Effects of partial borate autocausticizing on kraft recovery operations

By H. Tran, X. Mao, N. Lesmana, S.H. Kochesfahani, C.M. Bair, R. McBroom

The technology is particularly good for boilers that are thermally limited

The partial borate-autocausticizing technology uses a small quantity of sodium borate to causticize a portion of sodium carbonate (Na₂CO₃) in a recovery boiler, and then completes the causticization of the remaining Na₂CO₃ in a conventional recaust plant with a reduced quantity of lime. Since the technology requires no capital investment, it can be an attractive alternative for kraft mills where incremental causticizing and limekiln capacity are required [1].

Over the past three years, the technology has been tested at a BCTMP mill [2] and at three kraft pulp mills [3,4]. Results of these trials, which lasted from one day to 18 months, have been encouraging. Lime consumption was lowered during kraft mill trials, and no effects of borate on pulp quality, effluent quality, chemical recovery process equipment, and digester and limekiln operations were reported. Although several problems, directly or indirectly related to borate in the liquors, were experienced in the operation of evaporators, recovery boilers and recaust plants, most have been rectified.

Before the trials, there was little information with respect to how borate may affect the recovery operation. Since borate is highly soluble in water, it circulates with the liquor through the recovery cycle. Its presence was often “blamed” for any operational problems and abnormalities that occurred during the trials, as well as being credited for any positive results that were obtained. The learning curve has been steep for people involved. The effects of borate on virtually every aspect of recovery operations have been closely monitored, and when necessary, laboratory experiments were conducted to obtain a better understanding of how borate may have caused a particular problem observed during the trials.

This paper focuses only on major problems experienced during the trials, and discusses results of laboratory studies conducted to examine these problems, and the implications for recovery operations.

Recaust Operation

Effect of Borate on Standard ABC Titration Method: The main operating problem experienced in recaust plants during the early mill trials was the interference of borate with the standard ABC titration method used to determine the composition of white liquor. Borate has a pH buffering effect. When the liquor is titrated with HCl, the presence of borate may alter the titration endpoints and cause errors in the liquor analysis.

A systematic study was performed to examine the extent to which borate may affect the results of the standard ABC titration method [5]. Tests were performed on both green and white liquors that had been doped with various concentrations of borate. Since similar results were obtained in both cases, only the tests on white liquor are discussed here.

Figure 1 shows two titration curves for a white liquor sample: one for the liquor “as is”; the other for the liquor doped with 64.3 g/L of NaBO₂ (10,560 ppm or mg/L B). For the liquor with no borate (as-is), three endpoints (or inflection points) A, B and C were observed on the titration curve with HCl. The sharp decrease and increase in pH near endpoint A was due to the addition of formaldehyde as part of the analytical procedure. For the liquor with borate, there were also three endpoints A’, B’ and C’, plus a fourth endpoint D’.

The first endpoints A and A’ appear to be at the same position, whereas the second and third endpoints B and C are shifted respectively to B’
and C' by the same amount (i.e., BB' = CC'). These results are not surprising considering the buffering effect of NaBO₂ at a pH between 8 and 10. Thus, borate affects only the endpoints B and C, which occur at a pH below 8.

In the standard ABC titration method, the effective alkali (EA) of the liquor is determined based on the amount of HCl solution that has been consumed up to endpoint A. The active alkali (AA) is based on the amount of HCl required up to endpoint B, while the total titratable alkali (TTA) is based on the amount of HCl required up to endpoint C. Therefore, the standard ABC titration method, as is, cannot be used to determine the composition of a liquor that contains borate. Although the EA value is unaffected by borate (no change in the endpoint A position), the AA and TTA values will appear to be higher than the actual values.

Figure 2 shows the EA, AA and TTA values of a white liquor determined by the standard ABC titration method, as a function of borate concentration in the liquor. There is no change in EA, whereas AA and TTA increase by an equal amount and linearly with an increase in borate concentration.

Since the apparent increase in AA and TTA values is caused by the increase in the amount of HCl used to neutralize NaBO₂ in the liquor, it can be estimated as follows:

\[ F = \frac{[B]}{(2 \times 10.8) \times 62/1000} = 0.00287[B] \]

where \( F \) is the increase factor in g/L Na₂O, and [B] is the boron concentration in the liquor in ppm or mg/L. Using this increase factor, the corrected AA and TTA values can be obtained by subtracting the increase factor from the measured values. Thus,

\[ \text{EA} = \text{EA}_{\text{measured}} = \text{NaOH} + \frac{1}{2} \text{Na}_2\text{S} \]

\[ \text{AA} = \text{AA}_{\text{measured}} - F = \text{NaOH} + \frac{1}{2} \text{Na}_2\text{S} \]

\[ \text{TTA} = \text{TTA}_{\text{measured}} - F = \text{NaOH} + \frac{1}{2} \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 \]

The data presented in Fig. 3 are the same as in Fig. 2, except that in Fig. 3, the corrected values were used instead of the measured values. The independence of the corrected values with borate concentration clearly suggests that the standard ABC titration method can be used to determine the composition of borate-containing liquor, if the boron concentration is known.

