

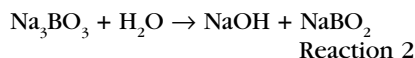
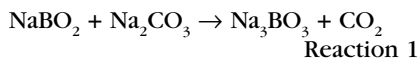
Partial borate autocausticizing trial increases capacity at Swedish mill

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ABSTRACT: A full-scale partial borate autocausticizing trial has been running continuously and successfully since November 2002 at the Stora Enso Norrsundet mill in Sweden. The objective has been to off-load the lime kilns and reduce the amount of purchased lime and subsequent lime mud disposal costs. The total lime requirement has been reduced by about 7% while the autocausticizing level averaged around 9%-11% over this period. Overall, the presence of sodium borate in the liquors had little effect on the mill operations and the pulp properties and quality were unaffected. Results suggest that borates may enhance the pulp yield.

Application: Partial borate autocausticizing is an easy way for a recausticizing-limited mill to increase its capacity without new equipment.

The use of sodium borates to causticize smelt directly was first suggested by Janson in the late 1970s [1] and refined by Tran et al. [2] in the 1990s. The principal autocausticizing (AC) reaction that occurs in the recovery boiler is between sodium metaborate (NaBO_2) and sodium carbonate (Na_2CO_3) in the molten smelt to form trisodium borate (Na_3BO_3) (Reaction 1). Na_3BO_3 reacts with water in the smelt dissolving tank to form sodium hydroxide (NaOH) and regenerate NaBO_2 (Reaction 2).



If sodium borates are added to the kraft liquor at sub-stoichiometric levels, partial AC could be achieved, which allows an incremental increase in the causticizing capacity of the liquor cycle. This concept has been tried earlier in a number of North American mill trials [3-5]; however, the Stora Enso Norrsundet mill in Sweden is the first European mill to conduct a mill trial of borate AC.

The mill produces 800 air dried metric tons (admt) per day of bleached kraft pulp from softwood (spruce and pine). The recovery process consists of two parallel sets of multiple-effect evaporators, one concentrator, two recovery boilers, two lime kilns, one slaker, and five causticizers. The lime kiln operation is the bottleneck in the mill's recovery cycle. Fresh lime has to be purchased to overcome this constraint. Additional costs are incurred as the excess lime mud is sent to an external company for reburning.

The main objective for Norrsundet to run a partial borate AC trial was to off-load the lime kilns and reduce the amount of purchased lime. The trial commenced in November 2002 and had been running continuously and successfully for at least 15 months.

TRIAL PREPARATION

Laboratory Studies

The first ever mill trial with borate AC was conducted at the Stora Enso Kotka mill in 1982 using the Janson chemistry [1]. The trial was unsuccessful due to a large drop in pulp yield and an increase in the black liquor viscosity. Consequently, before the current trial was initiated, Stora Enso conducted laboratory studies to investigate the effects of borate at a level equivalent to providing 15% AC.

Pulping studies on softwood chips showed no difference in cooking yield, bleachability, beatability, or pulp properties when borate was added to the pulping liquor. The black liquor viscosity was also unaffected below 77% dry solids. The as-fired black liquor concentration at Norrsundet is typically 71% dry solids. Combustion studies similar to those described by Hupa et al. [6] showed a decrease in swelling of the black liquor droplets during combustion at AC levels <20%. A clear decrease in the char burning times was observed for the Norrsundet liquors, although the pyrolysis time was unchanged.

Borate Loading

The mill used sodium tetraborate pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) as the source of sodium borate during the trial.

The sodium borate was introduced into the weak black liquor stream before the evaporators. Initial loading of the liquor cycle to 12% AC was completed over a one month period. Make-up of sodium borate is required and has been calculated to be about 2.5% of the borate inventory per day. The make-up was added at the same location as initial loading and typically occurred for 6 h/day on alternate days.

Pulp Liquor Analysis

The addition of sodium borate to pulping liquors affects the analysis of white liquor (WL) and green liquor (GL) by the conventional ABC-titration method [7]. Borax installed automatic dual-titrator systems, which calculate not only typical liquor properties (i.e., effective alkali, active alkali, total titratable alkali, causticity, and sulfidity), but also the boron concentration.

