EFFECT OF HIGH SULPHATE CONTENT ON FLUIDITY OF RECOVERY BOILER MOLTEN SMELT

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ABSTRACT

A systematic study was conducted to examine the effect of high sulfate content on the freezing tempeture of molten smelt and how this may contribute to the formation of viscous jellyroll smelt in recovery boilers. The results show that even for recovery boilers with a smelt reduction as low as 70%, the sulfate content in smelt has no or little effect on smelt freezing temperature, and hence, on molten smelt fluidity. The perceived adverse effect of high sulfate content on smelt fluidity and on jellyroll smelt formation comes from the high sulfate content in deposits that have fallen from the upper furnace. Fallen deposits may or may not form jellyroll smelt depending on whether or not they can melt and be well-mixed with molten smelt by the time they reach the smelt spouts. It is not the high sulfate content in smelt resulting from the low smelt reduction efficiency that makes molten smelt viscous and forms jellyroll smelt, but rather, it is the incomplete melting of fallen deposits that results in jellyroll smelt formation.

KEYWORDS

Recovery Boiler, Reduction Efficiency, Jellyroll Smelt, Fluidity, Freezing Temperature, Sulfate.

INTRODUCTION

In recovery boiler operation, molten smelt flows out of the boiler smoothly through several smelt spouts. It is shattered by steam jets into small droplets before entering a dissolving tank underneath the boiler where it is dissolved in water to form green liquor. This highly fluid molten smelt stream can occasionally become sluggish, forming a viscous blob that either moves slowly or stops moving on the spout trough as shown in **Figure 1**. Such viscous smelt is known as "*jellyroll*" smelt [1].

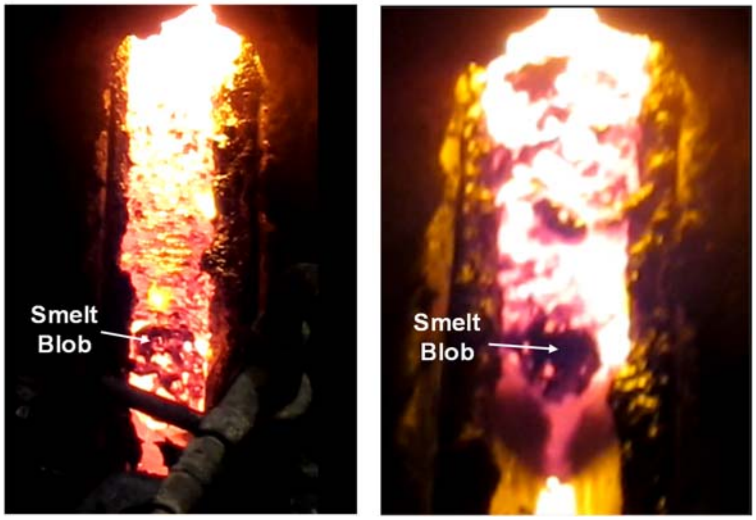

Figure 1. *Jellyroll smelt blobs on spout troughs in two recovery boilers* [1].

Jellyroll smelt can completely block the smelt flow, allowing a large pool of molten smelt to accumulate behind the spout opening. This can make spout cleaning a hazardous task for recovery boiler operators. As the molten smelt pool behind the blockage becomes larger and deeper, it eventually pushes the smelt blob off the trough, resulting in a massive amount of molten smelt pouring into the dissolving tank at once. Such heavy smelt run-offs [2] can be violent, shake buildings/structures nearby, and in severe cases, lead to smelt-water explosions that can cause equipment damage and even personnel fatality [3,4].

It has been shown that jellyroll smelt is likely formed by three main mechanisms: 1) the partial freezing of molten smelt caused by a temperature drop in the lower furnace, 2) the inclusion of deposits that have fallen from the upper furnace (mostly the superheater region and the furnace roof), and 3) the inclusion of a large amount of unburned char [1]. These formation mechanisms result in a sudden increase in the molten smelt viscosity that hinders the molten smelt flow.

Smelt consists mainly of sodium (Na), carbonate (CO_3) and sulfide (S), with small amounts of sulfate (SO_4), potassium (K), chloride (Cl) and inerts. The composition is determined by the composition of the black liquor burned in the boiler and the boiler reduction efficiency. Of the minor components, the SO_4 content is of particular interest in this study because it is the largest component and varies greatly from <1 wt% for boilers with 98% reduction efficiency to as high as 10 wt% for boilers with 70% reduction efficiency. These low and high SO_4 contents increase proportionally with increasing liquor sulfidity or sulfur content in the black liquor.

