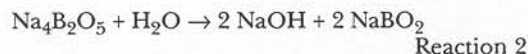
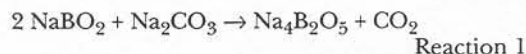


Autocausticizing of smelt with sodium borates

Less borate might be required, the authors suggest

BY H. TRAN, X. MAO, J. CAMERON AND C.M. BAIR

THE USE OF SODIUM BORATES to causticize smelt directly in soda and kraft recovery boilers was first suggested by Janson in the late 1970s [1-3]. Janson proposed that the "autocausticizing" process is attained by reacting sodium carbonate (Na_2CO_3) in the molten smelt with sodium meta-borate (NaBO_2) to form disodium borate ($\text{Na}_4\text{B}_2\text{O}_5$), which subsequently is hydrolysed to form sodium hydroxide (NaOH) and to regenerate NaBO_2 in the dissolving tank:



The process is attractive in that it produces NaOH directly in green liquor, thus potentially eliminating the need for slakers, causticizers and the lime kiln.

Besides sodium borates, there are several compounds that may be used as autocausticizing agents: for example, alumina (Al_2O_3), silica (SiO_2) and disodium phosphate ($\text{Na}_4\text{P}_2\text{O}_7$) [2], ferric oxide (Fe_2O_3), titanium dioxide (TiO_2) and ilmenite (FeTiO_3) [4-6]. Two basic differences between borates and most other autocausticizing compounds are: i) borates are water-soluble while the others (except for $\text{Na}_4\text{P}_2\text{O}_7$) are not; and ii) the decarbonization of Na_2CO_3 (Reaction 1) and the hydrolysis of the resulting higher-Na/B-ratio borates (Reaction 2) occur rapidly in the borate case because they happen in solution and are not the result of solid-solution interactions. Furthermore, borates do not react with sulphide in smelt, and thus can be used in kraft process [3].

A full-scale plant trial was carried out at the Enso Gutzeit liner board mill in Kotka, Finland, in 1982. While the results were inconclusive, the trial provided some insights into the feasibility of the process. A review of various autocausticizing processes conducted by Grace [7] suggested that full-scale implementation of the borate process is technically difficult and economically unattractive, due primarily to the large amount of borate "deadload" in the liquor cycle, and to the low heating value and the high viscosity of the resulting borate-containing black liquor [8].

For mills which require incremental causticizing and lime kiln capacities, partial autocausticizing may be an attractive alternative since it re-

quires a proportionately smaller borate load. However, it was suggested by Janson [2] that Reaction 1 would be severely hindered if the Na:B molar ratio (or Na/B) of the reactants is greater than 1.5:1 (or 1.5); and that it would not even occur if Na/B is greater than 3. This means that partial autocausticizing is technically not feasible because Na/B is likely to be much greater than 3. The development work involving borates became dormant by the end of the 1980s.

In 1990, US Borax Inc., in search of new applications for borate products, began to re-examine technologies that involve the use of borates in the pulp and paper industry. Previous research work on borate-autocausticizing was reviewed, and numerous in-house experiments were performed. This, along with the positive results of recent studies on the effect of borates on kraft, kraft-AQ and soda-AQ cooking of black spruce [9,10], led to the initiation of a large research program to examine the effects of borates on various processes in kraft pulping and chemical recovery. The program involved several independent research groups including: Econotech Services Inc., Vancouver, BC, Western Michigan University, Kalamazoo, MI, Institute of Paper Science and Technology, Atlanta, GA, Oregon State University, Corvallis, OR, and the University of Toronto. At the same time, Sandwell Inc., Vancouver, B.C. was asked to conduct an economic analysis of the borate-autocausticizing process.

Work by Econotech Services suggests that the use of borate may produce better quality pulp, and pulp which shrinks less during bleaching. The study at the University of Toronto, as will be discussed in detail below, shows that in air, sodium borates can react with molten Na_2CO_3 at any Na/B value, and that the reaction product is likely to be trisodium borate, $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ (or Na_3BO_3). These findings imply that partial autocausticizing with borate may now be technically feasible.

This paper discusses the results and practical implications of the recent study at the University of Toronto, and those of the unpublished work conducted at the Institute of Paper Chemistry in 1987 on autocausticizing reactions between Na_2CO_3 and sodium borates.