Norrsundet has an in-line titrator, which is used for process control of the recausticizing plant. It was necessary to reprogram the calculation of liquor composition in the system to accommodate the presence of boron so that the automatic process control could be maintained. The boron concentration was analyzed in-house by atomic absorption spectroscopy (AAS) and used to correct the in-line titrator analysis results. The boron and sodium concentrations were analyzed frequently by AAS during the initial loading phase to confirm the level of AC and borate loading requirement.

TRIAL RESULTS

The trial has been running successfully at Norrsundet mill for more than 15 months. **Figure 1** shows the variations in the level

RECOVERY

Parameter	Unit	Pre-trial Period, 2/15/2002 to 11/15/2002	Trial Period, 12/1/2002 to 2/15/2004	Change, %
Effective alkali (EA) charge to digesters	kg NaOH/ admt pulp	430	416	-3.4
EA charge to oxygen delignification		20	27	34.0
Total EA usage		450	442	-1.7
Total solids in BL	kg/admt	1788	1780	-0.4
Total inorganic solids in WL or BL	pulp	706	732	3.7
Total organic solids in BL		1082	1049	-3.1
Estimated* yield of brownstock pulp	% of moisture	47.5	48.3	1.7
Estimated* yield of final pulp	free wood	43.7	44.4	1.7

* Assuming 8% fiber yield loss during bleaching and 10% moisture content in the air-dried pulp.

I. Calculated pulp yield using measured black liquor (BL) total solids and white liquor (WL) inorganic solids per metric ton of pulp.

Evaporator Parameter	Unit	Pre-trial Period, 2/15/2002 to 11/15/2002	Trial Period, 12/1/2002 to 2/15/2004	Change, %
Weak BL flow to evaporators	L/s	105	111	5.5
Total steam used in Effect-1	kg/s	19	20	7.9
Concentrated BL flow to both boilers	L/s	19.2	19.0	-1.2
Concentrated BL solid content	wt%	70.1	70.6	0.7
Concentrated BL solid flow to boilers	kg/s	18.0	18.4	2.0
Concentrated BL solids load	kg/admt	1788	1780	-0.4

II. Evaporator/concentrator load and black liquor (BL) flows.

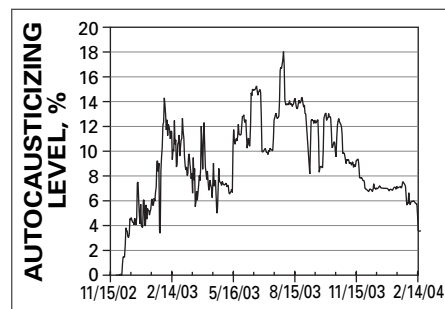
of partial AC during this period, which was controlled by the amount of make-up borate used. The AC level averaged 9%-11% for the initial 15 months of the trial. Overall, the total lime requirement per air dried metric ton of pulp was reduced and no negative effects have been noticed in the mill operations. The performance of the digesters, evaporator plant, recovery boilers, and recausticizing plant have been monitored during this period and are discussed in more detail below.

Digesters

Borate AC caused no change in pulp quality in terms of viscosity, brightness, or strength properties. Boron was not detected in the final pulp and no problems occurred in the operation of the digesters or in the rest of the fiber line.

To determine if the presence of sodium borates in the cooking liquor affect-

ed pulp yield, we calculated the organic content of black liquor solids for a 9 month baseline period and compared the results with those for the 15 month trial period. The concentrated black liquor flow rate and solids content (before addition of precipitator ash) are used to determine the total black liquor solids per metric ton of pulp. The WL flows and concentration are used to determine the inorganic solids content of WL per metric ton of pulp, which is equivalent to that in black liquor. Then, the organic solids content of black liquor per metric ton of pulp is calculated by the difference. To convert the organic solids per air dried metric ton to yield, we assumed that 1 admt is equivalent to 900 kg of bone-dried bleached pulp or 978 kg of brown-stock pulp (i.e., $(978\text{kg} - 900\text{kg})/978\text{kg} = 8\%$ yield loss during bleaching). The calculation results,



1. Variations in the theoretical auto-causticizing level during the trial.

presented in Table I, show that the average brownstock pulp yield has probably increased from a pre-trial value of 47.5% to the trial value of 48.3% on dried wood basis. The result is consistent with published laboratory studies [8,9], which suggest that there can be a 1%-2% yield increase when sodium borate is added to the cooking liquor.