Note that the AA and TTA values measured with the standard ABC titration method typically have an error of ±3 g/L Na₂O. Therefore, the increase factor \( F = 0.00284[B] \) can be considered to be negligible if the borate concentration in the liquor is lower than \( 3/0.00284 = 1,056 \text{ ppm B} \), that is, about 1,000 ppm B.

This finding is important, since it suggests that the effect of borate on the standard ABC test method is negligible if the boron concentration in the liquor is below 1,000 ppm, which is equivalent to a borate autocauticizing target of about 8%. This is particularly fortunate for mills that swap liquors with a borate mill. Consider a case in which Mill A is exchanging 15% of its liquor with Mill B where 25% borate autocauticizing is practised. Borate will be gradually transferred from Mill B to Mill A. At steady-state, Mill A will become a 3.75% (0.15*25%) borate autocauticizing mill. At this low level, there is no need for concern about the effect of borate on the standard ABC test method. The change in TTA and AA is too small to be detected.

Modified ABC Titration Methods: For mills that operate at a high boron level, it is important that the effect of borate is taken into account. This requires an accurate measurement of
boron concentration in the liquor. One possible way is to make use of the fourth endpoint D' located between the endpoints A' and B' on the standard ABC titration curve (Fig. 1). This endpoint is related directly to the borate concentration in the liquor, since D'B' represents the amount of HCl equivalent to the NaBO₂ present. Unfortunately, for liquors with a borate concentration below 800 ppm, endpoints D' and B' become indistinguishable, making it impossible to accurately determine the boron content.

The boron concentration can also be determined by means of Atomic Absorption Spectroscopy, which is available at many pulp mills. However, for mills where there is no such instrument, an alternative method is needed.

**Duo-Titration Method:** This method involves the use of a double or duo-titrator. It was developed specifically to eliminate the effect of borate on the AA and TTA data, and to replace the standard ABC titration method during the mill trials. In this method, the liquor sample is split into two parts: one is titrated with AgNO₃ to determine the sulphide content, while the other is subjected to a titration test with HCl. The resulting sulphide concentration and the titration endpoints are then used to estimate the EA, AA and TTA of the liquor, as well as the boron content.

The double titration method has been successfully developed and tested during mill trials. It was found to rapidly provide accurate results.

**EFFECTS ON EVAPORATOR OPERATION**

Few problems have occurred in the operation of black liquor evaporators during the borate trials. No apparent change in the over-all evaporator steam consumption and boiling point rise (BPR) was found. This is consistent with results of a recent laboratory study, which suggest that while the addition of borate may increase the BPR of slash pine black liquor [6], the effect is insignificant at low borate concentrations. As Fig. 4 shows, at a B/Na weight ratio below 0.04 (corresponding to <30% auto-causticizing), the BPR increase is less than 0.3°C.
During the borate trial at the mill where the black liquor concentrates were operated at 70-73%, the solids content determined by refractometers was found to be consistently lower than that measured gravimetrically with a moisture balance. While the moisture balance reading did not appreciably change with borate concentration, the refractometer reading decreased by about 1% dry solids for every 0.01 increase in B/Na weight ratio [4]. The cause of the discrepancy is not known. However, according to the manufacturer of refractometers, the decrease in refractometer reading may have been caused by the lower refractive index of sodium borate compared to that of other sodium compounds in the black liquor. At the mill where the final black liquor solids content was controlled at 63 to 65%, no discrepancy between the refractometer and the moisture balance measurements was found.

As black liquor becomes concentrated, the borate in the liquor is expected to be in the form of sodium metaborate dihydrate (NaBO$_2$·2H$_2$O), which is stable at temperatures prevailing in the evaporator. Since the hydrate contains 64.6% solids, which is comparable to the heavy black liquor from concentrators, its presence in the liquor would have no significant effect on the solids content.

No corrosion was found on coupons that had been exposed to the borate-containing heavy liquor in the first effect evaporator at one of the mills for 18 months.

