Floor tube corrosion in recovery boilers

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ABSTRACT: Lower sulfur emissions at a pulp mill result in higher sulfidity levels and in the enrichment of potassium in the mill's liquor system. The sulfidity values at Scandinavian kraft mills previously fluctuated between 28 and 35%; today they exceed 45%. Viscosity measurements show that the viscosity decreases drastically when the sulfidity increases from 30 mole% to 40 mole%, its potassium and chlorine levels are high enough, and the char bed is low, the smelt flows easily and may penetrate the char bed, approaching the floor tubes. In extreme cases, the hot smelt destroys the layer of solidified smelt on the floor tube's surface and reacts very rapidly with the floor tube.

KEYWORDS: Cracks, floors, recovery furnaces, smelt, stress corrosion, sulfidity, tubes.

The cracking of composite floor tubes in many recovery boilers has been the subject of discussion and active research in Finland and Sweden during the last three years. The TAPPI corrosion symposium, held in Orlando, FL, in November 1992, highlighted this problem *(1-5)*. The cracks, which are visible with a dye penetrant, go through the stainless steel layer. However, cracks have not occurred in the carbon steel portion of the composite tube. Although cracks have been observed in some units after just one year of operation, other boilers have been in service for 12 years before the cracks appeared.

Some researchers believe that the cracking is caused by water washing the floors, based on the fact that typical stress corrosion cracks have been found in the type 304L stainless steel layer of the composite tubes. The cracks, however, also have thermal fatigue features and occur when the smelt penetrates closer to the bottom tubes, where the bed height is low.

In order to discover the real causes of this corrosion phenomenon, it is appropriate to analyze the changes that have occurred at modern pulp mills during the last five years.

Boilers that were evaluated

Nine recovery boilers at seven pulp mills were selected for closer study. The normal day-to-day analyses carried out at the mills from 1987 to 1992 provided the basic data for this study. These data, together with a history of the composite tube cracking, were saved in a computer file on each mill.

Changes observed at the pulp mills

The changes observed in corrosion environments can be divided into two groups: the changes that occurred when a boiler was in use and those that affected a boiler during shutdowns or startups.

Boilers in use

Operational boilers displayed higher sulfidities due to the increased use of ClO_2 bleaching. The effective utilization of the by-products from ClO_2 generation has resulted in an overall decrease in chemical losses from the pulp mills. The by-products from the most popular methods used have high S/Na_2 ratios when compared with normal makeup chemicals. Since the production of these by-product salts or acids may take place sporadically, sulfidity levels may fluctuate widely at a given mill.

Higher sulfidities also result from an increase in recycled ash. Higher bed temperatures promote higher dust flow from the bed and, thus, reduced sulfur emissions from the boiler. At higher bed temperatures, there is obvious enrichment of K and Cl levels. If this recycled ash (mainly Na_2SO_4) is used as a makeup chemical and added to the black liquor, the sulfidity level of the liquor mixture will increase in the long run and, simultaneously, the K and Cl enrichment will take place.

Boilers in use also feature higher char bed temperatures due to (a) the

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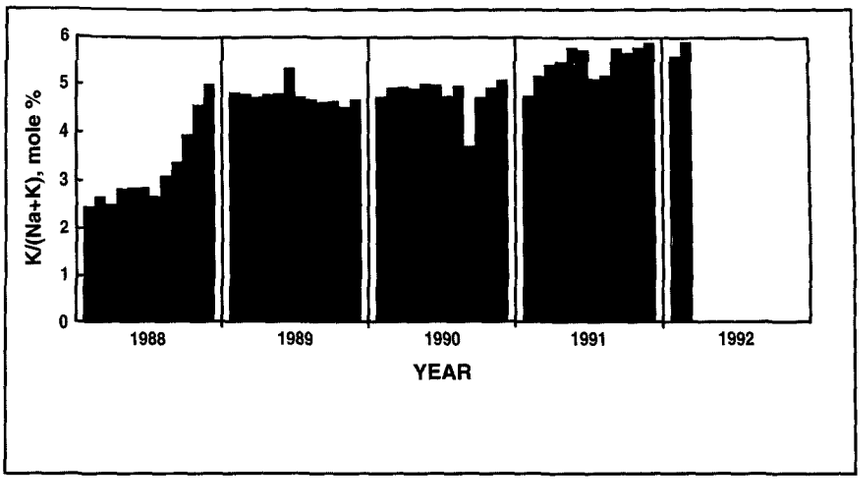
I. The equilibrium coefficient of Eq. 1 for sodium and potassium at different bed temperatures

