Effect of composition on the first melting temperature of fireside deposits in recovery boilers

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ABSTRACT

The first melting temperature (FMT) of fireside deposits—the temperature at which a deposit begins to melt—is a vitally important factor in minimizing superheater corrosion in kraft recovery boilers. This study examines the correlation between deposit composition and FMT. Chemical analysis of more than 150 deposits and precipitator dusts from various recovery boilers showed that of the minor components in the deposit, potassium has the greatest impact in lowering the FMT. Carbonate can also lower the FMT, but the effect is much smaller than potassium. Sulfide has an even smaller effect. Since deposits usually contain some chloride, an increase in chloride content has little effect on the FMT. These differences in the effects of individual components on the FMT of boiler deposits can be explained using phase-equilibrium principles. A temperature contour map was constructed from the data. This map can be used to determine the FMT of a typical deposit as a function of potassium and carbonate contents.

Application: *Provides a method of predicting first melting temperatures of fireside deposits in the recovery boiler. Using this approach, mills can minimize superheater corrosion by operating below the identified temperature threshold.*

UNDERSTANDING THE MELTING behavior of fireside deposits in kraft recovery boilers is a critically important factor in boiler design and operations. The first melting temperature (FMT)—the temperature at which the deposit begins to melt—is particularly important in terms of superheater corrosion. Numerous field studies and mill experience have shown that superheater tubes undergo accelerated corrosion when the tube surface temperature exceeds the FMT of the deposit that covers the tube surface *(1–4)*, particularly when the atmosphere around the tube is reducing. The FMT is also important in boilers that burn high-chloride black liquor (>2.5 wt.% Cl on dry solids). In such boilers, because of the high chloride content [>8 mole% Cl/(Na+K)], the FMT is also the temperature at which the deposit becomes sticky, which leads to massive deposition *(5)*.

Deposits consist mainly of sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), with small amounts of sodium sulfide (Na_2S), sodium chloride (NaCl), and potassium (K) salts. The FMT typically varies between 520°C to 580°C, depending on composition. Because of the low FMT values and the corrosive nature of the deposits, recovery boilers are rarely operated at final superheated steam temperatures above 480°C (900°F).

In recent years, there has been a continuing trend toward minimizing chemical losses, producing more hardwood pulp, and operating recovery boilers at higher bed temperatures. As a result, the chloride and potassium contents in the liquor have increased over the years, and so has the carbonate content in recovery boiler deposits and precipitator dust. Such changes in deposit composition are expected to have a significant effect on the deposit melting behavior.

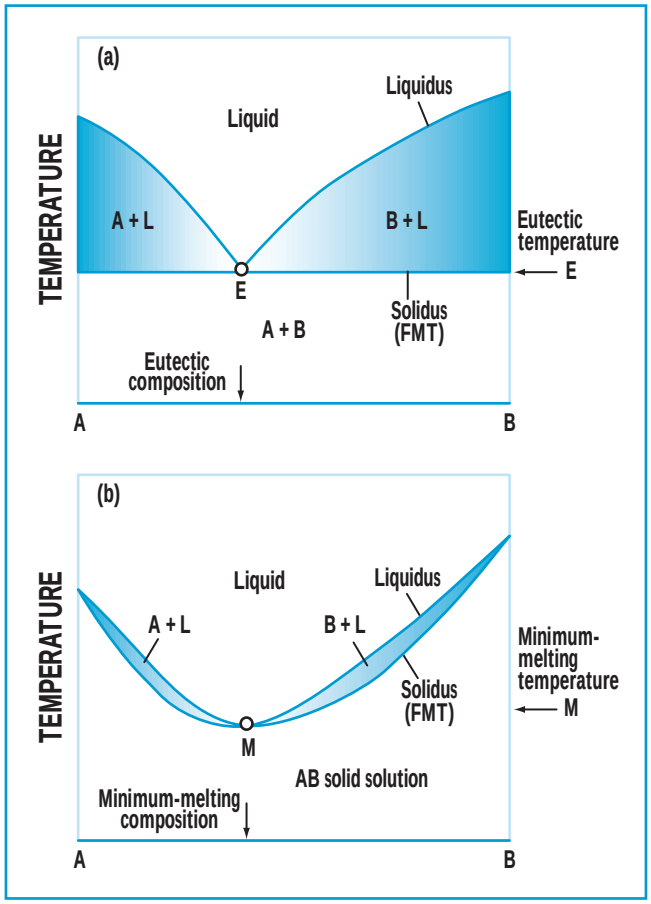
This paper discusses the results of a study into the effect of composition on the FMT. The study involved:

1. A theoretical analysis of the effect of individual deposit components on the FMT
2. An examination of the correlation between deposit composition and FMT for more than 150 boiler deposits and precipitator dusts
3. A systematic study using synthetic deposits to examine the effect of individual components on the FMT.

