Fireside behavior of black liquors containing boron

MIKKO HUPA, MIKAEL FORSSÉN, RAINER BACKMAN, ADRIAN STUBBS, AND ROLAND BOLTON

ABSTRACT: Partial autocaustization using boron has become an interesting option for debottlenecking the recausticizing department in the chemical recovery cycle of kraft pulp mills. Several full-scale trials in North America have shown that the autocaustization concept using boron works efficiently in recovery boilers. However, more detailed information is needed about the influence of boron on the operation of the recovery boiler.

This paper presents initial information about the effects of meta-borate addition on the liquor burning properties, smelt bed melting behavior, and fireside deposit characteristics in superheaters. The information is based on multiphase chemical equilibrium calculations of the furnace processes and results obtained at the Åbo Akademi single droplet burning test facility.

The presence of boron lowers the melting temperature range of the smelt and the carry over liquor residue particles. Larger boron additions also changed the burning behavior of the black liquor studied. The characteristic swelling during the devolatilization stage decreased, resulting in somewhat longer burning times. The measured release of carbon and the formation of NO and SO_2 from the burning droplet were not changed significantly.

Application: Initial testing shows that mills may benefit from boron to debottleneck the caustication segment of their recovery boiler operations.

Jansson first suggested the use of sodium borates to causticize the black liquor recovery boiler smelt directly in the furnace in 1977 [1]. This so-called autocausticizing process involved the reaction between the sodium carbonate in the bed and the added sodium metaborate ($NaBO_2$) to form disodium borate ($Na_4B_2O_5$). The disodium borate would hydrolyze in water to sodium hydroxide (NaOH), and to the original sodium metaborate. This process would produce sodium hydroxide directly in the green liquor, thus eliminating the need for the recausticizing plant, including the lime kiln.

Recently, Tran et al, studied this autocausticizing process further. [2,3]. They showed that the key borate formed in the furnace is trisodium borate (Na_3BO_3), instead of the disodium borate as originally suggested by Jansson. In water the trisodium borate hydrolyzes to form NaOH and $NaBO_2$.

This finding implied that only half a mole of boron (metaborate) is required to produce one mole of NaOH in the green liquor, as opposed to one mole of metaborate per mole of NaOH as in the Jansson concept. This 50% reduction in borate requirement has made the borate autocausticizing process much more attractive. Especially interesting is the possibility to partially convert the carbonate in the smelt to borate with a small amount of metaborate, and then complete the causticizing of the remaining sodium carbonate in the recaust plant with a reduced amount of lime. This partial autocausticizing technology is an attractive alternative for kraft mills where the capacity of the recaust plant or the lime kiln is limiting the total production [2,3].

The presence of sodium metaborate in the black liquor changes the recovery furnace chemistry. Besides changing the smelt bed composition by replacing a part of the alkali carbonate with trialkali borate, the boron will also influence other furnace processes. This paper presents some initial information about the influence of metaborate addition on the liquor burning properties, smelt bed melting behavior, and fireside deposit characteristics in superheaters. The information is based on multiphase chemical equilibrium calculations of the furnace processes and results obtained at the Åbo Akademi single droplet burning test facility.

LOWER FURNACE GAS AND BED CHEMISTRY

Figure 1 shows the equilibrium composition of the smelt bed and the lower furnace gas phase as function of temperature. These equilibrium calculations are based on thermodynamic data of the relevant compounds in the recovery boiler furnace we have collected previously including the data base for the non-ideal condensed phases as produced by Backman [4]. Figure 1A shows results for normal kraft liquor with no boron addition.

The main compounds in the bed are sodium monosulfide (Na_2S) and sodium carbonate (Na_2CO_3) with small amounts of NaOH at higher temperatures. In the gas phase the main sulfur species are H_2S(g) and COS(g), and the main sodium compounds are NaOH(g) and Na(g). These results are consistent with similar previous calculations [5,6].

