

EFFECT OF PARTIAL BORATE AUTOCAUSTICIZING ON THE CAUSTICIZING RATE AND EQUILIBRIUM

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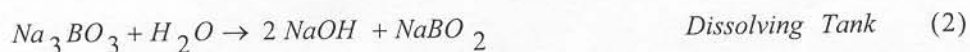
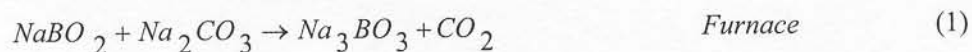
ABSTRACT

Borate auto-causticizing can replace - total auto-causticizing, or supplement the kraft lime cycle - partial auto-causticizing. Partial auto-causticizing has recently been commercialized in one kraft mill and is undergoing trials in several additional mills. In the on-going partial borate auto-causticizing trials, a common but unexpected observation is that the causticizing efficiency increases. The objectives of this study are to determine the effect of borate on the causticizing rate, equilibrium, and rate controlling parameters with the aim of defining the conditions that can increase causticizing efficiency. The causticizing experiments were conducted using analytical grade sodium carbonate, sodium borate, sodium sulfide and commercial burnt lime. The major findings are that when the degree of completion of the causticizing reaction is rate limited (which is true in commercial operations), partial borate auto-causticizing can increase causticizing efficiency due to the higher initial hydroxide content. Temperature was found to be a critical variable for achieving high causticizing efficiencies after partial borate auto-causticizing.

INTRODUCTION

Borate Auto-causticizing: Auto-causticizing processes are non-conventional causticizing processes based on the use of amphoteric salts that release carbon dioxide (CO₂) from sodium carbonate (Na₂CO₃) in the kraft furnace and generate sodium hydroxide (NaOH) in the green liquor-dissolving tank. The most promising of the auto-causticizing processes is borate-based auto-causticizing. Borate-based auto-causticizing can supply either part or all of the sodium hydroxide requirements in the kraft pulping process. When auto-causticizing supplies the entire hydroxide requirement, the calcining/causticizing process is eliminated, and when auto-causticizing supplies part of the hydroxide, the material and energy burden for calcining and causticizing are reduced.

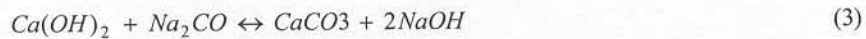
Recently, Tran, et al. [1] published experimental data showing that the borate auto-causticizing reactions are considerably more efficient than were proposed by Janson [2-5]. Among the more sufficient finding of Tran's et al. work is that borate auto-causticizing proceeds through the reaction of sodium metaborate and sodium carbonate in the furnace to form trisodium borate (Na₃BO₃), and generate carbon dioxide, reaction 1. On dissolving, the trisodium borate reacts with water to form sodium hydroxide and generate the metaborate, reaction 2.



In addition to suggesting the new stoichiometry, Tran et al. also proposed that borate auto-causticizing offers the possibility of only partially converting the sodium carbonate to sodium hydroxide with the remaining conversion occurring in lime cycle. This provides an easy method for causticizing limited mills to increase their causticizing capacity without installing new equipment. Based on this new understanding, several mill trials with partial auto-causticizing were recently conducted and confirmed this new stoichiometry.

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Conventional Causticizing: In the causticizing reaction, slaked lime (Ca(OH)_2) reacts with sodium carbonate (Na_2CO_3) forming calcium carbonate (CaCO_3) and sodium hydroxide NaOH – reaction 3.



Both sodium carbonate and sodium hydroxide are soluble, while calcium hydroxide (slaked lime) and calcium carbonate (lime mud) are limited in solubility and essentially take part in the reaction as solids. Since calcium carbonate is more insoluble than calcium hydroxide, the reaction is driven to the right. The equilibrium for this reaction may be written as hydroxide ion squared over carbonate ion as shown in equation (4)

$$K = \frac{[\text{OH}^-]^2}{[\text{CO}_3^{2-}]} \quad (4)$$

The most significant feature of this equilibrium equation is that the numerator – the hydroxide ion – is squared, while the denominator – the carbonate ion is not. Because of this, the numerator increases faster than the denominator as the initial liquor concentration increases, which reduces the degree of completion for this reaction or causticizing efficiency, equation (5).

$$\text{Causticizing Efficiency} = \frac{\text{NaOH}}{\text{Na}_2\text{CO}_3 + \text{NaOH}} \quad (5)$$

(with Na_2CO_3 and NaOH defined in terms of Na_2O)

Sometimes the causticizing efficiency is corrected by subtracting from both numerator and denominator the sodium hydroxide already present in the green liquor. Because of the large amount of hydroxide formed through auto-causticizing with this study, such a correction would be misleading and therefore is not made for the data presented in this paper.

