Field studies on fume chemistry and deposition in kraft recovery boilers

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ABSTRACT

The chemistry and rate of accumulation of fume deposits at various locations in two recovery boilers at different mills were investigated using a fume deposition probe. Similar results were obtained at both boilers. In the lower furnace, fume deposits contained as much as 26 wt.% alkali hydroxides (NaOH + KOH). In the upper furnace, no hydroxide was found; the chloride and potassium contents were relatively constant, whereas the carbonate content increased progressively towards the back end of the boiler. The study also indicates that the majority of solid fume starts forming at a location near the entrance of the generating bank, where the flue-gas temperature is about 600°C.

Application:

Results of two field trials on different recovery boilers show that carbonate in fume increases toward the back end of the boiler and that most fume deposits form where the temperature is about 600°C, typically near the entrance to the generating bank.

THE DEPOSITION OF FUME ON tube surfaces in the upper furnace of kraft recovery boilers has been intensively studied over the last two decades. Fume deposits have a drastic effect on boiler thermal performance, corrosion, and fouling and plugging of flue-gas passages. Fume chemistry is particularly important, since it greatly affects the thermal behavior and the reactivity of deposits.

In a previous field study that we conducted in a CE recovery boiler at a kraft pulp mill in Ontario *(1)*, it was found that the composition of fume deposits varies greatly with location in the boiler. Fume deposits in the lower furnace contained as much as 26 wt.% of alkali hydroxides (NaOH + KOH). In the upper furnace—from the bullnose elevation onward—deposits contained no hydroxide and had relatively constant chloride and potassium contents. The carbonate content increased gradually in going from the bullnose elevation through to the secondary superheater platens, remaining relatively constant at this location onward. The study also indicated that the majority of solid fume starts forming at a location close to the entrance of the generating bank, where the flue-gas temperature is in the range of 550–650°C.

The detection of such a large amount of hydroxide in fume deposits in the lower furnace supports the belief that hydroxides are responsible for the localized corrosion of composite tubes around air ports in the lower furnace *(2, 3)*. The low carbonate content in fume deposits at the bullnose elevation compared with that in the superheater region and in the precipitator dust is inconsistent with the general observation that the carbonate content decreases (not increases) toward the back end of the boiler. Precipitator dust, which consists mostly of fume, generally contains less carbonate than the deposits in the superheater region, where carryover deposition is dominant *(4)*.

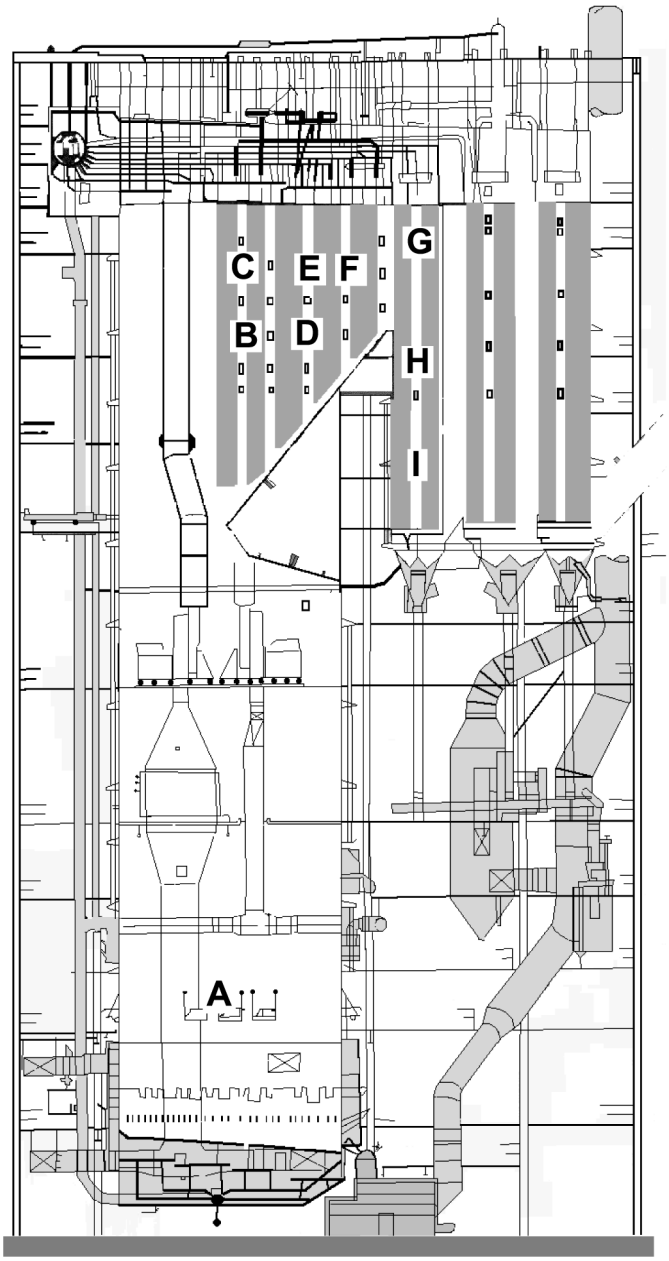
Of all the individual fume components, potassium chloride has the lowest melting temperature, 775°C. Thus, all solid fume should be formed in the first section of the superheater, where the flue-gas temperature is below 775°C. The sudden formation of large amounts of fume near the generating-bank inlet found in this case is difficult to explain. However, if it is true, the phenomenon will have a significant impact on our understanding of how deposits form and grow at various locations in the boiler.