Work published as early as 1965 suggests that sodium borates can retard cellulose peeling reactions [10]. This hypothesis is under investigation to understand how borates reduce the peeling reactions. One possible explanation is the formation of temporary complexes between sodium metaborate and the vicinal hydroxyl groups of the mannose units at C-2 and C-3 positions in the glucomannans. The data from the Norrsundet mill trial are the first mill evidence that support the concept that sodium borates could enhance pulp yield. This effect still needs to be quantified because other operational changes have been made in the digester during this trial period.

Evaporators

The evaporators at Norrsundet typically produce about 19 L/s of concentrated black liquor at 70%-71% solids for the two recovery boilers to burn. As with earlier reported partial borate AC trials [3-5], the operation of the evaporators during the trial was relatively smooth. The weak black liquor flow and steam consumption at the evaporators increased somewhat (Table II). This was due to three contributing factors: (i) 2.4% increase in pulp production; (ii) the increase in concentrated black liquor solids content from 70.1% to 70.6%; and (iii) some extra water that was used to load the sodium borate instead of using the originally planned weak black liquor.

The concentrated black liquor solids throughput has shown about a 2% increase, which is about the same level as the extra sodium borate load in the liquor, so it may seem that the increase is due to the load of borate. However, the concentrated black liquor load per air dried metric ton of pulp (Table II) shows a small decrease. Therefore, we concluded that the additional black liquor solids load is due to increased pulp production. The additional load of borate could have been compensated for by the 1.7% decrease in effective alkali charge and 3.1% decrease in black liquor organic content (Table I). We have seen no evidence of increased scaling in either the evaporators or the concentrator.

Recovery boilers

Norrundet has two recovery boilers: SP#65 is a 1965 Maskinverken unit and SP#70 is a 1970 Gotaverken unit. Both recovery boilers handled the borate black liquor reasonably well. Table III summarizes the main operating parameters of both boilers during the trial as compared to the pre-trial period.

Despite the added load of borate and higher average production, the averaged firing black liquor solids flow to both recovery boilers decreased by about 1%, while the steam production increased, as shown by both steam and feed water flows to the boilers. This suggests a potential improvement in the firing black liquor heating value or the boiler thermal performance. One explanation for this improvement is a decrease in the recovery boiler dust load that was observed in earlier mill trials of borate AC [5].

Table IV summarizes the result of boiler dust load calculations obtained by subtracting the concentrated black liquor from the firing black liquor per air dried metric ton of pulp production. The averaged dust load calculated for both boilers shows a substantial decrease of about 50% during the borate trial, which overcompensates for the extra inorganic load of borate in the liquor. This is a significant decrease that was partially related to an attempt made to decrease the bed temperature in boiler SP#70 to improve the boiler stack opacity (pre-trial condition). However, the major contributing factor in decreasing the dust load is expected to be the presence of borate and the AC reaction that reduces

Operating Parameter	Recovery Boiler, SP#65	Recovery Boiler, SP#70
<i>As-fired Black Liquor</i>		
Volumetric flow, L/s	-1.6% (decrease)	-1.1% (decrease)
Solids flow, kg/s	-1.1% (decrease)	-1.3% (decrease)
Solids content	+0.4% Point (increase)	No data
Temperature	+1.8°C (increase)	+1.9°C (increase)
<i>Steam</i>		
Superheated steam flow	+3.2% (increase)	+1.8% (increase)
Feed water flow	+3.5% (increase)	+1.9% (increase)
Temperature	-5°C (decrease)	-15°C (decrease)
Pressure	Small increase	Small increase
Steam/BL ratio	+1.6% (increase)	+1.8% (increase)
Temperature gain across primary superheater	-12°C (decreased heat transfer)	-3°C (decreased heat transfer)
<i>Flue Gas Temperature</i>		
Before generating bank	-23°C (increased SH heat transfer)	+29°C (decreased SH heat transfer)
After generating bank	+7°C	-3°C
Temperature loss across generating bank	-30°C (decreased heat transfer)	+32°C (increased generating bank heat transfer)
<i>Air</i>		
Primary air ratio	+1% point (increase)	+0.7% point (increase)
Secondary air ratio	-1.4% point (decrease)	+2.7% point (increase)
Tertiary air ratio	No change	-3.6% point (decrease)
Total air	+2.1% (increase)	-1.4% (decrease)
Air/BL ratio	No change	-1.4% (decrease)
Excess O ₂	+0.4% Point (increase)	+0.2% Point (increase)

III. Changes observed in the average values of main operating parameters of the recovery boilers during the borate trial as compared to the pre-trial period.