The presence of sulfide in the liquor results in the formation of additional sodium hydroxide, reaction 6, which participates in the equilibrium and also reduces the conversion or causticizing efficiency.



Several authors, including Lindberg and Ulmgren [6], have published causticizing equilibrium curves. Figure 1, based on data from contained in the description of white liquor preparation by Grace [7], shows that the causticizing decreases with increased concentration, expressed as TTA, and increased sulfidity.

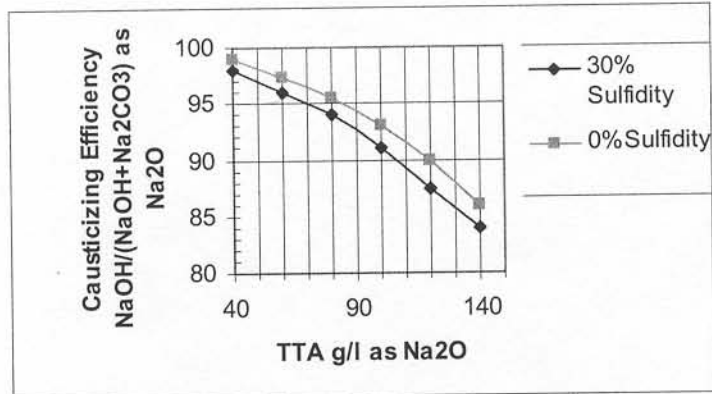


Fig. 1. Effect of Increasing Concentration of Liquor and Sulfidity on Causticizing Efficiency

Actual mill causticizing efficiencies are 5 to 15% less than the equilibrium efficiencies shown in figure 1 [7]. There are several reasons for mills not achieving equilibrium efficiencies, these include; rate limitations due to incomplete mixing, and low local temperatures.

Conventional Causticizing after Partial Borate Autocauticizing: With partial borate autocauticizing, only part of the sodium carbonate reacts with sodium metaborate in the recovery furnace, reaction (1) and the remaining sodium carbonate is converted into sodium hydroxide through the conventional lime cycle. Mills trials have reported an increase in the causticizing efficiency with partial borate autocauticizing. The objective of this research is to determine the conditions where partial borate autocauticizing can increase the causticizing rate or equilibrium.

Two factors, a higher initial hydroxide level (that is, less carbonate to convert) and the presence of additional ionic species may affect the causticizing efficiency. As mentioned above, since mill operations are rate limited, the causticizing reaction never reaches the equilibrium constraint. Therefore, if the initial hydroxide concentration (causticizing efficiency) is higher, the final causticizing efficiency will also be higher.

Studies of the effect of other soluble salts on the equilibrium constant have yielded mixed results. For example, Lindberg and Ulmgren [6] reported that the equilibrium constant of the causticizing reaction decreases with increasing cation concentration, while, other researchers report no effect of increasing sodium chloride concentration [7]. Therefore the effect of the sodium metaborate (the borate product of autocauticizing) is difficult to estimate.

EXPERIMENTAL

Experimental Reagents: Synthetic green liquor, representing borate-autocauticizing liquor, was prepared using reagent grade sodium carbonate, sodium borate, and sodium hydroxide and commercial burnt lime. As described by Holman et al. [8], the use of mill burnt lime is important for applied calculations.

Experimental System: The experimental system used for this study is shown in Figure 2, and consists of a stirred temperature controlled reactor. Sodium carbonate, metaborate and sodium hydroxide were dissolved in deionized water and heated 5 to 10 °C below the desired causticizing reaction temperature. Since the slaking reaction between burnt lime (CaO) and water is highly exothermic, the addition of the

burnt lime raised the reactor temperature to the target temperature and the reactor was then held at this temperature through the course of the reaction. Small samples were periodically withdrawn under vacuum from the reactor, filtered – inline, and analyzed, using a duo-titrator ion analyzer developed by U.S. Borax Inc. (variant of the TAPPI standard ABC titration method).

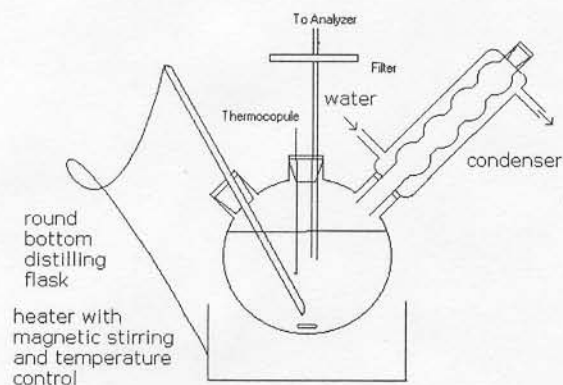


Figure 2. Causticizing Reactor

RESULTS AND DISCUSSION

The experimental conditions described in this paper are shown in Table 1, and were designed to delineate the effects of concentration, sulfidity, temperature, and metaborate level.