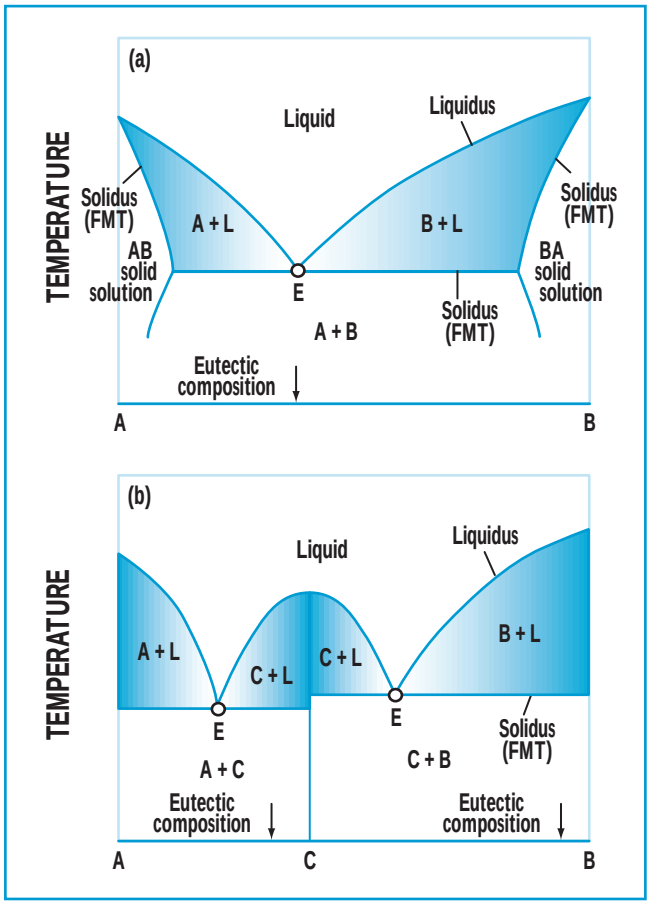
THEORETICAL ANALYSIS

The phase equilibrium involved in multicomponent ionic melts, such as recovery boiler deposits, is an extremely complex subject that is beyond the scope of this paper. However, it is important to have a basic understanding of phase diagrams and how ionic materials behave at high temperatures so that the effect of individual components on the FMT can be understood.

For pure compounds, the FMT is the same as the complete melting temperature of that compound. Thus, given sufficient time, a pure ionic compound will melt completely at its melting temperature. For example, Na_2SO_4 begins to melt at 884°C (FMT) and becomes completely molten at 884°C, while NaCl begins to melt and becomes completely molten at 800°C. For a mixture of compounds, the FMT is usually much lower than the melting temperatures of individual compounds. For example, a mixture of 90 mole% Na_2SO_4 and 10 mole%



1. Basic phase diagrams for binary systems: (a) eutectic and (b) minimum melting



2. Basic phase diagrams for binary systems with (a) limited solid solutions and (b) compound formation

NaCl begins to melt at 628°C (FMT), but it is not completely molten until the temperature is above 850°C.

Phase diagrams

In a simple binary system involving ionic Compounds A and B containing a common cation (e.g., Na_2SO_4–Na_2CO_3 or K_2SO_4–KCl) or a common anion (e.g., Na_2SO_4–K_2SO_4 and NaCl–KCl), there are two basic types of mixtures: eutectic and minimum melting. In a eutectic mixture, Compounds A and B usually have different crystal structures and are always in their individual crystal forms at temperatures below the eutectic temperature, as seen in **Fig. 1a**. In the liquid-phase region of the diagram, A and B dissolve in each other, forming a melt that contains individual ions. When the ionic melt is cooled to a temperature below the eutectic temperature, it solidifies and becomes a mixture of two original Compounds A and B. Examples of binary systems that form eutectic mixtures are Na_2SO_4–NaCl, K_2SO_4–KCl, and Na_2CO_3–NaCl.

In a minimum-melting mixture, the melt remains "well mixed" after it solidifies, as seen in **Fig. 1b**. A and B form a complete solid solution with each other and no longer have their original crystal structures. A complete solid solution usually occurs when A and B have the same crystal structure, the same ionic charge, and the size difference between their cations or between their anions are not large (<30%). Examples of such systems are Na_2SO_4–Na_2CO_3, Na_2SO_4–K_2SO_4, and NaCl–KCl.