Another field study was therefore performed to verify the findings of the first study. The objective was to determine whether similar results could be obtained for boilers at different mill sites and with different operations. If the results were similar, then conclusions on fume chemistry and deposition could be drawn with greater confidence. In this paper, results of the second field study are discussed and compared with the previous study. Conclusions are drawn based on results obtained from both studies.

TEST PROCEDURE

The second field study was carried out at a mill in the southern United States. The boiler, shown in **Fig. 1**, is a 1992 single-drum B&W unit designed to burn 2,475,000 kg of black-liquor dry solids per day and to produce 400,000 kg/h superheated steam rated at 482°C and 112 bar. At the time of this study, the boiler was operated at only 89% of its rated dry-solids capacity. This boiler is about 1-1/2 times larger than the CE boiler in the previous study.

The fume deposition probe used in this study was the same as that in the previous study. As shown in **Fig. 2**, the probe consists of three concentric Type 310 stainless steel tubes (outer, central, and inner tubes) equipped with a five-plate screening impactor at the probe hot end to remove carryover particles. Flue gas from the boiler is drawn through the space between the outer tube and the central tube,



1. Schematic of the B & W recovery boiler and locations where deposits were collected during the second field study

and fume deposits are collected on the surface of the central tube.

The probe was exposed at various sites within the boiler. The sites are illustrated in **Fig. 1**. Site A was next to a black-liquor gun port. Sites B, C, D, E, and F were access doors in the superheater region; and Sites G, H, and I were access doors in the generating bank. To minimize the effect of thermophoresis on fume deposition, no cooling air was used to cool the central tube of the probe during the tests in the upper furnace. Only at Site A—in the lower furnace—was cooling air used. This was done to avoid excessive corrosion of the fume-deposition surface. At each test site, two or more runs were carried out. Before each test, the probe was exposed for 5–10 min to allow the temperature to reach a steady state. When this temperature was reached, the test was started by activating the vacuum pump to draw the flue gas through the probe. After 10 min of gas withdrawal, the probe was taken out of the boiler, and the outer tube was removed. The surfaces of both the outer tube and the central tube were thoroughly examined and photographed. Three or more samples of deposits were collected along the probe length and analyzed. Details of the probe design and operation, the deposit collection procedure, and analytical methods have been described previously *(1)*.

DEPOSIT APPEARANCE

Examination of the deposits on a probe at Site C revealed some interesting findings. The cold end (back half) of the probe's central tube was covered with a layer of white, dustlike deposits, typical of fume deposits, while the hot end (front half) appeared to be deposit free. The windward side of the outer tube was covered with a thick layer of deposits that were partially fused. The deposits contained some pink particles characteristic of those formed mostly by carryover. At locations further downstream, deposits on the central tube looked the same as those observed at Site C. On the other hand, deposits on the outer tubes were somewhat different; they appeared to contain more white, dustlike deposits.

The appearance of deposits and the results of SEM examinations performed on selected samples show that deposits on the central tube consist mostly of fume, whereas deposits on the outer tubes are a mixture of carryover and fume. The results also confirm that fume is the dominant type of deposit in the back end of the boiler.

