Formation of blue deposits in kraft recovery boilers

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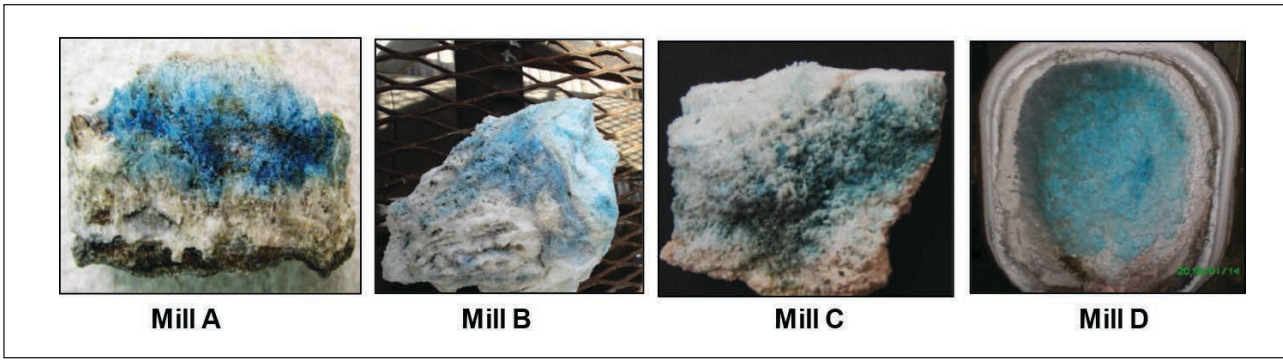
ABSTRACT: Fireside deposits in recovery boilers are typically white, red, pink, grey, black, or occasionally yellow, depending on where they are in the boiler, the mechanisms by which they are formed, and the environment to which they are exposed. Although rare, blue deposits have been reported, and some were "bluer" than others. This study systematically examines the cause of the blue coloration of deposits in recovery boilers. The results show that for a deposit to become blue, it must a) contain sodium carbonate, b) contain a small amount of manganese, c) be molten or partially molten, and d) have exposure to an oxidizing atmosphere. Because deposits always contain sodium carbonate and manganese, these requirements suggest that blue deposits can form only in the superheater region of the recovery boiler when oxidizing conditions prevail. Blue coloration is thus more likely to be observed in boilers operating at a reduced firing load with a high excess oxygen target.

Application: Blue deposits have more or less the same chemical and thermal properties as normal pink or white deposits, and should be treated in the same way.

Fireside deposits form on heat transfer tube surfaces in kraft recovery boilers because of the high ash content of the fuel (black liquor) and low melting temperature of the ash [1]. Deposits can be different colors at different locations in the boiler as a result of the various mechanisms through which they form and the specific gas environment to which they are exposed. In the lower superheater near the bullnose region, deposits are formed mainly by inertial impaction of carryover, entrained molten or partially molten smelt, and unburned char particles in the flue gas. They are usually red or pink (**Fig. 1**) and often speckled with black char particles. In the upper superheater region upstream of the generating bank, deposits are essentially a mixture of better-burned carryover and condensed alkali salts (fume). They are usually pinkish, greyish, or silver-white. In the generating bank and economizer regions, deposits become whiter and whiter toward the economizer outlet because they contain increasingly more fume and less carryover.

Regardless of where and how they form, deposits consist of mainly sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), with a small amount of sodium chloride (NaCl), sodium sulfide (Na_2S), and potassium salts (potassium sulfate [K_2SO_4], potassium carbonate [K_2CO_3], potassium chloride [KCl], etc.) [1]. Because all of these compounds are white, what makes smelt and carryover deposits red or pink is not well understood. In their study of the Na_2S-Na_2SO_4 phase diagram by reducing Na_2SO_4 to Na_2S in hydrogen (H_2) at constant temperatures, Tran and Barham [2] observed that the resulting Na_2S-Na_2SO_4 melt was always red. However, when the gas stream was switched from a strong reducing H_2 gas to an inert neutral nitrogen (N_2) gas, the melt color turned quickly from red to white, even though the melt composition was unchanged. They postulated that the red coloration of the melt results from the presence of sodium sulfoxylate (Na_2SO_2), an intermediate reduced-sulfur compound that is stable in a reducing atmosphere but not in a neutral or oxidizing atmosphere. The postulation is consistent with field ob-

1. Pink and white deposits at different locations in a recovery boiler.



2. Blue deposits from recovery boilers at four different kraft pulp mills (A, B, C, and D).

servations that freshly formed carryover deposits have a smelt-like red or pink color, but they slowly oxidize and become white or grey if mixed with black liquor char. Similarly, when a red molten smelt sample is scooped out of the boiler and left to cool uncovered on a floor nearby, the red color slowly fades and the smelt turns grey as it oxidizes or reacts with moisture in the air.

In some recovery boilers, bright yellow deposits also have been observed. The cause of yellow coloration is not known. It might result from the presence of a small amount of elemental sulfur (yellow) or polysulphides (orange). At a kraft mill where petroleum coke was burned in the lime kilns, bright yellow deposits were observed on a recovery boiler manhole. Results of chemical analysis showed that the yellow deposit contained five times more yellow vanadium pentoxide (V_2O_5) than the white deposit nearby [3].

