-necked round-bottomed flask. This particular reaction vessel was chosen after carefully considering the variables and the parameters that had to be measured and monitored throughout the system. Since the reaction vessel was limited in size, the total volume of the reactants was always kept close to or less than 1L.

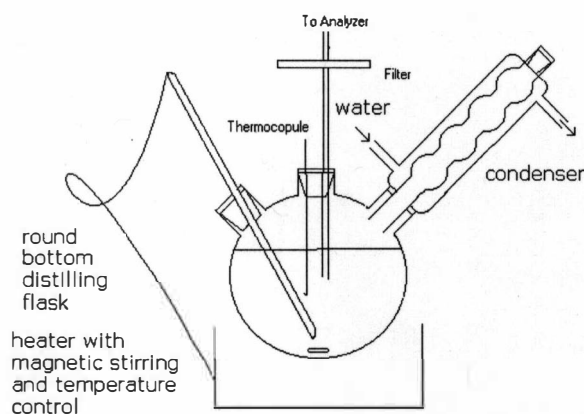


Figure 5. Experimental System.

One of the necks was fitted with a vapor condenser to condense any vapor that was produced during the reaction and hence to avoid any change in the concentration of the liquor under study by preventing the escape of any vapors. The other neck had a temperature probe fitted, which was connected with the heater to maintain the set temperature throughout the reaction. The last neck had two thermocouples connected to the computer through a DAQ board to monitor and measure the temperatures throughout the reaction using Microsoft Excel. The code for acquiring and recording the temperature was written in Visual Basic and the same was used for this study. The neck was also fitted with a custom made fitting to remove samples from the reaction system for further analysis in a titrator. Since sample to be used in the titrator has to be free of any suspended lime particles, it has to be filtered simultaneously while removing it from the reaction system. A special needle/filter attachment was designed for this purpose. The fitting consisted of a long surgical needle with deflected tips from Cole-Parmer Instrument Company fitted with an inline Acrodisc syringe filter with a pore size of $5\text{ }\mu\text{m}$, membrane diameter of 32mm and effective filtering area of 5.8 cm^2 ordered from the same company. This inline filter attachment aided in filtering the sample of any suspended lime particles even while drawing it from the reaction system. A 20 ml laboratory purpose disposable syringe was used in removing the sample using the

needle/filter attachment. The filters had to be changed after every 2 filtrations since the suspended lime particles plugged the pores of the membrane.

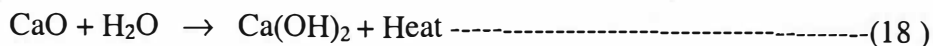
The heater in which the reaction vessel was seated was ordered from Cole-Parmer Instrument Company. It had variable heating with temperature ranges of 0 and 200° C. It also had an inbuilt magnetic stirring with options to vary the stirring rate between 0 and 1000 rpm.

The setup by itself was totally unique to run the causticizing reaction in the laboratory and with the flexibilities to vary reaction parameters such as the temperature and the mixing. The inline filter method used in obtaining the samples from the reaction system was unique too. So far there have been no reports on the use of such a design to run the causticizing reaction in the laboratory.

Experimental

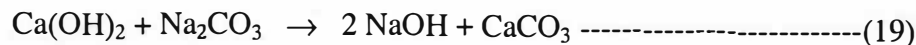
A typical slaking/causticizing reaction was carried out as follows: A known volume of green liquor was prepared using the reagent grade chemicals such as the sodium carbonate, sodium sulfide, sodium metaborate, and sodium hydroxide by dissolving it in deionized water in a tightly closed round-bottomed flask using a magnetic stirrer. The stirring aids in the uniform mixing of the system throughout the experiment and also to maintain uniform temperature distribution throughout the system. The mixing greatly influences the rate of slaking, causticizing and settling [5]. The stirring rate was always kept at 200 rpm for all the runs during slaking and causticizing to ensure uniform temperature in the liquor and to prevent any settling of the lime particles. The reaction mixture simulates the actual contents of green liquor in a causticizer. A known volume of green liquor was withdrawn from the sample and kept aside for later analysis. The contents are heated in a hot plate with a rheostat to 5 to 10 degrees centigrade less than the target temperature since the slaking reaction is highly exothermic, reaction and it

heats up the system to the target temperature.



Once the system reaches the desired temperature freshly ground stoichiometric commercial burnt lime was introduced into the system using a funnel through one of the openings and, after addition, the opening was tightly closed.

The slaking reaction, Reaction 18, which follows the lime addition, increases the temperature of the system by 5 to 10 degree centigrade to reach the target temperature and is maintained at this point throughout the course of the reaction by the heater thermostat. The reaction is timed once it reaches the target temperature. The sodium carbonate in the green liquor reacts with lime to form sodium hydroxide. The overall reaction can be written as follows:



Samples were removed at 5 min intervals through one of the openings using a 20 ml syringe fitted with a needle/filter attachment. The filter attachment aids in the simultaneous filtering of the sample. A syringe with a volume much larger than needed was used to prevent any plugging of the coarse particles at the mouth. Between sampling, the opening was sealed with a rubber cork. Reaction time of 70 to 90 minutes was selected because it corresponded to the mean residence time of the lime in the causticizers in the mills.

The samples were cooled instantly in an ice bath to arrest any further reaction and later analyzed at room temperature using a Metrohm Dosimat titrator, provided by the US Borax Inc. The Dosimat titrator is a variant of the ABC titration according to TAPPI Standard Method T624 os-68 to determine the amounts of carbonate, hydroxide, borates and sulfides. Three repetitions were performed at each sample point and the mean value is

taken for the calculations. The standard deviation of the repetitions was kept at a minimum and the values were tabulated in an Excel sheet. The progress of the reaction can be monitored by following the carbonate conversion, which is numerically equivalent to the causticizing efficiency [4].

The causticizing efficiency at each sample point was calculated using the following formula:

$$\text{Causticizing Efficiency:} = \frac{\text{NaOH}}{\text{Na}_2\text{CO}_3 + \text{NaOH}}$$

The rate and the equilibrium of each causticizing reaction were followed by calculating the causticizing efficiency at each sample point and the comparisons were made by plotting the values for control run against the test run.

CHAPTER VI

METHODOLOGY

The methodology followed in this study can be categorized into three phases. They are as follows:

Phase 1

The first step in phase 1 was to measure the lime activity (% CaO) of the commercial burnt lime, obtained from the industry to be used in all the calculations involving lime addition. The primary objectives of phase 1 experiments were to develop a good idea in running the conventional causticizing experiments and to gain confidence in varying the reaction parameters and authenticity of the data obtained.

This was achieved by conducting several runs of the causticizing reactions at different temperatures, concentrations, lime additions and studying the causticizing reaction rate and equilibrium. The data obtained were compared with previously published results to verify the experimental approach and to develop confidence in performing the experiments for the study.

Phase 2

The objective of phase 2 experiments was to study the effect of borate on the causticizing reaction without simulating autocausticizing. The interest was in looking at any possible changes in the causticizing reaction rate and equilibrium due to the presence of borate in the reaction. The effect was studied at an optimum autocausticizing level that

is being investigated in the mills.

The next step was to introduce sodium sulfide in the system to study its effects on causticizing reaction and equilibrium. The effect was studied on the conventional causticizing reaction and the data were compared with the previously published results.

Phase 3

The objectives of phase 3 experiments were to simulate borate autocausticizing and to study its effect on the causticizing reaction rate and equilibrium at mill conditions of temperature, concentration and sulfidity. Borate autocausticizing is simulated by the addition of sodium metaborate and sodium hydroxide into the reaction system and reducing the equivalent amount of sodium carbonate. The effect was studied at two different sulfidity levels, three different autocausticizing levels and two different temperatures. The data were compared with that of the conventional causticizing reaction.

CHAPTER VII

RESULTS AND DISCUSSION

The available CaO in the commercial burnt lime was determined potentiometrically by a titration with HCl. Samples were prepared according to a standard TAPPI test method T617 cm-84. The activity of the lime was found to be 85.833%. The lime activity was kept at 85.833% for the entire study and was tested for its reactivity from time to time.

The next step was to run the conventional causticizing reactions at different conditions. The following table summarizes the experimental conditions that were followed in the research and it was designed in such a way as to delineate the effects due to concentration, temperature, sulfidity, and borate levels. Table 1 presents the experimental conditions followed in the study.

Figure 6 shows the causticizing efficiency against time for a conventional causticizing reaction run at 60° C and 70.17 g/L Na₂O TTA and 86% stoichiometric lime addition. Refer to Appendix A for the experimental conditions, mean titration values, and causticizing efficiencies.

As mentioned earlier in the experimental part the contents of the simulated green liquor are heated to 5 to 10° C less than the target temperature. Once the lime is added the slaking reaction increases the reaction temperature and sets it at the target temperature. This temperature is maintained throughout the experiment with the aid of a heater thermostat with variable temperature settings.

Table 1. Experimental Conditions Followed in Conducting the Causticizing Reactions.

Run. No	Target	Na ₂ CO ₃	Na ₂ S	NaBO ₂	NaOH	TTA	CaO	Water
	Temp. °C	g/L as Na ₂ O	g/L as Na ₂ O	g/L as Na ₂ O	g/L as Na ₂ O	g/L as Na ₂ O	grams	In ml
1	60.00	70.17	0.00	0.00	0.00	70.17	55.99	800.00
2	60.00	77.50	0.00	0.00	0.00	77.50	65.24	800.00
3	80.00	77.50	0.00	0.00	0.00	77.50	65.16	800.00
4	70.00	77.50	0.00	0.00	0.00	77.50	65.17	800.00
5	70.00	77.50	0.00	10.85	0.00	77.50	65.17	800.00
6	70.00	120.00	0.00	0.00	0.00	120.00	101.01	800.00
7	70.00	120.00	0.00	21.00	0.00	120.00	101.02	800.00
8	70.00	76.21	0.00	21.00	41.96	118.19	65.66	800.00
9	95.00	120.00	0.00	0.00	0.00	120.00	101.02	800.00
10	95.00	77.97	0.00	21.00	41.99	120.00	65.70	800.00
11	95.00	77.97	0.00	0.00	41.99	120.00	65.70	800.00
12	95.00	84.00	36.00	0.00	0.00	120.00	70.72	800.00
13	95.00	54.60	36.00	14.70	29.40	120.00	45.96	800.00
14	95.00	102.00	18.00	0.00	0.00	120.00	86.37	800.00
15	95.00	67.06	18.00	19.98	36.11	120.00	56.45	800.00
16	95.00	63.00	36.00	19.98	21.00	120.00	53.03	800.00
17	95.00	71.40	36.00	12.60	12.60	120.00	60.11	800.00

The samples withdrawn every 5 minutes from the reaction system is cooled to room temperature and analyzed in a Dosimat titrator, which is a variant of the ABC titration test to measure hydroxide, carbonate, sulfide and borate ions. The results are tabulated and the mean and standard deviation of the measured hydroxide, carbonate and sulfide are calculated. The causticizing efficiency is calculated using the following formula:

$$\text{Causticizing Efficiency} = \frac{\text{NaOH}}{\text{Na}_2\text{CO}_3 + \text{NaOH}}$$

The calculated causticizing efficiency was plotted against time to study the causticizing rate and equilibrium. As it can be seen clearly from Figure 6, the reaction never goes to completion but rather reaches equilibrium. The overall equilibrium reaction can be written as,

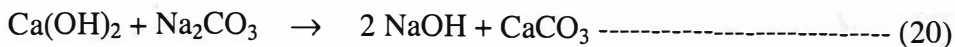


Figure 6 shows an equilibrium causticizing efficiency of 92.5% which compares very well with the published results for a TTA of 70.17 g/L as Na₂O. Since this was one of the first experiments ever tried on the designed experimental system, there were certain difficulties in controlling the reaction temperature at the exact target point.