DEPOSIT COMPOSITION

At all test sites, there was no significant difference in deposit composition along the probe length. **Tables I**

and II show the composition of fume deposits on the central tube and on the outer tube of the probe, respectively. Note that each composition is the average of all samples analyzed along the probe length and that no deposit composition in the lower furnace is presented in **Table II**. Sampling of deposits on the outer tube after exposure in the lower furnace was not possible because the tube surface had been severely corroded during exposure to the high temperature and corrosive environment in that region.

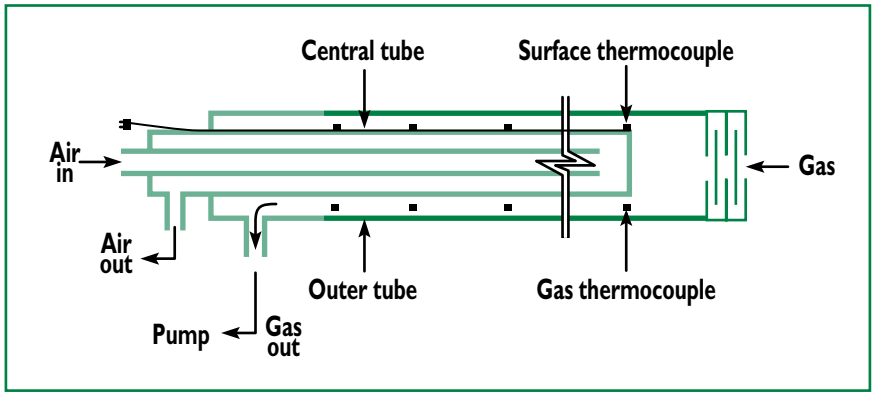
Note also that for all samples analyzed, the molar ratio of anions ($Cl_2+SO_4+CO_3+(OH)_2$) to cations (Na_2+K_2) is equal or close to one. This indicates that all or most of the alkali compounds in the deposits have been accounted for.

In order to compare the composition of the deposits and precipitator dusts obtained from the two test studies, molar units will be used throughout this paper. Since OH/(Na+K) mole%, Cl/(Na+K) mole%, and K/(Na+K) mole% are, respectively, equal to $(OH)_2/(Na_2+K_2)$ mole%, $Cl_2/(Na_2+K_2)$ mole%, and $K_2/(Na_2+K_2)$ mole%, they will be used to describe the concentrations of hydroxide (OH), chloride (Cl), and potassium (K). Similarly, $CO_3/(Na_2+K_2)$ mole% and $SO_4/(Na_2+K_2)$ mole% will be used to describe the carbonate and sulfate contents, respectively.

Furthermore, since all the alkali compounds in the samples have been accounted for, the composition can be normalized to make the results clearer. For each sample, the sum of OH/(Na+K) mole%, Cl/(Na+K) mole%, $SO_4/(Na_2+K_2)$ mole%, and $CO_3/(Na_2+K_2)$ mole% is equal to 100%.

LOWER FURNACE

Figure 3 shows the normalized composition of the fume deposit on the central tube of the probe exposed in the lower furnace (Site A) and that obtained in the previous study *(1)*. The



2. Schematic of the fume deposition probe

Test site	CATIONS, wt.% Na	K	ANIONS, wt.% OH	Cl	SO_4	CO_3	A/C,[a] molar ratio
Lower furnace							
A	36.2	6.1	6.0	2.6	30.0	19.1	0.97
Upper furnace							
B	27.9	7.7	0.0	4.8	56.7	2.9	0.99
C	28.5	6.8	0.0	5.5	56.5	2.7	1.01
D	28.9	6.6	0.0	4.4	55.6	4.5	1.00
E	28.5	6.9	0.0	5.6	55.8	3.1	1.00
F	25.9	11.7	0.0	3.6	53.1	5.7	0.99
G	27.8	8.7	0.0	3.2	53.3	7.0	1.01
H	24.1	13.2	0.0	3.2	52.9	6.5	1.02
I	26.5	10.8	0.0	4.0	52.0	6.7	0.99
Precipitator[b]	30.8	6.4	0.0	3.3	46.3	11.3	1.00