BLUE DEPOSITS

This paper is about a type of deposit that has an unusual color: blue. Although rare, blue deposits have been observed from time to time. Over the years, we have received numerous samples and photographs of blue deposits from pulp mills and equipment suppliers asking about possible explanations for the strange coloration. **Figure 2** shows a few photographs of blue deposits collected from recovery boilers at different pulp mills. The intensity of blue coloration varies from boiler to boiler, and from location to location in the same boiler. Even in the same piece of deposit, the blue color is often unevenly distributed, with some parts of the deposit bluer than others. At mill B, blue deposits were observed over a large area of the superheater (**Fig. 3**).

Chemical analysis was thoroughly performed on several blue deposits. The results, however, failed to help explain what made them blue. In all the deposits examined, the blue part of the sample had a chemical composition similar to the white part.

In early 2013, a Canadian mill (mill E) sent us three deposit samples collected using an air-cooled probe inserted through an opening on the boiler front wall at an elevation between the bullnose and the furnace roof. The first sample was collected when the boiler was operated at full load

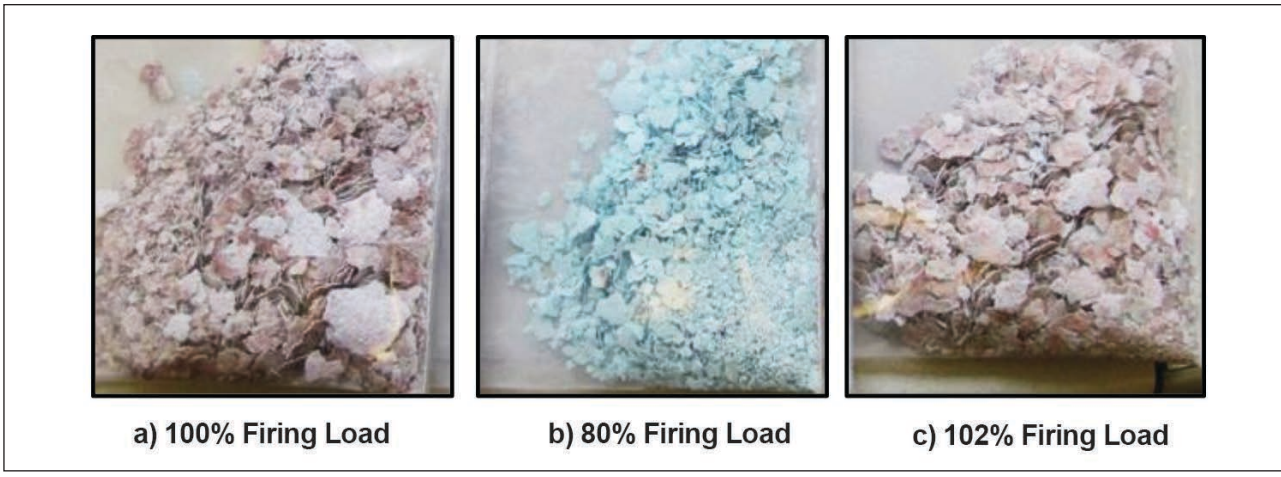
3. Blue deposits on secondary superheater platens in the recovery boiler at mill B.

(100%). It had a typical pink color (**Fig. 4a**). The second sample was collected a day-and-a-half after the first sample, when the boiler was fired at a reduced rate of 80%. That sample looked blue (Fig. 4b). The third sample was collected a day after the second sample, when the boiler was returned to its normal full load mode, and the color was pink again (Fig. 4c). Mill E had been monitoring its carryover buildup by collecting probe deposits daily at the same location. This was the first time that the boiler operator involved noted such a change in deposit color. The mill's questions were, understandably, what made the deposits blue? Could the blue coloration be related to the low liquor firing load?