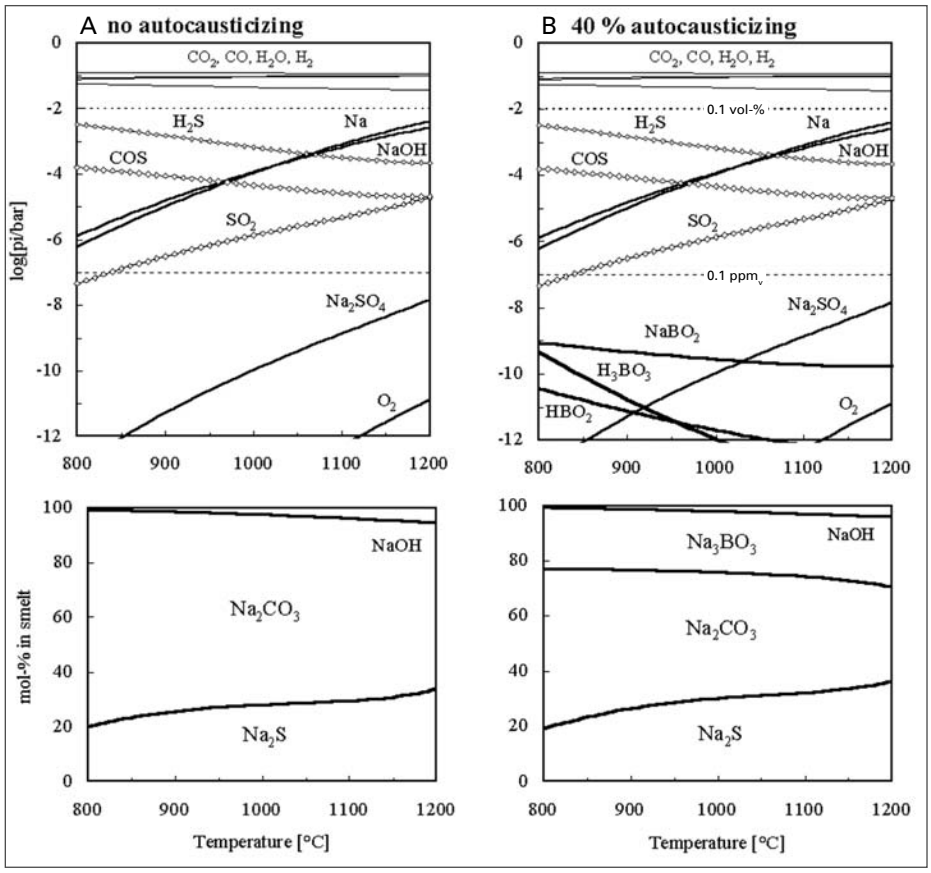
Figure 1B shows the same calculation for the case with the liquor containing boron. The boron addition was assumed to be 0.1 mole of boron per mole of Na, which corresponds to the stoichiometric addition of boron to achieve an autocaustization effect of 40%. In this calculation the previous thermodynamic database has been complemented with the relevant gaseous boron species, plus the condensed trisodium borate.

The boron additions are clearly seen in the bed composition. As expected, about 40% of the sodium carbonate in Fig. 1A has been converted to trisodium borate.

Note that the true equilibrium degree of the autocaustization is dependent on the temperature.

The main gas phase chemistry has not changed from the case with no boron. The calculations show very low partial pressures to any gaseous boron compounds.

These calculations show that—under equilibrium conditions—boron addition in the liquor will change the smelt bed composition significantly and result in trisodium borate formation which will be completely dissolved in the molten bed at the furnace temperatures. On the other hand, the boron addition will not affect the lower furnace gas composition, and no gaseous boron species are present in the furnace gases at any significant concentrations. This indicates that the condensed dust ("fume") also would remain practically boron free when boron is added to the liquor.



1.Calculated composition of the gas (above) and smelt bed (below) in the reducing part of the recovery boiler. Black liquor composition: $C_{10}H_{12}O_7Na_{2.4}S_{0.36}$. Stoichiometric air-to-fuel ratio: 0.7. Only the most relevant gaseous species are shown. A. (left): No borate, chlorine or potassium. B (right): Autocausticizing: 40%. No chlorine or potassium