AUTOCAUSTICIZING REACTIONS

In the study at the University of Toronto, dehydrated borax ($\text{Na}_2\text{B}_4\text{O}_7$) and dehydrated sodium meta-borate (NaBO_2) were used as a source of borate. Mixtures of Na_2CO_3 and $\text{Na}_2\text{B}_4\text{O}_7$ (or NaBO_2) with



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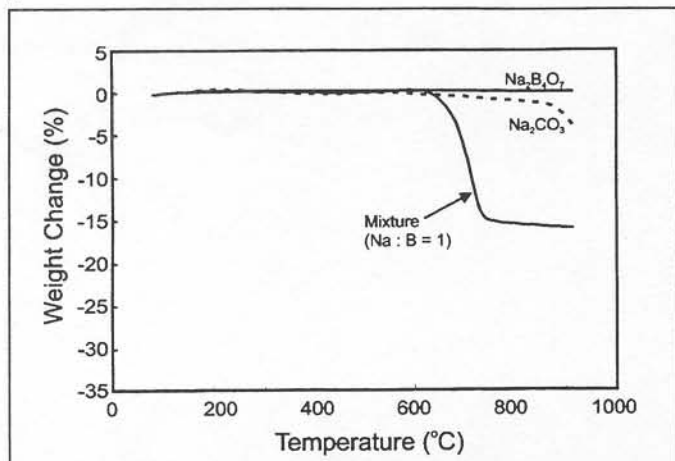


FIG. 1. TG curves of Na₂B₄O₇, Na₂CO₃, and Na₂CO₃-Na₂B₄O₇ mixture (Na/B=1) in air.

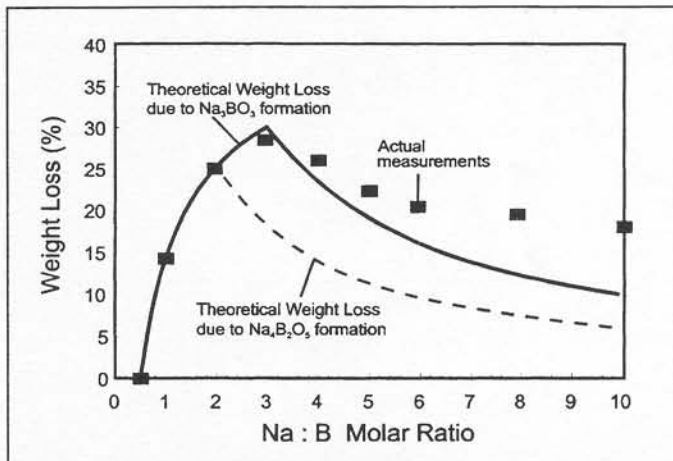


FIG. 2. Maximum weight loss of Na₂CO₃-Na₂B₄O₇ mixtures at various Na/B values heated in air to 925°C at 10°C/min.

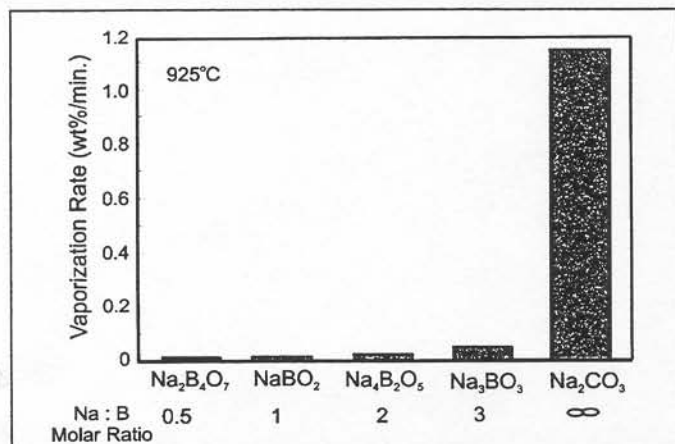


FIG. 3. Rates of vaporization of Na₂CO₃ and various sodium borate compounds at 925°C.

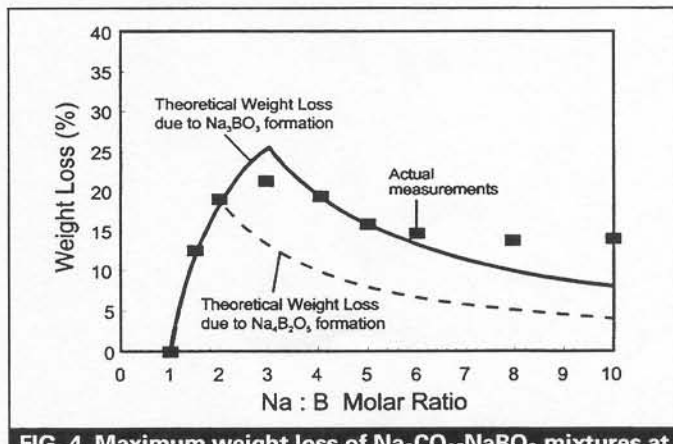


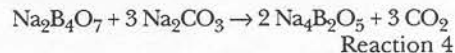
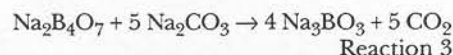
FIG. 4. Maximum weight loss of Na₂CO₃-NaBO₂ mixtures at various Na/B values after being heated in air to 925°C at 10°C/min.