Table 1, Experimental Conditions (CaO Activity = 85%)

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	70.17	0	0	0	70.17	55.99	800
2	60	77.5	0	0	0	77.5	65.24	800
3	80	77.5	0	0	0	77.5	65.16	800
4	70	77.5	0	0	0	77.5	65.17	800
5	70	77.5	0	10.85	0	77.5	65.17	800
6	70	120	0	0	0	120	101.01	800
7	70	120	0	21	0	120	101.02	800
8	70	76.21	0	21	41.96	118.19	65.66	800
9	95	120	0	0	0	120	101.02	800
10	95	77.97	0	21	41.99	120	65.7	800
11	95	77.97	0	0	41.99	120	65.7	800
12	95	84	36	0	0	120	70.72	800
13	95	54.6	36	14.7	29.4	120	45.96	800
14	95	102	18	0	0	120	86.37	800
15	95	67.06	18	19.98	36.11	120	56.45	800

The key experiment in this study is the comparison of the causticizing rate and equilibrium for typical mill conditions with and without borate auto-causticizing. Figure 3 presents such a comparison.

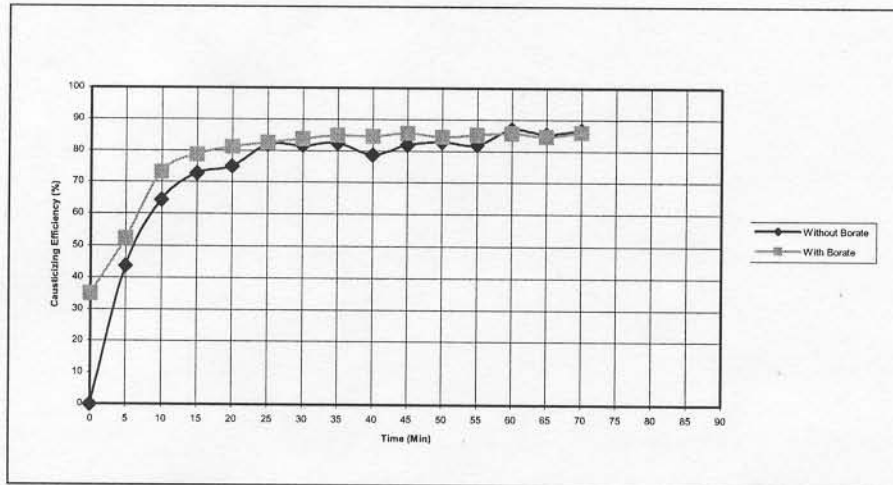


Fig. 3. Comparison of Causticizing Reaction with and without Borate Auto-causticizing 35% Auto-causticizing, 120 TTA g/l, 30% Sulfidity, 100 % Stoichiometric Lime Addition and 98 °C

The conditions shown in Fig. 3 simulate typical mill conditions at 35% auto-causticizing. The data show that borate-based auto-causticizing can provide higher causticizing efficiencies. At the conditions shown in Fig. 3, the increase in causticizing efficiency before equilibrium results from a higher initial hydroxide level. At equilibrium both causticizing reactions (that with and that without borate) reach 87% causticizing efficiency. Previous studies, such as those of Lindberg and Ulmgren [6] also show that the equilibrium reaches 87% under the conditions of 120 TTA, 30% Sulfidity and 100 °C. The similarity of this data with the previous published results provides confidence in the accuracy of the data and the experimental techniques.

Most mills achieve final causticizing efficiencies from 75 to 85% [7]. In figure 3, the causticizing efficiency with borate-based auto-causticizing is higher than conventional causticizing until the reaction reaches equilibrium at 87%. Since in mill operations equilibrium is rarely achieved, borate-based auto-causticizing will usually produce a higher causticizing efficiency. The main reason for this appears to be the higher initial hydroxide level with borate-based auto-causticizing.

Effect of Concentration, Sulfidity, Temperature and Extent of Auto-causticizing: Although Fig. 3 above clearly shows that the causticizing efficiency will either increase or remain unchanged with borate-based auto-causticizing, there is a need to understand the rate controlling parameters for the causticizing reaction following borate-based auto-causticizing. One of the concerns with causticizing following borate-based auto-causticizing is that since less burnt lime is required, the temperature rise across the slaker will be less. Therefore, the green liquor may need to be heated to ensure that the causticizing reaction nears completion. At lower temperatures, one would expect reduced causticizing efficiencies since the causticizing reaction is slower.

The effect of temperature on the causticizing reaction with and with partial borate auto-causticizing was studied by causticizing at different temperatures. The effect of auto-causticizing on the causticizing reaction at 70 °C and 0 % sulfidity is shown in Fig. 4.

