The sintering tendency of recovery boiler precipitator dust

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ABSTRACT: Fluffy dust and fume deposits on tube surfaces in recovery boilers may sinter and become resistant to sootblowing if they are exposed to high-temperature flue gases. The sintering tendencies of precipitator dusts from numerous kraft mills were examined with a novel technique and were ranked according to an index that relates closely to the dust sintered strength. The results show that chloride and potassium contents had the most significant effects on dust sintering, while highly sulfated dusts did not sinter appreciably below 600°C. The sintering tendency was strongly related to the first melting temperature and uncompacted bulk density of the dust. Black liquor firing load, solids content, and sulfidity also had an effect on dust sintering tendencies.

Application: Understanding the factors that cause fireside deposits to sinter and become resistant to sootblowing can help boiler operators to devise better strategies for minimizing fouling and plugging problems.

Sodium salt deposits sometimes block the gas passages in recovery boilers. These deposits reduce the heat transfer efficiency and the overall burning capacity of the black liquor. Considerable progress has been made toward eliminating superheater and economizer deposit problems during the past two decades. However, fine, sub-micron particles of alkali metal salt (fume or dust) continue to foul and block the gas passages of boiler banks.

These fume deposits are initially soft and are easily removed by sootblowing. However, they harden with time, sometimes rapidly, and they can become strong enough that sootblowing is not effective in removing them [1]. High-temperature sintering of fluffy dust and fume deposits in recovery boilers is the main mechanism by which these fireside deposits become hard and resistant to sootblowing.

It is important to know the sintering tendency of the fume particles that form these deposits. Deposits formed from fume particles begin to sinter and harden at about 300°C, and the rate of sintering increases rapidly with temperature. There is wide variation in both the sintering behavior and the composition of dust samples from different recovery boilers. The rates at which recovery boiler deposits sinter and harden are controlled by a combination of dust composition, particle packing density, and temperature. The time frame for nearly complete densification at a deposit temperature of 500°C (typically in the front half of the boiler bank) is from 15–20 min to more than an hour.

The composition of fume particles changes as they move through the upper furnace and superheater regions. These fine particles react with sulfur oxide (SO$_2$/SO$_3$) and oxygen in the flue gas, converting the carbonate and chloride within the particles to sulfate. Beyond the superheater region, however, the composition changes very little, and the composition of the fume that deposits on boiler bank tubes is essentially the same as the deposit sample was determined by heating the sample at a fixed temperature and measuring the change in sample dimension, specific surface area, or microstructure. Since this standard method is time-consuming, relatively few samples have been examined to date.

A new method has been developed to rapidly characterize the sintering behavior of recovery boiler precipitator dusts. Sixty-one dust samples from more than 40 recovery boilers of various types have been characterized, and their sintering tendencies have been ranked according to an index that relates to the strength of the sintered dust. Here, we discuss this method and look at how the sintering tendency may be affected by dust composition, physical properties, and the boiler operating conditions.

THE METHOD

Experimental procedure

Pellets (31.7 mm O.D. × 5.0 mm thickness) of each precipitator dust sample were prepared by pressing the dust in a circular mold. The pellets were tested one at a time using a sintering apparatus illustrated in Fig. 1. The pellet was placed in a muffle furnace and heated at a rate of 5°C/min.

The change in pellet diameter was monitored with a video camera that projected the image of the pellet on a TV monitor. The projected image diameter was measured from the monitor every 2.5°C, or every 30 s. Since the thickness of the pellet changed in proportion to the diameter and the mass of the pellet remained constant before and after the...
2. Density–thickness curve obtained for a typical precipitator dust.

The test, it was possible to calculate the density of the pellet from its projected diameter at each temperature. The calculated density was plotted against temperature for each dust sample.

Two tests were performed on each dust sample; similar results were obtained. Chemical and thermal analyses were performed on all samples to determine their composition and the first melting temperature.

Figure 2 shows a typical density–thickness curve. Up to about 400°C, the pellet density remained at its initial value (Di) of about 1.2 g/cm³. The density increased markedly with temperature, particularly above 450°C, reaching a peak value (Dpk) of 2.25 g/cm³ at about 550°C, and leveled off at this value. In this case, 400°C is considered the sintering initiation temperature, Ti, and 550°C is the sintering peak temperature, Tpk.