various Na/B values were prepared and the reaction was examined by means of simultaneous differential and thermogravimetric analysis (DTA/TGA). A small amount, about 20 mg, of the sample, was placed in a platinum crucible and heated in air up to 925°C at a constant heating rate of 10°C/min. The sample weight was continuously monitored. The total weight loss caused by the release of CO₂ as a result of the reaction was used to determine the degree of decarbonization of Na₂CO₃. It was assumed that no weight loss occurred due to evaporation. Experiments in air that contained 15% CO₂ were also carried out to examine the effect of CO₂ on the reactions.

Reactions between Na₂CO₃ and dehydrated borax: Figure 1 shows the thermogravimetric (TG) curves of Na₂B₄O₇, Na₂CO₃, and a mixture Na₂CO₃ and Na₂B₄O₇ which had a Na/B of 1. Na₂B₄O₇ shows no significant weight loss at temperatures up to 925°C. Na₂CO₃ begins to vaporize markedly at its melting temperature of about 850°C. In the case of the Na₂CO₃ and Na₂B₄O₇ mixture (Na/B=1), the weight loss began at about 600°C, reached 15 wt% at about 740°C and re-

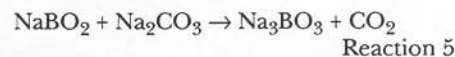
mained constant at higher temperatures. The maximum weight loss of this mixture is consistent with the theoretical weight loss for the complete decarbonization of the Na₂CO₃ in the sample. This suggests the reaction was complete under the test conditions. For mixtures with higher Na/B values, the maximum weight loss increased markedly with an increase in Na/B values, up to 3; then decreased thereafter, Fig. 2.

The solid curve in Fig. 2 represents the theoretical weight loss of the sample calculated on the assumption that the reaction product was trisodium borate (3 Na₂O·B₂O₃ or Na₃BO₃): Reaction 3. The broken curve is the theoretical weight loss of the sample if the reaction product are disodium borate (2 Na₂O·B₂O₃ or Na₄B₂O₅): Reaction 4. The weight loss data obtained follow more closely the solid curve than the broken curve, suggesting that the decarbonization of Na₂CO₃ occurs according to Reaction 3, with Na₃BO₃ as the reaction product.



It is interesting to note that the weight loss data in Fig. 2 at Na/B>3 was above the solid curve. This high weight loss is possibly due to the vaporisation of excess Na₂CO₃ in the Na₂CO₃-Na₃BO₃ mixture, since molten Na₂CO₃ is much more volatile than sodium borates, Fig. 3.

Reactions between Na₂CO₃ and dehydrated sodium meta-borate: Similar results were obtained for Na₂CO₃ and NaBO₂ mixtures, Fig. 4. The measured weight loss was highest at Na/B= 3. The data was, again, more consistent with the solid curve (Na₃BO₃ is assumed to be the reaction product, Reaction 6), than with the broken curve (Na₄B₂O₅ is assumed to be the reaction product, Reaction 1), as was suggested by Jansen [2]).



Note that the weight loss data in Fig. 4 fitted better with the solid curve at Na/B>3 than that in Fig. 2. This is because

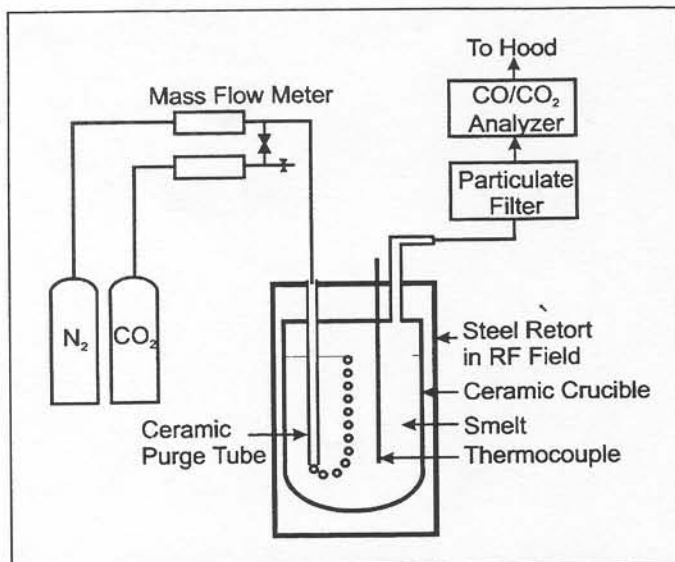


FIG. 5. Experimental apparatus at Institute of Paper Chemistry.