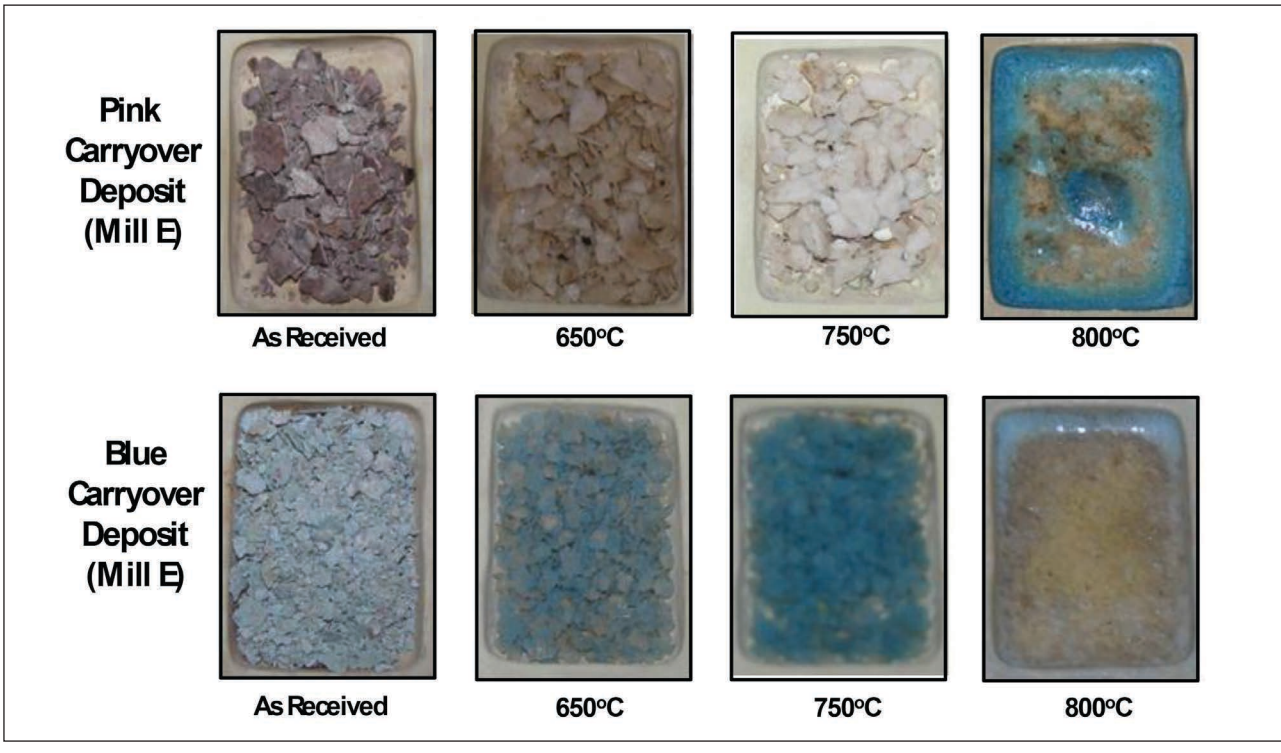
The event prompted us to conduct a systematic investigation to determine the possible cause(s) of the blue coloration and significance to boiler operations. This paper discusses the tests involved in the investigation, the results, and their practical implications.

EFFECT OF HEAT TREATMENT

In our earlier studies of deposit thermal properties [4,5] and precipitator ash sintering behaviors [6], we noted that when a sample of deposit or precipitator ash was heated in a crucible, it often turned blue when it melted. The first step in this investigation was, therefore, to determine if the blue coloration is in some way related to heat treatment.



4. Appearance of carryover deposits collected on an air-cooled probe inserted in the superheater region of a recovery boiler at mill E at different liquor firing loads.