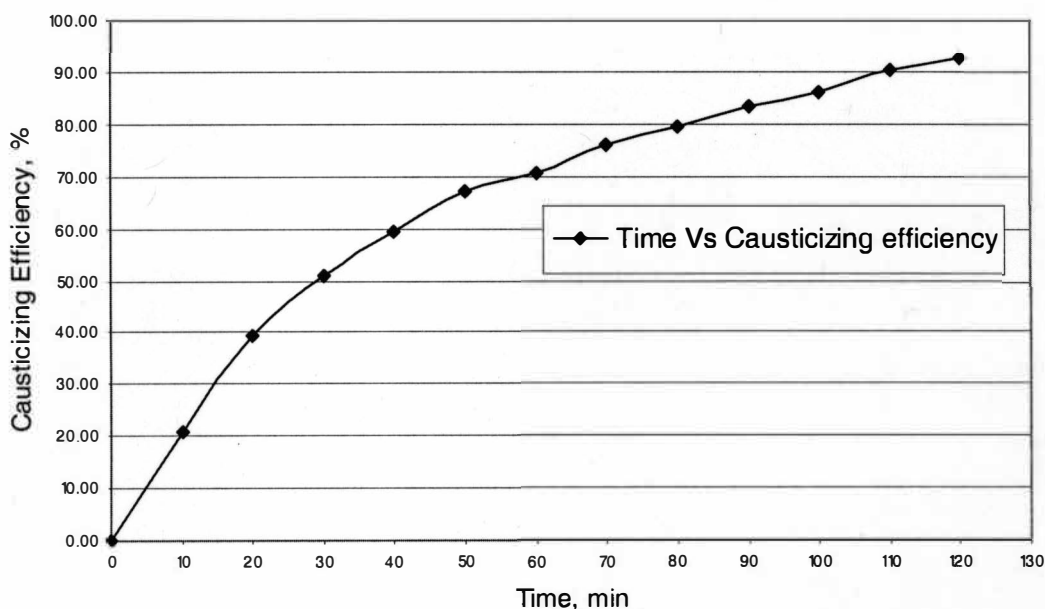


Figure 6. Effect of Time on Causticizing Efficiency for Run 1 at 60 °C and 70.17 g/L as Na₂O TTA and 86 % Stoichiometric Lime Addition

The reaction was repeated at the same temperature but the TTA was increased to 77.5 g/l Na₂O and the lime addition was 100% by stoichiometry.

Figure 7 shows the plot of causticizing efficiency versus time for run 2. The experimental conditions and results are provided in appendix B. This run shows an increase in the causticizing efficiency to 95.91%. It can be seen from the table that 95.91% causticizing efficiency was achieved only at 70.12 °C and the efficiency was

87.46% at 62.1 °C, which actually compares with previously published results. The difference can also be accounted on the increase in lime addition. These first few experiments gave a good idea on conducting the causticizing and varying the parameters such as the TTA, lime addition and the temperature.

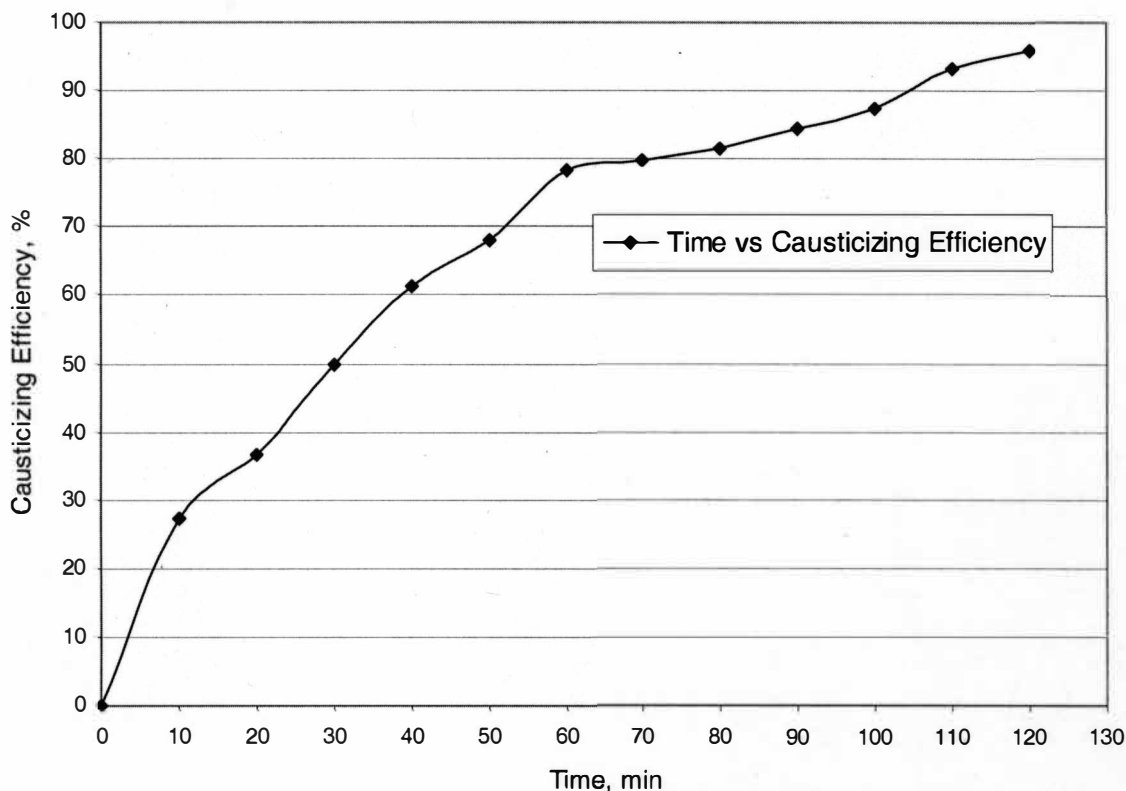


Figure 7. Effect of Time on Causticizing Efficiency for Run 2 at 60 °C and 77.5 g/L as Na_2O TTA and 100% Stoichiometric Lime Addition

Effect of Temperature on the Causticizing Reaction Rate and Equilibrium

Works done by Lindberg and Ulmgren [6] show that the reaction rate increases by 2 to 3 times for a 20 °C increase in temperature. Two experiments were performed at 70 °C and 80 °C at a TTA of 77.5 g/L as Na_2O . The plot of causticizing efficiency on time

was compared to find the effect of temperature on the causticizing rate and equilibrium.

Figure 8 shows the comparison plots for run no.2, 3 and 4. The experimental conditions are provided in appendix B, C and D. The equilibrium causticizing efficiency for the reaction at 60 °C was 95.9%, 70 °C was 97.3% and for 80 °C was 97.1%. It is evident from figure 8 that there is an increase in the causticizing reaction rate in reaching the equilibrium. Hence the data agrees with the works of Lindberg and Ulmgren. This provides confidence and authenticity in the data obtained and the method followed in conducting the reaction.

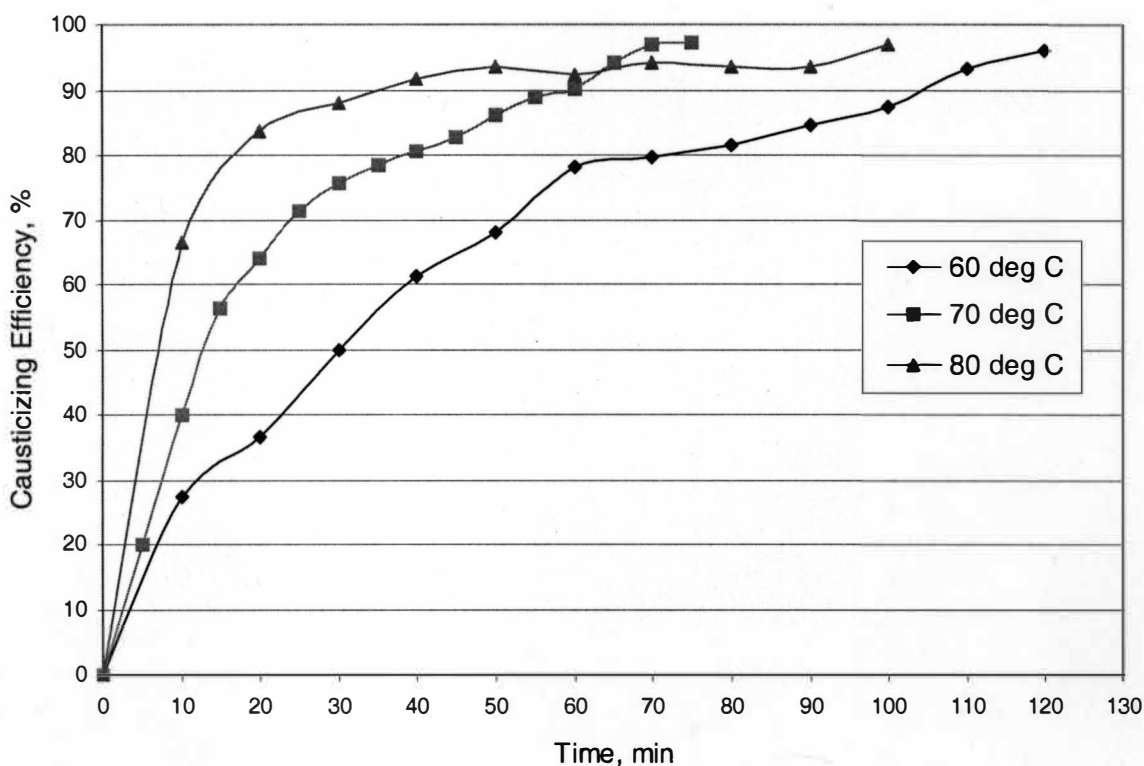


Figure 8. Effect of Time on Causticizing Efficiency for Runs 2, 3 and 4 at 60 °C, 70 °C and 80 °C Respectively and 77.5 g/l Na₂O TTA (Appendix B, C, D)

The effect of temperature was also studied at 70 °C and 95 °C by conducting the causticizing reaction at 120 g/L as Na₂O TTA, which is in the mill range of TTA concentrations (110-135) g/L Na₂O. As shown in figure 9 the increase in causticizing

reaction rate and equilibrium causticizing efficiency is seen for the reaction run at 95 °C over the 75 °C reaction. All these results provide more confidence in the dependability of the data and the experimental system.