**EFFECTS ON RECOVERY BOILER OPERATION**

The effect of borate on recovery boiler operation was less desirable. Although the borate-containing black liquor appeared to burn well during the trials, the endothermic nature of the auto-causticizing reaction may have caused the char bed temperature to decrease, particularly during periods when the boron concentration in the liquor was high. This, in turn, may have lowered the auto-causticizing reaction efficiency and made the boilers more susceptible to high SO$_2$ emissions.

The effect of borate on boiler fouling and plugging was not conclusive, since none of the boilers plugged because of borate during the trials. Only in one of the boilers did deposits appear to accumulate more in the superheater region. The increase in deposit build-up was due primarily to an increase in the auxiliary gas flow and combustion air during the trial. The steam production of this boiler during the trial was somewhat low, but the low liquor-firing load could have also caused it during the same period.

As with other minor compounds such as potassium and chloride in the deposit, borate is expected to lower the melting temperature of char particles, increase the particle liquid content, and make particles stickier. However, results from mill trials suggest that the effect of borate on deposit accumulation and plugging was insignificant, particularly when the borate concentration was low (<10% auto-causticizing).

No corrosion and cracking of tubes that could be related to borate was found in recovery boilers.

**BORATE-AUTOCAUSTICIZING REACTIONS**

**Effect of Make-Up Chemicals on Reaction Efficiency:** The principal auto-causticizing reaction that occurs in recovery boilers is the reaction between sodium metaborate (NaBO$_2$) and sodium carbonate (Na$_2$CO$_3$) in molten smelt to form tri-sodium borate (Na$_3$BO$_3$) (reaction i). In the dissolving tank, Na$_3$BO$_3$ reacts with water to form sodium hydroxide (NaOH) and regenerate NaBO$_2$ (reaction ii)

$$\text{NaBO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_3\text{BO}_3 + \text{CO}_2$$  (i)

$$\text{Na}_3\text{BO}_3 + \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 2\text{NaOH}$$  (ii)

If the borate makeup chemical, sodium tetraborate pentahydrate (Na$_4$B$_2$O$_7$·5H$_2$O), is introduced into the recovery cycle through mixing with green liquor or white liquor, it will react with NaOH to form NaBO$_2$ in the liquor (reaction iii). If the borate makeup is carried out through addition to black liquor, it will also react with residual NaOH in the liquor to form NaBO$_2$ before entering the boiler. However, if the amount of Na$_4$B$_2$O$_7$ added is stoichiometrically larger than that of the residual NaOH in the black liquor, the excess Na$_4$B$_2$O$_7$ will react with Na$_2$CO$_3$ in molten smelt to form Na$_3$BO$_3$ (Reaction iv).

$$\text{Na}_4\text{B}_2\text{O}_7 + 2\text{NaOH} \rightarrow 4\text{NaBO}_2 + \text{H}_2\text{O}$$  (iii)

$$\text{Na}_4\text{B}_2\text{O}_7 + 5\text{Na}_2\text{CO}_3 \rightarrow 4\text{Na}_3\text{BO}_3 + 5\text{CO}_2$$  (iv)

Reaction iv is expected to be the result of a sequence of reactions, producing first NaBO$_2$, then Na$_3$BO$_3$, and then the final product, Na$_3$BO$_3$; i.e.,

$$\text{Na}_4\text{B}_2\text{O}_7 + 2\text{Na}_2\text{CO}_3 \rightarrow 4\text{NaBO}_2 + \text{CO}_2$$  (v)

$$4\text{NaBO}_2 + 2\text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}_3\text{BO}_3 + 2\text{CO}_2$$  (vi)

$$2\text{Na}_2\text{BO}_2 + \text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}_3\text{BO}_3 + \text{CO}_2$$  (vii)

Thus, the overall auto-causticizing efficiency depends strongly on the type of borate compounds formed in the boiler. NaBO$_2$ yields twice as much NaOH compared to Na$_3$BO$_3$ when hydrolysed in water (Reactions ii and vii). Na$_3$BO$_3$ does not yield any NaOH, while Na$_2$B$_2$O$_7$, if still exists in the boiler, would react with NaOH from the weakwash to form NaBO$_2$ (Reaction iii). Thus, if the makeup chemical is not well mixed in the black liquor, or if the auto-causticizing reaction in the boiler does not occur uniformly over the char bed, or if the bed temperature is not sufficiently high, the resulting smelt would contain not only Na$_3$BO$_3$, Na$_2$B$_2$O$_7$, and NaBO$_2$, but also Na$_2$B$_2$O$_7$, which consumes NaOH. This would lower the overall auto-causticizing reaction efficiency in the dissolving tank.