SMELT AND SUPERHEATER DEPOSIT MELTING

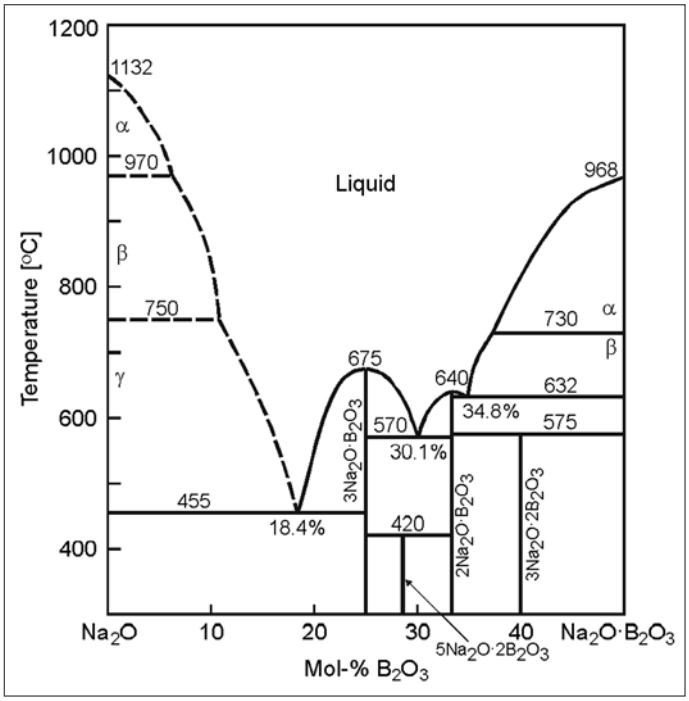
Sodium and boron form several compounds with each other. Figure 2 shows the phase diagram of the sodium oxide-boron oxide (Na_2O-B_2O_3)system [7]. There is no published information on the phase diagrams of the trisodium borate with other salts such as sulfide, carbonate, or chloride.

Figure 3 shows our first attempts to establish such phase diagrams based on the estimation of the thermodynamic data of melting of the trisodium borate. The figure indicates that the trisodium borate is readily soluble in the melts of sodium carbonate, sulfide, and chloride and forms eutectic systems with these three salts. This results in a steep decrease of the complete melting temperature of these three salts as a function of the borate addition. The first melting point (the eutectic temperature) seems to be around 630ºC-660ºC for all the three systems.

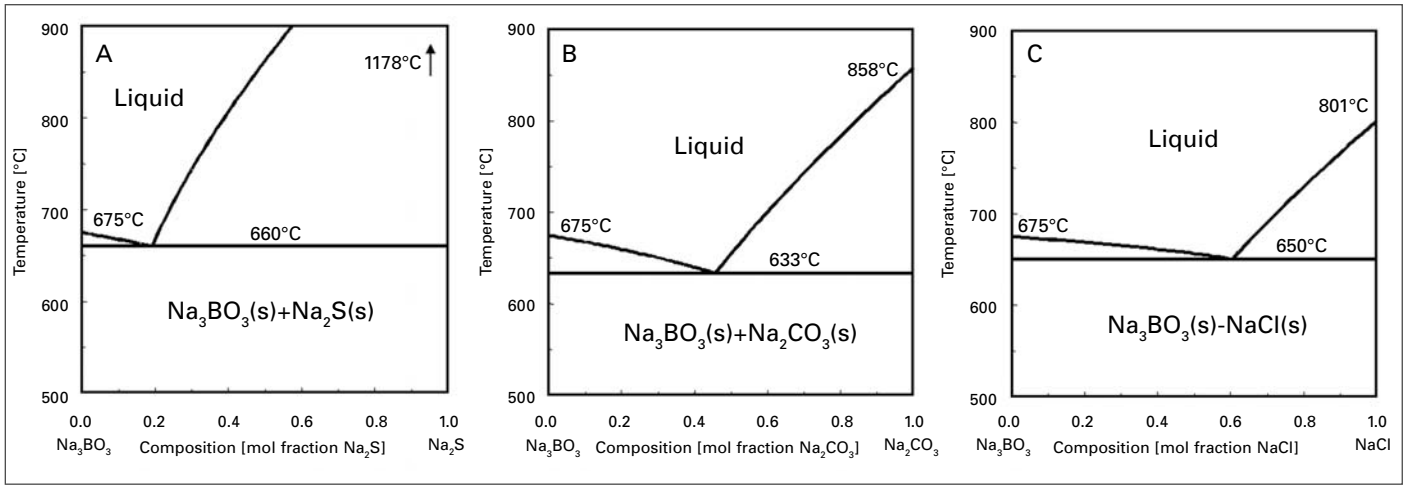
We estimated the melting behavior for a typical smelt bed (Fig. 4A) and superheater deposit caused by oxidized carry-over droplet residues (Fig. 4B) as a function of the boron content. The figures show the first melting temperature T_0, the "sticky temperature," T_{15}, the "flow temperature," T_{70}, and the complete melting temperature, T_{100}, respectively. These temperatures are defined and discussed elsewhere in more detail [8].