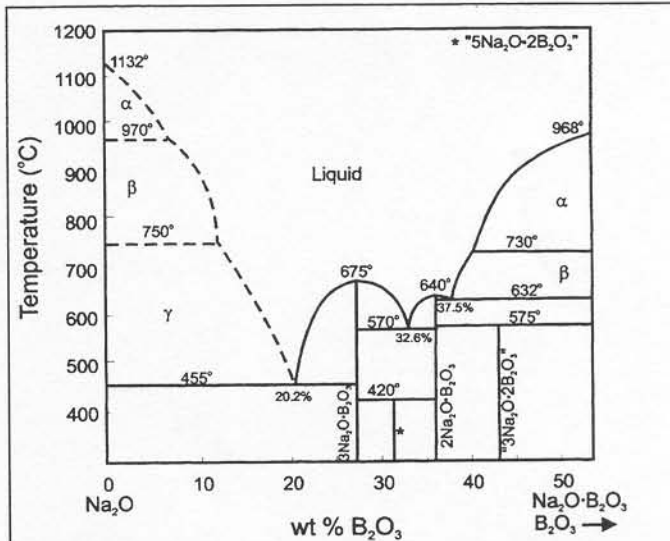


FIG. 6. The phase equilibrium diagram for the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ system [11].

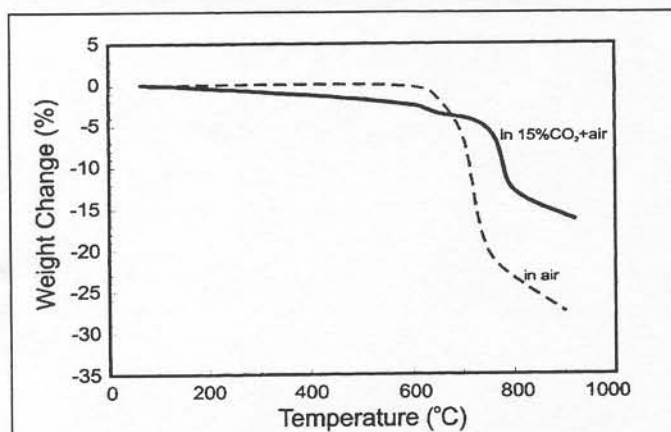


FIG. 7. TG curve of $\text{Na}_2\text{CO}_3-\text{Na}_2\text{B}_4\text{O}_7$ mixture (Na/B=3) in air containing 15% CO_2 .

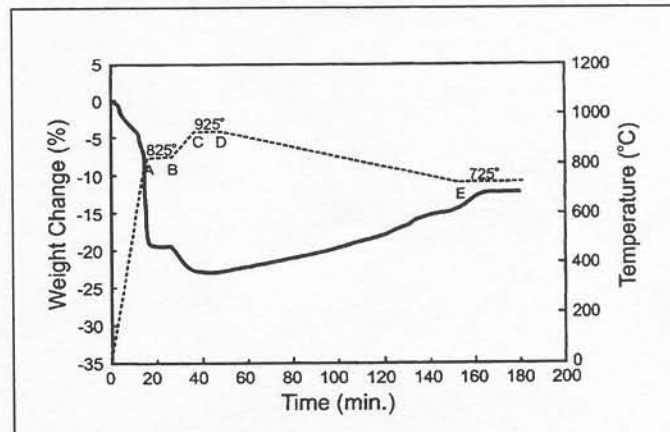


FIG. 8. Effect of temperature on the $\text{Na}_2\text{B}_4\text{O}_7 + 5 \text{Na}_2\text{CO}_3 \leftrightarrow 4 \text{Na}_3\text{BO}_3 + 5 \text{CO}_2$ reaction in air + 15% CO_2 .

the Na:B molar ratio in NaBO_2 is 1, whereas that in $\text{Na}_2\text{B}_4\text{O}_7$ is 0.5. At a given Na/B value, the amount of Na_2CO_3 used in the $\text{Na}_2\text{CO}_3-\text{NaBO}_2$ mixture was smaller than that used in the $\text{Na}_2\text{CO}_3-\text{Na}_2\text{B}_4\text{O}_7$ mixture. Therefore, the effect of vaporization of excess Na_2CO_3 in Fig. 4 is less than that in Fig. 2.