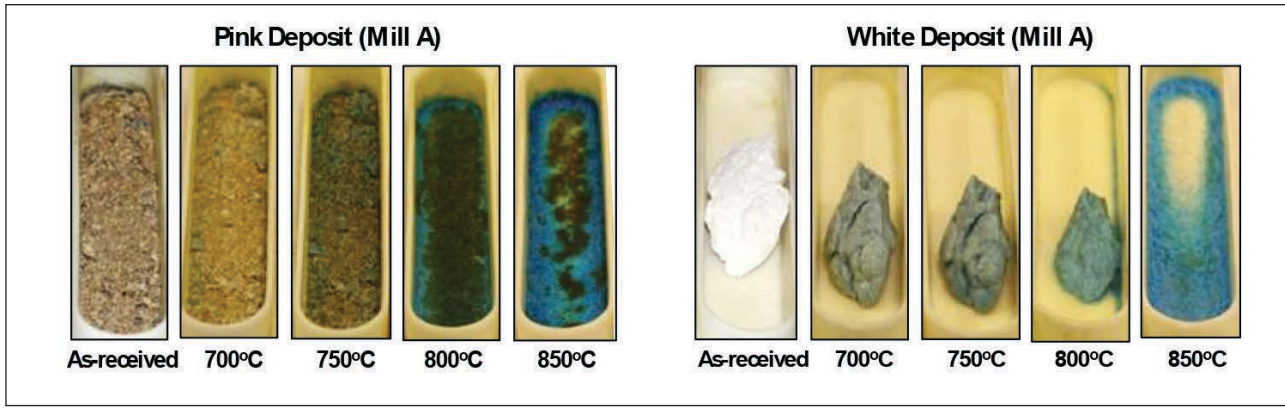


5. Appearance of pink and blue deposits from mill E after being heated at different temperatures in air for 30 min.

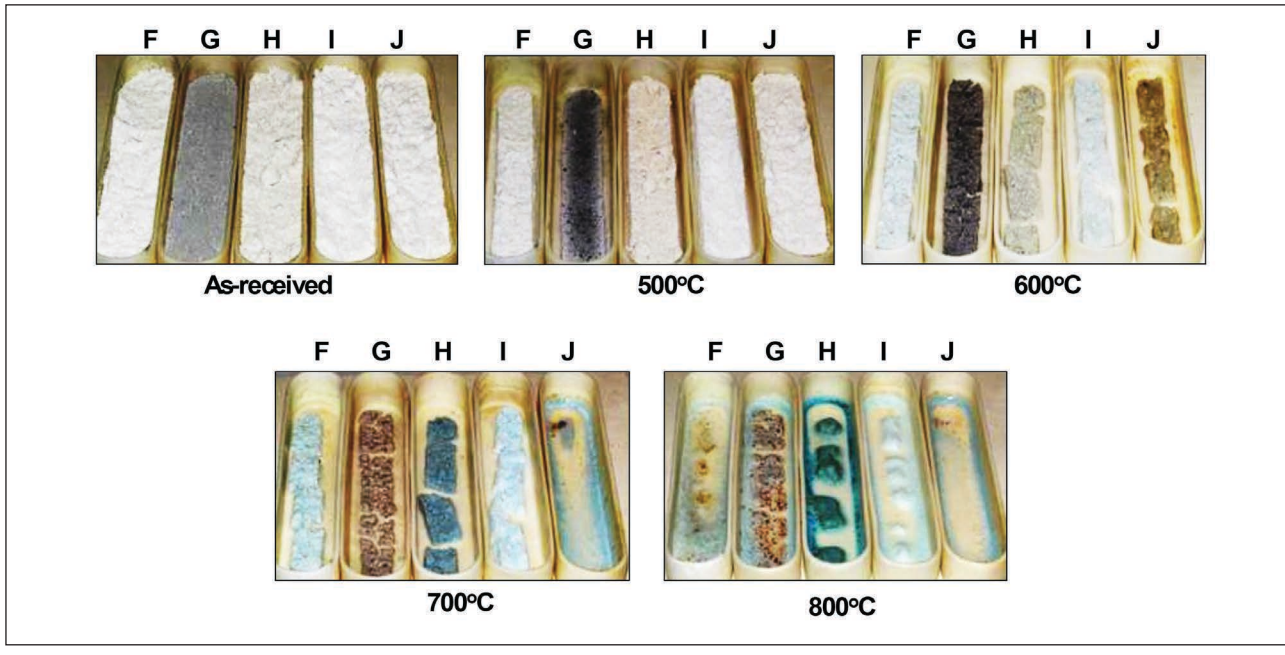
The tests began with the two pink and blue carryover deposits received from mill E. The deposits were heated in a muffle furnace in air at various temperatures for 30 min. As shown in **Fig. 5**, the pink deposit became pinkish at 650°C, pale white at 750°C, and blue at 800°C. The original blue deposit became bluer and bluer at 650°C and 750°C, but the blue color appeared to fade somewhat at 800°C. Similar results were obtained for two other pink and white deposits from mill A (**Fig. 6**).

Figure 7 shows the appearance of five precipitator ash samples from different pulp mills (mills F, G, H, and I) before and after being heat-treated at 500°C, 600°C, 700°C, and 800°C. Four of these ash samples were white as-received (before heat treatment), and one (from mill G) was grey, presumably because of inclusion of black liquor. All five samples turned blue at the end, but the black liquor-containing sample from mill G became blue only at a higher temperature than the other samples. The presence of black liquor in the sample appeared to have hindered the blue coloration of the ash.

Numerous samples of smelt, carryover deposit, and precipitator ash have been tested to date. Regardless of their initial colors (pink, grey, blue, white, or otherwise), they all turned blue when melted in air at high temperatures. It therefore can be concluded that melting at high temperatures is an



6. Appearance of pink and white carryover deposits from mill A after being heated at different temperatures in air for 30 min.



7. Appearance of precipitator ash samples from five mills (F to J) before and after being heated at various temperatures in air for 30 min.

important requirement for the blue coloration. The key question now is what compounds in the deposits make them blue at high temperatures? Our next series of tests were designed to address this question.

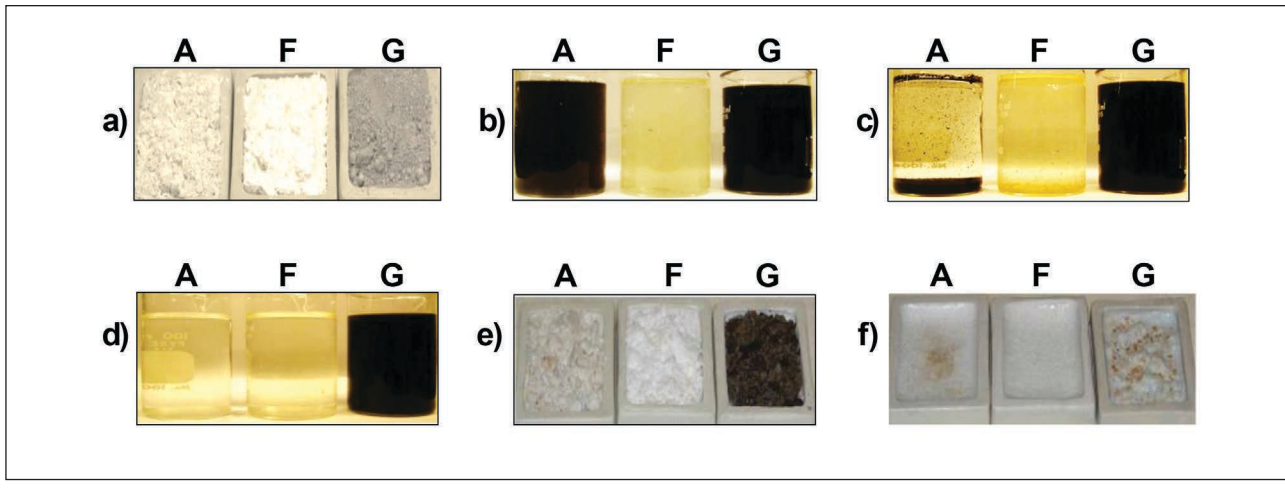
EFFECT OF DEPOSIT COMPOSITION

Recovery boiler deposits and precipitator ash are highly soluble in water. They typically contain more than 99 wt% water-soluble alkali salts (Na_2SO_4, Na_2CO_3, NaCl, and potassium salts) and less than 1 wt% water-insoluble matter, which consists of black liquor char (carbon) and compounds of nonprocess elements: aluminum (Al), calcium (Ca), cobalt (Co), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), silicon (Si), etc. Because alkali salts are all white, the blue-coloring compounds are likely to be present in the <1 wt% insoluble part of the deposits. To test this hypothesis, we needed to separate these two parts and test them individually.