Boron addition does not change the "freezing temperature" (the same as complete melting temperature) of the smelt bed to any significant degree (4A). For the pure Na_2S-Na_2CO_3 system with no potassium or chlorine compounds present, small additions decreased the freezing by some 50ºC, but larger additions will increase the freezing temperature again. Consequently, the boron addition will probably not negatively influence the flow of the smelt from the bottom of the furnace.

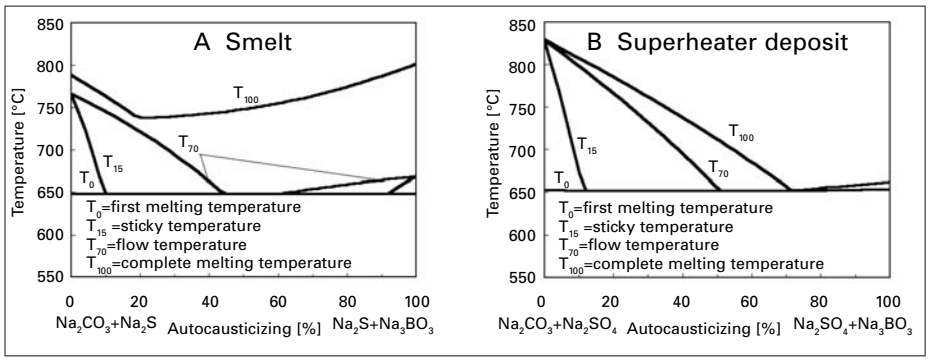
On the other hand, boron brings the first melting temperature of the smelt down to some 640ºC from about 770ºC for the pure Na_2S-Na_2CO_3 melt.



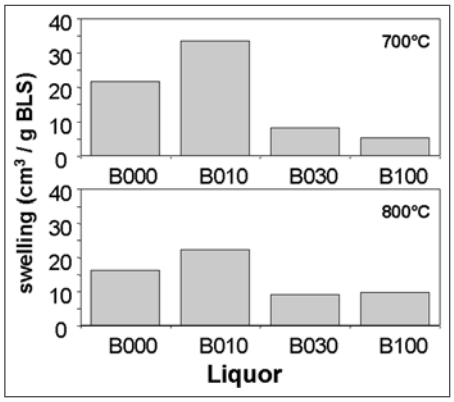
2. Experimental phase diagram for the system Na_2O-B_2O_3



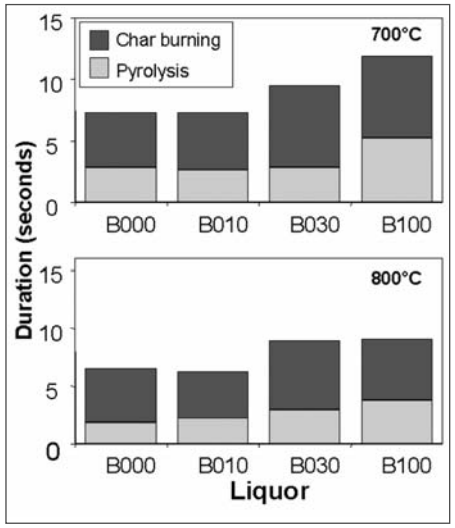
3. Calculated phase diagrams for a) Na_3BO_3-Na_2S, b) Na_3BO_3-Na_2CO_3, and c) Na_3BO_3-NaCl



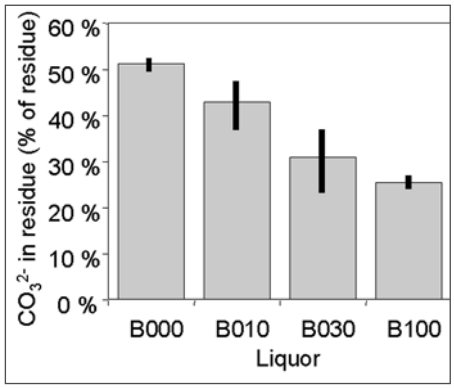
4. Calculated effect of borate on the characteristic melting temperatures for a) smelt bed and b) superheater deposits (oxidized smelt droplets, "carry-over")



5. Swelling at 700°C and 800°C, 21% O_2, average for 8 droplets (~10mg)



6. Combustion times at 700°C and 800°C, 21% O_2, average for 8 droplets (~10mg)



7. Carbonate in droplet residue after combustion at 800°C, 21% O_2

The influence of the boron on melting of the carry-over droplet residue particles is significant. The presence of the borate lowers the carry-over particle sticky temperature, T_{15}, especially, implying an increased potential of fouling in the cooler parts of the superheater area if significant boron additions are applied. In the case of the carry-over particles containing pure sodium carbonate-sodium sulfate (Na_2CO_3-Na_2SO_4) only (no potassium or chlorine), the presence of borate corresponding the autocaustization of 30% will drop the sticky temperature from around 750ºC to about 650ºC.