Intermediate (mixed) behaviors can occur when A and B have similar crystal structures and ionic charges, but their ionic sizes are greatly different. In such cases, B may form a limited solid solution with A at one end of the diagram, while A may form a limited solid solution with B at the other end, and the eutectic behavior is still shown in the middle of the diagram, as seen in **Fig. 2a**. The phase diagram becomes much more complex if A and B form a new Compound C at high temperatures. The basic principles, however, can still be applied by splitting the phase diagram into two subdiagrams A–C and C–B, as seen in **Fig. 2b**.

First melting temperature

The first melting temperature (FMT) of a binary mixture is essentially the solidus of the system (i.e., the temperature line below which the mixture is completely solidified). Consequently, the question of whether composition has any effect on the FMT depends on whether the mixture is a eutectic system or a minimum-melting system. In the eutectic

Mixture	Expected type [a]	EXPERIMENTAL RESULTS			
		Actual type [a]	Temperature,[b] °C	Composition,[c] mole%	Literature source
Na_2SO_4–K_2SO_4	M	M	823	20.0	Fig. 2889 in *(7)*
		M	832	25.0	Fig. 7018 in *(8)*
Na_2CO_3–K_2CO_3	M	M	710	41.0	Fig. 6979 in *(8)*
Na_2SO_4–Na_2CO_3	M	M	828	63.2	Fig. 7042 in *(8)*
K_2SO_4–K_2CO_3	M	M	901	100.0	Fig. 7036 in *(8)*
NaCl–KCl	M	M	657	49.4	Fig. 7256 in *(8)*
		M	667	50.7	Fig. 7257 in *(8)*
Na_2CO_3–NaCl	E	E	633	55.0	Fig. 7060 in *(8)*
K_2CO_3–KCl	E	E	629	43.4	Fig. 7058 in *(8)*
			640	63.0	Fig. 1813 in *(9)*
Na_2SO_4–NaCl	E	E	628	51.9	Fig. 7109 in *(8)*
K_2SO_4–KCl	E	E	690	66.6	Fig. 1772 in *(9)*
		E	690	66.6	Fig. 3834 in *(7)*
		E	690	73.7	Fig. 7105 in *(8)*
		E	694	73.0	Fig. 7106 in *(8)*
Na_2SO_4–Na_2S	E	E	740	40.0	*(10)*
		E, PSS	745	28.0	*(11)*
K_2SO_4–K_2S	E	E, PSS	610	23.0	*(12)*
Na_2CO_3–Na_2S	E	E	755	34.5	Fig. 6165 in *(13)*
		E, PSS	762	40.0	Fig. 6166 in *(13)*, *(14)*
K_2CO_3–K_2S	E	M	840	55.0	*(15)*
NaCl–Na_2S	E	E	710	22.0	*(16)*
KCl–K_2S	E	n/a [d]	n/a [d]	n/a [d]	

[a] E = eutectic, M = minimum melting, PSS = partial solid solution
[b] E or M temperature
[c] Percent of the second component
[d] Not available (no phase diagram for this system was found in the literature)

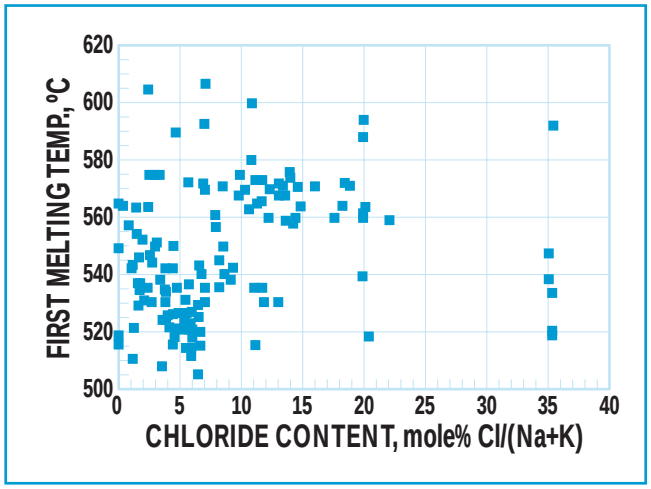
I. Expected types of mixtures and actual results obtained from the literature for binary systems

system, the FMT is the same as the eutectic temperature (the horizontal line in Fig. 1a). The composition of the mixture should therefore have no effect on the FMT, i.e., the mixture begins to melt at the eutectic temperature regardless of its composition. In the minimum-melting system, the FMT varies with composition. As shown in Fig. 1b, the FMT decreases as the composition of the mixture moves toward the minimum melting point (Point M).