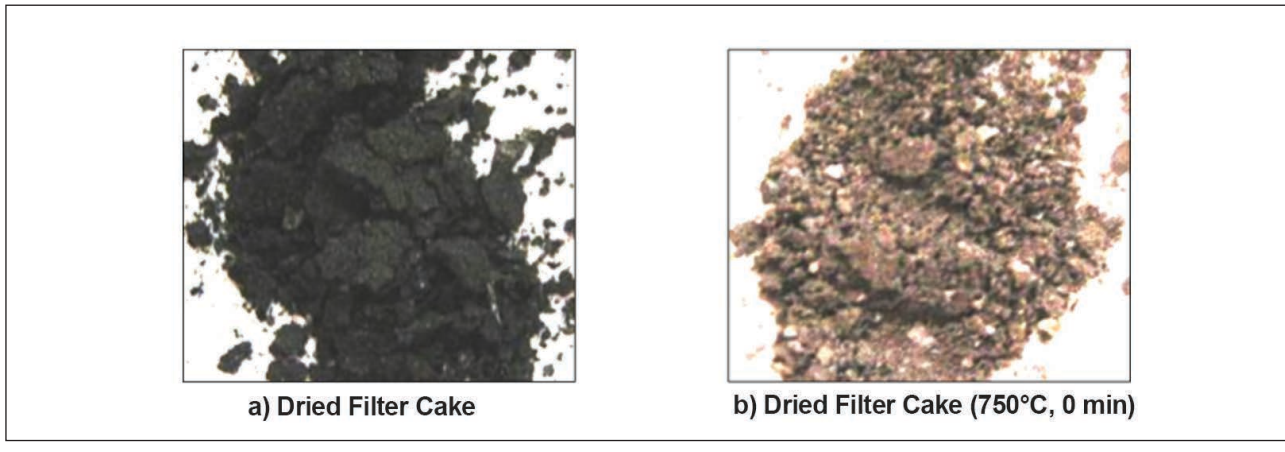
Water-solubles

In this series of tests, precipitator ash samples from three different kraft mills (A, F, and G) were used. These samples, as received, had slightly different colors: ivory-white, white, and grey (**Fig. 8a**). For each test, 1 g of sample was well mixed with 100 mL of hot de-ionized water in a glass beaker (Fig. 8b). The mixture was allowed to settle for 60 min (Fig. 8c) before being vacuum-filtered to separate the suspended solids from the water-solubles (solution). The filtrate was clear and free of suspended solids (Fig. 8d). It was subsequently concentrated and dried in an oven at 105°C. The dry mass (Fig. 8e) was essentially the water-solubles of the ash.

Note from Fig. 8d that the filtrate obtained from mill G ash was much darker than filtrates from mill A and mill F ashes. This is because the recovery boiler at mill G was an older unit equipped with direct contact evaporators. The ash was likely contaminated by raw black liquor as the flue gas passed



8. Procedures for separating water-soluble components from three precipitator ash samples obtained from mills A, F, and G: a) ash samples as received, b) ash solutions immediately after mixing, c) ash solutions after settling, d) filtrates, e) dried filtrate solids, and f) filtrate solids after heat treatment.



9. Dried filter cake obtained with mill A ash: a) as produced, containing black liquor char, and b) after being heat-treated at 750°C for 30 min to remove char.

through the direct contact evaporators. In contrast, the filtrate obtained with mill A ash was clear, even though this ash also contained partially burned black liquor char (Figs. 8b and 8c). This is understandable because char particles generally can settle and be filtered more readily than raw black liquor.

Figure 8f shows the appearance of water-solubles of mills A, F, and G ashes after being heat-treated at 750°C for 30 min. Mill A and mill F samples were white. The mill G sample was bluish, implying that it still contained a small about of water-insolubles. The results confirm that the water-soluble part of the deposits was not responsible for the blue coloration.

Water-insolubles

Because the water-insolubles content in precipitator ash is less than 1 wt%, a large amount of ash is needed to produce sufficient water-insolubles for use in various heat treatment tests. In this study, only mill A ash was used because it was available in a large quantity in our laboratory. The procedure for preparing water-insolubles was similar to that for the water-solubles, except that instead of the filtrate, the filter cake (the solids collected on the filter paper) was used. The cake was thoroughly washed and dried in an oven at 105°C. The dried cake (**Fig. 9a**) was essentially the insolubles of mill A ash. It was made of compounds of nonprocess elements and black liquor char that made it black.

A portion of the dried cake was heat-treated at 750°C in air for 30 min to burn off the char. The resulting brown "baked" cake (Fig. 8b) was considered to be the insolubles without char (or char-free insolubles) of mill A ash.