Temp.,°C	Na	K
900	0.0003	0.0049
950	0.0079	0.1158
1000	0.16	2
1050	2.5	28
1100	31	313
1150	324	2906
1200	2812	22,770

1. The slow increase in K/(K+Na) ratio at Mill A from 1988 to 1992



rotation of secondary air, (b) the higher dry solids content of the combustion liquors, and (c) the operation of boilers at overcapacity. These changes affect the char bed reactions, especially in cases where the bed has been low and the enrichment of potassium and chlorides has taken place. The lower melting points of K-enriched smelts facilitate the smelt penetration through the char bed, closer to the bottom tubes. This abnormal, hot-smelt penetration decreases the thermal insulation of the char bed. The hot, easily-flowing smelt has, in some cases, also locally destroyed the frozen smelt layer on the composite tube and aggressively corroded the tube's surface.

Boilers being shut down or started up

Shutdowns and startups generally provide an enrichment of sulfur. At the beginning of a shutdown, as a boiler cools, salt deposits on the superheaters fall onto the char bed. During the burndown of the char bed, these salts melt and mix with the original smelt, thereby enriching the smelt that is on the floor with potassium and chlorine. A sample salt layer compacted on the surface of a floor tube had 25 mole% of K/(K+Na), 3.2 mole% Cl/(K+Na), and a S/Na_2 molar ratio as high as 2.6. These ratios indicate that low-melting-temperature polysulfides may have been produced.

Sulfidity levels during startups may increase due to the use of oil burners. Hearth burners should not be used unless specifically required (e.g., for startup or burndown of the bed), since the excessive heat input in the lower furnace will accelerate corrosion.

In addition to sulfur enrichment, enriched compounds can be dissolved. When the boiler is washed with water, these enriched compounds, which are high in sulfur, potassium, and chlorides, dissolve into the washing water, creating a potentially more corrosive chemical solution.

Consequences of higher bed temperatures

Potassium and sodium have low melting points (Na: 98°C and K: 63°C) and low boiling points (Na: 883°C and K: 759°C) *(6, 7)*. The overall sodium reaction that takes place in the outer layer of a char bed can be described with the following equation:

$$Na_2SO_4(l) + 2C(s) + CO(g) + Na_2CO_3(l) = Na_2S(l) + 2Na(g) + 4CO_2(g) \quad (1)$$

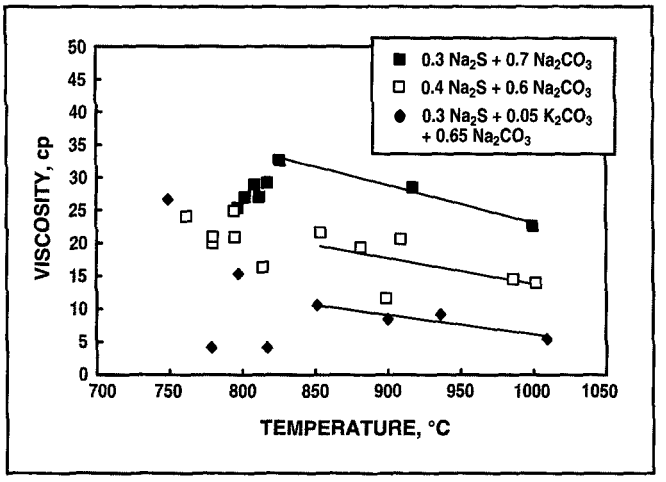
Table I provides the equilibrium coefficients for sodium reactions from Eq. 1 and for similar potassium reactions at different temperatures. The equilibrium coefficients indicate that potassium vaporizes more easily than sodium. However, when the bed temperature increases, the vaporization rate of K compared to that of Na does not increase.

