Borate autocausticizing: a cost effective technology

The technology has some very good practical applications


Janson initiated the use of borates for autocautosication in the pulp and paper industry in 1977 [1]. He postulated that borate autocautosication proceeds as shown in Reactions 1 to 3 [2], where one mole of sodium tetraborate (Na₂B₄O₇) produces four moles of caustic (NaOH). Reactions 1 and 2 describe the reactions occurring in the recovery boiler, while the smelt dissolving reaction is given in Reaction 3. In a kraft cook the borate will be in the form of sodium metaborate (NaBO₂), while the make-up borate would be sodium tetraborate pentahydrate (Na₂B₄O₇·5H₂O).

Based on this work, he concluded that the recausticizing lime cycle could potentially be eliminated. Further work was done in kraft pulping using the borated liquor and in autocautosication by Janson [3,4] and others [5] over the next few years. It was shown that the addition of borate to the black liquor had the potential to increase the black liquor viscosity [6], and decrease its heating value, thus rendering the process unattractive.

A full-scale plant autocautosiciozing trial performed in the Enso Gutseit linerboard mill in Kotka, Finland, in 1982 proved inconclusive in determining if borate autocautosication was feasible [7,8].

In 1990, US Borax Inc. began a search to find new uses for borates. One potential use was in autocautosicizing in the pulp and paper industry. A research program was initiated with the objective of determining the effects of borates on kraft pulping and chemical recovery [7]. It was discovered that the chemistry of borate autocautosication is different from that proposed by Janson. The autocautosication reactions were suggested to proceed as follows: Reactions 4 and 5 occur in the recovery boiler, and Reaction 6 occurs in the smelt-dissolving tank.

Reaction 4: Na₂B₄O₇ + 5Na₂CO₃ ↔ 4NaBO₂ + 5CO₂

Reaction 5: NaBO₂ + Na₂CO₃ → Na₂B₄O₇ + CO₂

Reaction 6: Na₂BO₃ + H₂O → 2NaOH + NaBO₂

In these reactions, one mole of sodium tetraborate produces eight moles of caustic, twice as much as proposed by Janson. This suggests that borate autocautosication requires only one half of the borate that was originally postulated, making the technology economically feasible.

In kraft pulping, autocautosicing has been proposed as a way to incrementally increase the amount of caustic available from the smelt. This process, dubbed "partial autocautosicing," involves adding sub-stoichiometric amounts of Na₂B₄O₇·5H₂O to the black liquor and firing in the recovery boiler. On dissolution the smelt produces green liquor that is enriched in caustic, Reaction 6. The unreacted sodium carbonate can still be reacted with lime as per the kraft lime cycle. A trial using partial autocautosicing was successfully done at Cariboo Pulp & Paper in Quesnel, BC, in the fall of 1998 and spring of 1999 [9].

In 1997, Millar Western Pulp (Meadow Lake) Ltd., Meadow Lake, SK, was approached by US Borax about the opportunities the autocautosicing technology might have for a BCTMP mill. The Meadow Lake mill is the world's first successfully operating zero-liquid effluent pulp mill with its effluent all being treated by fibre removal, effluent evaporation, concentration and incineration, Fig. 1 [10, 11]. Currently, 25-30% of the recovery boiler smelt is recycled and used for evaporator pH control and for chip impregnation.

Bleaching of mechanical pulp with peroxide does not require the high caustic charge of kraft pulping, and thus there is potential to fully autocautosize and replace purchased caustic with a sodium tetraborate make-up. In fact, there is another reaction that occurs between pH 9 and 10 that would be beneficial for peroxide bleaching.
of mechanical pulps, Reaction 7.

Reaction 7:

\[ 4\text{NaB}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaOH} \]

In this reaction, the sodium metaborate produced in the dissolving reaction in Reaction 6 reacts with water between pH 9 and 10 to produce caustic, thus buffering the bleaching reaction at its optimum pH. In this regard, the metaborate exhibits buffering properties similar to those of carbonate or silicate. Reaction 7 is not applicable to kraft pulping where the pH is maintained above 13 throughout the cook. For the peroxide bleaching of mechanical pulp, each mole of \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} \) can generate up to 10 moles of caustic, providing sufficient caustic for the bleaching reactions.