The formation of trisodium borate, Na_3BO_3 , rather than disodium borate, $\text{Na}_2\text{B}_2\text{O}_5$, from the reaction between Na_2CO_3 and NaBO_2 was also found in work performed at the Institute of Paper Chemistry in Appleton, WI, in 1987. The purpose of the work was to generate CO_2 in the smelt as a means of reducing the tendency of smelt to explode on contact with water. Although this method of reducing smelt-water explosions did not prove to be effective, the kinetics of the reaction between Na_2CO_3 and NaBO_2 were examined.

Mixtures of Na_2CO_3 and NaBO_2 were contained in an alumina crucible inside a

steel retort, Fig. 5. The retort was heated in a radio-frequency induction furnace, which allowed the mixture to reach the desired reaction temperature within a few minutes. In most of the experiments, a large excess amount of Na_2CO_3 was used relative to NaBO_2 , with an Na/B>50. The reaction temperature was varied from 1000 to 1200°K (727 to 927°C). During the experiment, the extent of the reaction was followed by purging the reactor with N_2 , and monitoring the CO_2 generated in the off-gases using an infrared spectrophotometer.

For each mole of NaBO_2 used, one mole of CO_2 was obtained. This suggests that Reaction 5 is the main reaction, and that Na_3BO_3 is the reaction product. With the CO_2 stripped from the reactor, the reaction could accurately be described as a second order irreversible reaction; first order with respect to both the borate and carbonate.

$$d[\text{CO}_2]/dt = k e^{\Delta E/RT} [\text{NaBO}_2][\text{Na}_2\text{CO}_3]$$

where

k is the reaction rate constant = 2580 ± 400 L/mol-sec;

ΔE is the activation energy = 35 ± 2.5 Kcal/mol;

R is the universal gas constant; and

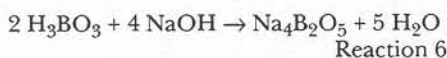
T is the absolute temperature of the reaction, in the range of 1000 to 1200°K.

In experiments where controlled levels of CO_2 were added to the purge gas, the rate of decarbonization reaction was lower.

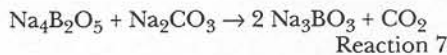
The above studies suggest that Reactions 3 and 5 can occur at any Na:B molar ratio, and that the reaction product is Na_3BO_3 . The conclusions contradict the original findings by Janson [2], which suggested that the reaction product is $\text{Na}_4\text{B}_2\text{O}_5$ (Reaction 1); that the reaction will be severely hindered if the Na/B value of the reactants is greater than 1.5; and that it will not even occur if Na/B is greater than 3. The contradiction is likely due to the following:

- The larger sample size, and the lack of a purge to remove CO₂ from the relatively large crucible used in Janson's experiments. Since CO₂ was not removed from the system, high levels could accumulate and prevent the reaction from going to completion.

- Janson's samples were prepared by adding an aqueous solution of NaOH to a constant amount of boric acid (H₃BO₃, 80 mmoles) and Na₂CO₃ (40 mmoles) to give the desired Na/B value. The addition of NaOH, instead of Na₂CO₃, to adjust Na/B in Janson's work was not realistic because: i) there is little or no NaOH in smelt; and ii) since NaOH is more alkaline and melts at a much lower temperature than Na₂CO₃, it would react rapidly with H₃BO₃ to form Na₄B₂O₅ (Reaction 6). Thus at Na/B>3, there would be no H₃BO₃ left to react with Na₂CO₃.



Janson suggested that Na₃BO₃ would not form from Reaction 7, because of the strongly basic character of the B₂O₅⁴⁻ anion in the melt [2]. The reaction, however, was not examined in Janson's work:



STABILITY OF Na₃BO₃

While trisodium borate (Na₃BO₃) is rarely mentioned in the borate-autocauticizing literature, this compound is known to exist. Phase equilibrium diagrams of the Na₂O-B₂O₃ system by Milman and Bouaziz [11] show that Na₂O and B₂O₃ form many compounds with different Na/B values. They are, in an order of increasing Na/B value: Na₂O·9B₂O₃, Na₂O·5B₂O₃, Na₂O·4B₂O₃, Na₂O·3B₂O₃, 2Na₂O·5B₂O₃, Na₂O·2B₂O₃, 2Na₂O·3B₂O₃, Na₂O·B₂O₃, 3Na₂O·2B₂O₃, 2Na₂O·B₂O₃, 5Na₂O·2B₂O₃, and 3Na₂O·B₂O₃. The large number of sodium borates implies the high affinity of borate to sodium compounds.