Sintering index

For a given deposit with fractional porosity, p, and density, D, the relative strength, S/Stheo, can be estimated using the following empirical correlation [4]:

\[
\frac{S}{S_{\text{theo}}} = e^{-6.2p} = e^{-6.2 \left( \frac{D}{D_{\text{theo}}} \right)}
\]  

(1)

where Stheo is the strength at the sintered dust at the theoretical density (or zero porosity). Because of the inevitable presence of pores, vacancies, and structural defects in the sintered mass, the relative strength may range from almost zero for an unsintered dust to a maximum value of 0.6 for a well-sintered dust, or for a dense, hard, and fused deposit in the superheater region.

In this work, the sintering index is defined as the average relative strength of the dust pellet at temperatures between 500°C and the sintering peak temperature (Tpk) that has been normalized to fit an arbitrary scale of 0 to 100, minus the equivalent initial relative strength of the dust pellet before sintering:

\[
\text{Index} = \frac{100 \times S_{\text{theo}}}{D_{\text{pk}}} - \frac{100 \times S_{\text{theo}}}{D_{i}} = 166.7 \times \left[ e^{-6.2 \frac{D_{\text{theo}}}{D_{\text{pk}}}} - e^{-6.2 \frac{D_{\text{theo}}}{D_{i}}} \right]
\]  

(2)

Substituting the porosity values with density values yields a sintering index that can be obtained directly from the change in pellet density during the sintering test:

\[
\text{Index} = 166.7 \times \left[ e^{-6.2 \frac{D_{\text{theo}}}{D_{\text{pk}}}} - e^{-6.2 \frac{D_{\text{theo}}}{D_{i}}} \right]
\]  

(3)

where Dpk and Di are the density of the pellet at 500°C and the peak temperature (Tpk), respectively. For dusts that do not sinter well, having a Tpk value higher than 600°C, the density of the pellet at 600°C is used instead. These temperatures were chosen because they correspond to the typical flue gas temperature at the generating bank inlet and to the temperature range in which maximum sintering typically occurs. They also represent the temperature range in which most of the fume starts forming in the boiler [6].

The theoretical density, Dtheo, is calculated based on the composition of the dust and the theoretical density of single crystals of sodium compounds (Na2SO4, Na2CO3, and NaCl). Potassium compounds are not considered because they have a density similar to that of their corresponding sodium compounds, and they are present at a much smaller concentration than sodium compounds are.

The resulting sintering index would have a value between 0 and 100. Dust with an index value of zero does not sinter at all at temperatures below 600°C, while dust with an index value of 100 develops the highest degree of sintering possible. Dust with an index below 10 would have less tendency to sinter or would develop only a low strength when sintered at temperatures between 500°C and 600°C. On the other hand, dust with an index above 40 would have a tendency to sinter rapidly and form a hard deposit that is more resistant to sootblowing.

Dust samples

We characterized a total of 61 dust samples from 42 recovery boilers at 35 mills. Of these, 48 samples from inland kraft mills were characterized by low chloride and low potassium. Two samples, with high chloride and low potassium, were from kraft mills on the west coast of Canada where sea-borne logs are used. One sample was a high-chloride, high-potassium dust from an inland kraft mill that had high chloride and high potassium concentrations in the liquor. Five samples were high in chloride potassium but were from coastal eucalypt kraft mills in Brazil. Four were high-carbonate dust samples from a BCTMP (soda) mill. One of the samples contained mostly sulfate from an NSSC mill.

Of the samples received, several appeared to be collected from either a generating bank or an economizer ash hopper. The ash hopper dust samples were lumpy and had high initial (uncompacted) bulk densities (>0.5 g/cm³) and high carbonate contents. Several of these dust samples contained matter not soluble in water.

SINTERING TENDENCY

Figure 3 shows the sintering tendencies of all 61 dust samples ranked according to index in ascending order. Most of these indices fall between 10 and 40. Dust samples with indices below 10 were those that sintered very slowly and had little strength, while those with...
4. Effect of chloride on sintering. (The broken curve connects data for dust samples collected from the same boiler but at different times.)

indices above 40 sintered rapidly and became hard deposits.

The lowest indices (almost 0) belonged to dust samples collected from ash hoppers, dust samples that contained no chloride, and the dust from the NSGC boiler. The highest index belonged to a sample from a coastal kraft mill in Brazil where eucalyptus were pulped. This dust had a relatively high potassium content and the highest chloride content of all dust samples examined.

**EFFECT OF DUST COMPOSITION**

We have used units of mole percent instead of weight percent so that the individual components in the dust can be readily related to those in the smelt, black liquor, green liquor, and/or white liquor.