In early 1998, it was decided to run a trial feeding \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} \) to the Concentrator Storage Tank, from which the borated liquor would be fired in the Recovery Boiler, Fig. 1. The success of the trial in terms of boiler operation and lab trials with the borated smelt in dissolution, clarification and use in peroxide bleaching of pulp, led the mill to run a large-scale trial in October 1998. In this trial, \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} \) was introduced to the effluent feeding the evaporators and the borated effluent was concentrated and burned. The smelt was dissolved and clarified, Fig. 2, and the borated green liquor (BGL) used as a partial caustic substitute in the pulp mill bleach plant, Fig. 3. The particulars of the two trials are reported in this paper.
BORATES

ANALYTICAL PROCEDURES

All samples from the trials were analysed in-house. Metals, silicon and boron were determined by microwave digestion of the samples in acid and then analysed on a Varian Spectra-10 Atomic Absorption Spectrophotometer (AAS).

The soluble anions were determined by filtering the samples through a 0.45-μm filter, diluting and then analysing them on a Waters HPLC system equipped with conductivity and UV-visible detectors.

Titrations, liquor heating values, solids values and pulp quality parameters were all determined using standard lab procedures.

Trial 1, June 1998 — Recovery Boiler:
A trial involving the addition of Na₂B₄O₇·5H₂O into the recovery system was performed on June 23 and 24, 1998. The chemical was added into the concentrated liquor before firing the liquor in the recovery boiler. The fired liquor BTU was observed to drop as the concentration of boron in the liquor increased, Fig. 4. There were only slight changes observed in the boiler operation. The main problem encountered came from trying to dissolve Na₂B₄O₇·5H₂O in the highly concentrated liquor.

The equilibrium of the non-process elements in the smelt did not change substantially. However, as expected, there was a major reduction in carbonate in the smelt, which was replaced by the borate. The trial was successful with the caustic concentration in the green liquor, derived from smelt dissolved in the lab, increasing 300%, Fig. 5. The caustic increase mirrored the metaborate increase and carbonate decrease.

Trial 2, October 1998 — Full Mill:
— Evaporators to recovery boiler: On October 14, 1998, the second borate trial proceeded with the addition of Na₂B₄O₇·5H₂O to the feed of the evaporators. The original trial displaced many concerns about changing liquor viscosity and evaporator problems that occurred in the original Finnish trial [8].

A sidestream of the evaporator feed was sent to a three-tank dissolving system. Na₂B₄O₇·5H₂O was transferred from bulk storage and dissolved in the evaporator feed. The borated evaporator feed was metered back into the Steam and Recovery process. The system was brought to a constant boron level and monitored for changes in the process. The borate dissolving process ran smoothly, however the increased pH of the evaporator feed caused some fouling problems in the preheaters. Samples of the material fouling the preheaters were taken and analysed. The samples were comprised of mainly calcium and magnesium silicates, with no boron being found. This suggests that the fouling mechanism was more likely caused by pH fluctuations than by the borate itself.

The main effect the borate had on the evaporators was increased flow, due to increased solids loading. The main flow increases were not experienced in the evaporator feed, but rather in the product discharge, primarily because of the 25% increase in the solids in the system due to the addition of borate. The sodium levels in the evaporator feed were maintained around 6,000 ppm, and the boron level equilibrated around 2,000 ppm.

A definite change in the evaporator distillate (MIDS) occurred with the addition of borate into the system. The conductivity of the MIDS doubled with the borate addition. Increasing the pH of the liquor to the normal operating range for one evaporator resulted in the conductivity of that evaporator’s distillate returning to normal values. The reason why pH control was not operating when the trial initially started was that the addition of borate increased the pH in the evaporator feed. Consensus was that this increased pH would be substantial enough to allow the evaporators to run at their normal pH range. This did not occur. It appears that the borate has a greater buffering
capacity than the sodium carbonate, and buffers at a slightly lower pH.

The boron did not appear to increase fouling in the concentrators. The viscosity changes were minimal and caused few problems with the pressures in the Fired Liquor loop.

The recovery boiler experienced the largest changes in the operating parameters. Most of these changes were predicted from the original trial experience. Due to a lowered liquor heating value, natural gas was required to maintain the boiler at regular operating conditions by stabilizing combustion. The large decrease in the fired liquor BTU value was due to the increased inorganic solids loading with the borate in the system. The value, tonnes of steam per tonne of solids fired, is calculated on-line, showing a decrease of about 15%. The liquor flows increased by 22%. The increased gas flow would be the significant operational cost to running borate in the system.