Inside the bed, where the temperature is lower, the vapor pressure of the potassium is much higher than that of the sodium. Therefore, it is much easier for K to form compounds like potassium polysulfides, which have extremely low melting points. The lowest melting point in the K_2S-S system has the eutectic of K_2S_3 and K_2S_4 at 115°C *(6)*, and in the Na_2S-S system, it has the eutectic of Na_2S_3 and Na_2S_4 at 236°C *(7)*.

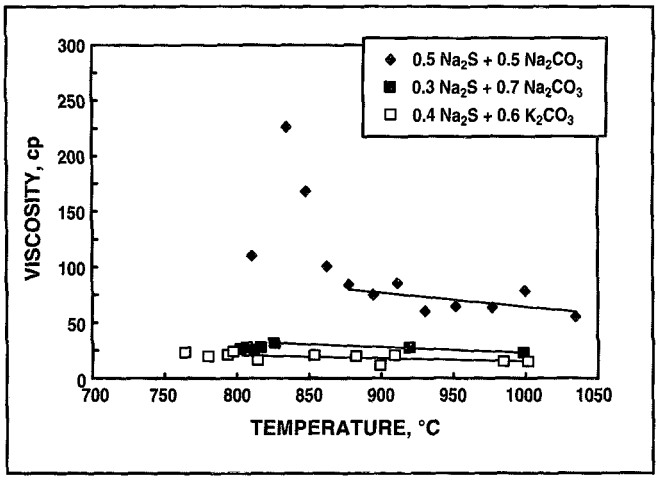
The equilibrium coefficients in Table I demonstrate the effect of changes in the char bed temperature: a temperature increase as low as 50°C drives the reaction strongly toward the creation of products. Thus, a higher bed temperature yields higher amounts of Na_2S (for better reduction) and higher Na vapor pressure. This vaporized sodium first captures CO_2; the Na_2CO_3 fume then reacts with sulfurous gases as it flows upward, forming sodium sulfate. If the bed temperature is so high that the sulfur emissions are extremely low, the concentration of sodium carbonate in the flyash increases.

When the sulfur emissions of the boiler diminish, the amount of flyash increases. The amount of potassium in