These calculations apply to the pure system, with no other salts present except those of sodium and sulfur. We are in the process of studying how the results change when the common "foreign elements" potassium and chlorine also are present.

DROPLET BURNING BEHAVIOR

We used our single droplet burning test facility to make some initial studies of the burning behavior of the black liquors containing boron. Our single droplet test system is described in our previous papers [9,10].

Table I shows results from a study of four liquor samples. The samples were produced in laboratory scale pulping of pine chips by adding a sufficient amount of sodium metaborate in a synthetic

BLACK LIQUOR	B000	B010	B030	B100
Dry-solids on arrival	19.0%	19.1%	19.1%	21.1%
Dry-solids in experiments	66.9%	69.5%	70.3%	69.1%
Replacement*	0%	10%	30%	100%
Content in dry solids				
boron	0%	0.23%	0.68%	2.01%
carbon	36.0%	34.9%	35.0%	31.3%
hydrogen	3.6%	3.4%	3.3%	3.4&
(Kjeldahl) nitrogen	0.049%	0.049%	0.050%	0.048%
sodium	18.9%	19.2%	19.7%	20.5%
potassium	0.065%	0.065%	0.064%	0.059%
sulfur	4.4%	4.4%	4.1%	3.8%
chloride	0.33%	0.35%	0.29%	0.33%
Heating value				
calorific	14.9	14.9	14.2	12.5
effective	12.75	12.82	12.22	10.54

** Replacement is explained in the text.*

I. Black liquors used in this work

white liquor to replace 0%, 10%, 30%, and 100% of the carbonate with the borate, respectively.

Figures 5 and 6 shows the relative swelling and characteristic droplet burning times for these four liquor samples during burning in air in a laboratory furnace at 700°C and 800°C respectively.The results are average numbers of 8-10 droplets of approximately 10 mg wet black liquor at each condition.

Small boron additions seem to slightly increase the swelling. However, large boron additions strongly reduce the swelling tendency of the liquor studied. These changes in swelling are reflected in the characteristic burning times. Increased swelling results in shorter burning times and vice verse.

Figure 7 shows our analysis results for carbonate in the droplet residues after burning in air at 800ºC. Because of the small amounts of sample for this analysis, the results are not accurate for all samples. However, the percentage of carbonate in the residue clearly appears to decrease as function of the boron addition. This effect may be explained partially by the diluting effect of the added boron, and perhaps because of the autcaustization effect taking place during the droplet burn-out. We plan to continue these types of tests in the near future.

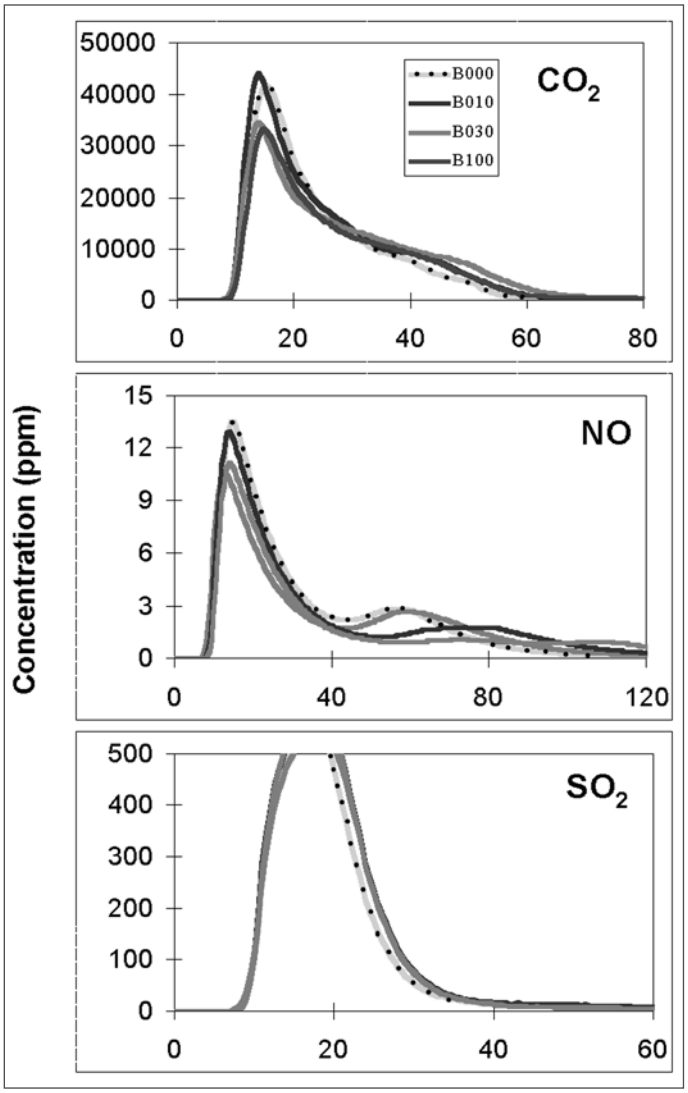
Figures 8 summarizes the single droplet tests for the four liquors at 900ºC and 10% oxygen using the on-line gas analysis system to follow the release of NO, SO_2, and CO_2. Each of the curves in Fig. 8 is an average of curves for four repeated droplets. The SO_2 analyzer was not able to detect higher concentration than 500ppm.