The oxygen in the flue gas decreased by 1%, due to increased carbon dioxide concentrations in the flue gas from the borate reacting with carbonate in the boiler hearth. The opacity of the emissions emanating from the boiler's stack became less erratic and decreased slightly. The borated liquor created less fume. The oxygen in the flue gas decreased by 8%, Fig. 6. The concentration (in mg/kg) obtained equilibrium at approximately 80% with the boron in the system. This was expected from the stoichiometry of the reaction.

The chloride in the smelt increased slightly, but the remainder of the anions did not change substantially during the trial. Changes in the precipitator ash were very distinctive. The amount of ash decreased by 50% and its chemical composition was extremely different when compared to pre-trial conditions. The amount of sodium and boron was relatively constant, with an average of 5,000 ppm of boron lost in the precipitator ash.

The potassium concentration in the ash doubled. The aluminium, calcium, silicon and magnesium all decreased slightly during the trial. The anions experienced marked changes, with the carbonate in the ash disappearing completely and sulphate becoming the major anion. The chloride in the ash remained consistent throughout the trial.

— **Green Liquor System**: The smelt was retrieved from the landfill and dissolved to produce borated green liquor. The liquor was then clarified and stored in temporary tanks that were being stored outside, for use in the pulp mill. There were several problems associated with the clarification process. The dissolved solids concentration of the borated green liquor was reduced from 30% to 20% in an effort to achieve better settling. The settling rates at the lower dissolved solids improved but were not equivalent to the carbonate settling rates. The settling of the borated slurry was slow, due to the small size of the dregs. When inspected under the microscope, the borated dregs particles were determined to be 5 μm or less.

### Table 1. Comparison of borated smelt and ash composition to the 1998 averages.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reported as</th>
<th>Smelt Composition*</th>
<th>Ash Composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1998 Average</td>
<td>Borated</td>
<td>1998 Average</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na⁺</td>
<td>41.4</td>
<td>35.5</td>
</tr>
<tr>
<td>Potassium</td>
<td>K⁺</td>
<td>1.09</td>
<td>1.56</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca²⁺</td>
<td>1.24</td>
<td>1.16</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg²⁺</td>
<td>0.92</td>
<td>0.82</td>
</tr>
<tr>
<td>Silicon</td>
<td>SiO₂⁻</td>
<td>1.73</td>
<td>1.85</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>&lt;0.005</td>
<td>5.19</td>
</tr>
<tr>
<td>Soluble</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>CO₃²⁻</td>
<td>35.8</td>
<td>8.16</td>
</tr>
<tr>
<td>Chloride</td>
<td>Cl⁻</td>
<td>0.99</td>
<td>1.46</td>
</tr>
<tr>
<td>Sulphite</td>
<td>SO₃²⁻</td>
<td>2.02</td>
<td>1.34</td>
</tr>
<tr>
<td>Sulphate</td>
<td>SO₄²⁻</td>
<td>2.51</td>
<td>2.80</td>
</tr>
<tr>
<td>Sulphide</td>
<td>S³⁻</td>
<td>5.02</td>
<td>5.49</td>
</tr>
<tr>
<td>Thiosulphate</td>
<td>SO₂₃⁻</td>
<td>0.72</td>
<td>0.30</td>
</tr>
</tbody>
</table>

*All values in wt %
The settling rate of particles is exponentially linked to the size of the particle, providing a theoretical settling rate of 8 ft/day. That assumes the particles are settling in water (density = 1.0 g/mL), and not a 20% dissolved solids solution (density = 1.19 g/mL), which hinders settling even more. Agglomerating the dregs particulate together could improve settling. Several polymers were examined and a product that would work with any consistency was not found.

The solution temperature is a significant factor in achieving good settling. Maintaining a constant temperature with the changing ambient temperatures and uninsulated settling tanks was virtually impossible. Temperature gradients caused thermal currents, which resulted in mixing in the tanks. When steam was injected into the tanks to keep the temperature constant, it created mixing. The best way to get the material to settle would be in a properly insulated settling clarifier. On November 16, 1998 the system was shut down due to low ambient temperatures.

In lab studies the dregs material did not compress well. When settling occurred, the dregs occupied approximately forty-five percent of the tank volume. The dregs material is light and porous, and would require some form of mechanical dewatering device. The sodium carbonate dregs are much heavier and compress to about five to eight percent of the clarifier on a volume basis.

The BGL addition rate (add rate) was initially set at 4.0% (as equivalent caustic) because lab studies had shown that more BGL than caustic was required to achieve the desired physical properties. After the first day, the BGL add rate was dropped to 2.5% as the tower temperatures and the tensile increased substantially and the peroxide residuals out of the P2 tower dropped. The EDTA was also turned on at this point to help stabilize the bleaching reaction. The BGL was reduced further to 2.0%, and again to 1.8% over the period of one day. By this time, the P2 tower temperatures had returned to normal levels and the peroxide residuals had recovered. The BGL add rate was then increased back to 2.5% and left there for the duration of the trial.