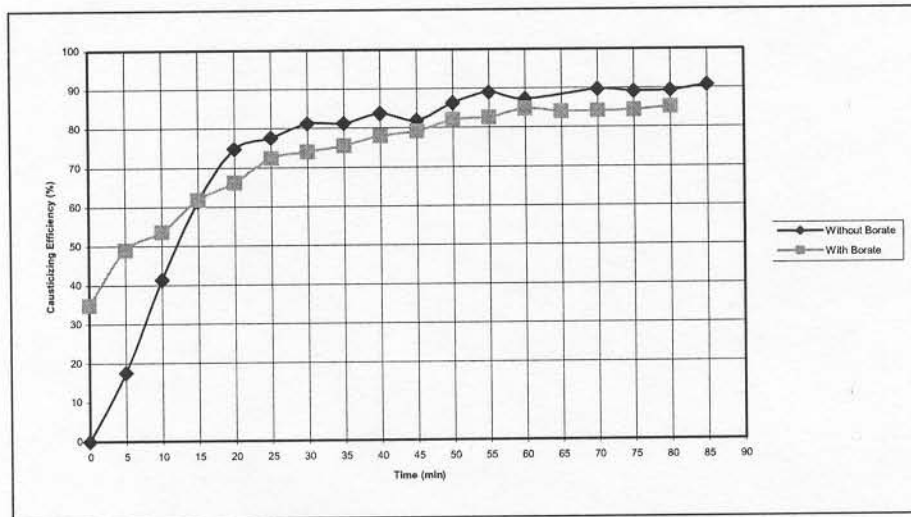


Figure 4, Comparison of Causticizing Reaction with and without Borate Autocausticizing; 35% Autocausticizing, 120 TTA g/l, 0% Sulfidity, 100% Stoichiometric Lime Addition and 70 °C

Here, the lower temperature (70 °C decreases the rate of both reactions, but appears to slow the causticizing following partial auto-causticizing to a greater degree than conventional causticizing. Although this is an extremely low temperature, it does show the need to maintain temperature following borate auto-causticizing.

Effect of Metaborate Addition without Simulating Autocausticizing: In the above figures, adding the equivalent amounts of sodium metaborate, and sodium hydroxide and reducing the sodium carbonate and burnt lime simulated borate-based auto-causticizing. In these experiments, the causticizing efficiency following borate auto-causticizing remained higher than without borate auto-causticizing until equilibrium was reached. In Figure 5, sodium metaborate was added to the green liquor without adjusting the other reagents.

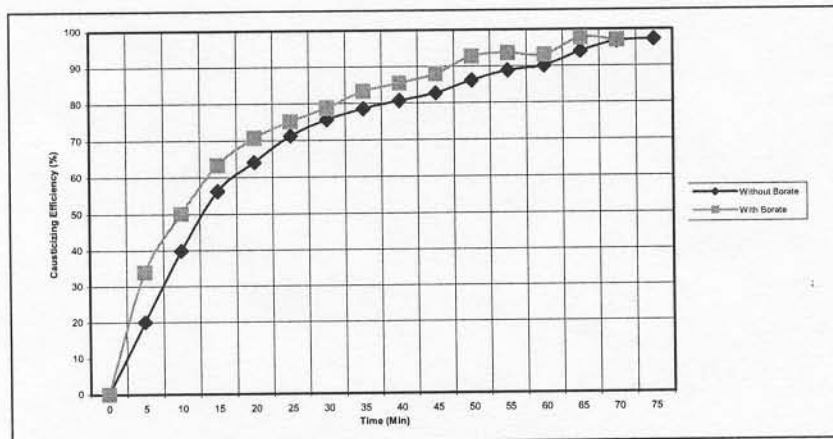


Figure 5, Comparison of Causticizing Reaction with and without Borate Autocausticizing; Meta Borate added Equivalent to 35% Autocausticizing, 70 g/l TTA, 0% Sulfidity, 100% Stoichiometric Lime Addition and 70 °C

A surprising result of this experiment is that the addition of the borate increases the causticizing rate. Although this was unexpected and might influence the final causticizing efficiency, both the temperature and TTA levels were relatively low. The increase in causticizing rate with borate was not observed at the commercial TTA level of 120 g/l

CONCLUSIONS:

The main conclusions from this study are:

- 1) The increase in causticizing efficiency with borate-autocausticizing results from the higher initial causticizing efficiency due to hydroxide formation through autocauticizing. Since causticizing in mill operations is typically rate limited, this initial level of hydroxide provides a step increase in causticizing efficiency and a higher final causticizing efficiency in rate limited causticizing.
- 2) The causticizing temperature is critical both for conventional causticizing and causticizing following borate autocauticizing. Since less lime is needed after borate autocauticizing, the temperature increase due to the slaking reaction is reduced and the green liquor temperature may need to be controlled through steam addition. If the green liquor temperature is allowed to decrease, a lower causticizing efficiency may be expected.

AKNOWLEDGMENTS

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