Deposits in the superheater region of the recovery boiler typically contain more than 40 wt% SO_4 and less than 1 wt% S [5]. This high SO_4 content and low S content in superheater deposits compared to those in smelt are due to the combination of the oxidizing atmosphere in the upper furnace that oxidizes the sulfide (S^{2-}) to sulfate (SO_4^{-2}) and the sulfation reactions that convert the CO_3 (and to some extent the Cl) into SO_4 as the deposits age on the tubes with time. The inclusion of fallen deposits can therefore drastically increase the SO_4 content of the smelt, at least locally. The amount of sulfate in smelt/deposit mixtures depends on the size of the deposits and the degree of mixing between the molten smelt and the deposits in the char bed.

In this paper, we will first review the correlation between smelt freezing temperature and viscosity, then examine the effect of SO_4 content on the freezing temperature and viscosity of molten smelt, and the role of SO_4-rich fallen deposits in jellyroll smelt formation.

SMELT FREEZING VERSUS VISCOSITY

Recovery boiler smelt has a freezing temperature between 740 and 780°C (1360 and 1440°F). Under normal boiler operation, since the smelt temperature typically varies between 820 and 830°C (1510 and 1630°F), the smelt must be completely molten. During boiler upsets, however, the lower furnace temperature may drop below the smelt freezing point, causing smelt to freeze/solidify. Freezing drastically increases the molten smelt viscosity, making the smelt less fluid.

Figure 2 shows the change in viscosity of five smelt samples from four kraft mills as they were cooled slowly from 960°C (1760°F) in a laboratory setting [6]. In all cases, the viscosity increased only slightly from 2 to 5 cP (centipoise) as the smelt temperature decreased to about 760 – 780°C (1400 – 1440°F), and then increased drastically as the temperature decreased further. The abrupt increase in viscosity of each smelt sample occurred at its respective freezing temperature. These results imply that as long as it is completely molten, smelt has a very low viscosity, roughly the same as that of milk at room temperature (3 cP), but will become much more viscous as it starts to freeze.

In general, the viscosity of a liquid increases logarithmically with decreasing temperature. It also increases drastically if the liquid contains or is mixed with fine solid particles. Coal-water slurry, clay slip, concrete mix, ice flurry, etc. are all good examples of solid/liquid mixtures.

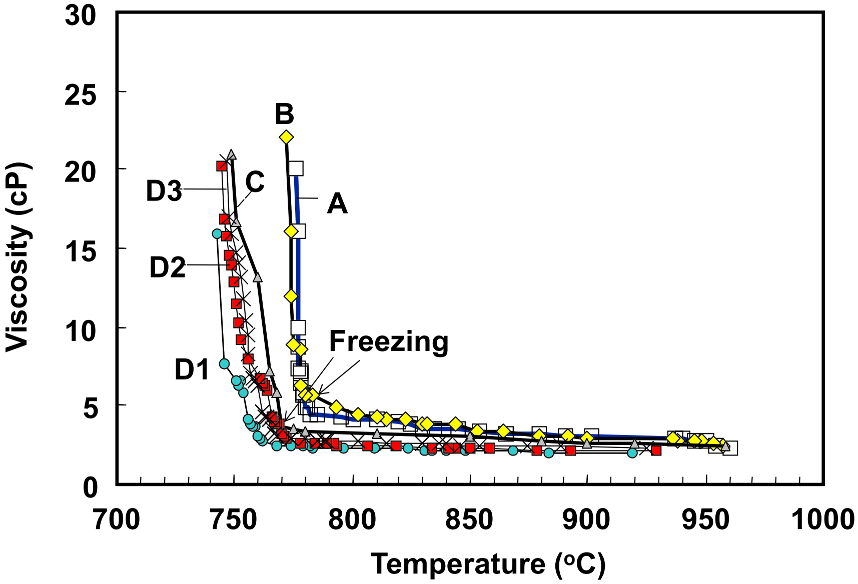

Figure 2. *Viscosity of smelt samples from four kraft mills [6]. Each smelt sample has a slightly different composition and thus a different break point (first freezing temperature).*

As mentioned above, kraft smelt is a mixture of sodium salts (mainly Na_2CO_3, Na_2S, Na_2SO_4 and NaCl) and their potassium counterparts (K_2CO_3, K_2S, K_2SO_4 and KCl). As the molten smelt cools and reaches its first freezing temperature[1] (or complete melting temperature), one of the salt components starts precipitating out, forming fine solid particles in the melt. As the smelt temperature decreases further, other components also precipitate, forming more solid particles. The more the solid particles are present in the molten smelt, the more viscous it becomes. As the temperature is cooled below the complete freezing temperature[2] (or first melting temperature) of the salt mixture, the whole mass is 100% solid. The abrupt increase in molten smelt viscosity shown in **Figure 2** is likely caused by the sudden appearance of a solid phase in the melt as it cools below its first freezing temperature. For simplicity, the first freezing temperature in this paper is referred to simply as the "freezing temperature".