As the trial progressed, it was discovered that the BGL in the storage tank had stratified into different concentration layers due to caustic contamination. The concentration of the BGL decreased throughout the trial as the level dropped in the storage tank. That resulted in physical property control difficulties, as the amount of alkali being added to the system was inconsistent and the flowrate of BGL needed to be adjusted continuously.

TABLE II. Finishing line quality comparison: caustic and borate at P2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Caustic at P2</th>
<th>Borate at P2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td>std. dev.</td>
</tr>
<tr>
<td>Bright (% ISO)</td>
<td>84.8</td>
<td>0.51</td>
</tr>
<tr>
<td>Tensile (m)</td>
<td>3259</td>
<td>379</td>
</tr>
<tr>
<td>Bulk (cm³/g)</td>
<td>2.22</td>
<td>0.13</td>
</tr>
<tr>
<td>COD (kg/adt)</td>
<td>6.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Freeness (mL CSF)</td>
<td>283</td>
<td>17</td>
</tr>
<tr>
<td>0.004-in. debris (%)</td>
<td>0.238</td>
<td>0.074</td>
</tr>
<tr>
<td>0.006-in. debris (%)</td>
<td>0.013</td>
<td>0.004</td>
</tr>
</tbody>
</table>

*interpolated from regression analysis

FIG. 7. Kinetic study of borate vs. caustic bleaching — brightness profile.

The chemical make-up of the dregs differs substantially from the liquor. Two dregs samples were analysed. The first was dregs directly from the dissolving system, and the second was a dregs sample that was sufficiently washed to remove all dissolved material. The dregs from the bottom of the settling tank were approximately 26.5% total solids. The dregs from the sodium carbonate green liquor system average 52% total solids. This shows the major compression discrepancy between the dregs from the two processes. In a dried, unwashed sample of borated dregs, 77% is soluble.

Bleach Plant Trial:

— Steam and Recovery operation: The sodium hydroxide in the borated green liquor increased significantly, which was the goal of this trial. The material was successfully used as a caustic replacement in the pulp mill (vide infra). The effluent streams from the pulping process were monitored during the bleach plant trial. The results were very encouraging as the amount of boron returning to the P2 bleach tower. EDTA was also piped up to the P2 tower in case the BGL caused instability in the bleaching reaction.

The BGL addition rate (add rate) was initially set at 4.0% (as equivalent caustic) because lab studies had shown that more BGL than caustic was required to achieve the desired physical properties. After the first day, the BGL add rate was dropped to 2.5% as the tower temperatures and the tensile increased substantially and the peroxide residuals out of the P2 tower dropped. The EDTA was also turned on at this point to help stabilize the bleaching reaction. The BGL was reduced further to 2.0% and again to 1.8% over the period of one day. By this time, the P2 tower temperatures had returned to normal levels and the peroxide residuals had recovered. The BGL add rate was then increased back to 2.5% and left there for the duration of the trial.

As the trial progressed, it was discovered that the BGL in the storage tank had stratified into different concentration layers due to caustic contamination. The concentration of the BGL decreased throughout the trial as the level dropped in the storage tank. That resulted in physical property control difficulties, as the amount of alkali being added to the system was inconsistent and the flowrate of BGL needed to be adjusted continuously.
The P2 tower behaved normally when substituting BGL for caustic. High BGL add rates caused higher temperatures and lower peroxide residuals at the outlet of the P2 tower as peroxide decomposition occurred. As the BGL add rate was reduced to 2.5% from 4.0%, the temperatures dropped and the peroxide residuals increased to normal levels.

Three days into the trial, the EDTA was completely used up. Even without the EDTA, the peroxide residuals and finishing line brightness remained on target. The peroxide add rate was not changed during the entire trial. The only hardship incurred was the fluctuating BGL concentration. Overall, the trial ran well and showed a promising future for BGL at the mill.

— Finishing line quality: The in-process and finishing line brightness did not change significantly before, during or after the trial. This is a positive result for this trial and supports the kinetic studies done in the lab. That is also contradictory to the initial bag bleaches that had been done prior to the trial which suggested that the brightness would be significantly lower than the bag bleaching with caustic.

Table II shows the average finishing line quality values with and without BGL added to the P2 tower.

