How does a kraft recovery boiler become plugged?

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ABSTRACT In kraft recovery boilers, flue gas passages often plug for no obvious reasons. The phenomenon has puzzled the industry for years and needs to be understood because of the substantial production loss caused by forced shutdowns. The fundamental characteristics of fireside deposits and their impact on plugging help to explain how deposits form, grow, and become resistant to sootblowing. Knowledge that can help kraft mills discover better solutions to their boiler plugging problems.

The plugging of flue gas passages as a result of massive deposit buildup has been a headache, particularly when there is only one production line. Plugging often occurs unpredictably and has puzzled boiler operators, manufacturers, and academics for years. The questions of why, when, and how plugging occurs need to be answered because of the high cost associated with forced boiler shutdowns.

Because of its unpredictability and complexity, plugging has been attributed to almost everything related to the boilers: high solids content load, high flue gas temperature, high air flow rates, poor air distribution, poor bed conditions, upset of liquor properties, poor sootblowing efficiency, poor boiler design, etc. Logically, overload would seem to be the most important cause of plugging because it often results in increased carryover and high flue gas temperature. Nevertheless, a recent survey on boiler plugging in Canada showed no conclusive correlation between firing load and the severity of plugging (1).

One thing that is clear is that plugging occurs because of massive deposit accumulation. Deposits often accumulate heavily only at some specific location in the boiler, while there is almost no accumulation at other locations. It is therefore crucial to understand the characteristics of deposits and how deposits form and grow in different regions in the boiler, to discover ways to control them and to optimize boiler operation.

Deposit formation

Deposits are derived from two distinctly different sources (2):

1. Carryover. Smelt and/or partially burned black liquor particles physically entrained in the flue gas.

2. Condensation. Fume or dust resulting from the condensation of compounds volatilized from the lower furnace. The condensation occurs either directly on cooled surfaces or indirectly in the flue gas stream, forming particles that subsequently are transferred to the cool surfaces.

Carryover and condensed material form a dust stream, which is collected by ash hoppers and electrostatic precipitators and ultimately returned to the system by being added to the strong black liquor (Fig. 1). This "internal recycling" has been estimated to account for about 10% of the total inorganic content in the black liquor (3). Portions of it remain as deposits on heat transfer surfaces, and a small amount is lost with the stack gas.

Thus, deposits are a mixture of carryover and condensation in proportions that vary with location in the furnace. In the lower superheater, the flue gas temperature is too high for most vapors to condense. Carryover is dominant, forming hard, fused, and smelt-like deposits. In the upper superheater and the region upstream of the generating bank, the flue gas temperature is lower, allowing some vapors to condense. Condensation takes place on cooled tube surfaces, forming a layer of fluffy, white deposits. It can also take place in the flue gas stream, forming dust that is transported to the tube surface, where it mixes with the carryover. As a result, deposits in this region normally contain condensed material, the amount of which increases as the flue gas temperature decreases. In the generating bank and the economizer region where the flue gas temperature is low enough, almost all vapors condense to form dust, while carryover is completely solidified and will not stick readily on tube surfaces. Thus, deposits in this region consist mainly of condensation.

Chemical composition of deposits

Deposits consist of more than 99.8% by weight of water-soluble compounds. These are mainly sodium sulfate and sodium carbonate, with small amounts of sodium chloride, sodium hydroxide, potassium salts, and reduced sulfur compounds. Since deposits are basically a mixture of carryover and con-
densation materials, their composition depends on the relative proportion of these two types and consequently varies widely with location in the boiler.

**Carryover**
Carryover material, which originates from physically entrained smelt and/or unburned black liquor particles, originally consists of 20–30% by weight of Na₂SO₄, 60–70% Na₂CO₃, and some unburned organic material—a composition similar to that of smelt that has been fully oxidized (Fig. 2). As the carryover travels to the upper part of the boiler, Na₂CO₃, NaOH, and other alkali compounds react with sulfur species in the flue gas to form Na₂SO₄.