We estimated the end of char burning using the slope of the CO_2 curves at the end of the experiment (at 50-55 seconds).This gives a total combustion time of 48 s, 52 s, 52 s, and 59 s, for liquors B000, B010, B030 and B100, respectively.The boron addition prolonged somewhat the total burning time also in these tests. However, the boron addition did not change the formation of the gases CO_2, SO_2 and NO during the droplet burnout.

Based on these first tests with one typical kraft liquor the boron addition would not change the overall flue gas chemistry in the recovery boiler. The NO formation and sulfur release/reactions in the furnace are not expected to change significantly.

DISCUSSION AND CONCLUSIONS

Addition of boron in the recovery cycle to achieve partial autocaustization will influence the recovery boiler fireside behavior



8. CO_2, NO, and SO_2 formed during combustion, 900°C, 10% O_2, ~40mg WBL.

in several ways.This paper reports the first results of our studies using thermodynamic modeling and laboratory burning tests to establish some of the effects caused by boron.

The thermodynamic analysis of the lower furnace chemistry supports the findings by Tran et al [2,3] that trisodium borate will replace alkali carbonate in the smelt almost in the expected stoichiometric ratio. The borate in the smelt causes only minor changes in the smelt bed freezing temperature, thus indicating no significant effects on the flow of the smelt from the furnace.

The composition of the condensed dust, or fume, will probably stay unchanged due to the very low volatility of all the potential gaseous boron compounds. Consequently, the fouling tendency of the fume would not change.The carry-over droplet residues will contain the added borate, and this will result in a lowering of the melting range of these particles. Especially the sticky temperature T_{15} of the carry over particles will decrease due to the presence of boron.This may result in carry over particles remaining sticky somewhat deeper down in the flue gas duct than in the case with no boron in the liquor.

The characteristic swelling associated with the burning process of kraft liquors decreased for the particular liquor studied when we added boron. This decrease in swelling resulted in somewhat longer characteristic burning times, as also expected, based on our previous experience [9,10]. However, the rest of the burning behavior, including the release of carbon and the formation of NO and SO_2 from the burning droplet, did not change significantly.

More work is required to test the validity of the conclusions to a larger number of liquors. The interaction between boron compounds and potassium and chlorine also needs to be studied more to establish more generally the expected changes in the smelt and superheater deposit melting properties. **TJ**

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INSIGHTS FROM THE AUTHORS

Boron is under serious consideration for commercial use to debottleneck the chemical recovery plant in kraft pulp mills. Initial mill trials have been made, but there is lack of fundamental information about how the added boron will influence the recovery boiler operation. This work is a contribution to developing that information.

Until now, there has not been published information on potential changes in the black liquor burning behavior when boron is used as an added autocaustization chemical. Our work gives fundamental information on this based on laboratory burning tests and advanced thermodynamic modelling.

The most difficult aspect of this research was the lack of any previous information. We had to start from the scratch and start developing a thermodynamic database for boron compounds in recovery boiler conditions.

The overall picture of boron chemistry in the recovery boiler was very interesting and useful. The influence of boron on the melting of salts in the recovery furnace was exciting to study, also.

We plan to expand our studies to include systems where potassium and chlorine levels are higher, and thus may give a different result on the influence of boron.

— Mikko Hupa

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