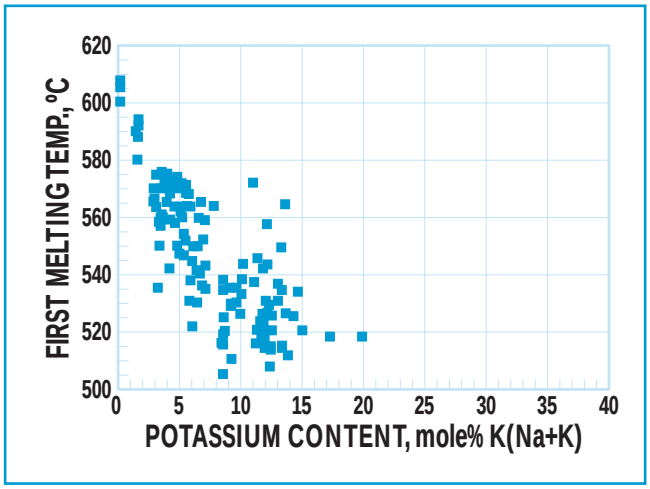
In general, the tendency to form a eutectic or a minimum-melting mixture depends on the ionic size and the valency of elements that constitute the compounds. Ions that have the same charge (e.g., Na^+ and K^+, CO_3^{2-} and SO_4^{2-}) and ions that have a comparable size (e.g., CO_3^{2-} and SO_4^{2-}) are able to mix well, and thus they tend to form solid solutions with each other. Therefore, compounds containing such ions tend to form minimum-melting mixtures. On the other hand, ions that have different charges (e.g., Cl^- and CO_3^{2-}) and/or sizes (e.g., Cl^- and SO_4^{2-}) tend not to form solid solutions. Compounds containing such incompatible ions tend to form eutectic mixtures.

In recovery boilers, the main ions contained in deposits and smelt are Na^+, K^+, CO_3^{2-}, SO_4^{2-}, S^{2-}, and Cl^-. Since Na^+ and K^+ have the same charge (+1), sodium compounds tend to form solid solutions with their potassium counterparts. Examples of this are Na_2SO_4–K_2SO_4, Na_2CO_3–K_2CO_3, and KCl–NaCl, which are all minimum-melting systems. Similarly, since SO_4^{2-} and CO_3^{2-} have the same charge (–2), sulfate and carbonate tend to form solid solutions with each other, as exemplified by Na_2SO_4–Na_2CO_3 and K_2SO_4–K_2CO_3 systems.

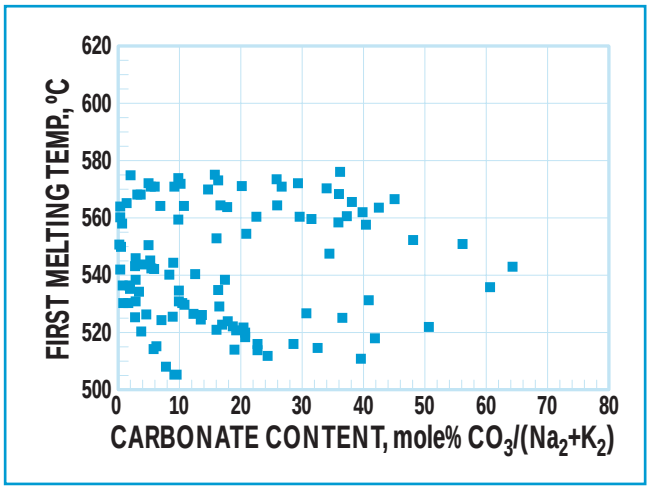
Sulfide has a somewhat different behavior. Although it is divalent (–2) like carbonate and sulfate, sulfide has the smallest ionic size (i.e., $SO_4^{2-} > CO_3^{2-} > S^{2-}$) because of the absence