Similarly, the chloride and potassium content in the carryover is originally the same as that in the oxidized smelt. Although its reaction with sulfur compounds is slow, chloride is also converted to sulfate at high temperatures.

Potassium, on the other hand, is not depleted by reactions with sulfur compounds. However, it can be removed from carryover deposits along with chloride by vaporization at high temperatures.

As a result, carryover material has a composition close to that shown in Fig. 3, consisting of about the same or slightly less chloride and potassium but more sulfate and less carbonate than the oxidized smelt.

**Condensation**
Condensation material originates from vapors that condense to form sub-micrometer-sized fume. The fume's high specific surface area makes it extremely reactive in the oxidizing sulfur-bearing flue gas, converting most of its alkali compounds to sulfates. Condensation material normally has a composition as is shown in Fig. 4. It contains mostly Na₂SO₄, is enriched with chloride and potassium salts, has only a small amount of carbonate, and contains no reduced sulfur compounds and hydroxides. The chemical composition of the condensation material is influenced by sulfidity, concentration of volatile components in the black liquor, and bed and smelt temperatures in the lower furnace.

Higher bed temperature results in more sodium and less sulfur in the flue gas (4). The excess of sodium with respect to sulfur in the flue gas results in the formation of Na₂CO₃, which in turn decreases the Na₂SO₄ content in the condensation material. High bed temperatures also cause more chloride and potassium salts to vaporize out of the smelt, enriching these salts in the condensation. Liquor of lower sulfidity, particularly in conjunction with high bed temperature, produces less gaseous sulfur in the flue gas and results in a lower Na₂SO₄ content and a higher chloride content in the condensation material.

**Deposits**
Since deposits are a mixture of carryover and condensation materials, their composition lies between that of these two, with sulfate and carbonate content varying widely with location in the boiler. In the superheater, where the carryover is dominant, the composition is close to that of the carryover material, with some reduced sulfur compounds. In the generating bank and the back side of the boiler, where the condensation becomes more pronounced, the deposit composition is close to that of the condensation material.

On aging, deposits further react with sulfur compounds in the flue gas, converting some carbonate, hydroxide, and chloride to sulfate. Figure 5 shows typical compositions of deposits at various locations in the boiler. The ratio of sulfate to carbonate in deposits increases dramatically toward the back side of the boiler.

**Thermal properties of deposits**
Since deposit composition varies with location in the boiler, thermal properties also vary. Deposits, like most mixtures of chemical compounds, have two distinct melting temperatures. The first melting temperature is the
temperature at which the liquid phase first appears, while the complete melting temperature is the temperature at which the deposit is completely molten.

Between these two temperatures, there are at least two other temperatures that are important from the accumulation standpoint. First, the sticky temperature is the temperature above which the deposit contains enough liquid phase to become sticky. Second, the radical deformation temperature is the temperature above which the amount of liquid phase in the deposit is sufficient to make the deposit fluid. In Fig. 6, these temperatures are depicted as changes in the appearance of cones made of deposits.

**Sticky temperature**
Deposit stickiness is one of the main factors that determines the rate of deposition in the region upstream of the generating bank. Stickiness is affected by many variables, of which deposit temperature, composition, surface conditions, particle size, and flue gas velocity are the most important. The influence of surface conditions on stickiness is difficult to determine, but carryover particles are less sticky when they are covered with a layer of condensation and/or if they are mixed with a large amount of unburned black liquor particles.

For a deposit to be sticky, it must contain a certain amount of liquid phase, which increases with both temperature and chloride content at temperatures above the first melting temperature (5). As the amount of liquid phase reaches 70% at the radical deformation temperature, deposit accumulation ceases because fresh deposits melt and run off.