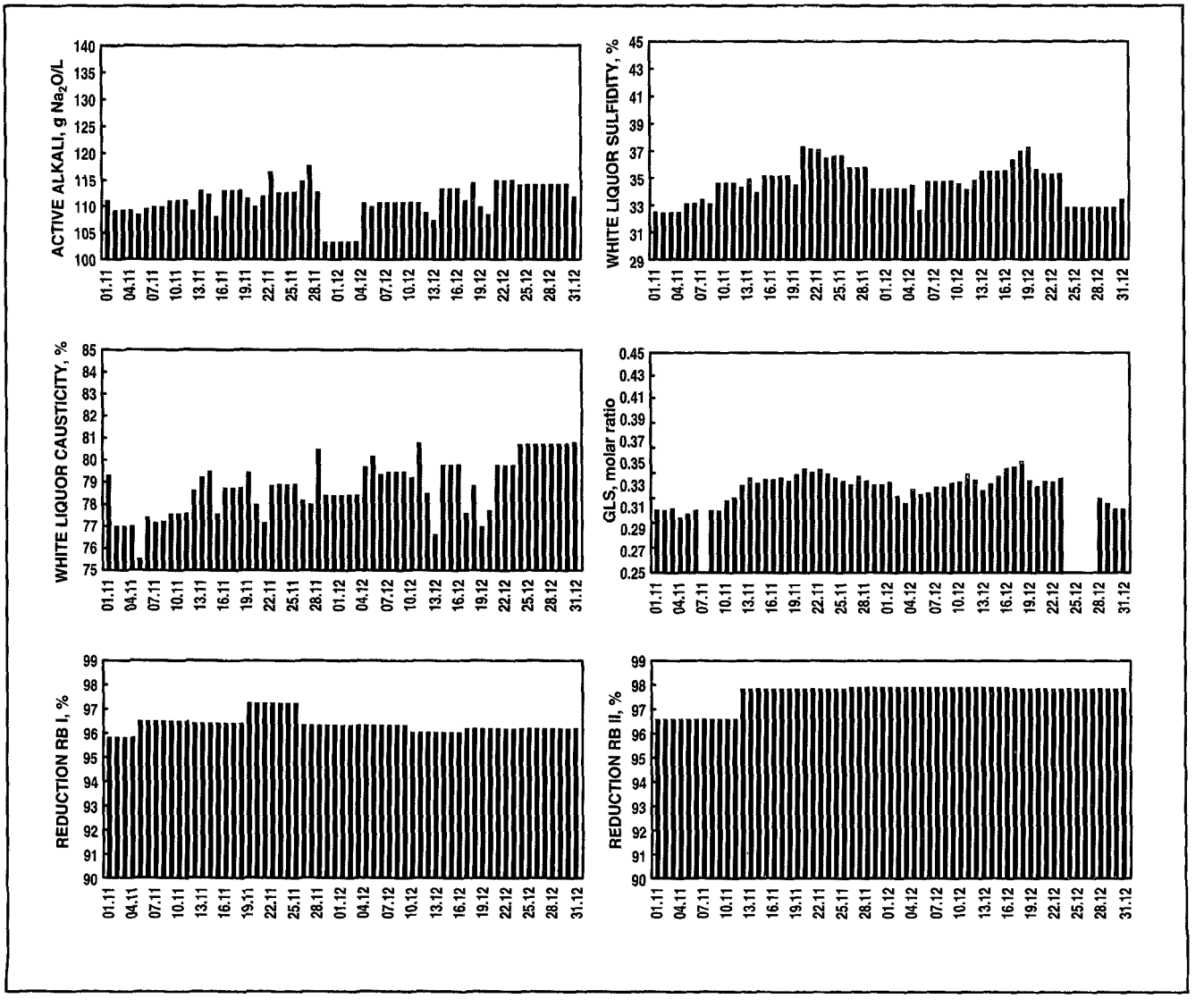
2. Viscosity of Na_2S-Na_2CO_3 melts at two sulfidity levels, with and without 5 mole% K-substitution