$$\text{Na}_3\text{BO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaBO}_2 + 2\text{NaOH}$$  (viii)

**Effect of Borate on Reaction Efficiency:** The reaction between Na$_2$CO$_3$ and NaBO$_2$ to form Na$_3$BO$_3$ (Reaction i) requires heat to occur. Under a given condition (temperature and time), the reaction is expected to be more difficult to complete as the borate content in the mixture increases. Figure 5 shows results of a laboratory study on the effect of borate content on the auto-causticizing reaction at 900°C for 1 hour. The experiments were performed in air using an isothermal gravimetric apparatus. The degree of completion of the reaction was based on the weight loss of the mixture, assuming Na$_3$BO$_3$ is the reaction product. The weight loss was assumed to be due to CO$_2$ release. The results confirmed that, under the experimental conditions, the reaction occurred completely (100% completion) only for mixtures with a B/Na weight ratio of below 0.0157, which corresponds to about 9.5% auto-causticizing. Above this B/Na weight ratio, the degree of completion decreased and appeared to level off at about 50-60% completion.

**Effect of Chloride and Potassium:** The effects of chloride and potassium on Reaction i were also studied by adding either NaCl or KCl to the mixture of Na$_2$CO$_3$ and NaBO$_2$ (B/Na weight ratio = 0.157). The results show that while both NaCl and KCl have an insignificant effect on the reaction rate, KCl causes the reaction to begin at a lower temperature; 560°C compared to over 600°C when there was no potassium present. This is probably because the presence of potassium salts lowers the first melting temperature of the mixture.

**Reactions between Borate and Hydroxide:** Results obtained from mill trials suggest that the auto-causticizing reaction occurred more completely in a recovery boiler environment than in the laboratory where mixtures of pure Na$_2$CO$_3$ and NaBO$_2$ were used. This is possible considering the presence of char (carbon) in the lower furnace environment, which helps break the Na$_2$CO$_3$ into Na$_2$O and CO, and thereby accelerating the
form of $\text{Na}_2\text{BO}_3$ (Reaction ix)

$$\text{NaBO}_2 + \text{Na}_2\text{CO}_3 + 2\text{C} \rightarrow \text{Na}_3\text{BO}_3 + 2\text{CO}$$  
(ix)

It is also possible that the formation of $\text{Na}_3\text{BO}_3$ in recovery boilers may follow a different path than the reaction between $\text{NaBO}_2$ and molten $\text{Na}_2\text{CO}_3$ in smelt. During black liquor combustion, some sodium is released as elemental Na, which reacts immediately with oxygen and water vapour to form $\text{Na}_2\text{O}$ and $\text{NaOH}$. $\text{NaOH}$ is highly reactive and may react with $\text{NaBO}_2$ or $\text{Na}_2\text{B}_4\text{O}_7$ to form tri-sodium borate, according to Reactions x and xi:

$$2\text{NaOH} + \text{NaBO}_2 \rightarrow \text{Na}_3\text{BO}_3 + \text{H}_2\text{O}$$  
(x)

$$8\text{NaOH} + \text{Na}_2\text{B}_4\text{O}_7 \rightarrow 4\text{Na}_3\text{BO}_3 + 4\text{H}_2\text{O}$$  
(xi)

Figure 6 shows the weight change of a $\text{NaOH}$ and $\text{NaBO}_2$ mixture with an Na/B molar ratio of 3, as it was heated gradually in air in a thermogravimetric apparatus. The weight loss value is close to the theoretical weight loss of the mixture (22.5 wt%) had all the $\text{NaOH}$ in the mixture reacted with borate to form $\text{Na}_3\text{BO}_3$.

Figure 7 shows the weight change of a $\text{NaOH}$ and $\text{NaBO}_2$ mixture (Na/B molar ratio=3) with time when it was heated at a constant temperature of 750°C. The reaction appeared to be essentially completed in about 5 minutes. Similar results were obtained for a $\text{NaOH}$ and $\text{Na}_2\text{B}_4\text{O}_7$ with the same Na/B molar ratio of 3.

The weight loss of mixtures of $\text{NaOH}$-$\text{NaBO}_2$ with different Na/B molar ratios after being heated at 750°C for one hour is shown in Fig. 8. The results were in a good agreement with the theoretical weight loss calculated based on Reaction ix. These results suggest that $\text{NaOH}$ can react readily and rapidly with $\text{NaBO}_2$ or $\text{Na}_2\text{B}_4\text{O}_7$ to form $\text{Na}_3\text{BO}_3$, and that the reaction can occur at any Na/B molar ratio.