EFFECTS OF SMELT COMPOSITION ON FREEZING TEMPERATURE

Since freezing can cause a sudden increase in molten smelt viscosity, it is important to understand how smelt freezing temperature is affected by composition.

Effects of Sulfidity, Potassium and Chloride

Figures 3 and **4** respectively show the freezing temperature of molten smelt as a function of smelt sulfidity and chloride content for softwood mills with a typical potassium content of 5 mole% K/(Na+K), and for hardwood mills with a typical potassium content of 10 mole% K/(Na+K) [1]. The freezing temperatures were calculated using FactSage, a commercially available thermodynamic program, assuming a 100% smelt reduction efficiency, i.e. no sulfate (SO_4) present in the smelt.

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[1] First freezing temperature of a molten salt mixture (melt) is the temperature at which a solid phase begins to appear in the melt as it cools. This temperature is the same as (or close to) the complete melting temperature of the same salt mixture as it is heated up.

[2] Complete freezing temperature of a molten salt mixture (melt) is the temperature at which the melt is completely solidified. Due to the supercooling effect, however, this temperature can be either the same as or somewhat lower than the first melting temperature of the same salt mixture as it is heated up.

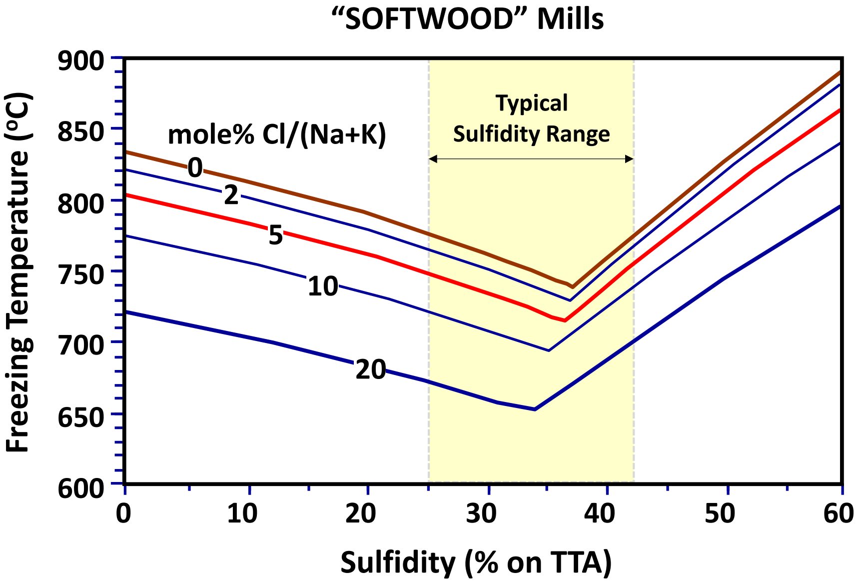

Figure 3. *Effect of sulfidity on freezing temperature of molten smelt at different Cl contents for typical softwood kraft mills with 5 mole% K/(Na+K) and 100% reduction efficiency.*