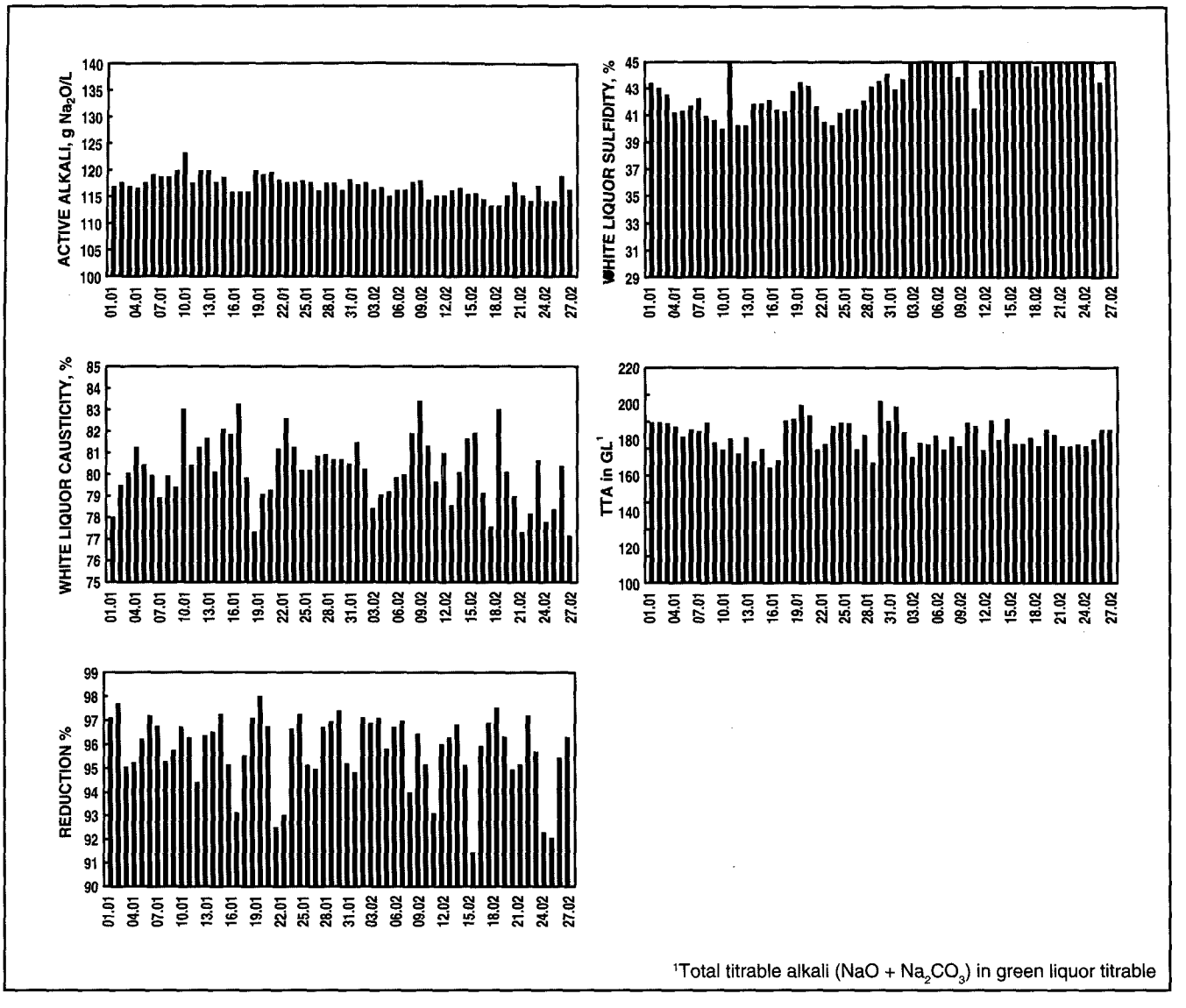
3. Viscosity of Na_2S-Na_2CO_3 melts at three sulfidity levels



4. Day-to-day analyses at Mill B (RB = recovery boiler)



5. Day-to-day analyses at Mill C



[1]Total titrable alkali (NaO + Na_2CO_3) in green liquor titrable

the liquor system simultaneously increases. **Figure 1** shows the K/(Na+K) molar ratio changes at Mill A from 1988 to 1992. The level of K/(K+Na) in the liquor system at a given pulp mill can be considered a measure of the closing degree of that mill. Chlorides have not been covered in this study because few chloride analyses were made during these years.