There is very little difference between the pulp produced with caustic and the pulp produced with BGL. The data from the BGL trial has a much higher standard deviation due to the difficulties experienced with the BGL concentration.

— Bleaching kinetic study: Pulp was gathered from the P2 rotomixer before and during the trial and placed in a water bath for four hours to determine the difference between bleaching with BGL and bleaching with caustic. Samples were pulled out at specified time intervals and the brightness and residual peroxide were measured. The bleaching conditions for each sample are as follows:

- Bath temperature = 65°C;
- peroxide add rate = 6.5%;
- Silicate add rate = 2.5%; and
- MgSO4 add rate = 0.5%

The caustic add rate was 2.4% for the caustic bleach and the BGL add rate was 2.5% for the BGL bleach. The results of the bleach study are shown in Table III and depicted graphically in Figs. 7 and 8.

The results of the bag bleaches show that there is essentially no difference between the BGL bleach and the caustic bleach. The BGL brightness was a little higher and the peroxide residuals were correspondingly lower. That was due to the fact that the BGL add rate was 0.1% higher than the caustic add rate which would result in higher brightness and lower peroxide residuals.

**IMPlications**

Operational Implications: The implications of this trial are enormous. The successful use of borated green liquor to replace caustic in the pulp mill could lead to a complete closure of the Steam and Recovery process. An effective trial in the pulp mill has the potential to make process closure a reality. The new process would completely eliminate the landfill of smelt, and would reduce the amount of ash going to landfill by more than half. The only inorganic materials that would be land-filled would be small amounts of ash and the dregs from the clarification process.

The implementation of a permanent system would eliminate the need for the existing tray conveyor, which causes a significant amount of downtime in the recovery boiler. The maintenance costs for the boiler would decrease substantially as a result.

The green-liquor system would run smoothly with more consistent flows and temperatures. Steady-state conditions would allow the insoluble material to settle in the clarifier that would work considerably better, with its slower rise rate, than the temporary tanks. The boiler operation would require only slight modification to run at the lowered fuel heating values. The recovery boiler would not be limited by the increased liquor flow because the steam load would remain consistent with normal operation. Natural gas costs would rise as the lower BTU value of the borated-fired liquor would not provide sufficient steam for the process. The required steam would have to be generated from the natural gas.

If completely successful, the borate would reduce the operational costs substantially. No caustic would need to be purchased and make-up sodium borate would be the only material required to ensure that the alkali to drive the process was available.

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Borate Requirements: The stoichiometric ratio of Na2B4O7·5H2O to caustic is 1:10. On a mass basis, roughly 1 kg of Na2B4O7·5H2O is required to produce 1 kg of caustic at a 70% reaction efficiency. Thus the borate mass needed during the initial system charge would be similar to the caustic normally required. The cost to initially charge the system would also be similar to normal caustic costs.

The major losses of boron from the system would occur in the dregs. Lab studies show that these losses could be 70% without proper washing and dewatering of the dregs. With dregs dewatering and washing the losses of boron in the dregs are around 9%. The ability to wash the dregs would substantially reduce the amount of boron required from external sources to keep the process levels constant.

The other points where minor amounts of boron are lost from the process are the precipitator ash and the pulp. Approximately 0.1 to 0.3% of the boron added during the trial was discharged in the precipitator ash. This would be an acceptable loss to maintain the system purge for the chlorides. The boron is quite soluble and the washing in the pulp mill is very efficient, therefore the amount of boron lost with the pulp will be fairly insignificant compared to the losses in the dregs.

The amount of Na2B4O7·5H2O required to maintain autocausticization in the system is approximately 10% of the caustic required in a year. This would reduce the variable costs of pulp production by 5%.

**CONCLUSIONS**

The borate autocausticization technology was demonstrated to work well in both the Steam and Recovery area, and in the bleach plant. In Steam and Recovery, few...
operational problems were encountered and the technology proved itself by providing an alkali stream, green liquor that had the required caustic strength.

In the bleach plant, the BGL worked well as a substitute for caustic in the P2 position on Line 2. The BGL exhibited the same bleaching kinetics as pure caustic and it was possible to produce the desired pulp properties at the finishing line with the BGL. This indicates that all of the pulp mill’s alkali needs could be met using BGL and that the current requirement to purchase caustic could be eliminated.

The recommendation has been made that this technology be further investigated and a full mill trial be tried in the future. Replacing all of the caustic addition points with BGL would verify that the recycle portion of the borate process works as well in practice as in theory.

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LITERATURE