Figure 7 shows the sticky temperature zone as a function of chloride content for a typical carryover deposit containing 5% by mole K/(Na + K), based on Isaak's data (6). The sticky temperature zone is bordered by the sticky temperature curve as a lower limit and the radical deformation temperature curve as an upper limit. In this zone, deposits are sticky, which increases deposit accumulation. Outside the range, deposits either do not contain enough liquid phase to be sticky or contain so much liquid phase that they slag and do not build up.

Figure 8 shows the sticky temperature of carryover deposits as a function of both chloride and potassium content. The sticky temperature is lowered as chloride content increases from 0% to 5% by mole Cl/(Na + K). The effect of potassium, on the other hand, is much less dramatic, particularly when the chloride content is below 1.5% by mole Cl/(Na + K). At low chloride content,
Radical deformation temperature

Like the sticky temperature, the radical deformation temperature is a function of the amount of liquid phase in deposits and is strongly influenced by the chloride content. This temperature is important for deposit accumulation because, in conjunction with steam temperature, it determines the thickness of deposits in the lower superheater, where high flue gas temperatures prevail (7). Increasing radical deformation temperature and/or decreasing steam temperature results in a thicker deposit. In regions where the flue gas temperature is between the sticky temperature and the radical deformation temperature, deposits accumulate and will not stop growing.

The effect of Na₂SO₄, Na₂CO₃, and NaS

Although Na₂CO₃ is one of the major components in deposits, particularly in the lower superheater, its effect on deposit thermal properties is insignificant. In the absence of chloride, deposit first melting and complete melting temperatures are close to each other, in the range of 825–870°C over the full range of carbonate content from 0% to 100% by weight (8).

In the lower superheater, where oxidation is not complete, the deposit may contain a small amount of NaS. This, however, has no significant effect on deposit thermal properties. The lowest first melting temperature of a mixture containing NaS, Na₂CO₃, NaCl, and potassium salt is about 520°C (9), about the same as that of a mixture without NaS.

The effect of chloride and potassium

Chloride and potassium content in deposits varies from boiler to boiler, depending on the input of these salts to the recovery cycle, the amount of internal recycling in the boiler, and the degree of closure of the mill. Typical chloride and potassium contents in carryover deposits for inland mills where there are no sources of chloride and potassium other than wood are 1–4% by mole Cl/(Na + K) and 4–7% by mole K/(Na + K), respectively. With input from other sources such as seaworn logs, makeup chemicals, and hardwood, chloride and potassium contents in deposits can be as high as 25% by mole Cl/(Na + K) and 20% by mole K/(Na + K), particularly for mills that have low chemical losses.

Both chloride and potassium can lower deposit melting temperatures, but their impact on deposit thermal properties is quite different. Chloride does not lower first melting temperature further once its concentration exceeds 1% by mole Cl/(Na + K). However, it increases the amount of liquid phase in deposits at temperatures higher than the first melting temperature. Potassium, on the other hand, lowers the first melting temperature as its concentration increases, but has little impact on the amount of liquid phase. This difference between chloride and potassium implies that the sticky temperature and radical deformation temperature, which are both a function of the amount of liquid phase, are strongly affected by chloride content in deposits and not by potassium.

Figure 9 summarizes the effect of temperature on a typical deposit containing 70% by weight of Na₂SO₄, 25% by weight of Na₂CO₃, 3% by mole of Cl/(Na + K), and 5% by mole of K/(Na + K).

How does plugging occur?

Plugging caused by carryover

Burning carryover particles are at a higher temperature than the surrounding flue gas. In the lower superheater, where the flue gas temperature is normally higher than 800°C, carryover particles will be at a much higher temperature than the radical deformation temperature. They will be molten droplets that strike and solidify on the tubes to form fused and hard deposits. As the deposit grows thicker, the outer surface temperature increases until it reaches the radical deformation temperature, at which point the surface becomes fluid, then slags, and thus stops growing. Under such conditions, deposit thickness is self-controlled; that is, no accumulation occurs after the deposit reaches a certain thickness. Plugging thus does not occur in this region despite the fused, hard, and adherent nature of deposits.