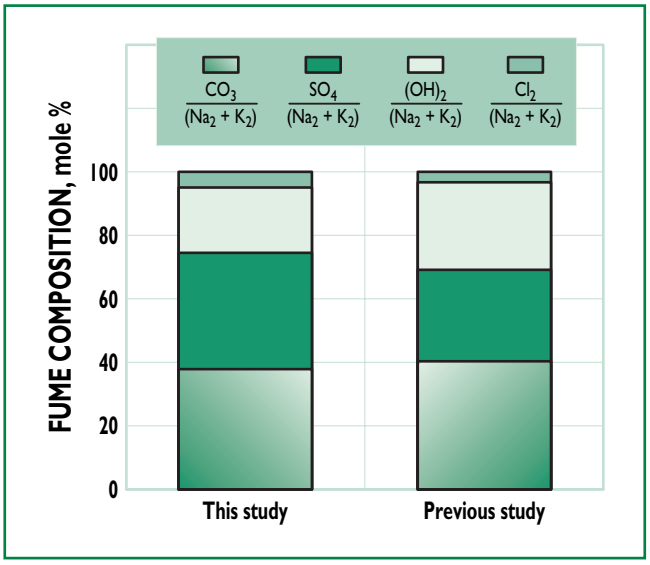
[a] A/C = molar ratio of anions to cations = $[Cl_2 + SO_4 + CO_3 + (OH)_2]/[Na_2 + K_2]$
[b] Analysis of dust collected from the precipitator

I. Composition of fume deposits collected on the probe's central tube

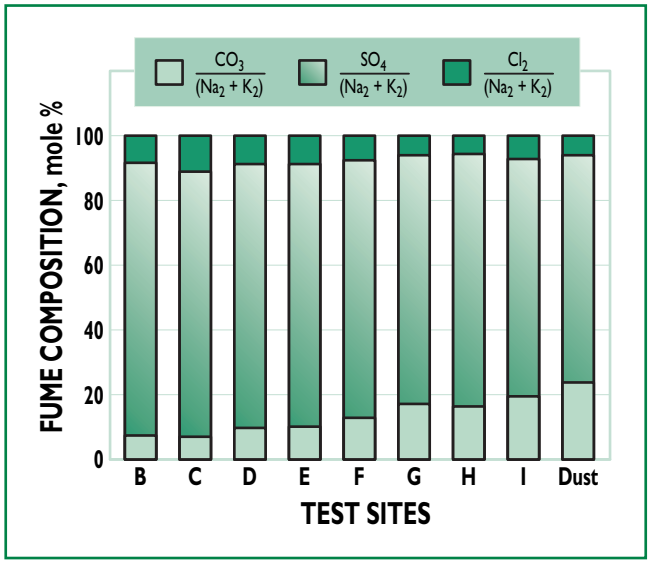
Test site	CATIONS, wt.% Na	K	ANIONS, wt.% OH	Cl	SO_4	CO_3	A/C,[a] molar ratio
Lower furnace [b]							
A	…	…	…	…	…	…	…
Upper furnace							
B	33.5	4.0	0.0	1.2	44.6	16.7	0.98
C	33.0	4.0	0.0	0.9	45.8	16.3	0.99
D	32.5	4.0	0.0	2.0	46.2	15.3	1.01
E	32.8	4.0	0.0	2.2	46.2	14.9	1.00
F	31.7	4.4	0.0	3.1	47.0	13.8	1.02
G	32.3	4.4	0.0	3.2	47.6	12.4	0.98
H	32.1	4.7	0.0	3.8	46.7	12.7	0.99
I	30.6	5.9	0.0	4.7	47.4	11.4	1.01
Precipitator[c]	30.8	6.4	0.0	3.3	46.3	11.3	1.00

[a] A/C = molar ratio of anions to cations = $[Cl_2 + SO_4 + CO_3 + (OH)_2]/[Na_2 + K_2]$
[b] Severe corrosion of the probe's outer tube during exposure in the lower furnace made it impossible to sample surface deposits.
[c] Analysis of dust collected from the precipitator

II. Composition of fume/carryover deposits collected on the probe's outer tube



3. Composition of fume deposits on the probe's central tube in the lower furnace for current study (B&W boiler) and a previous study (CE boiler)



4. Composition of fume deposits on the probe's central tube at various sites in the upper furnace and in precipitator dust (current study)

composition is virtually the same for both studies. The deposit contains a significant amount of hydroxide, 20.1 mole% OH/(Na+K), along with its usual components, chloride, carbonate, and sulfate. Assuming the anions (Cl, SO_4, CO_3, and OH) are bound proportionally to Na and K, the amount of alkali hydroxides can be estimated to be about 26 wt.% NaOH + KOH.