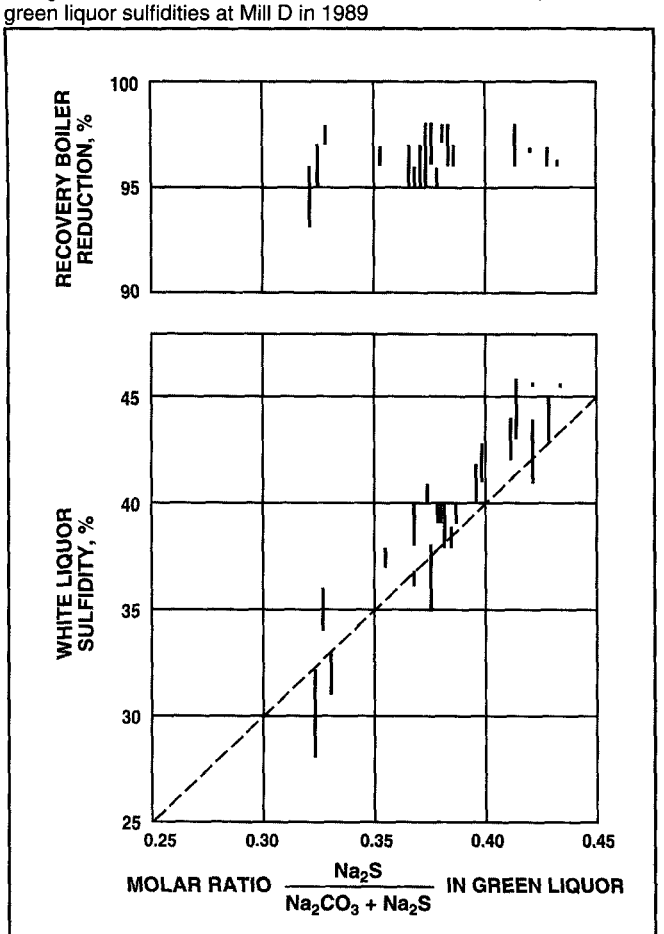
Consequences of higher sulfidity

In the long run, lower sulfur emissions at a pulp mill result in higher sulfidity levels in the mill's liquor system. The sulfidity values [or the ratio of Na_2S to active alkali (i.e., Na_2S+NaOH)] at Scandinavian kraft mills previously fluctuated between 28 and 35%; they now exceed 45%.

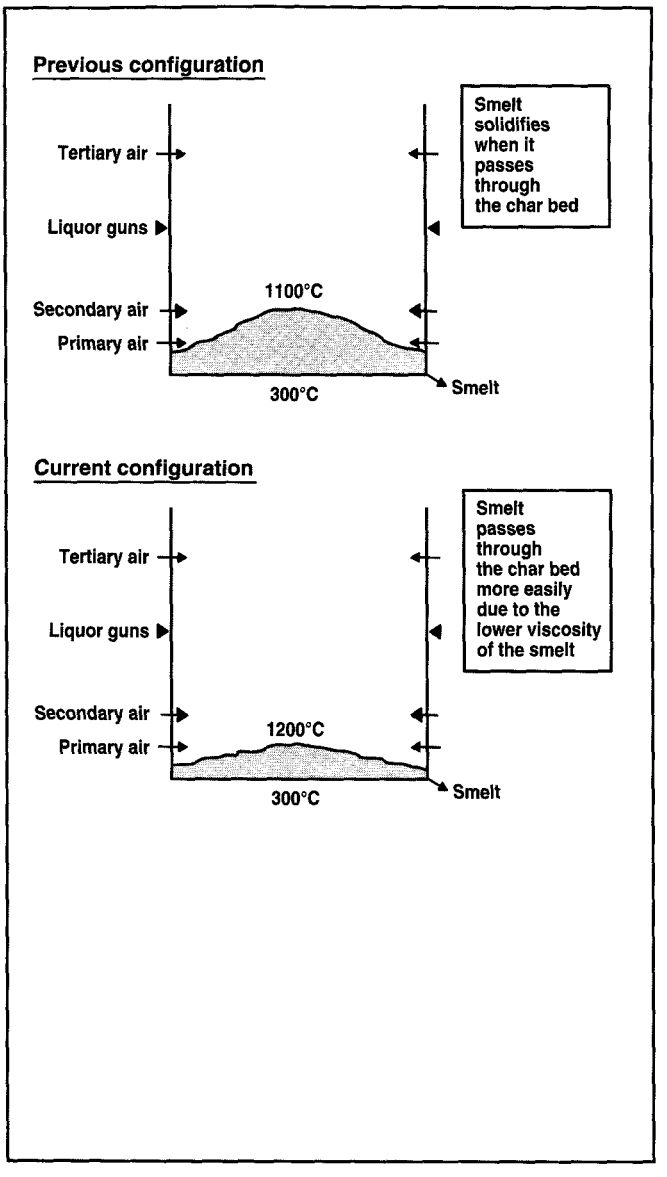
When considering the smelt and its behavior in the char bed, the viscosity of the smelt (Na_2S – Na_2CO_3) should be studied at different temperatures. Magnusson and Warnqvist *(8)* and Grace *(9)* have conducted viscosity measurements, and they have noted that the viscosity decreases when the sulfidity of the binary smelt increases. In this investigation, the viscosities of some binary solutions were measured by rotation viscometry, a procedure described in *(10)*.