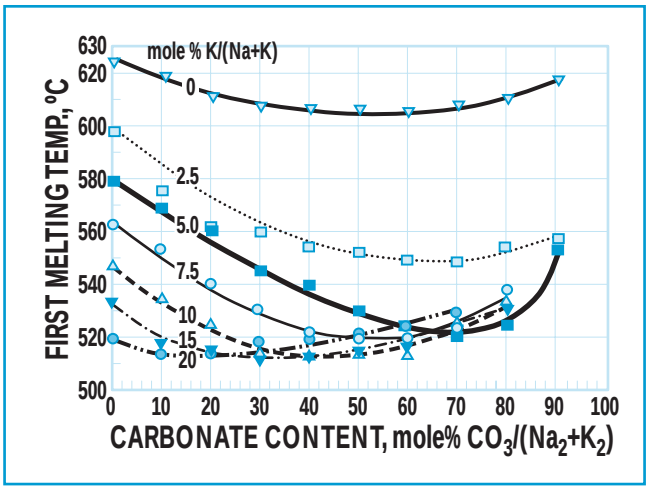
3. Effect of chloride on the FMT of boiler deposits and precipitator dusts



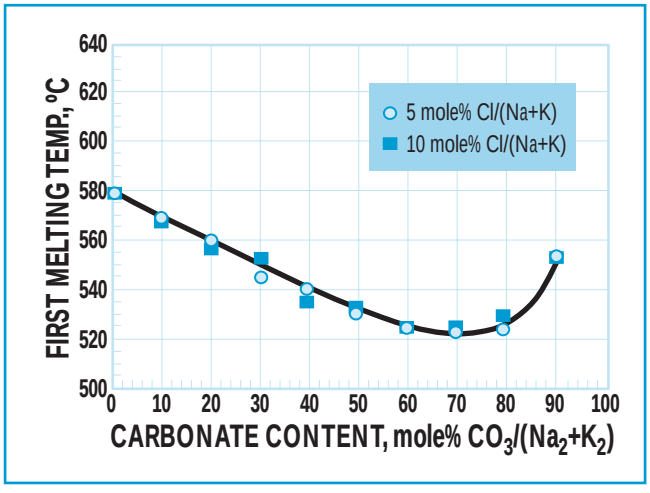
4. Effect of potassium on the FMT of boiler deposits and precipitator dusts



5. Effect of carbonate on the FMT of boiler deposits and precipitator dusts



6. Effect of carbonate on the FMT of synthetic deposits at different potassium levels [chloride content = 5 mole% Cl/(Na+K)]



7. Effect of carbonate on the FMT of synthetic deposits at two chloride levels [potassium content = 5% mole% K/(Na+K)]

of oxygen in its structure. Thus sulfide tends to form eutectics with sulfate and carbonate, but it can also form partial solid solutions with carbonate. Chloride is not only monovalent, but it is also much smaller than sulfate, carbonate, and sulfide. Therefore, chloride would form only eutectics with carbonate, sulfate, and sulfide.

For tertiary systems such as Na_2SO_4–Na_2CO_3–NaCl, the situation is more complicated. Nonetheless, this type of system can still be predicted by grouping Na_2SO_4 and Na_2CO_3 together as a solid solution and considering them as one compound, $Na_2(SO_4,CO_3)$. Thus the tertiary system becomes a pseudobinary system, $Na_2(SO_4,CO_3)$–NaCl, that should be a eutectic system, according to the above analysis. This is also consistent with the published Na_2SO_4–Na_2CO_3–NaCl phase diagram *(6)*.

Table I lists the expected melting types for all possible binary systems involving Na^+, K^+, CO_3^{2-}, SO_4^{2-}, S^{2-}, and

Cl^- based on the above theoretical analysis, along with actual results shown in phase diagrams reported in the literature. The agreement between the expected types and actual results is impressive.

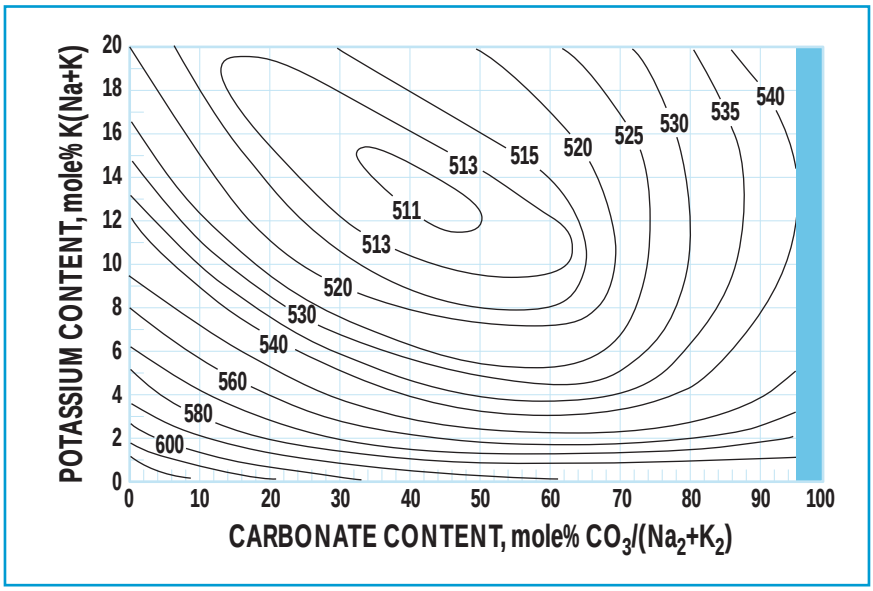
Sodium (Na^+) and sulfate (SO_4^{2-}) are, respectively, the major cation and anion in boiler deposits and precipitator dusts. The theoretical analysis suggests that—of the minor components—only potassium and carbonate are likely to have an effect on FMT because of their tendencies to form solid solutions with sodium and sulfate. Because deposits and precipitator dusts usually contain some chloride, an increase in chloride content above some minimum level would have no additional effect on the FMT of the deposit, since chloride forms eutectic mixtures with other anions. Similarly, sulfide would have little effect on the FMT because of its tendency to form eutectics, particularly with sulfate.