Evaporator Parameter	Unit	Pre-trial Period, 2/15/2002 to 11/15/2002	Trial Period, 12/1/2002 to 2/15/2004	Change, %
Concentrated BL solids load	kg/admt	1788	1780	-0.4
Firing BL solids load	pulp	1899	1831	-3.6
Total dust load of the recovery boilers		111	51	-54.4
Total load of sodium borates (as NaBO ₂)		0	34	—
Organic content of concentrated BL	wt %	60.5	58.9	-2.7
Organic content of firing BL		57	56.2	-1.3

IV. Calculated precipitator dust load of the recovery boilers for the pre-trial and trial periods as compared with the borate inorganic load.

the carbonate content of the char bed. (The char bed is known to be a major source of Na volatilization resulting in dust formation). While a decrease in dust load has positive effects on the boiler thermal efficiency, it reduces the sulfur capture function of the dust in the upper furnace and may increase SO₂ emission if it is not compensated for by some increase in the char bed temperature.

Interesting observations are found in the data presented in Table III for steam

and flue gas temperature and the air distribution, which suggests that the recovery boiler fouling pattern and behavior were affected. For SP#65, the flue gas temperature at the generating bank inlet shows that the overall heat transfer in the superheater is increased. However, we also noted a small decrease in primary superheater heat transfer. Therefore, the increase in heat transfer should have been mostly in the secondary superheater, which is placed at the

RECOVERY

Parameter	Unit	Pre-trial Period, 2/15/2002 to 11/15/2002	Trial Period , 12/1/2002 to 2/15/2004	Change, %
GL to slaker	L/s	38.0	38.8	2.1
GL density at boiler SP#65	g/L	1142	1166	2.1
GL density at boiler SP#70	g/L	1168	1178	0.9
Lime to slaker (using the screw rpm)	Metric ton/L	7.4	7.2	-3.1
Slaker Delta-T	°C	14.9	13.5	-9.5
Lime mud slurry flow to kiln/filter 64	L/s	9.0	8.7	-3.1
Lime mud slurry flow to kiln/filter 74	L/s	2.9	2.7	-7.5
Lime / GL ratio (using screw rpm)	kg/m3	92.4	87.4	-5.4
Lime / GL ratio (using slaker Delta T)	°C/m3	38.5	34.8	-9.6
WL filter pressure drop	kPa	88.1	88.6	0.6
Weak wash flow to SP#65	L/s	8.43	8.19	-2.9
Weak wash conductivity at SP#70	MS/m	105	60	-42.9
Dregs flow to filter	L/s	1.41	0.79	-43.9

V. Effects of autocausticizing trial on the recausticizing plant.

front end of the superheater where the platens are exposed to higher flue gas temperatures.

We observed similar trends in SP#70. However, this boiler suffered from a higher heat transfer loss at the primary superheater zone, which resulted in an overall decrease in the superheater heat transfer. This was partially related to a reduction in heat transfer surface in the primary superheater due to the removal of several superheater tube sections in this zone. In addition, SP#70 was retrofitted in May 2002 to increase the cross-sectional area of the hearth, which was followed with some changes in the boiler operating conditions that started before the borate trial and continued through the trial. This boiler runs at a high load and the mill has previously experienced issues of fouling, which motivated the retrofit.

To address the increased fouling in this boiler, Professor Mikko Hupa's group at Åbo Akademi in Turku, Finland, conducted a study in which the quantity and composition of carryover deposits were examined and the melting behavior of the borate-containing deposits were modeled. The main conclusion of this work was that the amount of carryover was dependent on the firing conditions rather than the boron content. However, the position of the fouling zone in the boiler could have been affected by borate towards a shift in fouling from the secondary superheater towards the pri-

mary superheater. As a result, the soot-blowing pattern was adjusted to target areas of high fouling potential.

The decrease in superheater heat transfer resulted in an increase in generating bank heat transfer (in SP#70) and vice versa, i.e., the increase in superheater heat transfer lowered the generating bank heat transfer (in SP#65). Generally, the effect of borate AC on boiler fouling was quite manageable, despite the prediction and observation of a shift in deposit accumulation towards the back end of the superheater and the generating bank inlet.