Figure 2 clearly shows the effect of the sulfidity increase from 30 mole% to 40 mole%: the viscosity decreases by almost 50%. The increased effect of the potassium is also quite noticeable. 5 mole% potassium in the smelt drastically decreases the viscosity. The effect of potassium on the smelt's melting temperature was shown by Grace *(9)* to decrease gradually with increasing potassium content. According to Grace, the eutectic melting temperature of the composition (66.3 mole% Na_2CO_3, 20.8 mole% Na_2S, and 12.9

6. High reduction and the correlation between the white liquor and the green liquor sulfidities at Mill D in 1989



7. Change in the char bed form



mole% Na_2Cl_2) dropped from 586°C to 525°C at 5 mole% potassium replacement. Higher potassium levels produce no essential changes in the eutectic melting temperatures.

According to Backman *(11)*, the melting points of Na_2S and Na_2CO_3 are 1180°C and 858°C, respectively. The eutectic point in that system is 762°C, with a composition of 40 mole% Na_2S and 60 mole% Na_2CO_3.

As seen in **Fig. 3**, when the sulfidity increases from 40 mole% to 50 mole%, the viscosity increases more than 100%. These data indicate that the viscosity decrease has its minimum near the eutectic point of the Na_2S–Na_2CO_3 system.

Analyses at pulp mills

Figures 4 and 5 show examples of day-to-day analyses from two pulp mills. Mill B, in Fig. 4, is running at a low sulfidity level, while Mill C, in Fig. 5, is running at extremely high sulfidity levels. These two boilers have had no significant problems with corrosion. Mill C, however, experienced some composite tube cracking when the sulfidity was near 40%. The green liquor sulfidity (GLS), or ratio of Na_2S to (Na_2 + Na_2CO_3) in green liquor, given in Figs. 4 and 5 was calculated from the titration analyses made from green liquor *(12)*.

Figure 6 shows Mill D's reduction rate and the sulfidity values in its white and green liquor. Mill D had been running for long periods close to the eutectic point of the Na_2S – Na_2CO_3 binary, i.e., 40 mole% Na_2S in the smelt. The height of the bed had, at the same time, been extremely low. As Fig. 6 shows, the sulfidity in the green liquor is lower than in the white liquor. The difference in sulfidities is due to limiting causticity to about 80%.

At Mill D (Fig. 6), the high reduction values, which indicate high bed temperatures, together with a smelt that had sulfidity close to 40 mole% for long periods of time, resulted in a smelt with very low viscosity values. These conditions produced an abnormal environment inside the boiler and lead to heavy corrosion of the composite tubes. The aggressive smelt had direct contact with the composite tubes and, therefore, the corrosion was pronounced.

Risks of abnormal smelt behavior

These data demonstrate that sulfidity levels close to the eutectic point in the binary $Na_2S - Na_2CO_3$ system should be avoided in a recovery boiler. If a unit operates close to the eutectic point of the smelt's composition and the potassium enrichment is over 5 mole% K/(K + Na), the smelt may demonstrate abnormal behavior. The risks of abnormal smelt behavior increase if the height of the char bed is kept low.

Figure 7 shows the most significant changes in the char bed forms during the last five years in Scandinavia. It is important to realize the effectiveness of a porous char bed in shielding floor tubes. When a smelt has a sulfidity close to 40 mole% and its potassium and chlorine levels are high enough, the smelt flows extremely easily at higher bed temperatures. Such a smelt has a low melting point and, thus, a low viscosity and may penetrate the char bed, getting close to the floor tubes.

This seepage of hot smelt through the char bed may create cracks that look like thermal fatigue cracks on the steel layer of the composite tubes. In extreme cases, the hot smelt may destroy the layer of solidified smelt on the floor tube's surface and react very rapidly with the floor tube.

Conclusions

To estimate the risks of abnormal smelt behavior and, thus, those of cracking and corrosion of composite floor tubes, the sulfidity and the concentrations of K and Cl in kraft mill smelts should be analyzed. A sulfidity level close to 40 mole% should be avoided, especially if the K/(K + Na) is over 5 mole%. If, however, circumstances are near this critical value, the boiler should be operated so the height of char bed is not concurrently reduced. ◼

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Received for review Jan. 14, 1993.

Accepted June 3, 1993.