FMT VS. COMPOSITION OF ACTUAL DEPOSITS

The FMT and composition of over 150 actual deposits and precipitator dust samples were examined. About half of these samples were fully analyzed for Na, K, Cl, CO_3, and SO_4; for the other half, only a partial analysis was available. From the data, the chloride, potassium, and carbonate contents were estimated (where applicable) and expressed, respectively, as mole% Cl/(Na+K), mole% K/(Na+K), and mole% $CO_3/(Na_2+K_2)$. These values are plotted against the FMT in **Figs. 3–5**, respectively. Note that because of the partial analysis, the number of data points in these figures does not add up to a total of 150.

No correlation was observed between the Cl content and FMT (Fig. 3). This is not surprising if the above explanation is considered. Because chloride forms a eutectic mixture with both carbonate and sulfate, the FMT of the mixtures are independent of the Cl content as long as the system contains some Cl. Potassium, on the other hand, shows a definite effect (Fig. 4). It markedly lowers the FMT of the deposits, from 610°C at zero mole% to about 520°C at 8 mole% K/(Na+K). These results are consistent with the previous explanation.

Although no clear correlation between carbonate and FMT was observed (Fig. 5), it is difficult to draw definite conclusions with respect to the effects of carbonate on FMT. This is not because the data were extracted from different sources but, rather, because of the large data scattering caused by interference from the effect of potassium. In an effort to isolate the effect of individual compounds, a systematic study was carried out using synthetic deposits.



8. Contour map (mole-percent units) showing combined effects of carbonate and potassium on the FMT of synthetic deposits [chloride content = 5 mole% Cl/(Na+K)]

FMT VS. COMPOSITION OF SYNTHETIC DEPOSITS

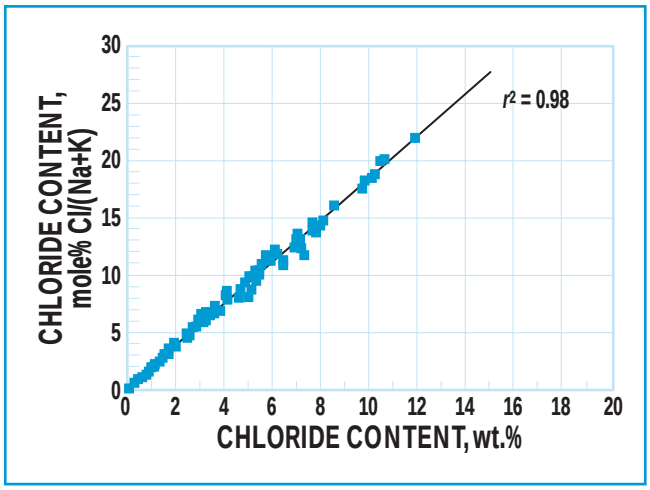
Synthetic deposits of desired compositions were prepared by mixing pure chemicals, melting the mixture at 800°C to 900°C for 20 min, cooling the melt, and then grinding the frozen melt. The FMT was determined by differential thermal analysis (DTA).

Figure 6 shows the effect of carbonate on the FMT of deposits containing 5 mole% Cl/(Na+K) and different K contents. The results show that, for samples with K contents below 7.5 mole% K/(Na+K), increasing the carbonate content, up to about 50 mole% $CO_3/(Na_2+K_2)$, decreases the FMT. A further increase in carbonate results in a higher FMT, which is consistent with the minimum-melting behavior of a carbonate–sulfate mixture. The results also show that the effect of carbonate is significant only when the K content is in the range of 2.5–7.5 mole% K/(Na+K). At high potassium levels, >15 mole% K/(Na+K), the effect of carbonate becomes minimal.