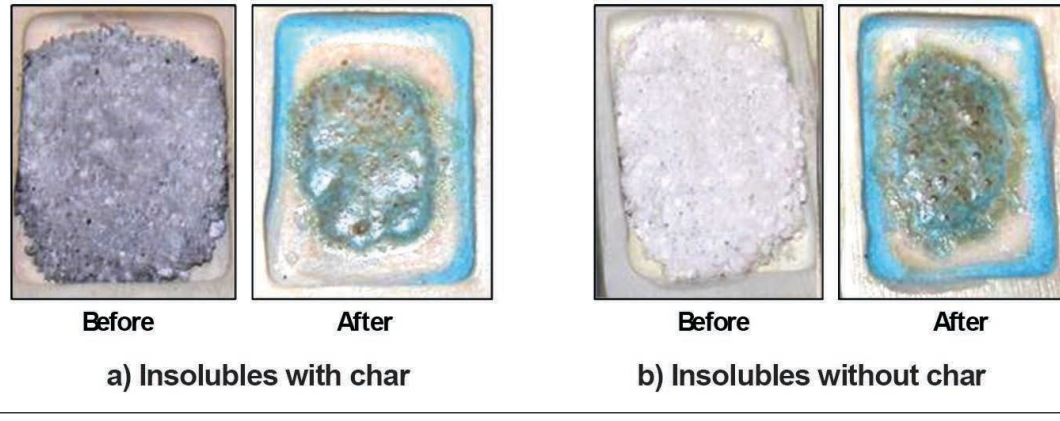
Table I summarizes the chemical composition on a dry basis of mill A ash and the analytical method used to determine each component. Mill A ash consists of 99.2 wt% solubles (alkali salts) and 0.8 wt% insolubles. Of the insolubles, slightly more than half were char residue, and the rest were presumably oxides or sulfates of calcium, iron, magnesium, manganese, and silicon. Other elements were either negligibly small (<20 ppm) or undetectable.

As shown in Fig. 8f, the soluble (or the major component)

Solubles			Insolubles			
	wt%	Method		wt%	ppm	Method
Sodium, Na	32.0	AAS	Char, as C	0.416	4160	TGA/DSC
Potassium, K	5.2	AAS	Magnesium, as MgO	0.134	1340	XRF
Sulfate, SO_4	42.8	IC	Silicon, as SiO_2	0.074	737	XRF
Carbonate, CO_3	18.0	TIT	Manganese, as MnO	0.042	424	XRF
Chloride, Cl	1.2	IC	Calcium, as CaO	0.035	347	XRF
Total	**99.2**		Sulfur, as SO_3	0.078	780	XRF
			Iron, as $Fe2O_3$	0.012	115	XRF
			Aluminum, as Al_2O_3	0.002	24	XRF
			Phosphor, as P_2O_5	0.002	24	XRF
			Titanium, as TiO_2	0.001	7	XRF
			Vanadium, as V_2O_5	< 0.001	4	XRF
			Total	**0.80**	**7960**	

AAS = atomic absorption spectrometry; IC = ion chromatography; TIT = titration;
TGA/DSC = thermogravimetric analysis/differential scanning calorimetry; XRF = X-ray fluorescence spectrometry.

I. Composition of mill A ash (dry basis).



10. Synthetic deposits mixed with a) 1 wt% insolubles with char, and b) 1 wt% insolubles without char, before and after being heated at 750°C for 30 min in air.

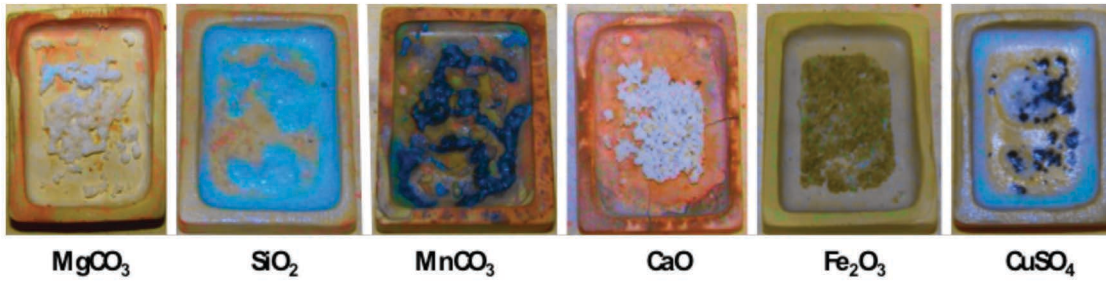
part of the ash is not responsible for the blue coloration. The investigation focus was shifted toward the effect of the insoluble part of the ash. Tests were performed by heating a synthetic deposit mixed with 1 wt% of insolubles from mill A ash at 750°C for 30 min in air. The synthetic deposit was prepared from pure chemicals: Na_2SO_4, Na_2CO_3, NaCl, and K_2SO_4. The deposit had a composition of 30.7 wt% Na, 5.2 wt% K, 51.3 wt% SO_4, 8 wt% CO_3, and 4.8 wt% Cl.

Figure 10 shows the appearance of the synthetic deposit doped with 1 wt% insolubles with and without char, before and after the heat treatment. Both turned blue after the heat treatment. The blue color was more intense in tests where the insolubles content was increased to 3 wt%. Because the blue coloration occurred with or without char, it must have been caused by the oxide part of the insolubles, not by the char part.