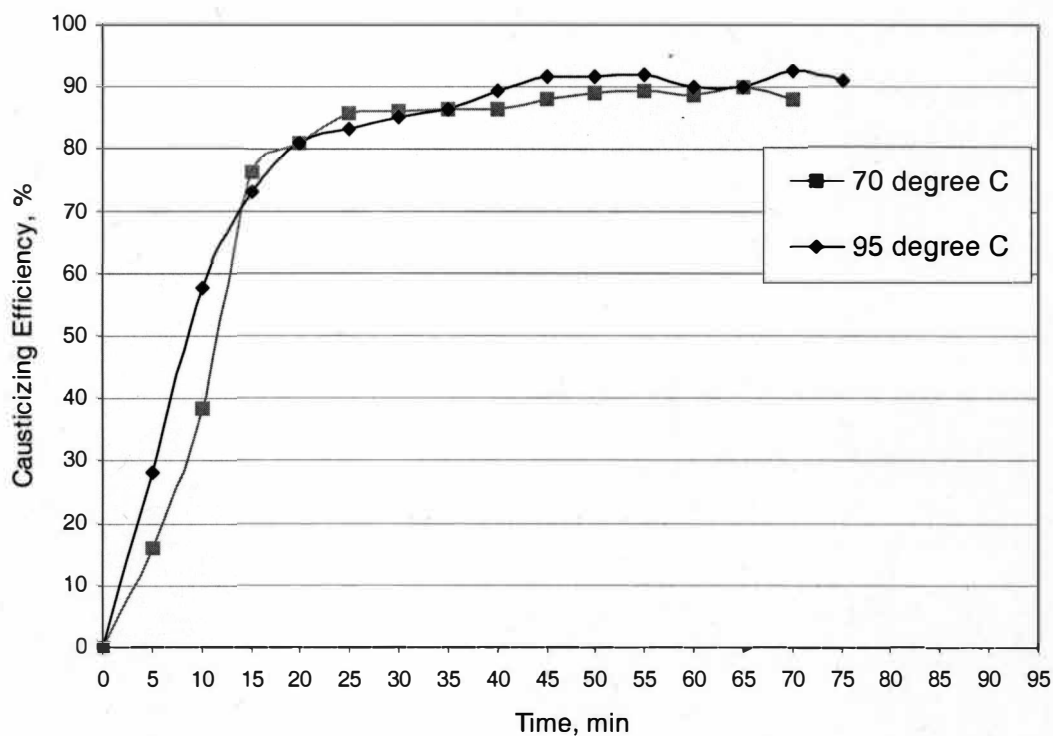


Figure 9. Effect of Time on Causticizing Efficiency for Runs 6 and 9 at 70 °C and 95 °C Respectively and 120 g/l as Na₂O TTA (Appendix F and I)

Effect of Concentration on the Conventional Causticizing Reaction Rate

Works of Dorris and Allen [3] suggest that the equilibrium causticity decreases by about 5% as the concentration is increased. To study this effect on concentration two runs were conducted at 70 °C and two different TTA's of 77.5 g/L as Na₂O and 120g/L as Na₂O.

Figure 10 shows the decrease in equilibrium causticizing efficiency as the TTA is increased from 77.5 g/L as Na_2O to 120 g/L as Na_2O .

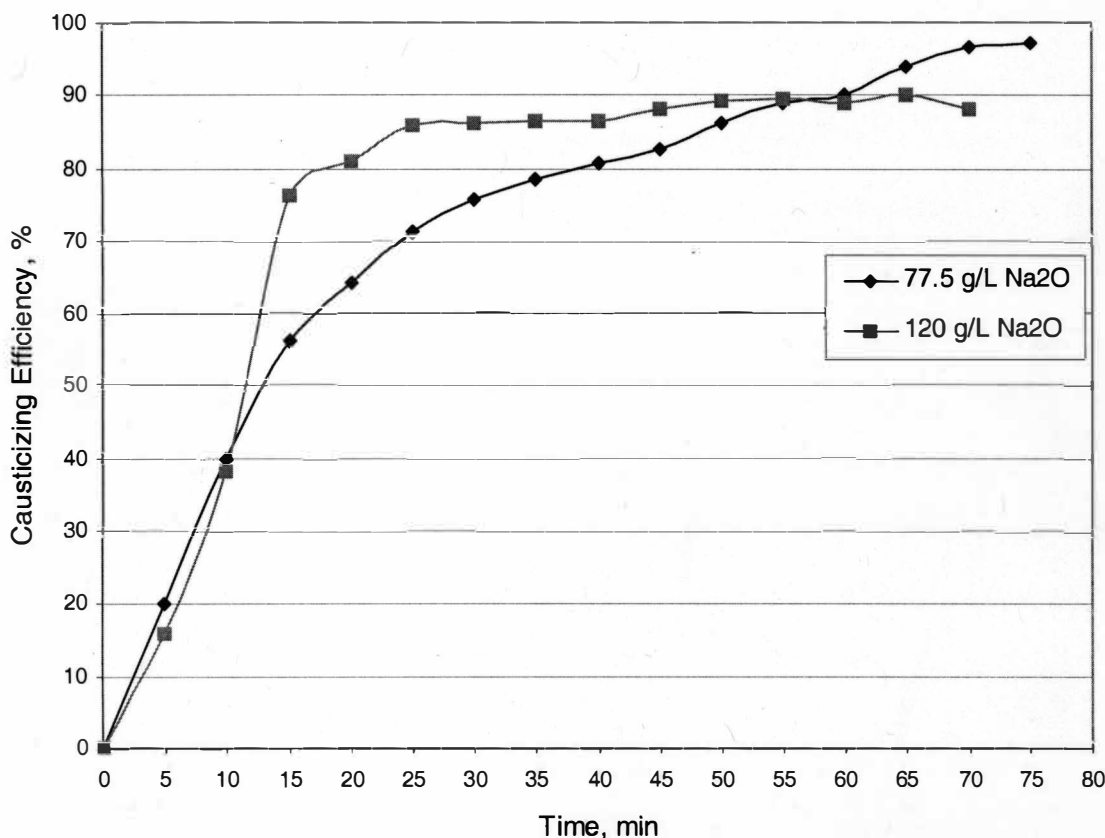


Figure 10. Effect of Time on Causticizing Efficiency for Runs 4 and 6 at TTA 77.5 g/l Na_2O and 120 g/l as Na_2O Respectively (Appendix D and F).

Effect of Borate Addition on the Causticizing Reaction Rate and Equilibrium

The primary objective of the research being the effect of borate on the causticizing reaction, the next phase of experiments was to study the effect of borate addition. The interest was to look at any possible changes in the causticizing equilibrium and rate due to the presence of borate.

Experiments were conducted without simulating autocausticizing but with the

presence of sodium metaborate in the system, i.e. without changing the amounts of other reagents but by just adding sodium metaborate into the system and were compared against the conventional causticizing reaction. Borate was introduced into the system at 35% and at two TTA levels of 70 g/l as Na_2O and 120 g/l as Na_2O at 70 °C.

In Figure 11 the causticizing efficiency was almost the same as the conventional one, except near the end. The surprising result of this experiment is that the presence of borate increased the equilibrium causticizing efficiency slightly. Though it was unexpected it might influence the final causticizing efficiency but both the temperature and TTA were relatively low.

Figure 12 appears to show that borate reduces the causticizing rate and equilibrium at 70 °C and 120 g/l TTA as Na_2O . The reason for the increase in the causticizing rate at 70 °C was very strange and has to be studied further.

Effect of Sulfidity on the Causticizing Reaction Rate and Equilibrium

Dorris and Allen also suggest that the causticizing rate and equilibrium decreases as the sulfidity increases [3]. Figure13 shows the causticizing curves for three different sulfidities of 0%, 15% and 30%, which was conducted in the conventional style. As seen the causticizing rate and equilibrium is less for 15% sulfidity than 0% and that for 30% sulfidity is below the two.

Effect of Borate Autocausticizing on the Causticizing Reaction

In the Figures 14 and 15 below, the borate autocausticizing is simulated by adding equivalent amounts of sodium metaborate, sodium hydroxide and reducing the sodium

carbonate and burnt lime.

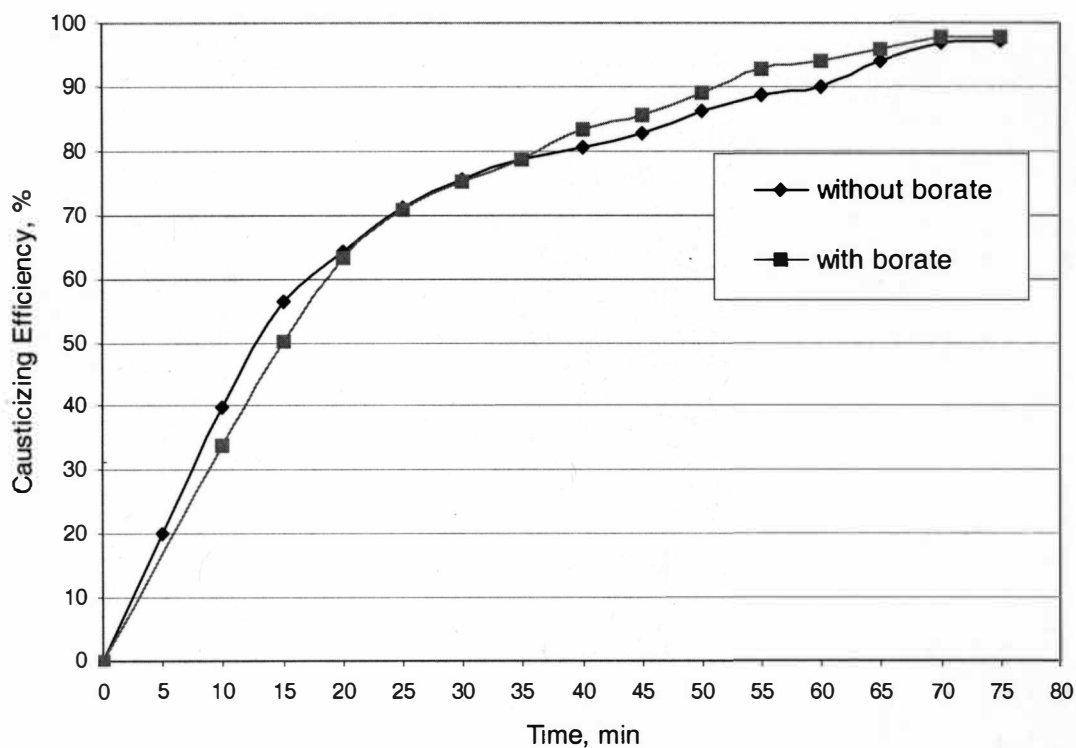


Figure 11. Comparison of Causticizing Reactions with and without Borate at 70 °C and 70 g/l Na₂O (Appendix D and E)

Figures 14 and 15 illustrate that the initial causticizing rates are high for borate based autocausticizing at 70 °C and 120 °C respectively, the final rates and equilibrium are less when compared to the conventional causticizing. This may be due to the higher initial hydroxide content of the borate based autocausticizing reactions.

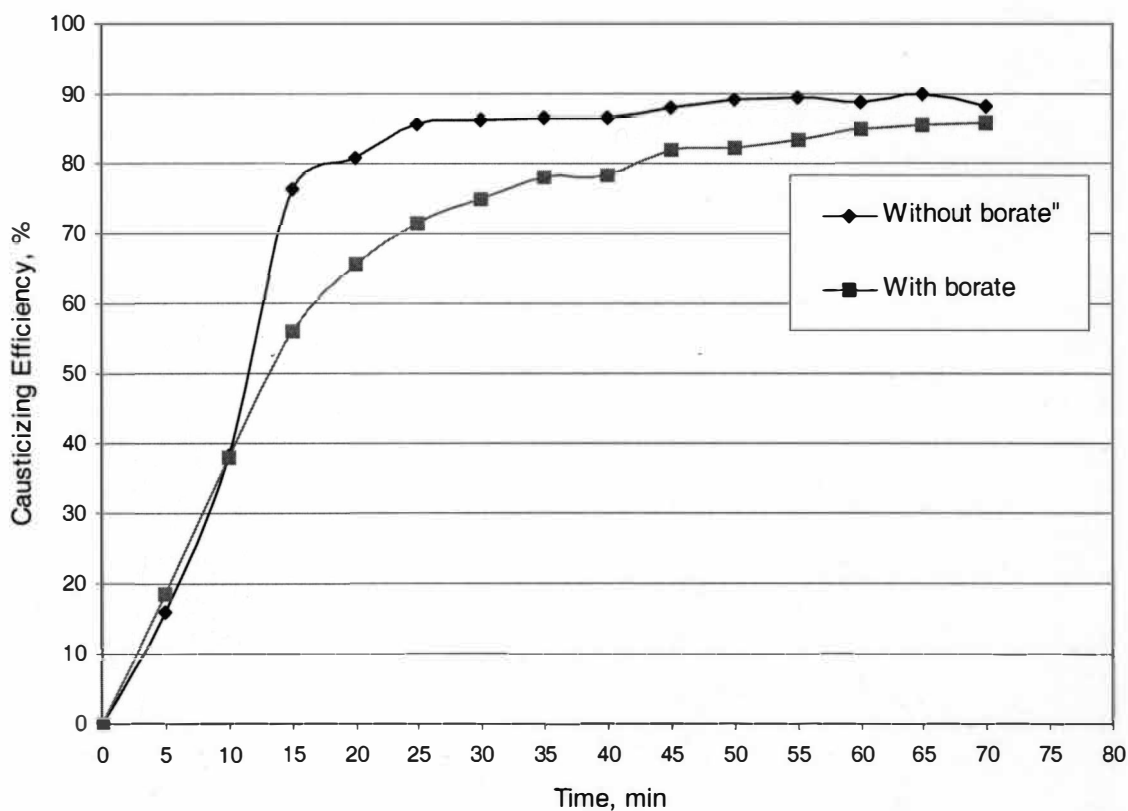


Figure 12. Comparison of Causticizing Reactions with and without Borate at 70 °C and 120 g/l Na₂O (Appendix F and G)

Effect of Initial Hydroxide Content

To study the increase in causticizing reaction rates before reaching equilibrium in the borate autocausticizing reaction, a run was conducted with the initial hydroxide but without the presence of borate in the system. This was to determine whether the increase in the rate was due to the presence of borate.