**Chloride**

Figure 4 shows the effect of chloride content on dust sintering. Dust samples with higher chloride contents generally sintered more rapidly than dusts with low chloride contents. Dust samples containing less than 2 mol % Cl/(Na+K) generally did not sinter well; only 3 out of 15 of such dust samples had a sintering index above 10.

The scattering of data indicates that high chloride was not the only factor that caused rapid sintering; the potassium content and the dust particle size also affected the rate. However, the effect of chloride on sintering was more apparent among samples taken from the same coastal mill but taken at different times (the dotted line in Fig. 4).

**Potassium**

At a first glance, potassium by itself did not seem to have an effect on sintering (Fig. 5). However, the effect of K became more apparent if the data points for dust samples from ash hopper and dust samples with less than 2 mol % Cl/(Na+K) were excluded. At a chloride content above 2 mol % Cl/(Na+K), the sintering index increased as the K content increased.

The effect of potassium on sintering followed a similar pattern as that of the first melting temperature (FMT) of the dust [7]. This effect, along with that of chloride, implies that the combination of high chloride and high potassium can drastically increase sintering. This explanation is plausible since sodium and potassium chlorides have high vapor pressures relative to other dust components. In addition, potassium helps lower the FMT and thus lowers the temperature at which significant vaporization occurs.

**Carbonate**

As shown in Fig. 6, carbonate by itself did not appear to have an effect on sintering.

**EFFECT OF THE FIRST MELTING TEMPERATURE**

Figure 7 shows the relationship between the sintering index values for the dust samples and the first melting temperatures of those samples. There is a clear trend for more rapid sintering at lower FMTs. This inverse relationship between the sintering tendency of a dust and its FMT has been observed earlier [5].

The FMT of recovery boiler dust is very high (above 780°C) if the dust contains no chloride. It is dramatically lower, down to below 600°C, if there is a small amount of chloride in the dust. Once the chloride content has reached a threshold value of 1-2 mol % Cl/(Na+K), a further reduction in the chloride content would not lower the FMT any further. The FMT of dust samples that contain chloride would be affected mainly by potassium and, to a lesser extent, by carbonate. This complicated correlation between dust composition and FMT is one reason the sintering index does not correlate well with the carbonate content of the dust samples.

**EFFECT OF UNCOMPACTED BULK DENSITY**

Figure 8 is a plot of sintering index vs. the initial (as received), uncompacted bulk density of the dust samples. It shows a trend of decreasing sintering index with increasing bulk density of the
uncompacted dust. The fluffiest dust samples (toward the left side of graph) sintered more, while the more dense dust samples from ash hoppers (toward the right side of the graph) sintered very little.

Several factors could influence the as-received, uncompacted bulk density of recovery boiler dust samples collected from electrostatic precipitators. One is the extent to which the dust samples have sintered prior to the bulk density measurements. For dust samples that have undergone moderate to extensive sintering, the extent of sintering would be indicated by an increase in the size of grains to a substantially larger size than individual fume particles [8]. For low-sintering dust samples, the extent of sintering would be indicated by the apparent density of agglomerates of individual particles. If a dust had already sintered, as in the case of the ash hopper dust, it would sinter less and have a smaller sintering index in laboratory sintering tests.

Another factor is the extent to which the dust samples have been sulfated. As shown in Table I, dust samples with higher sulfate contents tend to be denser and have a lower sintering index.

### EFFECT OF BOILER OPERATION ON DUST SINTERING

The dust composition (and hence thermal properties) and particle size can be affected greatly by how boilers are operated. High-solids firing typically results in high bed temperatures, low SO2 concentrations in the flue gas, and dust samples with fine particle size and high carbonate content. Overloaded boilers tend to produce dust samples that have high carbonate contents because of the high bed temperature and the inclusion of smelt carryover in the dust. The sulfidity of the liquor also plays an important role since it is directly related to the amount of SO2.
available for the sulfation of alkali compounds. Therefore, these parameters were expected to have a significant effect on the sintering behavior of the dust samples.