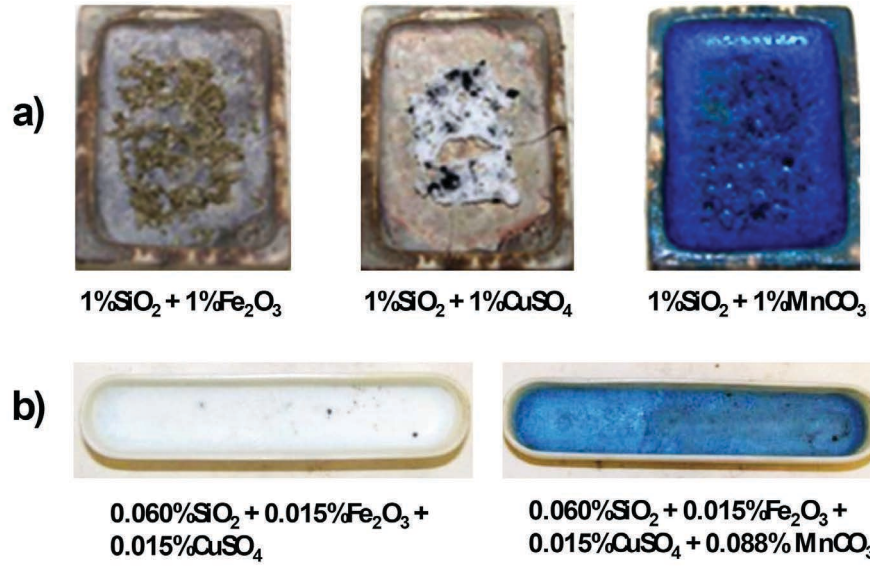
Blue coloration compounds

To determine which compounds in the oxide part of the insolubles are responsible for the blue coloration, heat treatment tests were performed on mixtures of the synthetic deposit and 1 wt% of compounds containing calcium, iron, manganese, and silicon, the main nonprocess elements in the insolubles. The compounds used for these nonprocess elements were $MgCO_3$, silicon dioxide (SiO_2), manganese carbonate ($MnCO_3$), calcium oxide (CaO), and iron oxide (Fe_2O_3), respectively. Although copper was not detectable in the insolubles of mill A ash, copper sulfate ($CuSO_4$) was also used in this study for comparison because it is known to be blue.

Figure 11 shows the results of the heat treatment tests. Samples doped with magnesium and calcium remained white after the heat treatment, confirming that magnesium and cal-



11. Appearance of mixtures of 1 wt% pure chemicals ($MgCO_3$, SiO_2, $MnCO_3$, CaO, Fe_2O_3, and $CuSO_4$) and the synthetic deposit after being heated at 750°C for 30 min in air.



12. Appearance of a) mixtures of 1 wt% SiO_2, 1 wt% other (Fe_2O_3, $CuSO_4$, or $MnCO_3$) and 98 wt% synthetic deposit, and b) mixtures of synthetic deposit and 280 ppm Si, 105 ppm Fe, 60 ppm Cu, and 420 ppm Mn after being heated at 750°C for 30 min in air.

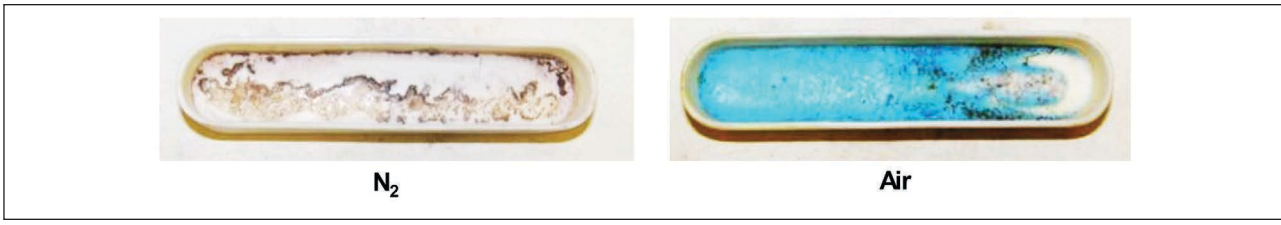
13. Appearance of pure Na_2CO_3 or Na_2SO_4 mixed with 1 wt% $MnCO_3$ after being heated at 920°C for 30 min in air.

cium are not contributing to the blue color. The sample doped with iron turned brownish. The samples doped with silicon, manganese, and copper became light blue, dark blue, and black, respectively.

Tests were also carried out to examine the combined effect of copper, iron, manganese, and silicon by adding 1 wt% SiO_2 and 1 wt% of another chemical to the synthetic deposit (**Fig. 12a**) and the combined effect of copper, iron, manganese, and silicon at a much smaller dosage (Fig. 12b). The absence of blue color in samples containing no $MnCO_3$ and the brilliant blue coloration of the samples containing $MnCO_3$ clearly suggest that manganese is the main element causing the blue coloration of the synthetic deposit.

Deposit major components

Although manganese has been singled out as the main culprit of the blue coloration, it is not clear which major components in the deposit manganese associates with to make the deposit blue. Tests were therefore performed on mixtures of 1 wt% $MnCO_3$ and 99 wt% individual major components. The results show that of the four major components, Na_2SO_4, Na_2CO_3, NaCl, and KCl, only Na_2CO_3 doped with 1 wt%



14. Effect of gas atmosphere on the color of synthetic deposit containing 1 wt% insolubles after being heated at 750°C for 30 min in N_2 and air.