UPPER FURNACE

Figure 4 shows the normalized compositions of fume deposits at various locations in the upper furnace, along with that of precipitator dust collected during this study. No hydroxide was detected in the deposits. The Cl content was relatively constant, about 10 mole% Cl/(Na+K). The carbonate content increased from about 6 mole% $CO_3/(Na_2+K_2)$ after the inlet of the second pass of the secondary superheater platens (Sites B and C) to about 10 mole% $CO_3/(Na_2+K_2)$ at the entrance of the third pass of the primary superheater platens (Sites D and E). It further increased towards the back end of the boiler, reaching 15–20 mole% $CO_3/(Na_2+K_2)$ in the generating bank (Sites G, H, and I). Carbonate content was 25 mole% $CO_3/(Na_2+K_2)$ in the precipitator dust. The sulfate content of the deposits decreased as the carbonate increased.

The results were consistent with those found in the CE recovery boiler in the previous study, confirming that the carbonate content in fume deposits increases towards the back side of the boiler.

A similar graph for the composition of carryover/fume deposits collected on the outer tube of the probe in the upper furnace is shown in **Fig. 5**. The Cl content appeared to be lower in the superheater region, presumably because of the vaporization of NaCl and KCl from the deposit at high temperatures. Unlike the results shown in **Fig. 4**, in this case, the carbonate content decreased towards the back end of the boiler, which is consistent with conventional belief. Note that towards the back end of the boiler, the composition of fume deposits (**Fig. 4**) becomes increasingly similar to that of the carryover/fume deposits (**Fig. 5**).

It can therefore be concluded that the composition of fume deposits is different from general observation; that is, the carbonate content increases toward the back end of the boiler while the sulfate content decreases, and the Cl and K contents are relatively constant throughout the boiler.

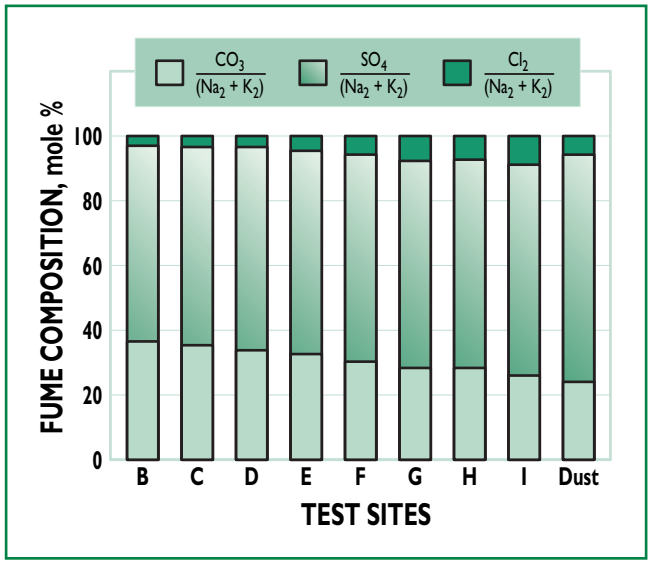
DEPOSITION RATE

Examination of the probe's central tube showed a clear transition point between the hot end, where little or no deposit was observed, and the cold end, where a white deposit was observed. The flue-gas temperature at the transition point during the test was about 600°C. Consistent with the appearance, the mass of fume deposits collected in 10 min along the probe length was about 10 mg/m² on the hot end, significantly less than that on the cold end, which was more than 300 mg/m².

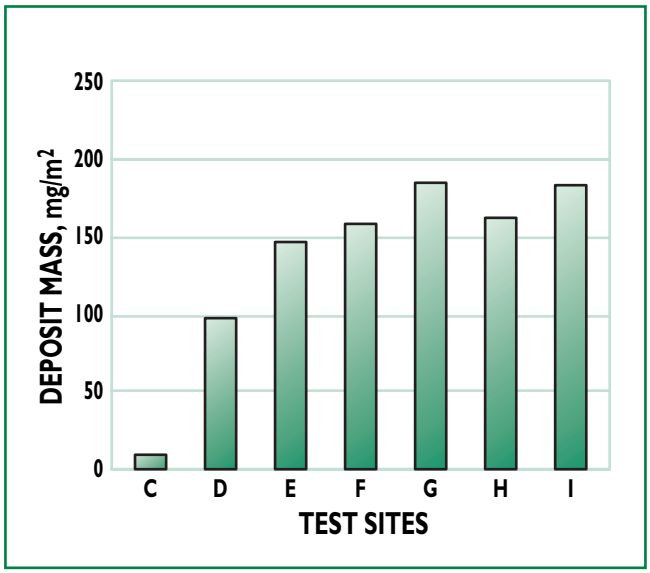
Figure 6 shows the amount of fume deposits collected on the cold end of the central tube at various test sites in the upper furnace. The amount increased markedly from about 10 mg/m² at Site C to about 150 mg/m² at Site E. It then increased further, although at a much lower rate, reaching about 180 mg/m² in the generating bank (Sites G, H, and I).