As it can be seen from Figure 16, the causticizing rate is more for 35% NaOH at the beginning and as the equilibrium is reached it slows down. This is very similar to the effect noticed in the borate based autocausticizing. Hence the increase in the causticizing rate before reaching equilibrium can be attributed to the higher initial hydroxide content

of the borate based autocausticizing reactions.

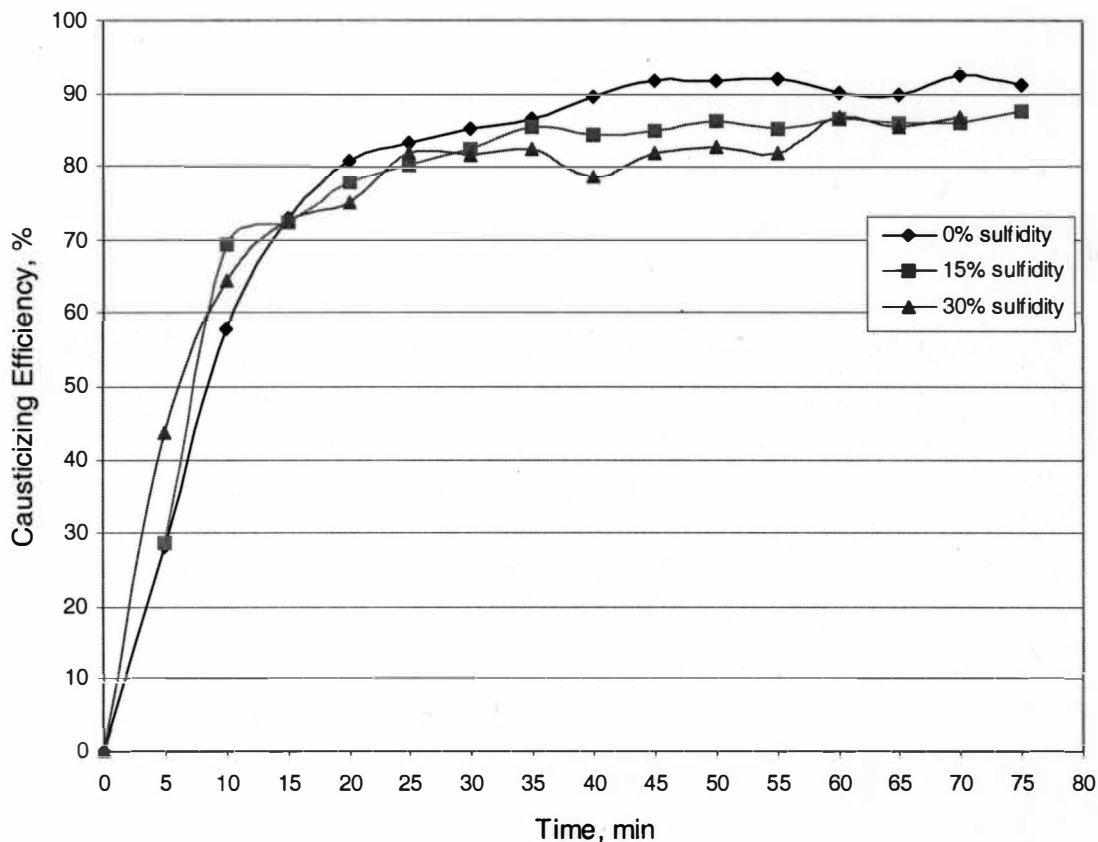


Figure 13. Effect of Time on Causticizing Efficiency for Runs 9, 12, 14 at 0%, 15% and 30% Sulfidities Respectively (Appendix I, L, N)

Effect of Temperature on Borate Autocausticizing

One concern about the causticizing reaction following borate based autocausticizing is that the temperature rise across the slaker will be less since the amount of burnt lime added into the system will be less. This temperature loss may have to be compensated by additional steam heating of the green liquor to ensure the completion of the causticizing reaction. Previously published results of Lindberg and Ulmgren [6] suggest that the causticizing efficiency is reduced at lower temperatures.

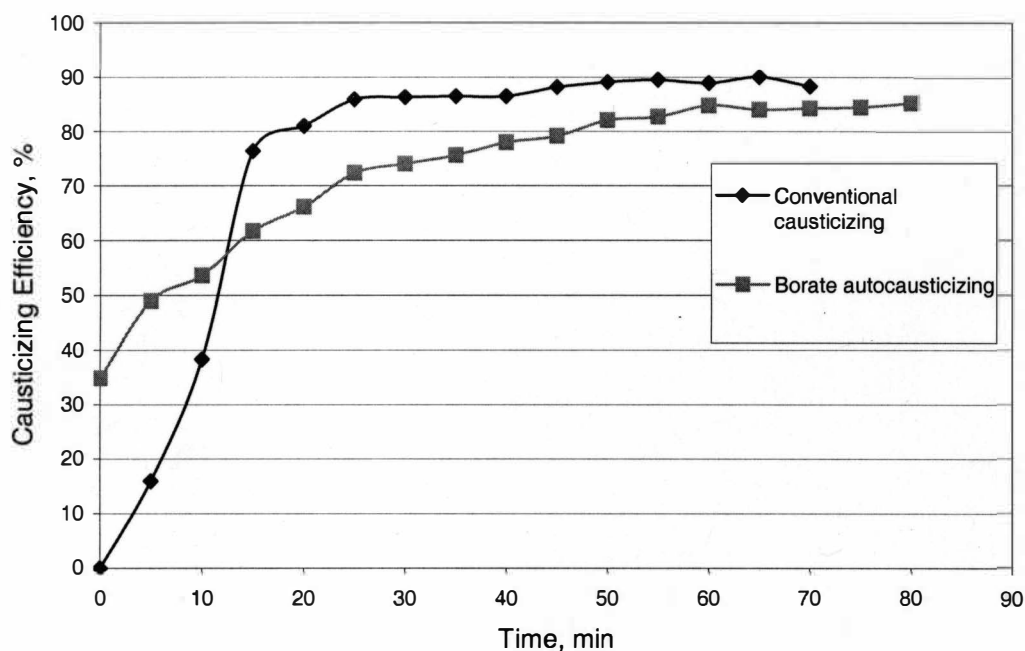


Figure 14. Effect of Time on Causticizing Efficiency for Conventional Causticizing and Borate Autocausticizing at 70 °C (Appendix F, H)

Figure 17 illustrates the borate based autocausticizing reactions at 70 °C. The plot clearly shows that the causticizing efficiency is lowered as the temperature is decreased to 70 °C. The effect is more pronounced on the causticizing reaction following partial borate autocausticizing than on the conventional causticizing as seen in the earlier figures. But this effect is seen only at 70 °C, which is a very low temperature for a causticizing reaction, and this shows that the temperature should be maintained following borate autocausticizing.

Comparison of the Causticizing Rate and Equilibrium for Typical Mill Conditions

One of the primary objectives of this research was to compare the causticizing rate and equilibrium for reactions with and without borate autocausticizing at typical mill

conditions. Figure 18 shows such a comparison.

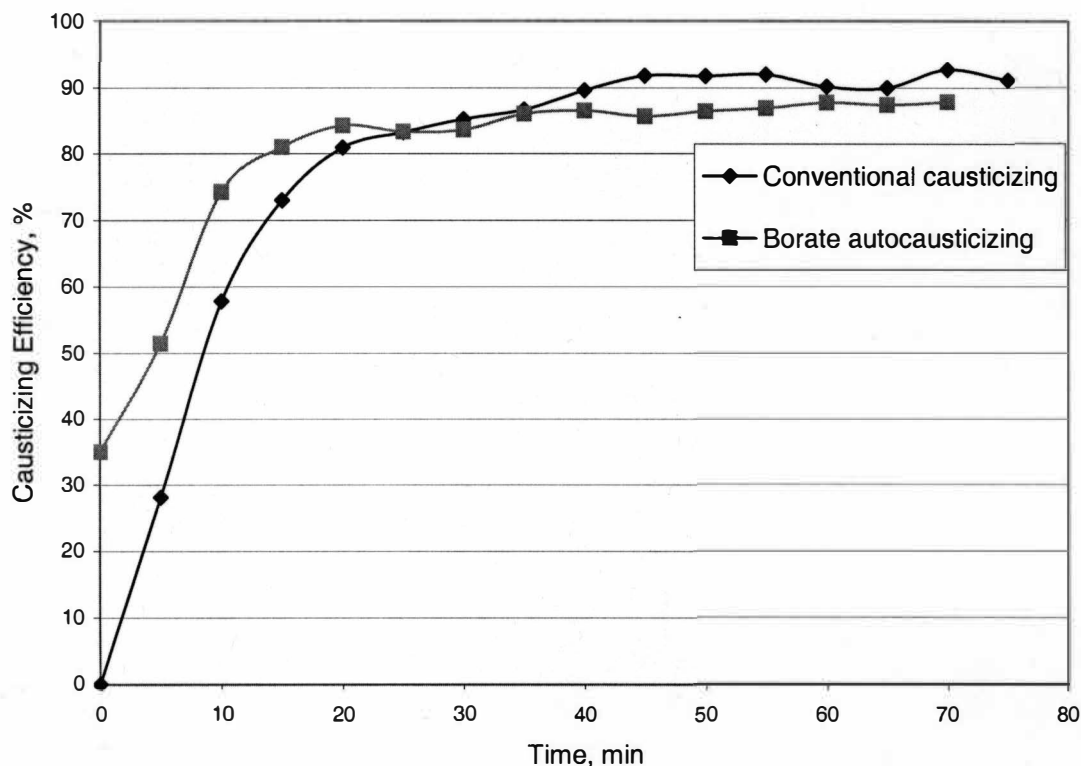


Figure 15. Effect of Time on Causticizing Efficiency for Conventional Causticizing and Borate Autocausticizing at 95 °C (Appendix I, J)

In this discussion the comparisons were made against simulated autocausticizing reactions. Autocausticizing is simulated by adding equivalent amounts of sodium hydroxide and sodium metaborate and reducing the equivalent amount of sodium carbonate that is being added into the system. This resulted in higher causticizing efficiencies before the equilibrium is reached since the initial causticizing efficiency is high due to the higher hydroxide content. The conditions shown in Figure 18 simulate typical mill conditions of 120 g/L as Na_2O TTA, 30% sulfidity, 100% stoichiometric lime addition and 95 °C, with and without borate autocausticizing.