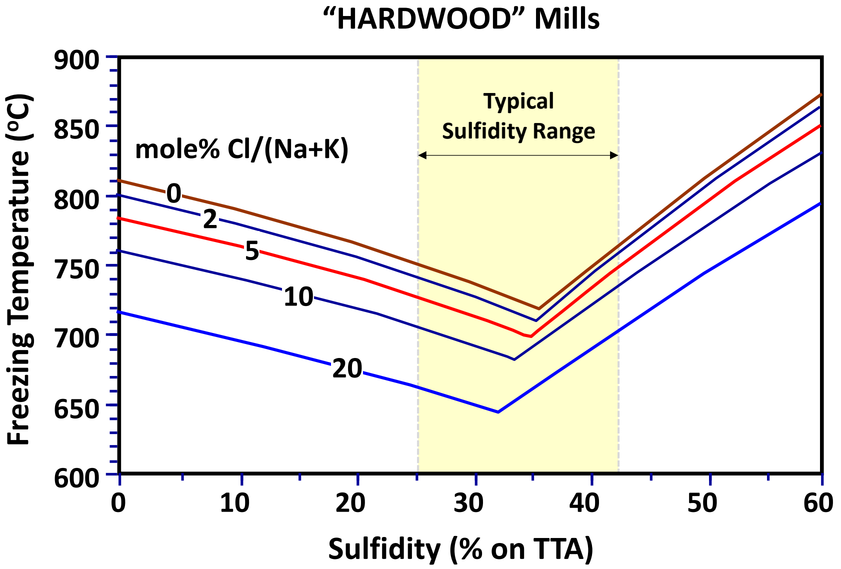

Figure 4. *Effect of sulfidity on freezing temperature of molten smelt at different Cl contents for typical hardwood kraft mills with 10 mole% K/(Na+K) and 100% reduction efficiency.*

In both cases, the freezing temperature decreases as the sulfidity increases up to 32 – 36% on TTA (total active alkali), depending on the Cl content. Beyond this point, which is essentially the eutectic of the system, the trend reverses; the freezing temperature increases with an increase in sulfidity. At a given sulfidity and chloride content, softwood smelt (**Figure 3**), due to its lower potassium content, has a higher freezing temperature than hardwood smelt (**Figure 4**). At a given liquor sulfidity and potassium content, on the other hand, increasing the chloride content from 2 to 5 mole% Cl/(Na+K) in smelt (equivalent to 0.6 to 1.5 wt% Cl in black liquor dry solids) would lower the smelt freezing temperature by 18 degrees C (32 degrees F).

Effect of Sulfate Content

The freezing temperatures shown in **Figures 3** and **4** are for smelt with 100% reduction efficiency (i.e., 0% SO_4 or no sulfate). Since the sulfate content in smelt can vary from as little as <1 wt% for boilers with 98% smelt reduction efficiency to as high as 10 wt% for boilers with 70% smelt reduction efficiency, it is worthwhile to examine how this wide variation in SO_4 content may affect the smelt freezing temperature and viscosity.

The effect of sulfate content on the smelt freezing (or complete melting) temperature can be evaluated with the aid of the Na_2CO_3-Na_2S-Na_2SO_4 ternary phase diagram shown in **Figure 5**. The three apexes of the triangle are the freezing temperatures of Na_2CO_3 (850^{o}C), Na_2S (1190^{o}C) and Na_2SO_4 (890^{o}C). The sides of the triangle correspond to the three binary systems: the Na_2CO_3-Na_2S eutectic system, the Na_2S-Na_2SO_4 eutectic system, and the Na_2CO_3-Na_2SO_4 minimum melting system. The curves within the triangle are isotherms in degrees Celsius. On each isotherm curve, mixtures of these three components have exactly the same freezing temperature.

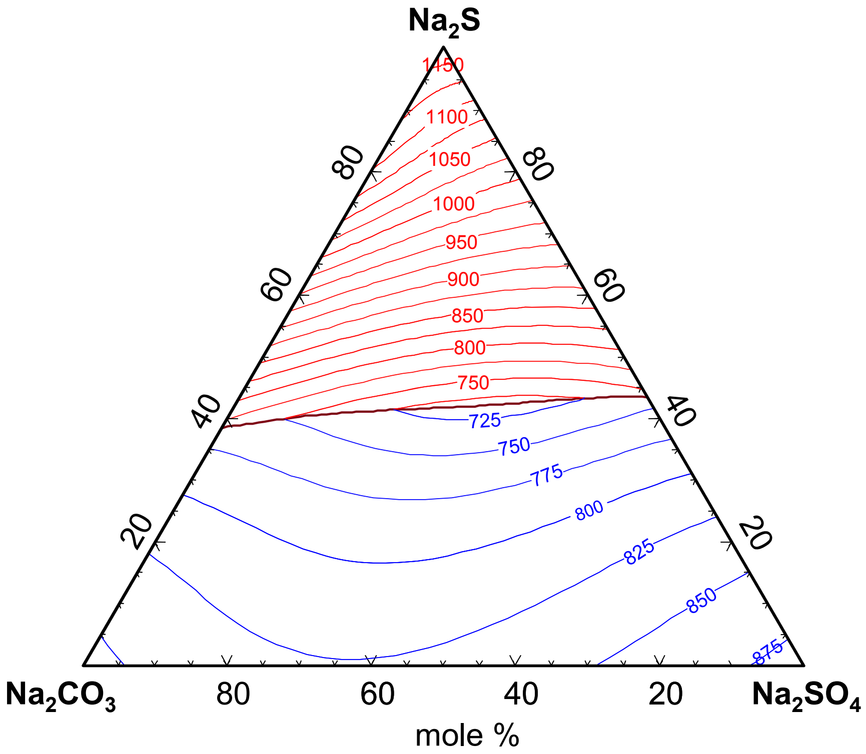

Figure 5. The Na_2CO_3-Na_2S-Na_2SO_4 Phase Diagram [7].