**Black liquor solids**
The second two rows in the table show the sintering indices for dust samples collected from two different boilers at Mill A. Although these two boilers processed the same virgin black liquor, Boiler 1 burned low-solids black liquor, 62–65% dissolved solids, whereas Boiler 2 burned high-solids black liquor, 78–80% dissolved solids. The dust from the high-solids firing boiler has a sintering index of 24, compared to only 2 for the dust from the low-solids firing boiler. This difference means that the Boiler 2 dust would sinter at a lower temperature and a higher rate than the dust of Boiler 1. Chemical analysis also shows that Boiler 2 dust contained much more carbonate (less sulfate) and somewhat more chloride than Boiler 1 dust contained. Furthermore, Boiler 2 dust had a much lower bulk density than that of Boiler 1 dust. A similar result was also found at another Kraft mill where dust samples from two different boilers had quite different sintering behaviors.

**Firing load**
Also summarized in the table are the results of three dust samples collected from Mill B. Dust samples from Boilers 1, 2, and 3 were collected during the time when the boilers were operating at 65%, 95%, and 107%, respectively, of the design firing capacity. The results show that the dust from Boiler 1 did not sinter at all, the dust from Boiler 2 sintered only slightly, and the dust from Boiler 3 sintered at a higher rate.

Both carbonate and chloride contents were lowest in the dust from Boiler 1 and highest in that from Boiler 3. The uncompacted bulk density decreased with the firing load. These results are consistent with those obtained at Mill A, where liquor solids content was a variable. This outcome is understandable since an increase in either the firing load or the liquor solids would result in higher bed temperatures. In turn, higher bed temperatures would produce dust samples that are lighter and that have higher carbonate and chloride contents and a lower sulfate content.

**NCG combustion**
The effects of burning concentrated non-condensible gases (CNCG) in a kraft recovery boiler at Mill C are summarized in the table. Two dust samples were taken during CNCG combustion (normal operation), and two were taken after CNCG combustion had been halted for at least 8 h.

Burning CNCG had an insignificant effect on dust properties, although a slight increase in sulfate content was observed. This increase in sulfate content is consistent with the increase in uncompacted bulk density and the lower sintering tendency during CNCG combustion.

**CONCLUSIONS**
A novel technique has been developed to characterize the sintering behavior of precipitator dust samples. Sixty-one dust samples from over 40 recovery boilers have been tested, and their sintering tendencies have been ranked according to an index that relates closely to the strength of the sintered dust. These rankings led to a number of findings.

Sintering increased with the chloride and potassium contents of the dust as long as the chloride level of the dust was greater than 2 mol % Cl/(Na+K). Carbonate had no direct effect on sintering, although dust samples with higher carbonate contents tended to also contain high chloride, which increased sintering. Dust samples that had a very low chloride content, dust samples that were completely sulfated, and dust samples that had previously sintered did not sinter appreciably below 600°C.

Changes in boiler operating conditions that impact bed temperatures and/or the chemical composition inside the boiler may affect dust sintering behavior. For a given boiler, dust samples with higher sulfate contents have less tendency to sinter.

Apparently, the tendency for dust particles to sinter and form hard deposits in recovery boilers increases with a decrease in dust uncompacted bulk density and in the first melting temperature of the dust. The results support earlier findings that the first melting temperature may be a good indicator of sintering tendency.

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**LITERATURE CITED**

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Sintering is important to boiler operation, but it has not been systematically studied before. The method we used to determine the sintering tendency of dust is a novel one that produces faster results and provides more information than other methods used in previous research.

Our most difficult task was to relate the laboratory findings to mill experience. We did so by performing tests on a large number of samples collected from many pulp mills and comparing the results with mill operating data and experience. The findings were intriguing, confirming the important role of composition and density of fume and dust particles in the sintering behavior of deposits.

Mill engineers may be able to use the data and information provided to determine the sintering tendency of dust in their recovery boilers and to optimize their sootblowing operations. What’s next? This project has been brought to a satisfactory completion, and there are no plans to take this research further.

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A simple and fast procedure for estimating the elapsed time since tree felling (seasoning time) has been developed. The procedure is suitable for logs or wood chips. The method involves squeezing wood chips at high pressure and analyzing the resultant exudate for its glycerides content by an enzymatic colorimetric test. Fully seasoned chips yield a yellow coloration, whereas fresh or partially seasoned chips yield a pink coloration, the intensity of which is a function of the seasoning time.

Results can be obtained in about 20 minutes. The procedure can distinguish between fresh and seasoned wood. It was used to monitor laboratory seasoning of several wood species.

Sitholé and Allen are with Paprican, 570 Boul. St.-Jean, Pointe Claire, Québec, Canada. Email Sitholé at bsithole@paprican.ca. This paper appears in full in the electronic subscription version of TAPPI JOURNAL, on pages E33 through E45.

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