$MnCO_3$ turned blue after it was heat-treated at 920°C for 30 min in air (**Fig. 13**). The appearance of NaCl and KCl doped with 1 wt% $MnCO_3$ after heat treatment was similar to that of Na_2SO_4. No blue coloration was observed.

Effect of gas atmosphere

As discussed, pink carryover deposits gradually become grey as they oxidize. In this study, tests were performed to examine if and how the gas atmosphere affects blue coloration. **Figure 14** shows the appearance of the synthetic deposit mixed with 1 wt% insolubles obtained from mill A ash after being heat treated at 750°C for 30 min in air (oxidizing atmosphere) and in N_2 (neutral atmosphere). Only the mixture heated in air turned blue. The results imply that the blue coloration can only occur in an oxidizing environment.

Table II summarizes the results of tests performed on synthetic deposits and pure chemicals. The blue coloration appears to occur on samples that contain Na_2CO_3 and manganese and that have been molten in an oxidizing atmosphere.

CONCLUSIONS AND IMPLICATIONS

This study systematically analyzed the composition of recovery boiler deposits and precipitator ash samples obtained from kraft pulp mills and investigated the main components in the

Base Material	Additives (weight basis)	Gas	Color
Synthetic deposit	1% insolubles with char	Air	Blue
Synthetic deposit	1% insolubles without char	Air	Blue
Synthetic deposit	1% $MgCO_3$	Air	White
Synthetic deposit	1% CaO	Air	White
Synthetic deposit	1% SiO_2	Air	Slight blue
Synthetic deposit	1% $MnCO_3$	Air	Dark blue
Synthetic deposit	1% $MnCO_3$	Nitrogen	White
Synthetic deposit	1% Fe_2O_3	Air	Grey
Synthetic deposit	1% $CuSO_4$	Air	White/black spots
Synthetic deposit	1% SiO_2 + 1% Fe_2O_3	Air	Brownish
Synthetic deposit	1% SiO_2 + 1% $CuSO_4$	Air	White/black spots
Synthetic deposit	1% SiO_2 + 1% $MnCO_3$	Air	Blue
Synthetic deposit	0.060% SiO_2 + 0.015% Fe_2O_3 + 0.015% $CuSO_4$	Air	White
Synthetic deposit	0.060% SiO_2 + 0.015% Fe_2O_3 + 0.015% $CuSO_4$ + 0.088% $MnCO_3$	Air	Blue
Na_2SO_4	1% $MnCO_3$	Air	White
Na_2CO_3	1% $MnCO_3$	Air	Blue
Na_2SO_4	1% insolubles with char	Air	Grey
Na_2CO_3	1% insolubles with char	Air	Blue
NaCl	1% insolubles with char	Air	Grey
KCl	1% insolubles with char	Air	Grey

II. Colors of deposits after heat treatment.

deposits that make them blue. The results show that for a deposit to become blue, it must 1) contain Na_2CO_3 and a small amount of manganese, and 2) have been molten or partially molten in an oxidizing atmosphere.

The first requirement is always met; deposits contain more than sufficient amounts of Na_2CO_3 and manganese to make them blue. The second requirement implies that blue deposits can form only in the superheater region of the recovery boiler where the flue gas temperature is high enough for them to melt, and during the time when oxidizing conditions prevail. This means that blue deposits are more likely to form in boilers operating at a reduced firing load with a high excess O_2 target. The finding is consistent with the experience at mill E, where blue deposits were observed during the time when the boiler was operated at a reduced load.

Because blue deposits have the same chemical composition as normal pink or white deposits, they should have the same thermal property as normal deposits, and thus should be treated as such. The blue coloration, however, might suggest that the environment around such deposits was oxidizing. **TJ**

ABOUT THE AUTHORS

We chose this topic to research because blue deposits have been occasionally observed in recovery boilers, but what makes them blue and what impact they may have on boiler operation were not known.

Mao

This research compliments previous research by our group and other groups. The focus, however, is only on the mechanism of blue coloration.

The most difficult aspect of this research was to decide where to start the investigation. We addressed that by systematically conducting experiments to identify the main causes of blue coloration through process of elimination.

Tran

Temperature and gas atmosphere can dramatically change the deposit color. The most interesting finding was that at high temperatures and under an oxidizing condition, deposits will all turn blue.

Mills may use the information to indirectly determine the environment prevailing in the recovery boiler.

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ACKNOWLEDGEMENTS

This work was conducted as part of the research program on "Increasing Energy and Chemical Recovery Efficiency in the Kraft Process – III," jointly supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and a consortium of the following companies: Andritz, AV Nackawic, Babcock & Wilcox, Boise, Carter Holt Harvey, Celulose Nipo-Brasileira, Clyde-Bergemann, DMI Peace River Pulp, Eldorado, ERCO Worldwide, Fibria, FPInnovations, International Paper, Irving Pulp & Paper, Kiln Flame Systems, Klabin, WestRock, StoraEnso Research, Suzano, Tembec, Tolko Industries, and Valmet. The authors also thank numerous kraft pulp mills and equipment suppliers for sending us deposit and ash samples, blue or otherwise.

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