The phase diagram can be made more user-friendly particularly for pulp mill engineers by adding two sets of lines as shown in **Figure 6**. The first set consists of **iso-sulfidity** (orange) lines that connect a point on the Na_2CO_3-Na_2S side of the triangle to the Na_2SO_4 apex. Mixtures of Na_2CO_3, Na_2S and Na_2SO_4 along each orange line have the same sulfidity. The second set consists of **iso-reduction efficiency** **(green)** lines that connect a point on the Na_2S-Na_2SO_4 side of the triangle to the Na_2CO_3 apex. On each green line, the reduction efficiency is the same for all mixtures.

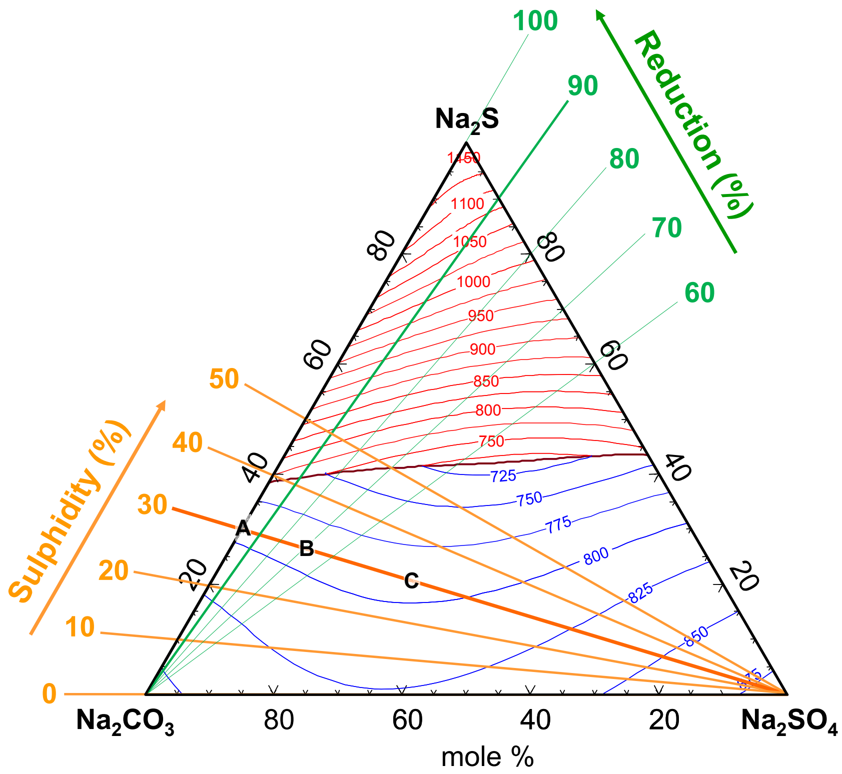

Figure 6. Iso-Sulfidity and Iso-Reduction lines in the Na_2CO_3-Na_2S-Na_2SO_4 Phase Diagram.

For example, on the 30% iso-sulfidity line, all mixtures have the same sulfidity at 30% on TTA but with a different reduction efficiency. The mixture at Point A has a sulfidity of 30% with 100% reduction efficiency (or 0 mol% Na_2SO_4). The mixture at Point B also has a sulfidity of 30%, but with 70% reduction efficiency (or 30 mol% Na_2SO_4). Thus, moving from Point A to Point B will lower the reduction efficiency from 100% to 70% or increase the sulfate content from 0 to 30 mol%.

Using the nearest isotherms 775^{o}C and 800^{o}C (**blue curves**) on both sides of the AB line, the freezing temperatures of the mixtures at Point A and Point B can be estimated to be 793^{o}C and 790^{o}C, respectively. This suggests that for a melt with 30% sulfidity, lowering the reduction efficiency from 100% to 70% (or increasing the sulfate content from 0 to 30 mol %) will lower the freezing temperature by only 3 degrees C (5.4 degrees F), which is insignificant.