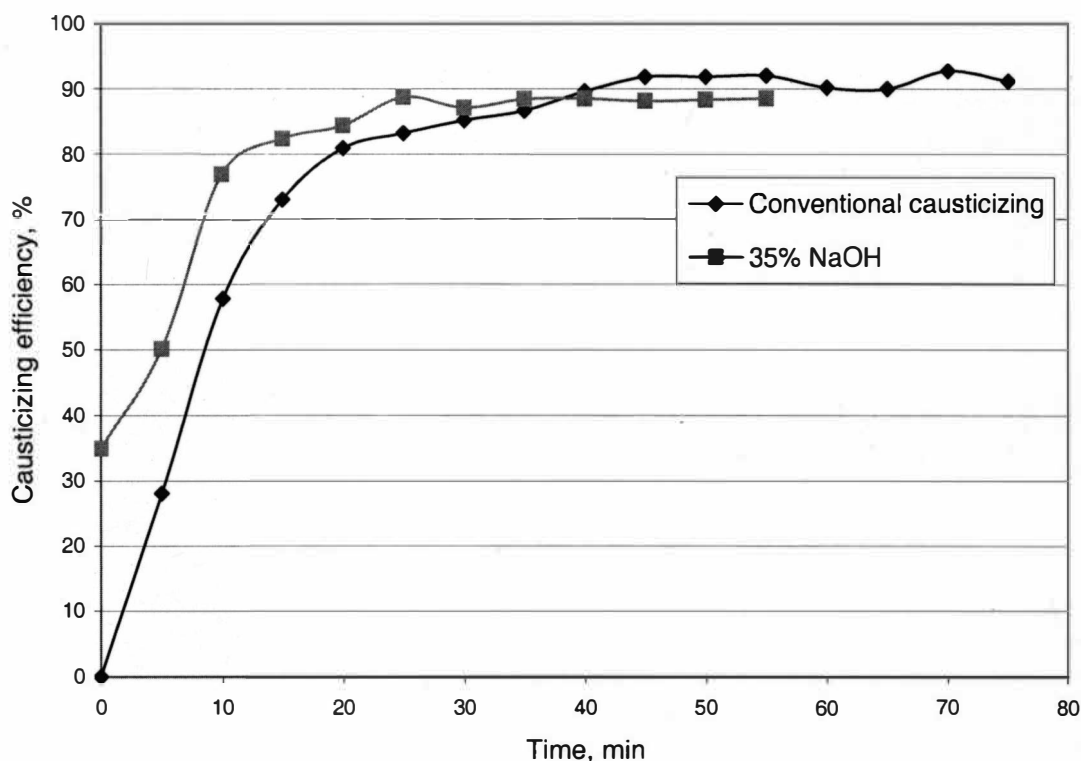


Figure 16. Effect of Initial Hydroxide Content on the Causticizing Rate and Equilibrium (Appendix I and K)

The autocausticizing level was maintained at 35%. The conditions shown in Figure 18 illustrates that the borate autocausticizing produces higher causticizing efficiencies compared to conventional causticizing, before the equilibrium is reached. This increase in causticizing efficiency is due to higher initial hydroxide level of the borate causticizing reaction. At equilibrium both the reactions reach 87% causticizing efficiency. This data also matches with the work done by Lindberg and Ulmgren, in which 87% causticizing efficiency is reached under the same conditions of 120 TTA, 30% sulfidity and 100 °C. The similarity of this data with the previously published results provides confidence in the accuracy of the results and the method followed in conducting the reaction.

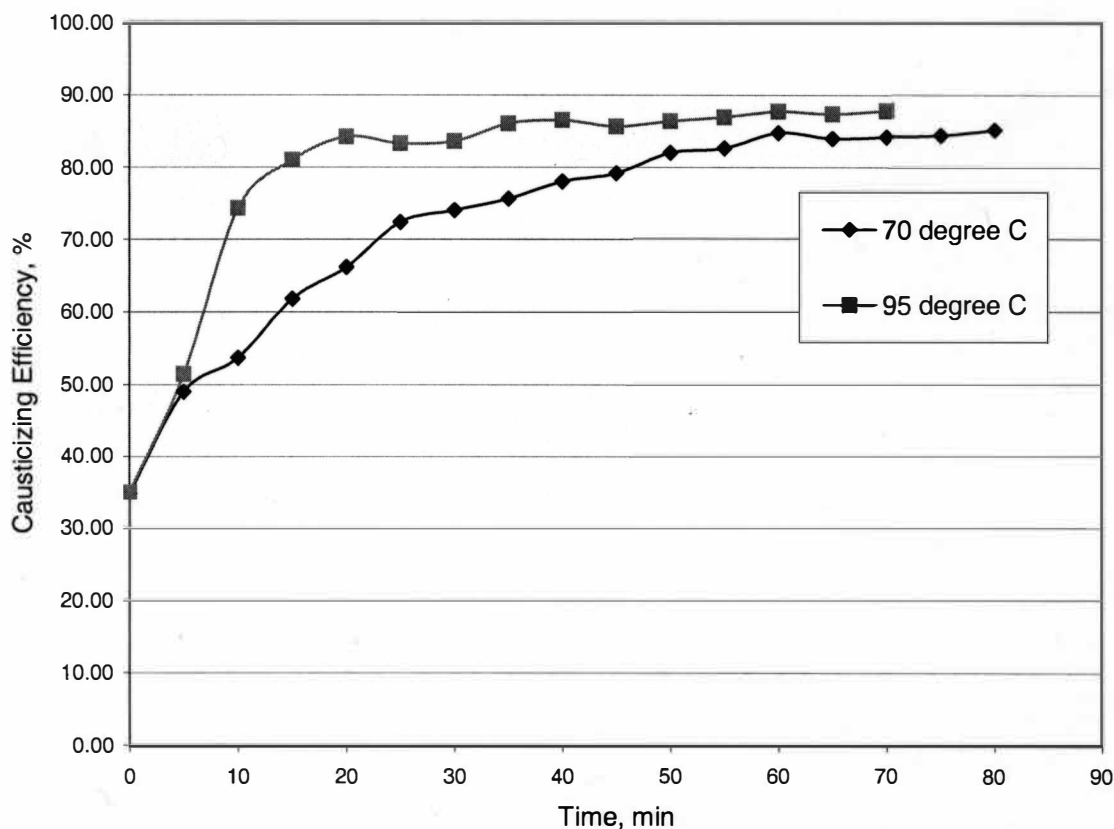


Figure 17. Effect of Temperature on Borate Based Causticizing Reactions (Appendix H, J)

As it can be clearly seen from the plots the borate autocausticizing produces higher causticizing efficiencies before equilibrium is reached. This can be a huge advantage to the mills in achieving better causticizing efficiencies compared to the conventional causticizing reaction since the reaction rarely reaches equilibrium in the mills for various reasons.

Though borate autocausticizing produces higher causticizing efficiencies before equilibrium is reached at typical mill conditions, there is a need to understand the effect of parameters like sulfidity and the extent of autocausticizing.

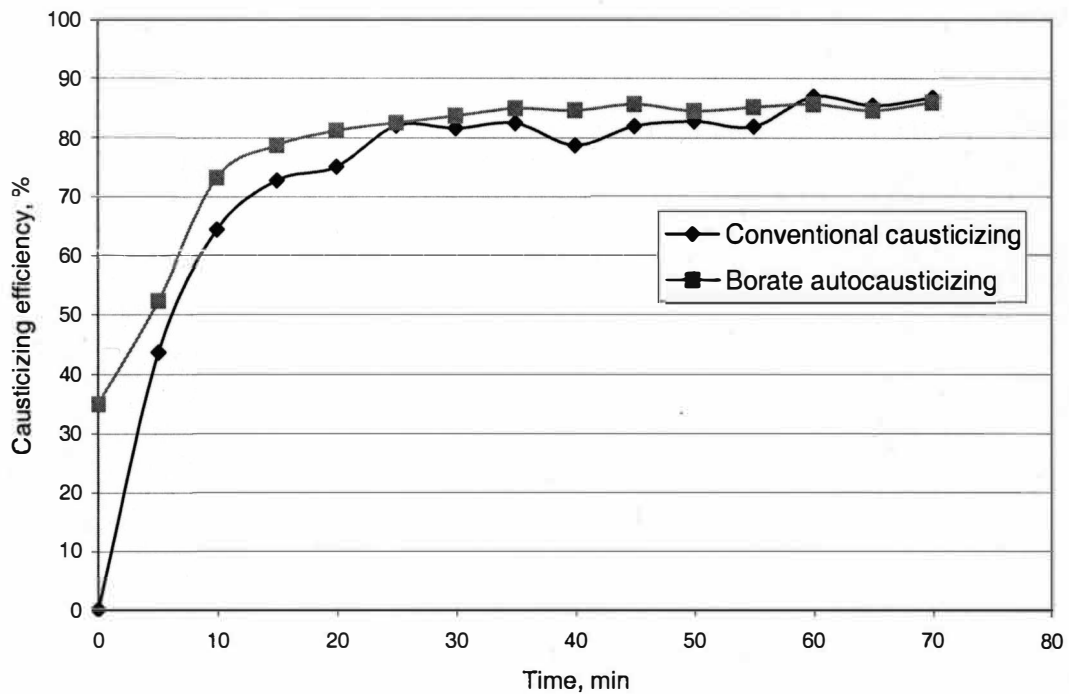


Figure 18. Comparison of Causticizing Reactions with and without Borate Autocausticizing (Appendix I and M)

Effect of Sulfidity on Causticizing Rate and Equilibrium at Mill Conditions

As illustrated in Figure 19 the effect of sulfidity on the causticizing rate and equilibrium is less pronounced for borate based causticizing reactions than the conventional ones. This is a strange and an unexpected effect, which may be due to the presence of borate in the system. This effect is not seen in the conventional causticizing runs. This has to be studied further to get a better insight.