We noted negatives and positives in the boiler operation during the borate trial, which could be the subject of a more detailed study. Overall, the boilers handled the borate liquor reasonably well and the operation was satisfactory. During the annual mill shutdown, the recovery boilers were examined for signs of increased corrosion: none was observed.

Recausticizing and lime kilns

The effects on the recausticizing plant were quite apparent (Table V). They included some increase in the GL flow and a clear decrease in lime usage, as seen in the reduced speed of the lime conveyor, reduced temperature difference or ΔT at the slaker (normally ΔT is directly proportional to lime added to the slaker), and the lime mud slurry flow. The ratio of lime/GL is normally a good

measure of the lime usage. On average, the lime/GL ratio shows a 5.4% decrease using the lime screw data and a 9.6% decrease using the slaker ΔT data. The discrepancy between the two measures of lime usage and the variation in purchased lime requirement due to a number of kiln operational issues has made it difficult to obtain a quantitative measure of the AC performance.

Other positive effects in this area include an apparent increase in the lime mud-settling rate, noticed by the mill operators as a decrease in the pressure drop at the WL pressure disk filter at the start of the trial. This improvement is not clear in the data shown in Table V because a subsequent increase in WL flow through the filter increased the pressure drop. The positive effect on lime mud separation is also observed as a reduction in weak wash (WW) concentration (as shown in WW conductivity) measured at the recovery boiler SP#70 and a decrease in WW flow rate measured at recovery boiler SP#65. The decrease in both concentration and flow of WW indicate improved lime mud separation, i.e., more efficient WL filter operation, which could be expected because of the reduced lime mud load in WL.

We also noted a decrease in the dregs content in both the unclarified and clarified GL, which is now more stable than before the start of the trial. The average dregs content in the unclarified GL is reduced by 40%, from 1200 mg/L to 750 mg/L, which is consistent with a 44% decrease in the flow to the dregs' filter (Table V).

Environmental Impact

Borates are naturally occurring minerals. They are an essential micronutrient for all plant life, essential for aquatic life, and probably essential to humans. Borates are present in soils (10-20 ppm borate), rocks (5-100 ppm borate) and in inland freshwaters at relatively low concentrations (typically < 1 ppm borate). Scandinavian rivers have been reported to contain 0.01 ppm borate. Seawater contains higher concentrations (typically 5 ppm borate) [11]. Norrsundet is situated on the coast of the Gulf of Bothnia in Sweden. The Swedish limit for boron in effluent to a water recipient is 10 ppm [12]. The effluent streams at the mill pass through an activated treatment plant before being discharged to the sea.

The trial has had no effect on the treatment plant and the boron concentration in the effluent has been measured to be less than 4 ppm during the trial period. According to the European Union technical guidance document for risk assessment, for coastal discharges the initial dilution will be around 10-fold and a total dilution of 100 may be assumed [13]. Borates do not bioaccumulate in aquatic animals, therefore we anticipate that there will be no impact on the marine environment.

CONCLUSIONS

A partial borate AC trial has been conducted at the Stora Enso Norrsundet mill in Sweden for a period of more than 15 months. The results show that the addition of sodium borate to the liquor cycle was effective in producing caustic directly and thus reducing the total amount of lime in the cycle. Some evidence also suggests that pulp yield has increased. No negative effects were found on pulp quality or pulp properties. The effects on the recovery boilers were quite positive for steam production, though changes in the boiler fouling pattern were observed. The comparison of the black solids flow at the concentrator and recovery boiler shows significant decreases of about 50% in the electrostatic precipitator dust load

for the trial period. There has been no evidence of increased corrosion or cracking in the recovery boilers, evaporators, digesters, or other equipment. Overall, sodium borate in the liquors had little effect on the mill operations. The trial has been considered successful and Norrsundet continued to evaluate the true benefits for a further year. **TJ**

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INSIGHTS FROM THE AUTHORS

Partial borate autoausticizing has been studied by different researchers to provide information about the behavior of borates in kraft liquors. This paper takes these research findings one stage further: a long-term mill trial.

The most difficult aspect of this research was distilling cause and effect from the everyday process parameters. The trial revealed good translation of the technology from the laboratory to full-scale production, including being able to quantify other benefits. We believe that this is a good reference for other, similarly recausticizing-limited mills. The next step is to develop this technology worldwide and explore the potential to replace higher levels of caustic.



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