It is important to note that up to Point C (the intersection between the 30% iso-sulfidity line and the 40% reduction efficiency line), the 30% iso-sulfidity line is almost parallel to both the 775^{o}C and 800^{o}C isotherms. This means that there is little change in freezing temperature with decreasing reduction efficiency or increasing SO_4 content. From Point C to the Na_2SO_4 apex, however, the 30% iso-sulfidity line starts to deviate toward a higher freezing temperature. Such an increase in freezing temperature at a sulfate content greater than 60 mol% is plausible because the melt composition is in the SO_4-rich region of the phase diagram.

Similarly, the 25% and 40% iso-sulfidity lines in **Figure 6** are almost parallel to 775^{o}C and 800^{o}C isotherms up to 60% reduction efficiency. This implies that within the typical kraft mill sulfidity range of 25 - 42% on TTA, the smelt freezing temperature does not change much up to 60% reduction efficiency or 40 mol% SO_4 content.

Since kraft smelt also contains some chloride (Cl) and potassium (K), the freezing temperature is expected to be lower than that of the pure system shown in **Figure 5**. By adding appropriate amounts of NaCl, KCl, K_2S and K_2SO_4 to the above Na_2CO_3-Na_2S-Na_2SO_4 tertiary system, the freezing temperature of salt mixtures containing various amounts of Cl and K can be estimated using FactSage. The results are shown in **Figure 7** for a typical kraft smelt with 30% sulfidity on TTA. In all cases, lowering the smelt reduction efficiency from 100 to 70% (or increasing the sulfate content from 0 to 30%) results in only a slight decrease in freezing temperature.

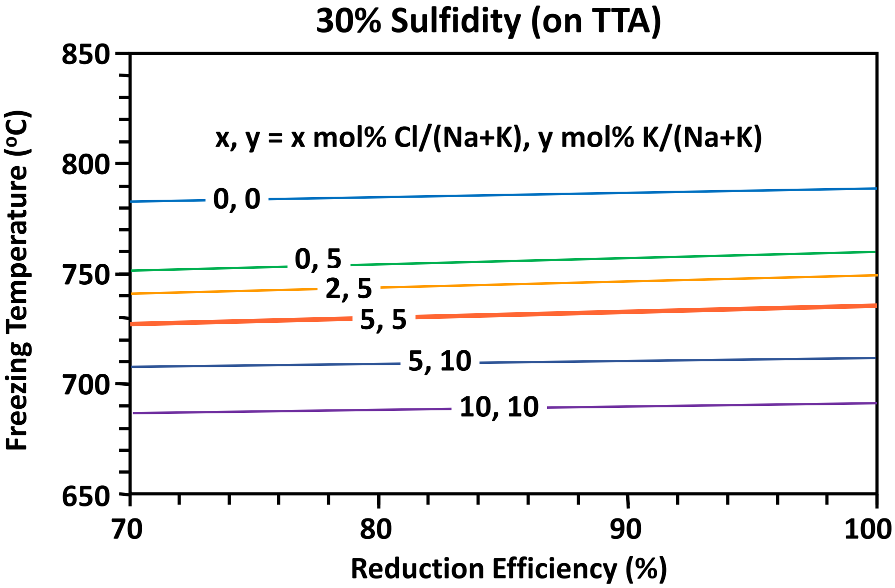

Figure 7. Effect of reduction efficiency on the freezing temperature of kraft smelt with 30% sulfidity and various Cl and K contents. Note that potassium contents of 5 and 10 mol% K/(Na+K) are typical for softwood and hardwood liquors respectively.

Most recovery boilers operate at 90 – 95% reduction efficiency. Even during boiler upset conditions, the reduction efficiency rarely drops below 80% (20 mol% sulfate) causing the freezing temperature to decrease, at the most, 3 degrees C. This again implies that the sulfate content in molten smelt has no significant effect on smelt freezing temperature, and by extension, on smelt viscosity as long as the smelt is completely molten.

Effect of Fallen Deposits Under Steady State Conditions

Depending on the location in the boiler and the position on the tube surface, superheater deposits contain 35 – 75 mol% Na_2SO_4, 25 – 70 mol% Na_2CO_3, some Cl and K, and little or no sulfide [8]. Such a high sulfate content is expected to affect the freezing temperature of smelt. Figure 8 conceptually shows the change in composition of a fallen deposit after it has landed on the char bed and mixed with molten smelt, with the aid of the Na_2CO_3-Na_2S-Na_2SO_4 phase diagram.