The subsystem Na₂O-Na₂O·B₂O₃ in the Na₂O-B₂O₃ system is shown in Fig. 6 [11]. Note that the dashed lines in the diagram refer to metastable equilibrium, while the compounds in quotation marks, "3Na₂O·2B₂O₃" and "5Na₂O·2B₂O₃," are not certain and might correspond to 5Na₂O·3B₂O₃ and 7Na₂O·3B₂O₃, respectively. Disodium borate (2Na₂O·B₂O₃ or Na₄B₂O₅) and trisodium borate (3Na₂O·B₂O₃ or Na₃BO₃), respectively, melt at 640°C and 675°C, and they form a eutectic at 570°C. This eutectic temperature is consistent with the temperature at which the weight loss of carbonate-borate mixtures began in most of tests conducted in air at the University of Toronto, when Na/B>2. This implies that the decarbonization of Na₂CO₃ by borate in air would initially result in the formation of both

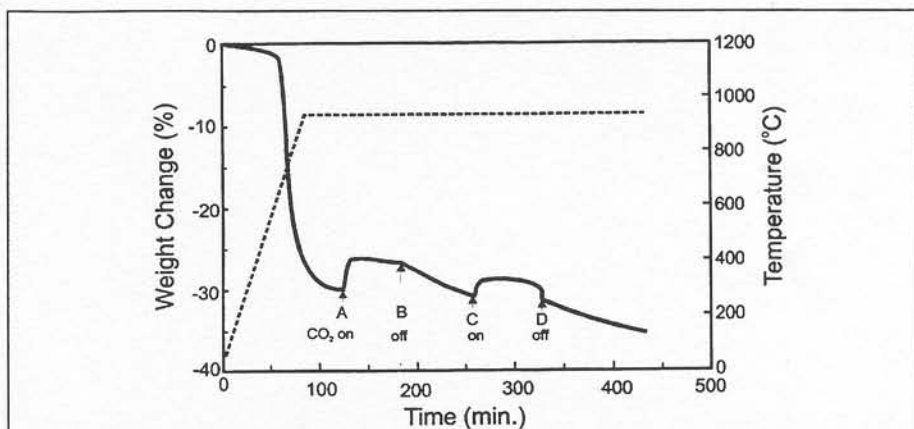


FIG. 9. Effect of CO₂ on the carbonation of Na₃BO₃ at 925°C.

Na₄B₂O₅ and Na₃BO₃. For mixtures with an initial Na/B(3), the resulting Na₄B₂O₅ would react further with Na₂CO₃ to form Na₃BO₃ (Reaction 7).

EFFECT OF CO₂

Sodium borates, particularly those with high Na/B values, such as Na₄B₂O₅ and Na₃BO₃, might be expected to be carbonated if they are exposed to CO₂. This is because the Na₂O component of the compounds might react with CO₂ to form Na₂CO₃. Since the kinetics of Reactions 1, 3, 4 and 5 is slower in CO₂ than in air. The two main reactions in this study, Reactions 3 and 5, should be rewritten as follows:

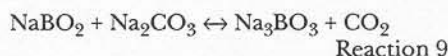
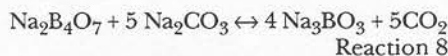


Figure 7 shows TG curves of a Na₂CO₃-Na₂B₄O₇ mixture (Na/B=3) in air and in air plus 15% CO₂. The total weight loss of the mixture in air that contained 15% CO₂ after the test was only 60% of that in air. This adverse effect of CO₂ on decarbonization is a strong function of temperature. As shown in Fig. 8, during the period when the reaction temperature was kept constant at 825°C (from Point A to Point B), the weight loss of the melt stabilized at about 18 wt%. The weight loss increased to 22 wt% as the temperature was increased to 925°C (Point C). However, as the temperature was gradually decreased from 925°C (Point D) to 725°C (Point E), the sample gradually regained weight to a final value of 13 wt%, and remained at this value as the temperature was maintained at 725°C.