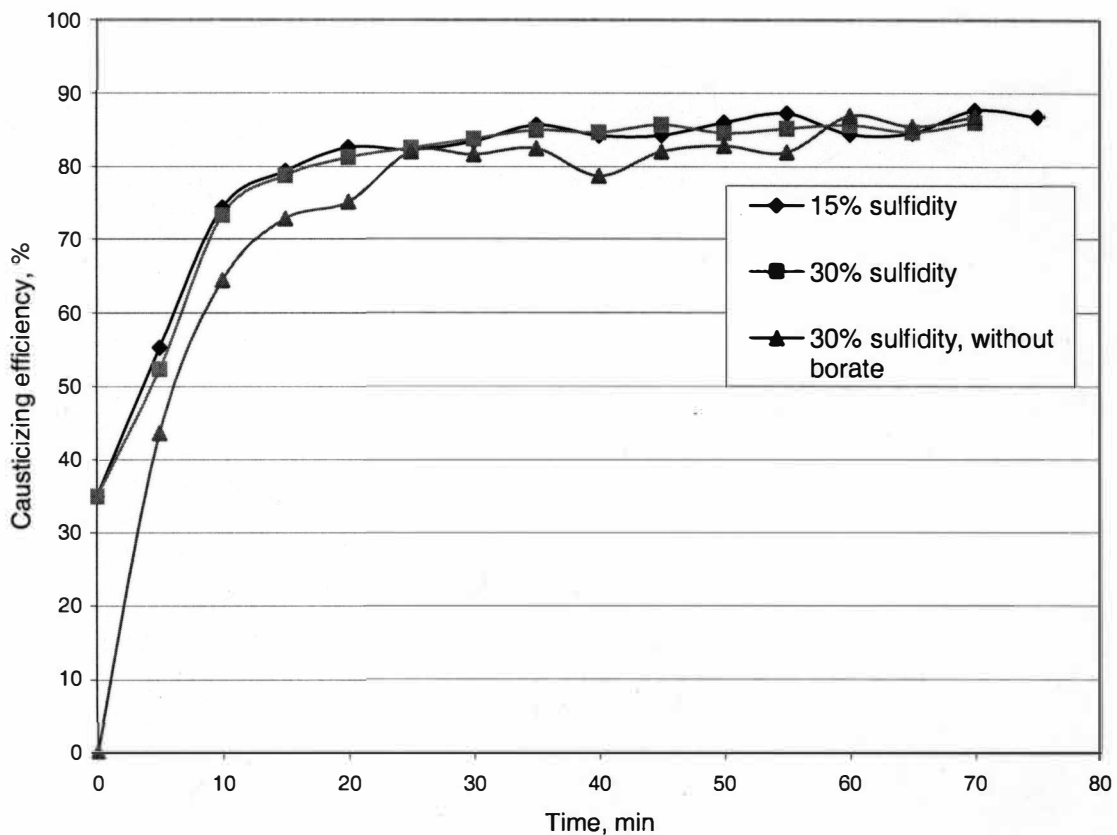


Figure 19. Effect of Time on Causticizing Efficiency for Causticizing Reactions at 0%, 15% and 30% Sulfidity Levels (Appendix L, M and O)

Effect of Autocausticizing Levels at Mill Conditions

Figure 20 shows the causticizing curves at different autocausticizing levels of 15%, 25% and 35% at typical mill conditions of 95° C, 120 g/L as Na₂O TTA and 30% sulfidity. It can be noticed that although the final equilibrium is higher at 15% level the initial causticizing rates and equilibrium is higher at 35% than 15% and 25%. In mills the reactions never run to equilibrium for various reasons and it is the initial increase in rate and equilibrium that really matters to increase the overall efficiency of the system. Hence 35% autocausticizing level is the most preferable.

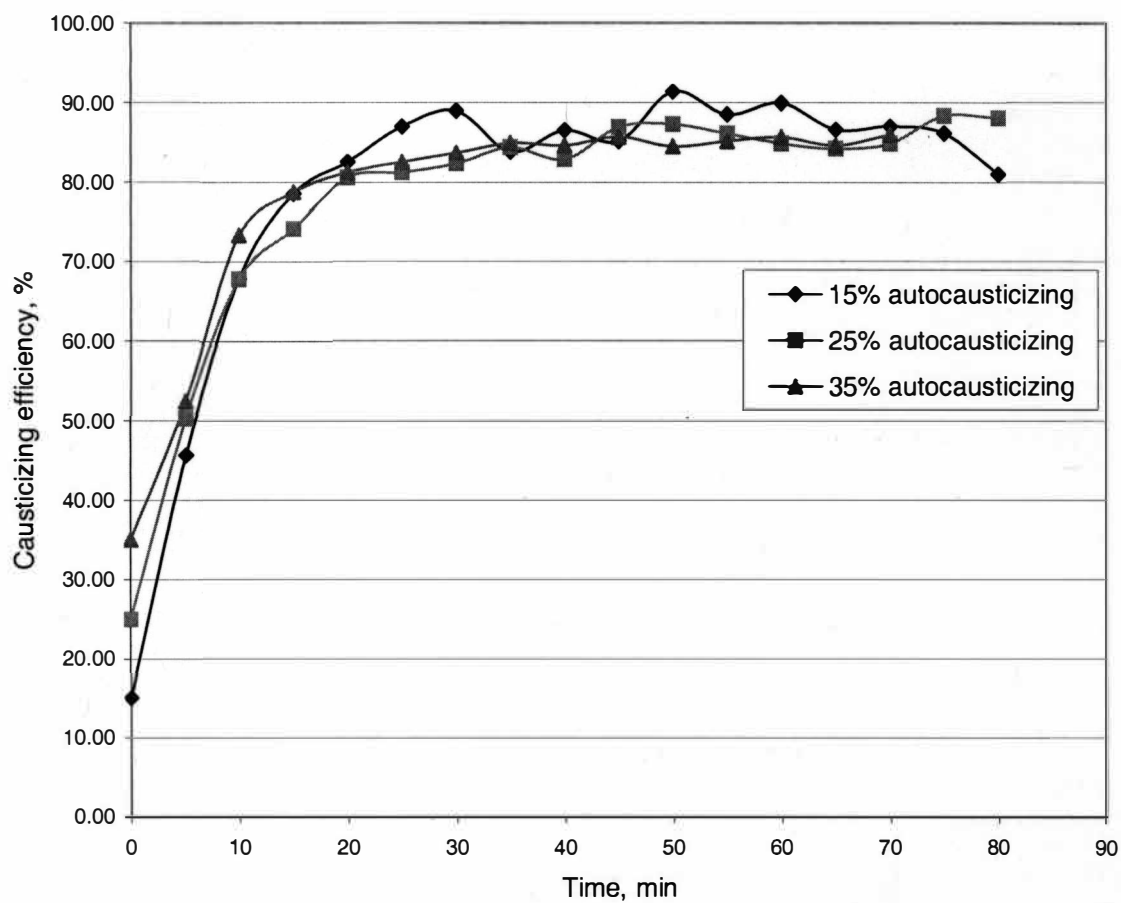


Figure 20. Comparison of Causticizing Rate and Equilibrium for the Causticizing Reactions at 15%, 25% and 35% Autocausticizing Levels (Appendix M, P, Q)

CHAPTER VIII

CONCLUSIONS

The major conclusions from this research can be summarized as follows:

1. The causticizing temperature is critical for both conventional causticizing and causticizing following borate autocausticizing. Since causticizing following borate autocausticizing uses less amount of burnt lime (CaO), the heat produced due to the slaking reaction is reduced and it is critical that the green liquor temperature is controlled through steam addition. If the green liquor temperature is allowed to decrease, a lower causticizing efficiency may be expected.
2. The addition of borate into the system at 70 g/l TTA and 70 °C without changing other reagents increased the causticizing rate and efficiency which is unexpected. The temperature and concentration are relatively low when compared with typical mill conditions. The same effect is not to be seen in the typical mill conditions of 120 g/l TTA and 95 °C.
3. The increase in causticizing efficiency with borate based autocausticizing results from the higher initial causticizing due to the hydroxide formation through autocausticizing. Since causticizing reactions in the mill rarely reach equilibrium and are rate limited, this provides a step increase in the initial causticizing efficiency and a higher final causticizing efficiency.
4. The effect of sulfidity on the reaction rate and equilibrium is less pronounced with the presence of borate in the system. This effect is unexpected and needs further investigation to get an insight.
5. 35% autocausticizing level seems to be the most preferable level of autocausticizing to get the benefits of initial increase in the causticizing rate and equilibrium.

APPENDICES

Appendix A
Experimental Run 1

Experimental Run. No. 1

Experimental Conditions

TTA = 70.17 g/L Na₂O

Target temperature = 60 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 86%

Starting Concentration

Na₂CO₃ = 70.17 g/L Na₂O

Burnt Lime = 55.9894 g/L Na₂O

Sample	Time	Temp	Mean		Standard Deviation		Causticizing
No.	min	deg.C	OH g/L	CO ₃ g/L	OH g/L	CO ₃ g/L	Efficiency %
			as Na ₂ O	as Na ₂ O			
Blank	0	67.58					0.00
1	10	67.84	14.01	52.58	2.06	0.68	21.04
2	20	65.82	23.24	35.49	1.05	4.46	39.57
3	30	62.13	31.84	30.47	0.89	1.54	51.10
4	40	60.21	35.46	24.11	1.85	0.47	59.53
5	50	59.82	42.39	20.8	1.67	1.97	67.08
6	60	60.92	45.1	18.79	1.67	2.43	70.59
7	70	60.62	49.18	15.45	1.57	2.71	76.09
8	80	61.92	55.77	14.36	1.86	2.32	79.52
9	90	60.08	55.76	10.95	3.71	1.72	83.59
10	100	60.88	57.44	9.17	0.71	0.78	86.23
11	110	60.48	54.3467	5.75	3.57	0.89	90.43
12	120	60.8	60.3467	4.84	2.13	1.67	92.58

Appendix B
Experimental Run 2

Experimental Run. No. 2

Experimental Conditions

TTA = 77.5 g/L Na₂O

Target temperature = 60 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting concentration

Na₂CO₃ = 77.5 g/L as Na₂O

Burnt Lime = 65.243 g

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean		Standard Deviation		Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	OH g/L	CO ₃ g/L	
Blank		60.72	-	-	-	-	0
1	10	61.13	21.92	58.30	0.60	2.57	27.32
2	20	60.25	28.98	50.23	3.34	3.49	36.59
3	30	61.25	38.64	39.07	1.50	1.87	49.72
4	40	60.17	45.94	28.92	1.74	2.67	61.37
5	50	61.33	52.38	24.54	1.94	1.31	68.10
6	60	60.21	49.47	13.77	1.94	3.10	78.23
7	70	62.29	60.33	15.37	3.15	1.18	79.70
8	80	60.98	64.33	14.49	4.98	3.10	81.62
9	90	60.58	66.34	12.16	3.54	4.45	84.51
10	100	62.10	71.49	10.25	4.39	1.73	87.46
11	110	64.49	79.78	5.81	17.42	2.96	93.21
12	120	70.12	73.72	3.14	4.57	0.18	95.91

Appendix C
Experimental Run 3

Experimental Run. No. 3

Experimental Conditions

TTA = 77.5 g/L Na₂O

Target temperature = 80 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 77.49 g/L as Na₂O

Burnt Lime = 65.16 g

Amount of water added = 800 mL

Sample	Time	Temp	Mean	Standard Deviation			Causticizing
No.	min	deg.C	OH g/L	CO ₃ g/L	OH g/L	CO ₃ g/L	Efficiency %
			as Na ₂ O	as Na ₂ O			
Blank	0	80.4	-	-	-	-	0
1	10	91.89	49.09	24.83	2.18	3.22	66.41
2	20	84.6	63.17	12.22	2.64	0.74	83.79
3	30	79.95	67.40	9.21	2.39	1.86	87.98
4	40	81.3	66.57	5.98	5.45	2.34	91.76
5	50	81.09	69.55	4.71	0.58	1.67	93.66
6	60	80.21	69.48	5.90	1.56	1.75	92.17
7	70	79.6	73.35	4.63	4.21	0.34	94.06
8	80	80.4	75.07	5.13	5.67	0.69	93.60
9	90	80.37	70.64	4.84	7.11	-	93.59

Appendix D
Experimental Run 4

Experimental Run. No. 4

Experimental Conditions

TTA = 77.5 g/L Na₂O

Target temperature = 70 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 77.4993 g/L as Na₂O

Burnt Lime = 65.1681 g

Amount of water added = 800 mL

Sample	Time	Temp	Mean		Standard Deviation		Causticizing
No.	min	deg.C	OH g/L	CO ₃ g/L	OH g/L	CO ₃ g/L	Efficiency %
			as Na ₂ O	as Na ₂ O			
Blank	0	70.50	1.88	74.37	-	-	0
1	5	74.38	14.75	58.60	1.63	0.84	20.11
2	10	77.42	29.18	43.91	1.38	1.17	39.92
3	15	76.05	43.00	33.39	1.80	1.37	56.29
4	20	73.75	49.51	27.71	1.38	1.61	64.12
5	25	71.18	54.20	21.82	3.18	2.92	71.30
6	30	69.58	55.47	17.82	0.73	0.53	75.69
7	35	69.42	57.94	15.82	0.51	0.37	78.55
8	40	69.15	60.93	14.62	1.51	1.57	80.65
9	45	68.99	63.19	13.20	3.18	2.64	82.72
10	50	68.79	64.12	10.33	1.39	2.51	86.12
11	55	68.42	66.43	8.33	2.06	3.44	88.86
12	60	68.10	67.36	7.39	1.17	2.38	90.11
13	65	67.79	67.82	4.29	2.38	1.85	94.05
14	70	67.69	68.41	2.25	1.51	1.48	96.82