Note that Sites C, E, F, and G are at

KEYWORDS
Black liquors, boilers, combustion, deposition, deposits, fumes, furnaces, heating equipment, recovery furnaces, solids content, spent liquors



5. Composition of carryover/fume deposits on the probe's outer tube at various sites in the upper furnace



6. Mass of deposits on the cold end of the probe's central tube at various sites in the upper furnace

the same elevation in the boiler, while Locations B, D, H, and I are at a lower elevation (**Fig. 1**). In this study, the flue-gas temperatures were measured using a temperature probe that was calibrated against a suction pyrometer. **Figure 7** shows the amount of fume deposits plotted against the flue-gas temperature for both this study (solid line) and the previous study (broken line). While Site D is in the lower superheated region, its flue-gas temperature was disproportionately low, presumably because of the large flue-gas recirculation zone above the bullnose. Therefore, if the data point at Site D is ignored, the results from the two studies are essentially the same. They both show a "break-point"—the temperature at which the majority of solid fume deposits form—at about 600°C. This is also the temperature at the transition point where deposition on the central tube of the probe increased dramatically.

These results are important, since they suggest that fume is suddenly precipitated out from the flue gas at a location where the temperature is about 600°C. This implies that, for a typical boiler, the majority of solid fume starts forming at a location near the superheater exit or the entrance of the generating bank.

IMPLICATIONS

Despite the difference in boiler design, operation, and liquor chemistry, the results obtained from both field studies are in agreement with each other. The implications of the results are thus worthy of further examination.

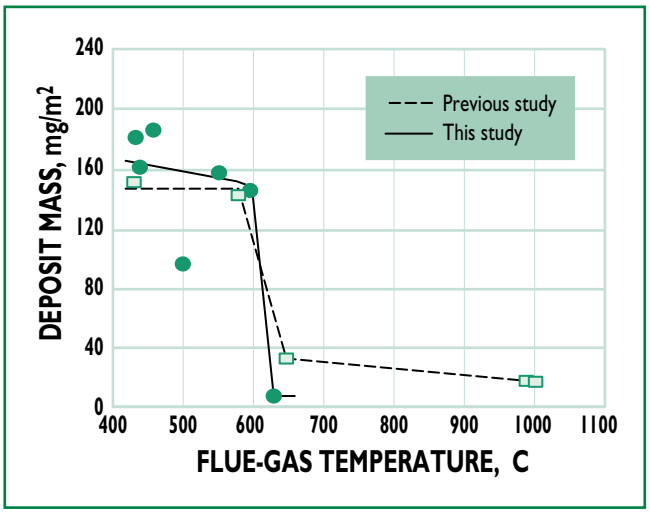
The carbonate content in the precipitator dust in both boilers was higher than 10 mole% $CO_3/(Na_2+K_2)$. This indicates that the concentration of sodium and potassium vapors released from the lower furnace was higher than the sulfur species, and that the bed temperature in both boilers was probably higher than 1050°C. At these temperatures, Na, K, NaOH, and KOH may exist in the flue gas, above the bed, at a combined concentration of about 3000 ppm. With about 10% CO_2 typically present in the flue gas, all hydroxides should be carbonated. The large amounts of hydroxide found in the lower-furnace fume deposits were probably due to the slow kinetics of the carbonation reaction of NaOH and KOH in the presence of 10% water vapor *(5)* and the short sampling time, 10 min, employed during the studies

It is important to note that the thermal behavior of alkali carbonate differs from that of other alkali compounds. As seen in **Fig. 8**, NaOH, NaCl, and Na_2SO_4 melt at their respective melting temperatures and then sublime to gaseous NaOH, NaCl, and Na_2SO_4 at temperatures above 750°C, 800°C, and 1200°C, respectively. Na_2CO_3, on the other hand, melts at 850°C and decomposes slowly (it does not sublime or vaporize) at about the same temperature into CO_2 and liquid Na_2O, which, in the presence of H_2O vapor, become gaseous NaOH, i.e.:

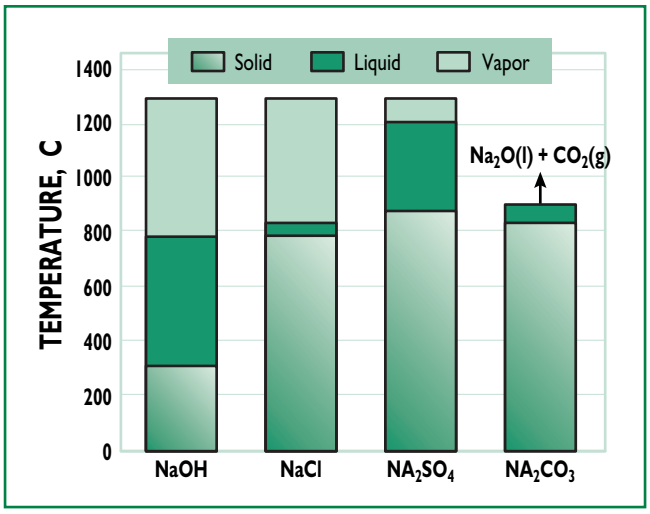
$$Na_2CO_3(s) \rightarrow Na_2CO_3(l) \rightarrow Na_2O(l) + CO_2(g) \rightarrow 2\ NaOH(g) + CO_2(g)$$

In the recovery boiler, the flue-gas temperature typically varies from 1200°C at the secondary or tertiary air level to about 1000°C at the bullnose elevation. In the region below the bullnose, the sodium compounds in the flue gas should be predominantly composed of NaOH and NaCl vapors and liquid Na_2SO_4 fume. There should be no Na_2CO_3 vapor and fume in the flue gas.

As the flue gas passes through the superheater, its temperature decreases, causing vapors of NaOH, NaCl, and Na_2SO_4 to condense into liquid or solid fume. Solid Na_2CO_3 fume is formed only when the flue-gas temperature is below 850°C as a result of the reaction between gaseous/liquid NaOH and CO_2, and not a result of condensation. Since liquid NaCl and Na_2CO_3 is stable in a very narrow temperature range,



7. Mass of deposits collected on the probe at various sites in the upper furnace as a function of the flue-gas temperature (current and previous studies)



8. Thermal stability of sodium compounds

there probably is little liquid NaCl and Na_2CO_3 fume in the flue gas. With the progression towards the back end of the boiler, the carbonate content in the fume increases as a result of the carbonation of hydroxide. The chloride and sulfate is high at first, then decreases as a result of dilution by the carbonate.

Although the melting point of the Na_2CO_3 is about 850°C, it is likely that Na_2CO_3 would precipitate out at a temperature much lower than 850°C through a supercooling effect. The driving force for the precipitation process increases as the deviation from the melting temperature increases. As the flue gas is cooled below 600°C, which is about the same as the first melting temperature of fume, some particles condense, providing nuclei (or seeds) on which Na_2CO_3 and other alkali compounds form and grow. This explains why large amounts of fume suddenly formed in the back end of the boiler.

Since the flue-gas temperature in the upper furnace depends strongly on boiler operation, the location in the boiler where the majority of fume forms may differ from boiler to boiler. For overloaded boilers, the flue-gas temperature in the upper furnace is usually high, and thus massive fume precipitation may occur inside the boiler bank. For boilers that are underloaded or that burn liquors of low heating value, the majority of fume precipitation is expected to occur in the mid superheater.

CONCLUSIONS

Results obtained from this and previous field studies on fume chemistry and deposition show that:

- In the lower furnace, fume deposits contained as much as 26 wt.% alkali hydroxides (NaOH + KOH) besides the usual components—Na_2SO_4, Na_2CO_3, NaCl, and potassium salts.
- In the upper furnace, fume deposits contain no hydroxide. The chloride and potassium contents of the deposits were relatively constant throughout the boiler.
- The majority of solid fume forms at a location where the flue-gas temperature is about 600°C. The location may differ from boiler to boiler because of differences in the flue-gas temperature.
- Kinetics play an important role in fume chemistry. **TJ**

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