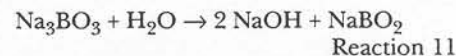
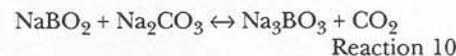
In the experiment shown in Fig. 9, the Na₂CO₃-Na₂B₄O₇ mixture was first heated in air from room temperature to 925°C, and then kept at that temperature for six hours. The weight loss stabilized at about 30 wt%, which is consistent with the theoretical weight loss caused by the formation of Na₃BO₃, Fig. 2. At 120 minutes (Point

A), the sample regained about 3% of its weight immediately as the gas atmosphere was switched from air to air plus 15% CO₂. The total weight loss was reduced to about 28 wt% and remained constant at this level until CO₂ was turned off (Point B). At that point, the sample began losing weight again until CO₂ was re-introduced (Point C). A small weight loss was observed again when CO₂ was off (Point D).

Based on the above results, it can be concluded that the kinetics of Na₃BO₃ formation reaction are a strong function of temperature, and are hindered by the presence of CO₂. However, once formed, Na₃BO₃ is relatively stable, and is not carbonated. Its vaporization rate at 925°C is about 1/50 of the vaporization rate of Na₂CO₃, Fig. 3.

IMPLICATIONS

These above studies indicate that both dehydrated borax (Na₂B₄O₇) and sodium meta-borate (NaBO₂) can readily react with Na₂CO₃ in air — even at Na/B>3 — and that the reaction product is Na₃BO₃. In water, Na₃BO₃ hydrolyzes to form NaOH and to regenerate NaBO₂, according to Reaction 11. Thus, regardless of the starting material, NaBO₂ is the main sodium borate compound in the solution. Since borax (Na₂B₄O₇·5H₂O) is less expensive and has a low Na/B value, its choice as a make-up chemical is a better one than sodium meta-borate. The over-all autocauticizing reactions can therefore be summarized as follows:



This reaction sequence suggests that only half a mole of borate is needed to produce one mole of NaOH in the liquor system. This is important because the amount of borate required would be half of that needed for the reaction sequence suggested by Janson [2], Reactions 1 and

2. Therefore, if the Reactions 9 and 11 can be fully attained, the amount of borate deadload in the system would be reduced by half. This, in turn, would significantly lower the black liquor viscosity and reduce other potential effects caused by borate.

Although CO_2 hinders the formation of Na_3BO_3 (Reactions 8 and 9), the practical implications of this are minimal. Equilibrium calculations [12] show that while the CO_2 content in the flue gas in the recovery boiler lower furnace may be as high as 15%, the CO_2 content in the char is very small, <1000 ppm, due to the presence of a large amount of carbon, and the equilibrium reaction, $\text{C} + \text{CO}_2 = 2 \text{CO}$ that consumes CO_2 at high temperatures. The decarbonization reaction of Na_2CO_3 to form Na_3BO_3 may proceed as an irreversible reaction within the furnace. Once Na_3BO_3 has been formed in the smelt, the effect of CO_2 becomes less important, as is shown in Fig. 9.

The occurrence of the decarbonization reaction (Reaction 9) at any Na:B molar ratio suggests that partial autocausticizing is technically feasible since it requires proportionally less borate. This may be an attractive alternative for the incremental capacity of the causticizing plant. However, the effect of borate in various causticizing processes needs to be thoroughly examined before such a technology can be implemented.

The much lower volatility of sodium borate compounds compared to Na_2CO_3 , Fig. 3 suggests that the amount fume formed will be significantly less in boilers burning borate-containing black liquor than boilers burning normal black liquor.

CONCLUSIONS

The basic reactions between sodium carbonate (Na_2CO_3) and sodium borates (NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$) at high temperatures were examined. The results show that:

- In air, both NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$ react readily with molten Na_2CO_3 at any Na/B value; and the reaction product is likely to be trisodium borate (Na_3BO_3), not disodium borate ($\text{Na}_2\text{B}_2\text{O}_5$), as was previously suggested.
- The reaction kinetics of Na_3BO_3 formation depends strongly on the sample size, temperature, the initial Na/B, and CO_2 concentration in the gas. Once formed, Na_3BO_3 is relatively stable, and the effect of CO_2 becomes insignificant.
- The kinetics of the decarbonization reaction can be increased by removing the CO_2 generated, and by using an excessive amount of sodium carbonate. In the

recovery furnace, the concentration of CO_2 in the char bed is low due to its conversion to CO ; consequently, the decarbonization reaction should proceed as an irreversible reaction within the furnace.

- The decarbonization reaction, as measured through CO_2 generation, can be described as a second overall reaction, first order with respect to both reactants. In the temperature range of 1000 to 1200°K, the reaction constant k and the activation energy ΔE are respectively $2580 \pm 400 \text{ L/mol-sec}$, and $35 \pm 2.5 \text{ Kcal/mole}$.
- The formation of Na_3BO_3 as a reaction product implies that only 0.5 mole of NaBO_2 is needed per mole of NaOH produced in the liquor system. The low borate requirement substantially reduces concerns over high black liquor viscosity and large deadload in the liquor cycle.
- The amount of fume formed is expected to be significantly less in boilers burning borate-containing black liquor than boilers burning normal black liquor.
- Partial borate-autocausticizing appears to be technically feasible and may be attractive economically.