Figure 7 shows the effect of carbonate on the FMT of deposits containing 5 mole% K/(Na+K) for two different chloride levels: 5 and 10 mole% Cl/(Na+K). No significant difference was found, confirming the insignificant effect of chloride on the FMT, at least for these two concentrations.

COMBINED EFFECTS OF CARBONATE AND POTASSIUM

Based on the data obtained in this study (Fig. 6) and the pertinent phase diagrams involving Na_2SO_4,



9. Correlation between wt.% Cl and mole% Cl /(Na+K) for deposits and precipitator dusts

K_2SO_4, Na_2CO_3, K_2CO_3, NaCl, and KCl (Table I), a FMT contour map was constructed to show the combined effect of potassium and carbonate, as seen in **Fig. 8**. From this map, the FMT of any deposit containing at least 5 mole% Cl/(Na+K) can be determined if its K, Na, and CO_3 contents are known. For example, a deposit with 5 mole% K/(Na+K) and 30 mole% $CO_3/(Na_2+K_2)$ would have a FMT of about 540°C. The FMT can be as low as 511°C for potassium contents between 11 and 15 mole% K/(K+Na) with carbonate contents between 31 and 50 mole% $CO_3/(Na_2+K_2)$.

UNIT CONVERSION

Chloride, potassium, and carbonate contents in the deposit are expressed respectively as mole% Cl/(Na+K), mole% K/(Na+K), and mole% $CO_3/(Na_2+K_2)$. Although these mole-percent units (which can include mole% $SO_4/(Na_2+K_2)$ for the sulfate content) are somewhat cumbersome, they are more useful than weight percent (or other weight-based units) for ionic mixtures such as recovery boiler deposits. The use of molar percent units makes it possible not only to compare the contents (particularly Cl and K) in deposits to those in precipitator dust, smelt, black liquor, green liquor, and white liquor within a pulp mill, but also to compare data obtained from various mills. Furthermore, it is possible to estimate the degrees of chloride and potassium enrichment in a boiler by comparing the mole% Cl/(Na+K) and mole% K/(Na+K) for the precipitator dust to those of smelt or as-fired black liquor. With weight-percent units, the degree of enrichment cannot be estimated, nor can comparisons of chloride and potassium contents between deposits, smelt, and precipitator dust be made.

Nonetheless, weight-percent units (i.e., Cl wt.% for chloride, K wt.% for potassium, CO_3 wt.% for carbonate, and SO_4 wt.% for sulfate) are often used in many mills because they are easy to obtain. In order to obtain the chloride content in the precipitator dust, the weight-percent unit needs only the analytical value of Cl, whereas the mole-percent unit requires the values of Cl, K, and Na. It is worthwhile, therefore, to devise a means of converting weight-percent units to mole-percent units without performing detailed chemical analysis.

Theoretically, no precise formulas for such unit conversions can be derived. However, using the chemical compositions of a large number of deposits and precipitator dusts, it is possible to devise empirical correlations between weight-percent units and mole-percent units. An example of this for chloride is shown in **Fig. 9**, which plots the wt.% Cl value against the mole% Cl/(Na+K) value of the samples. The relationship is linear, with a regression coefficient (r^2) of 0.98 and a line slope of 1.88. This means that for deposits or precipitator dusts, 1 wt.% Cl is equivalent to about 1.9 mole% Cl/(Na+K). Similar plots were also obtained for potassium, carbonate, and sulfate. From these plots, the weight-percent units can be converted to mole-percent units using the following empirical correlations:

Chloride:

$$1 \text{ wt.\% Cl} = 1.9 \text{ mole\% Cl/(Na+K)} = 1.9 \text{ mole\% } Cl_2/(Na_2+K_2)$$

Potassium:

$$1 \text{ wt.\% K} = 1.8 \text{ mole\% K/(Na+K)} = 1.8 \text{ mole\% } K_2/(Na_2+K_2)$$