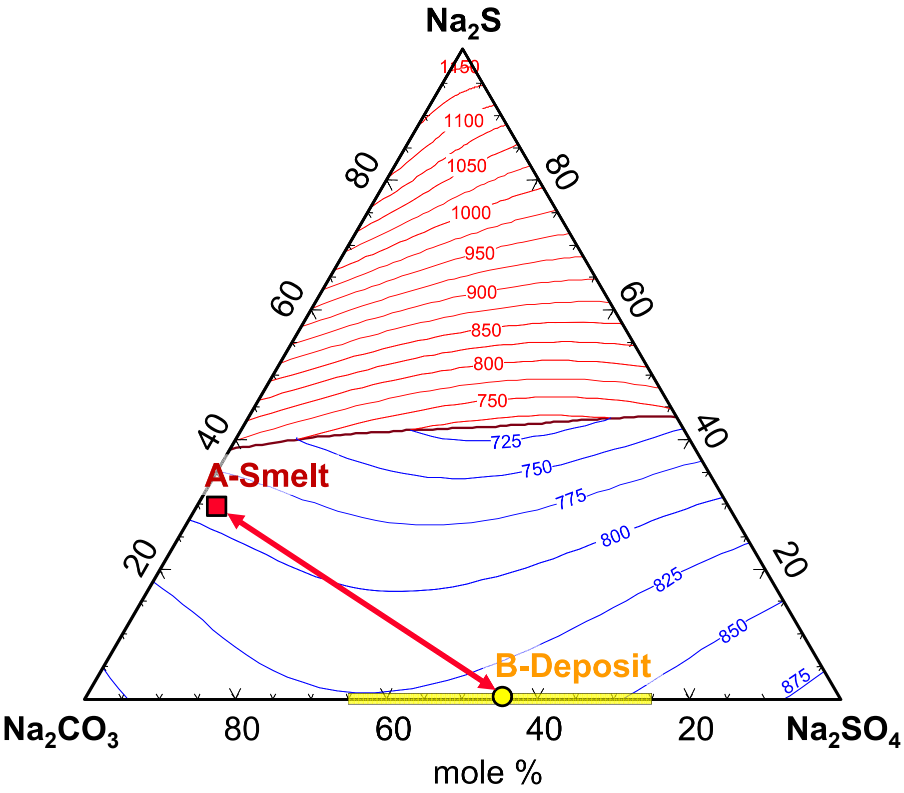

Figure 8. Change in freezing temperatures of smelt/fallen deposit mixtures in the Na_2CO_3-Na_2S-Na_2SO_4 phase diagram.

Points A and B on the diagram respectively represent the composition of a typical smelt with 30% sulfidity and 92% reduction efficiency, and the composition of the fallen deposit described above. As the deposit melts and mixes with the surrounding smelt, its sulfate content decreases as a result of dilution with molten smelt and reduction to sulfide under the strong reducing condition in the char bed. The composition of the smelt/deposit mixture would change along the red line that connects Point A and Point B.

The freezing temperature of the smelt at Point A is about 790°C, whereas the freezing temperature of the deposit at Point B is nearly 850°C. Up to about 40% reduction efficiency (or about 60 mol% sulfate), the red line is more or less parallel to the 800°C isotherm, implying that the freezing temperature of the smelt/deposit mixture is unchanged at 790°C. Beyond that point, the freezing temperature of the mixture increases abruptly from 800°C to 850°C as the composition gets closer to that of the deposit.

Under normal boiler operation, the amount of fallen deposits is typically much smaller than that of smelt. Thus, it is easy for them to melt, disperse, and eventually become part of the smelt. As such, there will be no appreciable change in smelt freezing temperature and viscosity.

Effect of Fallen Deposits Under Transient Conditions

Fallen deposits can have a great impact on smelt temperature, composition, freezing temperature, and hence viscosity, but only right after they land on the char bed and have not had sufficient time to melt and mix well with the surrounding molten smelt pool.

The flue gas temperature in the upper furnace varies from 900°C (1650°F) at the superheater entrance to 600°C (1110°F) at the generating bank inlet, while the tube surface temperature varies between 300 and 500°C (570 and 930°F) depending on location. This means that the deposit temperature, while still on the tube surface, varies between 300 and 700°C (570 and 1290°F). This temperature range is much lower than that of the molten smelt, 820 to 830°C (1510 and 1630°F), as mentioned earlier.

As deposits are removed from the tube surface in the upper furnace by sootblowers, they fall down onto the char bed and mix with molten smelt. **Figure 9** conceptually shows the "fate" of a chunk of colder deposit after it has dropped into the much hotter molten smelt pool [1].