ACKNOWLEDGEMENTS

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LITERATURE

1. JANSON, J. The Use of Unconventional Alkali In

cooking and Bleaching — Part 1. A New Approach to Liquor Generation and Alkalinity. *Paperi Ja Puu* 59(6-7): 425-430 (1977).

2. JANSON, J. The Use of Unconventional Alkali In cooking and Bleaching — Part 5. Autocausticizing Reactions. *Paperi Ja Puu* 61(1): 20-30 (1979).
3. JANSON, J. The Use of Unconventional Alkali In cooking and Bleaching — Part 6. Autocausticizing of Sulphur-containing Model Mixtures and Spent Liquors. *Paperi Ja Puu* 61(1): 20-30 (1979).
4. KIISKILA, E. Recovery of Sodium Hydroxide from Alkaline Puling Liquors by Smelt Causticizing — Part II. Causticizing of Molten Sodium Carbonate with Titanium Dioxide. *Paperi Ja Puu* 61(5): 394-401 (1979).
5. KIISKILA, E. Recovery of Sodium Hydroxide from Alkaline Puling Liquors by Smelt Causticizing — Part IV. Causticizing of Molten Sodium Carbonate with Ferric Oxide. *Paperi Ja Puu* 61(8): 505-510 (1979).
6. KIISKILA, E. Recovery of Sodium Hydroxide from Alkaline Puling Liquors by Smelt Causticizing — Part V. Causticizing of Molten Sodium Carbonate with Ilmenite. *Paperi Ja Puu* 61(9): 564-577 (1979).
7. GRACE, T.M. An Evolution of Non-Conventional Causticizing Technology for Kraft Chemical Recovery. Report One, A Progress Report to Members of the Institute of Paper Chemistry, January 30, 1991.
8. JANSON, J. and SÖDERHJELM, L. The Viscosity of Borate-Containing Black Liquor. *Nordic Pulp and Paper Research J. No. 2*: 107-110 (1988).
9. KORAN, C., WANTDEL, P. and KUBES, G., J. The Effect of Temperature on Borate-Based Kraft Cooking of Black Spruce. *Paperi Ja Puu — Paper and Timber* 78(9): 541-544 (1996).
10. PRIHODA, S., WANTDEL, P. and KUBES, G., J. The Effect of Borates on Kraft, Kraft-AQ And Soda-AQ Cooking Of Black Spruce. *Paperi Ja Puu — Paper and Timber* 78(8): 456-460 (1996).
11. MILMAN, T. and BOUAZIZ, R. Phase Diagrams for Ceramists. Ed. Levin, E.M. and McMurdie, H.F. *Ann. Chim.* 3 (4): 313-317 (1968).
12. HUPA, M. Recovery Boiler Chemistry. *Kraft Recovery Boilers*. Ed. Adams et al. Atlanta: TAPPI Press, 44 (1997).

Résumé: La technologie d'autocaustification utilisant du borate pour 'caustifier' le carbonate de sodium (Na_2CO_3) dans la soude caustique ou le salin kraft directement dans les chaudières de récupération, a été étudiée en réévaluant les réactions entre le Na_2CO_3 et les borates de sodium (NaBO_2 et $\text{Na}_2\text{B}_4\text{O}_7$) à haute température. Le NaBO_2 et le $\text{Na}_2\text{B}_4\text{O}_7$ ont tous deux réagi facilement au Na_2CO_3 fondu à n'importe quel Na:B molaire supérieur à 3:1 pour former du borate trisodique (Na_3BO_3). La formation de Na_3BO_3 comme produit de réaction signifie que la quantité de borate requise pour les réactions d'autocaustification peuvent être très inférieures à celles antérieurement suggérées.

Abstract: The autocausticizing technology involving the use of borate to "causticize" sodium carbonate (Na_2CO_3) in the soda or kraft smelt directly in recovery boilers was reviewed by re-examining the reactions between Na_2CO_3 and sodium borates (NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$) at high temperatures. Both NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$ were found to react readily with molten Na_2CO_3 at any Na:B molar larger than 3:1 to form trisodium borate (Na_3BO_3). The formation of Na_3BO_3 as a reaction product means that the amount of borate required for the autocausticizing reactions can be substantially lowered than previously suggested.

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