Carbonate:

$$1 \text{ wt.\% } CO_3 = 2.2 \text{ mole\% } CO_3/(Na_2+K_2)$$

Sulfate:

$$1 \text{ wt.\% } SO_4 = 1.5 \text{ mole\% } SO_4/(Na_2+K_2)$$

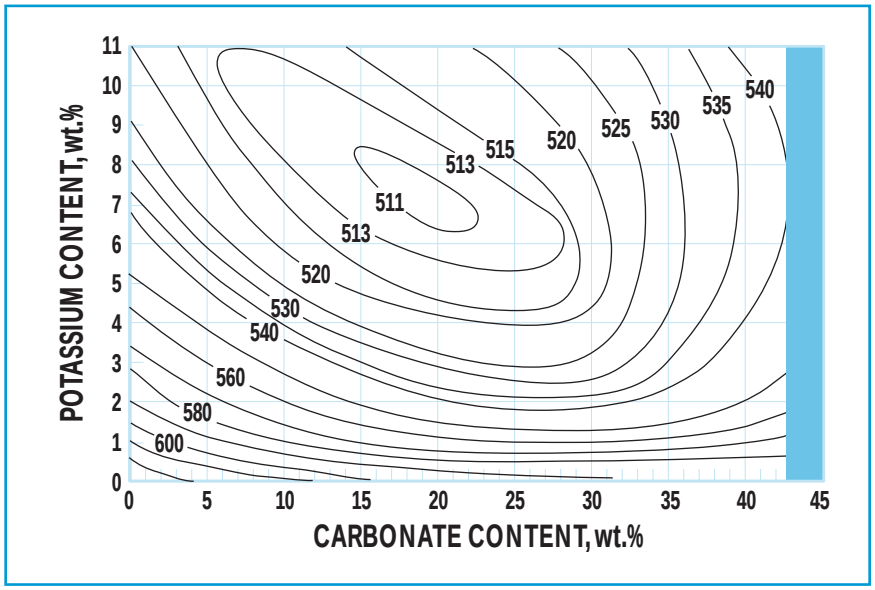
As a general rule, the mole-percent units for chloride, potassium, and carbonate can be approximately obtained by multiplying their respective weight-percent units by 2. Thus 1 wt.% Cl is equivalent to about 2 mole% Cl/(Na+K), 1 wt.% K to about 2 mole% K/(Na+K), and 1 wt.% CO_3 to about 2 mole% $CO_3/(Na_2+K_2)$.

Using empirical conversion formulas for potassium and carbonate, the contour map shown in Fig. 8 can be modified for estimating the FMT of deposits based on wt.% K and wt.% CO_3, as seen in **Fig. 10**.

IMPLICATIONS

This work clearly suggests that of all the minor components in the deposit, potassium compounds play the most significant role in lowering the FMT, followed by carbonate, sulfide, and chloride.

The potassium content in deposits is typically about 4–6 mole% K/(Na+K) for softwood mills and 10–15 mole% K/(Na+K) for hardwood mills *(17)*. The carbonate content, on the other hand, typically is within the range 10–50 mole% $CO_3/(Na_2+K_2)$, depending on the sulfidity of the liquor, the amount of carryover, and bed temperature. Thus increasing the carbonate content 10–50 mole% will lower the FMT from 570°C to 523°C for softwood mills, and from 545°C to 511°C for hardwood mills. This implies that for overloaded boilers and/or boilers operating at high bed temperatures at hardwood mills, the combination of high carbonate and high potassium contents can result in a FMT as low as 511°C. For such boilers, superheater tubes are susceptible to high-temperature corrosion from molten deposits if the boilers are operated at final superheated steam temperatures higher than 480°C.



10. Contour map (weight-percent units) showing combined effects of carbonate and potassium on the FMT of synthetic deposits (chloride content = 2.6 wt.%)

SUMMARY

The first melting temperature (FMT) of fireside deposits—the temperature at which a deposit begins to melt—in kraft recovery boilers is an important parameter for controlling superheater corrosion. This report presents the results of a systematic study that was performed to examine the effect of deposit composition on the FMT. The results show that:

- Of the minor components in the deposit, potassium has the greatest impact in lowering the FMT. Carbonate can also lower the FMT, but the effect is much smaller than potassium. Sulfide has an even smaller effect.
- Deposits usually contain some chloride, so additional chloride has a negligible effect on the FMT.
- The difference in the effect of individual components on the FMT can be explained using phase-equilibrium principles.
- For overloaded boilers and/or boilers operating at high bed temperatures at hardwood mills, the combination of high carbonate and high potassium contents can result in a FMT as low as 511°C. For such boilers, superheater tubes are susceptible to high-temperature corrosion when the boilers are operated at a final superheated steam temperature higher than 480°C.
- A temperature contour map (constructed from data obtained in this study) can be used to determine the FMT of a typical deposit as a function of potassium and carbonate contents.
- Empirical formulas were developed to convert weight-percent units to mole-percent units. TJ

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