Appendix E
Experimental Run 5

Experimental Run. No. 5

Experimental Conditions

TTA = 77.5 g/L Na₂O

Target temperature = 70 degree C

Sulfidity = 0%

Stoichiometric borate addition = 35%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 77.5014 g/L as Na₂O

Burnt Lime = 65.1656 g

NaBO₂ = 10.85 g/L as Na₂O

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean			Standard Deviation			Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	OH g/L	CO ₃ g/L	BO ₂ g/L	
Blank	0	70.58	0.84	68.88	2.16	-	-	-	
Borate	0	70.58	6.33	71.63	30.75	-	-	-	0.00
1	10	75.94	24.75	48.24	11.30	1.73	4.27	0.24	33.91
2	15	75.93	33.49	33.41	11.70	0.71	2.22	1.04	50.06
3	20	74.00	43.98	25.38	11.09	0.62	1.96	1.66	63.41
4	25	71.35	45.91	19.03	10.71	1.52	1.98	0.88	70.70
5	30	68.67	52.56	17.34	11.52	5.87	2.18	0.72	75.19
6	35	68.49	53.41	14.36	11.43	1.70	1.15	0.32	78.81
7	40	69.56	55.50	11.13	11.77	1.00	1.62	1.46	83.30
8	45	71.00	55.93	9.51	10.72	2.74	0.64	0.41	85.47
9	50	72.22	61.43	7.54	11.86	0.13	0.12	0.31	89.07
10	55	72.90	62.12	4.87	11.71	0.40	0.69	0.08	92.73
11	60	73.09	65.12	4.15	11.40	0.03		0.60	94.01
12	65	72.53	70.02	2.90	10.91	1.74		2.04	96.02
13	70	70.76	69.59	1.63	11.57	3.67	0.95	0.54	97.71
14	75	68.64	71.10	1.51	11.39	2.92	1.11	1.29	97.92

Appendix F
Experimental Run 6

Experimental Run. No. 6

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 70 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 120 g/L as Na₂O

Burnt Lime = 101.01g

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean		Standard Deviation		Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	OH g/L	CO ₃ g/L	
Blank	0	70.82			-	-	0
1	5	76.44	18.17	95.52	0.53	1.61	15.98
2	10	88.89	42.42	68.32	2.14	2.43	38.31
3	15	83.34	85.40	23.81	3.05	4.54	76.40
4	20	80.1	96.71	22.75	0.61	3.26	80.96
5	25	76.42	94.68	15.61	8.15	3.14	85.85
6	30	78.42	89.22	14.21	3.25	0.64	86.26
7	35	82.3	101.71	15.92	4.70	2.31	86.47
8	40	84.7	100.06	15.64	4.03	0.66	86.48
9	45	86.48	96.22	12.95	4.01	1.36	88.14
10	50	87.6	91.16	11.12	1.12	3.63	89.13
11	55	86	100.95	11.82	2.47	2.17	89.52
12	60	83.04	104.47	13.00	5.72	1.98	88.93
13	65	79.62	99.83	11.04	5.35	4.31	90.04

Appendix G
Experimental Run 7

Experimental Run. No. 7

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 70 degree C

Sulfidity = 0%

Stoichiometric borate addition = 35%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 120 g/L as Na₂O

Burnt Lime = 101.02 g

NaBO₂ = 20.995 g/L as Na₂O

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean			Standard Deviation			Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	OH g/L	CO ₃ g/L	BO ₂ g/L	
Blank	0								0
1	5	77.17	18.65	82.31	22.05	1.73	2.76	0.93	18.47
2	10	84.45	37.46	61.36	23.21	1.16	4.15	0.99	37.91
3	15	84.10	60.14	47.02	23.03	2.52	2.09	0.29	56.12
4	20	81.50	74.95	39.30	23.99	5.69	4.01	0.62	65.60
5	25	78.54	79.69	31.83	23.43	4.18	2.83	1.58	71.46
6	30	74.77	85.86	28.93	22.85	4.76	2.06	0.74	74.80
7	35	70.80	85.84	24.39	23.00	2.64	3.19	0.91	77.87
8	40	69.54	87.45	24.26	21.80	1.75	1.41	2.06	78.28
9	45	72.07	91.65	20.15	24.59	3.65	2.39	0.75	81.98
10	50	73.95	89.20	19.36	22.68	3.32	0.80	1.66	82.17
11	55	74.22	89.32	17.85	22.04	2.51	0.42	0.45	83.34
12	60	73.89	92.66	16.27	23.67	2.12	1.26	1.31	85.06
13	65	74.30	94.78	15.69	23.73	3.37	1.21	1.41	85.80
14	70	78.00	95.13	15.50	22.83	1.47	1.41	1.26	85.99

Appendix H
Experimental Run 8

Experimental Run. No. 8

Experimental Conditions

TTA = 118.19 g/L Na₂O

Target temperature = 70 degree C

Sulfidity = 0%

Stoichiometric borate addition = 35%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 76.21 g/L as Na₂O

Burnt Lime = 65.663 g

NaBO₂ = 20.9995 g/L as Na₂O

NaOH = 41.958 g/L as Na₂O

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean			Standard Deviation			Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	OH g/L	CO ₃ g/L	BO ₂ g/L	
Blank -1			40.85	72.81	1.90				
Blank -2	0		39.44	73.69	19.03				34.86
1	5	73.24	55.34	57.60	23.22	2.34	2.57	0.98	49.00
2	10	74.10	61.93	53.52	23.56	3.16	6.02	2.54	53.64
3	15	73.73	70.93	43.83	24.16	0.64	1.61	1.49	61.81
4	20	73.31	74.12	37.88	23.44	6.56	5.50	1.38	66.18
5	25	72.15	78.51	29.94	23.87	7.08	1.28	1.77	72.39
6	30	70.11	79.32	27.85	23.22	4.48	1.53	2.38	74.01
7	35	71.15	88.95	28.72	22.45	5.76	3.70	0.87	75.59
8	40	71.36	87.20	24.60	22.17	5.32	0.92	1.53	78.00
9	45	70.20	92.25	24.30	22.38	8.44	3.24	2.38	79.15
10	50	69.64	88.73	19.45	23.60	2.89	0.23	1.56	82.02
11	55	71.68	88.92	18.63	22.65	4.12	0.45	0.58	82.68
12	60	71.66	91.09	16.36	22.99	5.07	1.96	0.89	84.77
13	65	70.17	86.24	16.43	21.03	1.14	0.68	0.86	84.00
14	70	68.10	95.98	17.99	23.11	4.12	2.53	1.55	84.22
15	75	70.65	96.07	17.77	22.44	8.71	2.28	1.64	84.39

Appendix I
Experimental Run 9

Experimental Run. No. 9

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting concentration

Na₂CO₃ = 120 g/L as Na₂O

Burnt Lime = 101.0201 g

Amount of water added = 800 mL

Sample	Time	Temp	Mean	Standard Deviation			Causticizing
No.	min	deg.C	OH g/L	CO ₃ g/L	OH g/L	CO ₃ g/L	Efficiency %
			asNa ₂ O	asNa ₂ O			
	0						0
1	5	95.84	32.35	82.01	1.10	3.84	28.10
2	10	96.50	71.15	51.91	3.07	0.86	57.82
3	15	95.13	84.42	31.13	0.45	2.02	73.06
4	20	93.27	89.21	21.02	0.71	1.70	80.93
5	25	94.54	99.54	20.03	3.00	0.70	83.25
6	30	95.21	96.97	16.82	2.84	0.30	85.22
7	35	95.79	99.64	15.29	2.11	0.96	86.70
8	40	94.77	102.99	11.98	3.98	2.26	89.58
9	45	93.73	106.33	9.47	1.70	0.61	91.82
10	50	94.06	100.96	9.04	1.63	2.76	91.78
11	55	94.07	109.79	9.55			92.00
12	60	94.20	92.60	10.07	6.36	1.12	90.19
13	65	93.36	103.41	11.50	3.61	0.34	89.99
14	70	92.08	102.60	8.03	3.25	2.85	92.74

Appendix J
Experimental Run 10

Experimental Run. No. 10

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 0%

Stoichiometric borate addition = 35%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 77.97 g/L Na₂O

Burnt Lime = 65.6985 g

NaBO₂ = 20.9995 g/L Na₂O

NaOH = 41.9895 g/L Na₂O

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean			Standard Deviation			Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	OH g/L	CO ₃ g/L	BO ₂ g/L	
	0		41.99	77.97					35.00
1	5	89.88	55.74	52.58	21.36	2.80	2.73	1.39	51.46
2	10	95.55	83.06	28.71	21.76	1.48	2.01	1.44	74.31
3	15	94.91	91.67	21.49	23.16	0.99	0.28	0.95	81.01
4	20	95.02	92.84	17.34	22.71	0.78	1.85	1.22	84.26
5	25	94.96	97.93	19.57	20.77	6.76	0.23	2.02	83.34
6	30	94.82	93.23	18.23	19.83	8.70	1.47	2.14	83.64
7	35	94.14	82.14	13.30	18.64	0.54	1.30	0.78	86.06
8	40	94.20	85.44	13.26	18.99	12.93	3.07	1.75	86.57
9	45	94.37	98.57	16.50	21.48	1.95	1.46	1.85	85.66
10	50	94.13	89.18	14.01	19.32	7.22	2.15	1.97	86.42
11	55	93.96	96.25	14.44	21.38	0.49	1.19	1.30	86.95
12	60	92.71	82.22	11.46	18.13	0.88	2.36	0.67	87.77

Appendix K
Experimental Run 11

Experimental Run. No. 11

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 0%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 77.97 g/L as Na₂O

Burnt Lime = 65.6985 g

NaOH = 41.9895 g/L as Na₂O

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean		Standard Deviation		Causticizing Efficiency %
			OH g/L asNa ₂ O	CO ₃ g/L asNa ₂ O	OH g/L	CO ₃ g/L	
	0		42.01	77.98			35.01
1	5	92.3	56.175	55.815	0.94	1.24	50.16
2	10	96.13	88.38	26.48	2.33	2.97	76.95
3	15	94.89	97.73	20.8733	3.42	3.29	82.40
4	20	94.55	100.4	18.52	0.79	0.21	84.43
5	25	94.77	103.695	13.12	1.59	2.50	88.77
6	30	94.78	105.81	15.59	1.87	1.29	87.16
7	35	95.13	103.1	13.44	0.64	1.27	88.47
8	40	95.14	108.825	14.115	4.57	2.55	88.52
9	45	95.24	106.005	14.24	0.88	1.13	88.16
10	50	94.85	103.695	13.64	2.16	1.26	88.38
11	55	95.13	105.055	13.56			88.57

Appendix L
Experimental Run 12

Experimental Run. No. 12

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 30%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 84 g/L as Na₂O