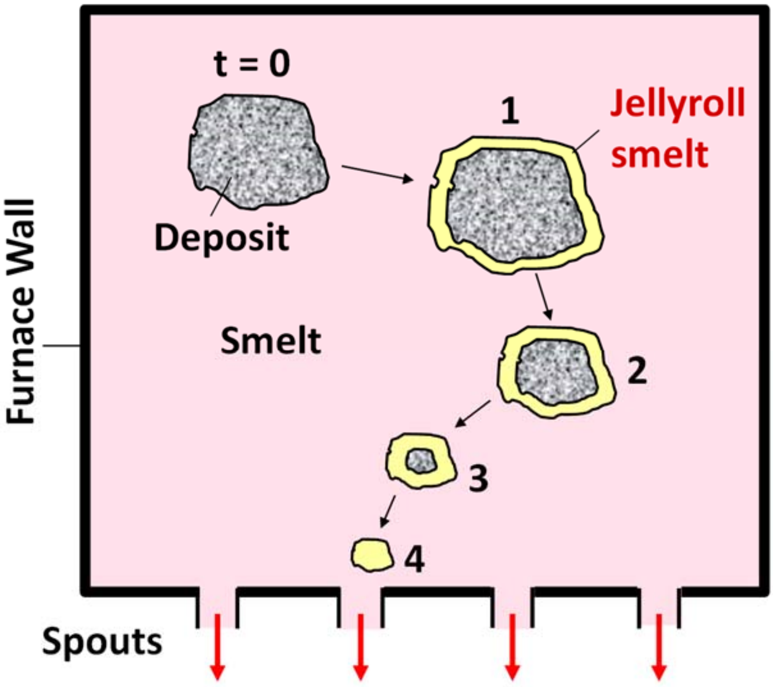

Figure 9. A postulated formation mechanism of jellyroll smelt by a fallen deposit.

At time 0, the deposit is heated up quickly by the surrounding molten smelt, and in the process, it lowers the temperature of the molten smelt with which it is in contact. The heat exchange between the low temperature deposit and the high temperature molten smelt causes the deposit surface to melt and the surrounding molten smelt to freeze. This results in the formation of a partially molten and viscous layer (jellyroll smelt) on the deposit surface, which temporarily increases the deposit size and mass (time 1). As time passes, the surface temperature increases causing the deposit to melt and become smaller and smaller (time 2 and time 3). It eventually becomes a viscous jellyroll smelt blob that partially floats and moves along with the molten smelt (time 4). If such a smelt blob does not melt completely by the time it reaches the smelt spouts, it may block a spout opening or sit on the spout trough, as shown in **Figure 1**.

Whether or not a fallen deposit can melt completely and be well mixed with smelt by the time it reaches a smelt spout depends on its size, composition, temperature, and residence time, as well as the temperature, composition, and the movement of the molten smelt. Small pieces will melt and become part of the molten smelt quickly, while large pieces will take a much longer time to melt and so are more likely to form jellyroll smelt. Furthermore, small pieces will add less sulfate to the surrounding smelt pool compared to large pieces, and hence will not appreciably change the smelt freeing temperature.

The above formation of jellyroll smelt caused by fallen deposits is consistent with mill experience that the problem is more severe during the boiler start-up after a non-waterwash shutdown (thermal shedding events) when more and larger pieces of deposits fall [9], and that the problems are worse for boilers burning low sulfidity black liquor, because the smelt freezing temperature is higher, making it easier for the molten smelt to freeze on the surface of fallen deposits and form viscous jellyroll smelt blobs.

SUMMARY

The sulfate content in molten smelt in recovery boilers is typically small, <1 wt% SO_4, but can be as high as 10 wt% when the smelt reduction efficiency is only 70 wt%. For smelt that is mixed with deposits that have fallen from the superheater region, the sulfate content can be as high as 40 wt% SO_4. This study examines the effect of sulfate content on the freezing tempeture of molten smelt and how the high sulfate content may contribute to the formation of viscous jellyroll smelt in recovery boilers. The results show that:

- Even for recovery boilers operating at a reduction efficiency as low as 70%, the sulfate content in smelt has no or little effect on smelt freezing temperature, and hence, on molten smelt fluidity.
- The perceived adverse effect of high sulfate content on smelt viscosity and on jellyroll smelt formation comes from the high sulfate content in deposits that have fallen from the upper furnace. Fallen deposits may or may not form jellyroll smelt depending on whether or not they can melt and be well mixed with molten smelt by the time they reach the smelt spouts.
- It is not the high sulfate content in smelt resulting from the low smelt reduction efficiency that makes molten smelt viscous and forms jellyroll smelt; but rather it is the incomplete melting of fallen deposits (which happen to contain a large amount of sulfate) that results in jellyroll smelt formation.

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