In the upper superheater, where the flue gas temperature is about 700°C, carryover particles are above the sticky temperature and are always sticky, forming tenacious deposits. These deposits will continue to grow and will not be self-controlled, because the deposit surface temperature is lower than the radical deformation temperature. Massive deposits can result, and plugging is highly likely in this region if sootblowing is not sufficient.

At the boiler bank inlet, the flue gas temperature is in the range of 550–700°C, close to the minimum deposit sticky temperature. The carryover material may or may not be sticky depending on its composition and whether or not it is mixed with condensation material. Furthermore, since the spacing between tubes in the generating bank is much narrower than in the superheater region, sootblowing efficiency is rather low. Therefore, complete plugging in this region is highly likely when the carryover material is sticky.

In the boiler rear bank and economizer regions, carryover particles are not sticky, since the flue gas temperature is normally lower than the sticky temperature. Furthermore, the carryover material is mixed with a large amount of condensation material, making it easy to remove. Plugging in this region resulting from sticky carryover is unlikely.

Plugging caused by condensation

Under suitable conditions, fluffy condensation deposits can become extremely hard through "sintering," a molecular diffusion process that normally occurs at temperatures below the deposit first melting point. Sintering is highly temperature-dependent and can be promoted by a small amount of liquid phase. Laboratory tests of precipitator dust sintering have shown that the dust starts to sinter at about 300°C and becomes hard in less than 1 h if it is exposed to temperatures above 500°C (10).

Consider a case of a 900-psi steam pressure boiler where the flue gas temperature entering the boiler bank is 600°C and is leaving it at about 400°C. In the boiler front bank, the flue gas temperature is in the range of 500–600°C. The boiler bank tube surface temperature is about 320°C. This low temperature allows volatilized materials to condense on the tubes to form condensation deposits. As the deposit layer thickens, its outer surface temperature rises and sintering occurs. The outer layer would become hard in 1 h if its temperature were to exceed 500°C, while the inner layer adjacent to the tube remains unsintered, soft, and friable. Under normal conditions, such deposits can still be
removed from the tubes by sootblowers because of the weak bonding between the soft, friable inner layer and the tubes.

However, large pieces of deposits, which have been removed from the tubes in the upper part of the boiler by sootblowers, fall and occasionally bridge the tubes in the lower part. These "jammed" deposits receive little or no cooling from the tubes and become hard because of sintering. They then become a new site for deposition, upon which deposits build, harden, and become difficult to remove.

Figure 10 shows an SEM photograph of a cross-section of a deposit collected between tubes in the boiler front bank of a plugged boiler. The inner layer is sintered and becomes a dense mass, while the outer layer, presumably newly formed, still remains dust-like. This hardening mechanism of the dust by sintering makes deposits difficult to remove and eventually can lead to complete plugging of flue gas passages.

The mud drum is usually the most susceptible site for falling deposits because of the "dead space" on the drum. In some cases, plugging starts from the mud drum and spreads toward the steam drum.

Plugging caused by dust sintering can also be accelerated by high flue gas temperatures which result from the insulation effect caused by massive buildup of carryover deposits in the superheater region. In some boilers, plugging starts in the superheater region and propagates rapidly to the boiler bank.

In some cases, acidic deposits have been found in the economizer region. These deposits are believed to contain sodium bisulfate, which forms at high SO₃ concentrations in the flue gas, particularly in boilers that burn high sulfidity liquor and have low bed temperatures.

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The temperature zone in which the deposit is sticky is different from boiler to boiler. It is a function of chloride and potassium content. At a chloride content of less than 1.5% by mole Cl/(Na + K), potassium has a minimal effect on deposit sticky temperature once its concentration in deposits exceeds 6% by mole K/(Na + K).

Precipitator dust and condensation deposits can sinter and become hard in less than 1 h if their temperature is higher than 500°C.

Summary

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