The reactivity of $\text{NaBO}_2$ with $\text{NaOH}$ was much greater than with $\text{Na}_2\text{CO}_3$, Fig. 9. At 750°C, for instance, $\text{NaOH}$ can completely react with $\text{NaBO}_2$ in 10 minutes, while the case of $\text{Na}_2\text{CO}_3$, only 70% completion was achieved after more than three hours. Even at 900°C, the reaction was only 80% complete after two hours. The high reactivity of $\text{NaOH}$ compared to $\text{Na}_2\text{CO}_3$ suggests that the direct reaction between $\text{NaOH}$ (or $\text{Na}_2\text{O}$) and $\text{NaBO}_2$ between during black liquor combustion may play an important role in the formation of $\text{Na}_3\text{BO}_3$ in the boiler.

**SUMMARY**

Trials on partial autocausticizing using borate have been conducted at several kraft pulp mills. The results show that the lime consumption was lowered as predicted and there were little or no effects on pulp quality, effluent quality, and evaporator, limekiln and digester operations. The presence of borate in the liquor, however, has a significant effect on the standard ABC titration test method used to determine the EA, AA and TTA of green and white liquors. This problem has been successfully solved with the use of a duto-titrator for liquor analysis.

Several problems were experienced in the recovery boiler operation at one of the mills, including occasionally high SO$_2$ emissions and lowered steam production. These problems were caused by a combination of the low firing load (low heat input) of the boilers during the trial period, and by the greater heat requirement for the borate autocausticizing reaction.

In principle, borate may have an effect on boiler fouling; however, results obtained from mill trials were inclusive. There was no indication of fouling increase at one mill, while at the other mill, deposit accumulation in the superheater region appeared to be worse than normal. This increase in fouling, however, was due primarily to an increase in the auxiliary gas flow and combustion air during the trial. No plugging occurred during all trials.

Results of laboratory studies show that the efficiency of the borate autocausticizing reaction that occurs in recovery boilers increases as the boron concentration in the liquid decreases. This implies that it is easier to achieve maximum reaction efficiency at a lower percentage autocausticizing target.

The main reaction product, $\text{Na}_3\text{BO}_3$, may be formed rapidly by the reaction between NaOH formed during black liquor combustion and $\text{NaBO}_2$ or $\text{Na}_2\text{B}_4\text{O}_7$ in the black liquor.

Since the autocausticizing reaction requires heat, the technology is good for boilers that are thermally limited. For boilers that have low heat input (i.e., low firing load and/or low heating value liquid), it may be difficult to achieve high reaction efficiency.

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**LITERATURE**


Résumé: Des essais sur l’autocaustification partielle avec du borate effectués dans plusieurs usines de papier indiquent une réduction de la consommation de chaux, et aussi que le borate n’a eu aucun effet sur la qualité du papier ou de l’effluent, le matériel de récupération des produits chimiques, et le fonctionnement du lessiveur et du four à chaux. Nous avons rencontré des problèmes d’exploitation avec les évaporateurs, les ateliers de recaustification, et les chauffières de récupération, mais la plupart ont été résolus. Les résultats des études en laboratoire suggèrent que l’efficacité de la réaction de l’autocaustification avec borate survenant dans les chauffières de récupération s’accord à mesure que la teneur en bore diminue dans la liquore. Puisqu’il faut de la chaleur pour l’autocaustification, la technologie peut se révéler utile dans les chauffières dont le capacité thermique est limitée. Pour les chauffières à faible apport de chaleur, il sera difficile d’obtenir une réaction très efficace.

**Abstract:** Trials on partial borate autocausticizing conducted at several kraft pulp mills showed that lime consumption was lowered and there were no effects of borate on pulp quality, effluent quality, chemical recovery process equipment, and digestor and limekiln operations. Several problems were experienced during operation of evaporators, recast plants and recovery boilers, but most have been overcome. Results of laboratory studies suggest that the efficiency of the borate autocausticizing reaction that occurs in recovery boilers increases as the boron concentration in the liquor decreases. Since the autocausticizing reaction requires heat, the technology may be beneficial for boilers that are thermally limited. For boilers that have a low heat input, it will be difficult to achieve a high reaction efficiency.


**Keywords:** CFK Mills, Kraft Pulps, Recovery Plants, Causticizing, Borates, Recovery Furnaces, Heat.