Burnt Lime = 70.7221 g

Na₂S = 36 g/L as Na₂O

Amount of water added = 800 mL

Sample No.	Time min	Temp deg.C	Mean			Standard Deviation			Causticizing
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	S g/L as Na ₂ O	OH g/L	CO ₃ g/L	S g/L	Efficiency %
	0		0	84					0
1	5	101.83	39.39	50.83	26.00	4.25	5.62	1.11	43.66
2	10	101.15	44.70	24.67	30.72	5.06	3.14	5.15	64.44
3	15	97.29	57.88	21.62	32.92	1.70	5.25	5.52	72.81
4	20	94.01	61.28	20.30	31.24	3.79	4.60	3.72	75.12
5	25	94.13	57.00	12.47	33.79				82.05
6	30	95.01	63.83	14.35	34.56	2.37	2.67	2.10	81.64
7	35	96.56	57.19	12.14	29.65	8.26	2.85	3.37	82.49
8	40	95.46	54.54	14.73	22.51	2.87	1.52	0.63	78.74
9	45	96.81	66.73	14.61	31.11	1.20	0.84	1.53	82.04
10	50	96.26	54.85	11.36	24.92	9.84	3.54	2.81	82.84
11	55	96.20	52.31	11.50	22.44	6.09	1.29	2.83	81.98
12	60	96.40	67.58	10.14	34.50	0.82	2.27	3.21	86.95

Appendix M
Experimental Run 13

Experimental Run. No. 13

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 30%

Stoichiometric borate addition = 35%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 54.6 g/L as Na₂O

Burnt Lime = 45.9634 g

Na₂S = 36 g/L as Na₂O

Amount of water added = 800 mL

NaBO₂ = 14.7 g/L as Na₂O

Sample No.	Time min	Temp deg.C	Mean				Standard Deviation				Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	S g/L as Na ₂ O	OH g/L	CO ₃ g/L	BO ₂ g/L	S g/L	
	0		29.4	54.6							35
1	5	89.74	41.86	38.06	15.49	31.30	2.83	4.47	2.31	1.38	52.38
2	10	93.09	55.48	20.22	14.24	32.50	11.17	9.28	2.45	4.70	73.29
3	15	94.11	65.29	17.62	15.49	34.34	2.87	0.78	0.61	1.48	78.75
4	20	94.73	61.37	14.17	13.81	30.46	3.27	1.51	0.71	0.28	81.24
5	25	96.25	63.41	13.37	13.53	29.57	1.08	0.99	1.22	3.44	82.59
6	30	96.68	66.29	12.83	14.10	30.42	1.44	1.67	2.57	1.24	83.78
7	35	95.89	65.37	11.54	14.33	32.48	2.02	0.04	0.21	1.37	85.00
8	40	96.47	68.42	12.38	14.46	32.00	2.35	0.32	0.54	0.59	84.68
9	45	95.46	65.62	10.92	13.94	32.21	1.16	1.31	1.72	2.28	85.73
10	50	96.42	70.53	12.86	15.13	30.03	0.68	1.11	0.60	4.73	84.58
11	55	95.20	67.22	11.67	13.59	31.07	4.47	4.04	1.04	2.60	85.21
12	60	96.72	72.88	12.16	15.11	33.24	7.17	4.87	1.23	3.51	85.70

Appendix N
Experimental Run 14

Experimental Run. No. 14

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 15%

Stoichiometric borate addition = 0%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 102 g/L as Na₂O

Burnt Lime = 86.3745 g

Na₂S = 18 g/L as Na₂O

Amount of water added = 800 mL

Sample	Time	Temp	Mean			Standard Deviation			Causticizing
No.	min	deg.C	OH g/L	CO ₃ g/L	S g/L	OH g/L	CO ₃ g/L	S g/L	Efficiency %
			as Na ₂ O	as Na ₂ O	as Na ₂ O				
			0	102					0
1	5	100.03	28.64	71.59	18.32	4.31	0.45		28.57
2	10	100.68	61.03	27.03					69.31
3	15	97.04	74.11	28.06	17.13	5.11	2.82	1.48	72.54
4	20	92.27	72.32	20.41	16.81	1.22	1.80	1.68	77.99
5	25	91.74	79.70	19.61	16.63	0.81	0.44	0.12	80.25
6	30	95.21	83.96	17.77	18.27	1.42	0.67	0.19	82.53
7	35	96.68	83.62	14.10	19.91	0.01	1.28	1.73	85.57
8	40	95.43	91.29	16.76	18.16	9.44	2.83	0.63	84.49
9	45	93.48	84.11	14.88	16.77	0.49	2.35	2.69	84.97
10	50	94.84	83.06	13.21	17.20	5.90	0.28	1.63	86.28
11	55	95.10	89.07	15.58	15.97	2.84	1.72	1.27	85.11
12	60	94.22	89.45	13.93	17.27	1.43	2.38	2.33	86.53
13	65	95.12	78.99	12.80	14.13	14.45	2.11	2.72	86.06

Appendix O
Experimental Run 15

Experimental Run. No. 15

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 15%

Stoichiometric borate addition = 35%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 67.06 g/L as Na₂O

Burnt Lime = 56.4535 g

Na₂S = 18 g/L as Na₂O

Amount of water added = 800 mL

NaBO₂ = 19.98 g/L as Na₂O

NaOH = 36.1088 g/L as Na₂O

Sample No.	Time min	Temp deg.C	Mean				Standard Deviation				Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	S g/L as Na ₂ O	OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	S g/L as Na ₂ O	
	0		36.11	67.06							35.00
1	5	99.42	51.68	41.78	19.06	18.33	2.19	1.19	0.54	0.87	55.30
2	10	96.70	75.57	27.06	17.71	16.47	0.68	0.40	0.90	0.07	74.35
3	15	95.45	80.94	21.00	18.80	16.72	1.38	2.23	0.81	1.12	79.40
4	20	96.06	82.23	17.28	18.80	17.64	1.21	0.21	0.42	1.27	82.63
5	25	96.39	84.57	18.16	17.40	15.61	1.56	2.21	1.24	1.30	82.32
6	30	96.27	86.53	17.18	18.21	16.65	2.73	2.91	1.32	2.42	83.43
7	35	96.64	78.27	13.10	17.68	16.69	5.85	0.06	2.17	1.90	85.66
8	40	96.87	81.66	15.27	16.39	15.91	0.54	0.47	0.07	0.29	84.25
9	45	97.27	85.43	15.94	16.87	15.45	10.62	2.65	1.90	2.02	84.28
10	50	97.53	83.55	13.56	18.36	16.67	2.35	1.53	0.13	1.07	86.04
11	55	97.64	83.32	12.17	18.68	17.86	1.17	0.16	0.00	0.40	87.26
12	60	97.96	92.63	17.09	19.74	15.40	4.48	0.59	0.34	0.86	84.42
13	65	98.48	89.02	16.22	17.47	16.18	2.05	1.36	0.18	0.04	84.59
14	70	98.62	83.03	11.64	18.84	17.44	0.75	1.05	0.95	0.99	87.70

Appendix P
Experimental Run 16

Experimental Run. No. 16

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree C

Sulfidity = 30%

Stoichiometric borate addition = 25%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 63 g/L as Na₂O

Burnt Lime = 56.4535 g

Na₂S = 36 g/L as Na₂O

Amount of water added = 800 mL

NaBO₂ = 19.98 g/L as Na₂O

NaOH = 21 g/L as Na₂O

Sample No.	Time min	Temp deg.C	Mean				Standard Deviation				Causticizing Efficiency %
			OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	S g/L as Na ₂ O	OH g/L as Na ₂ O	CO ₃ g/L as Na ₂ O	BO ₂ g/L as Na ₂ O	S g/L as Na ₂ O	
	0		21.00	63.00							25.00
1	5	94.80	39.56	39.20	11.30	34.46	0.44	0.37	0.91	2.43	50.23
2	10	94.60	54.78	25.99	9.74	31.75	0.03	0.54	0.15	0.35	67.82
3	15	96.90	65.20	22.77	18.85	20.99	3.26	6.79	10.19	19.66	74.12
4	20	96.80	65.42	15.75	10.97	34.11	2.85	7.29	3.65	6.30	80.60
5	25	95.70	69.02	15.91	10.15	32.63	4.24	5.56	2.04	3.96	81.27
6	30	95.80	69.33	14.80	9.89	31.67	0.31	2.53	1.77	3.36	82.41
7	35	96.40	66.40	12.22	9.94	31.20	1.63	4.15	2.00	4.14	84.46
8	40	96.70	73.37	15.11	9.49	32.10	3.34	1.47	1.65	3.73	82.92
9	45	96.80	69.30	10.41	12.05	32.81	0.39	1.48	0.47	1.85	86.94
10	50	96.70	69.07	10.03	11.47	33.25	2.59	2.43	0.54	0.77	87.32
11	55	96.50	72.89	11.72	11.04	32.89	1.06	2.38	1.12	3.02	86.15
12	60	97.30	72.06	12.79	10.10	31.22	1.05	1.85	0.64	1.53	84.93
13	65	97.50	68.86	12.85	8.98	28.76	1.07	1.56	0.54	1.75	84.27
14	70	98.25	69.75	12.36	9.43	29.29	3.22	2.25	0.34	1.58	84.95
15	75	99.07	66.72	8.78	11.15	31.80	1.80	1.95	1.40	0.64	88.37

Appendix Q
Experimental Run 17

Experimental Run. No. 17

Experimental Conditions

TTA = 120 g/L Na₂O

Target temperature = 95 degree

Sulfidity = 30%

Stoichiometric borate addition = 15%

Stoichiometric lime addition = 100%

Starting Concentration

Na₂CO₃ = 71.40 g/L as Na₂O

Burnt Lime = 60.11 g

Na₂S = 36 g/L as Na₂O

Amount of water added = 800 mL

NaBO₂ = 12.6 g/L as Na₂O

NaOH = 12.6 g/L as Na₂O

Sample	Time	Temp	Mean				Standard Deviation				Causticizing
No.	min	deg.C	OH g/L	CO ₃ g/L	BO ₂ g/L	S g/L	OH g/L	CO ₃ g/L	BO ₂ g/L	S g/L	Efficiency %
			as Na ₂ O	as Na ₂ O	as Na ₂ O	as Na ₂ O	as Na ₂ O	as Na ₂ O	as Na ₂ O	as Na ₂ O	
	0		12.60	71.40							15.00
1	5	96.82	37.58	44.79	6.01	31.25	2.01	3.34	1.08	1.18	45.62
2	10	97.58	58.46	27.70	5.28	30.55	1.15	1.20	0.28	0.19	67.85
3	15	93.64	60.04	16.39	7.89	35.08	2.91	4.27	2.23	3.61	78.56
4	20	93.00	62.73	13.21	8.00	35.48	4.27	6.67	3.17	6.24	82.60
5	25	94.76	64.69	9.65	8.67	37.27	1.34	2.11	0.98	1.52	87.02
6	30	95.77	67.44	8.35	9.41	39.16	5.06	5.69	2.05	4.21	88.98
7	35	97.00	70.54	13.55	6.23	32.36	4.30	2.70	1.18	2.99	83.89
8	40	97.36	68.48	10.64	6.99	32.51	3.56	1.37	0.81	2.96	86.55
9	45	97.07	65.62	11.39	5.91	28.89	4.06	4.40	2.12	2.81	85.21
10	50	97.42	63.71	6.04	8.80	33.34	1.58	0.79	0.95	1.65	91.34
11	55	98.62	69.52	9.00	7.50	33.40	0.54	2.57	0.95	2.98	88.54
12	60	100.32	68.39	7.66	8.51	34.54	4.77	7.94	3.89	6.99	89.93
13	65	98.72	72.08	11.13	5.97	31.75	3.97	2.48	1.56	1.11	86.62
14	70	95.73	71.67	10.68	6.49	31.00	0.47	1.43	1.06	2.06	87.03
15	75	94.32	69.79	11.19	5.91	28.86	2.83	4.18	1.58	3.63	86.18

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