Effects of SO_2 on superheater fouling in kraft recovery boilers

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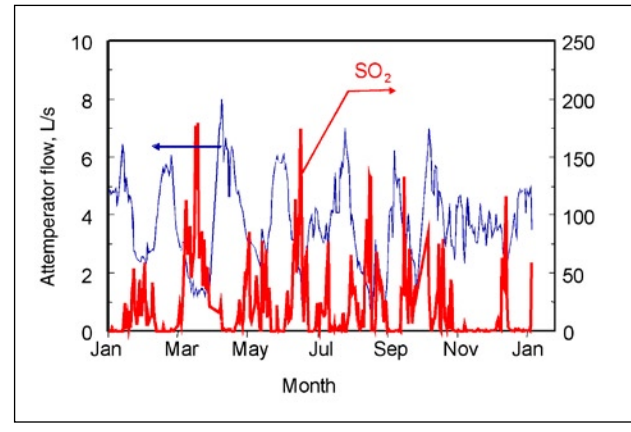
ABSTRACT: Researchers used an entrained flow reactor (EFR) to examine the effect of SO_2 concentration in combustion gas on the deposition rate, composition, and adhesion strength of carryover deposits produced from burning dried black liquor. The results indicate that SO_2 is not the main cause of fouling in the superheater region of recovery boilers. High SO_2 may even be beneficial, as it helps produce deposits more easily removed by sootblowers. In recovery boilers where high SO_2 and excessive carryover fouling are observed at the same time, it is likely that they are a result of other boiler operating factors.

Application: When excessive fouling occurs in the recovery boiler, mills may look for causes other than SO_2.

In some recovery boilers, rapid deposit accumulation in the superheater region has been observed when the concentration of sulfur dioxide (SO_2) in the flue gas was high. An example of this is shown in **Fig. 1**. The attemperator flow in a recovery boiler, which is often used as an indication of superheater fouling, correlates well with SO_2 emissions from the boiler stack. The phenomenon has led to a general belief that a high SO_2 concentration in the flue gas is a cause of superheater fouling [1]. A possible explanation for this is that the carbonates (Na_2CO_3, K_2CO_3) and, to a much lesser extent, the chlorides (NaCl, KCl) in the deposit react with SO_2 and O_2 in the flue gas to form sulfates (Na_2SO_4, K_2SO_4) [2,3,4], which may make a deposit harder and more resistant to sootblowing; i.e: $Na_2CO_3 + SO_2 + ½\ O_2 = Na_2SO_4 + CO_2$ (Reaction 1).

However, it has also often been observed that during an upset in the lower furnace, high SO_2 emissions from recovery boilers often coincided with high carryover, which is the main cause of rapid deposit accumulation on superheater tubes. For instance, when there is a large char bed build-up in the lower furnace, the bed temperature is usually low, resulting in high SO_2 emissions. The high bed problem is usually rectified by increasing the primary/secondary air flow to burn off the bed, and/or by increasing the liquor firing temperature to produce finer sprays. These remedial actions inevitably lead to increased entrainment of carryover particles, and hence, increased superheater fouling. Thus, the high SO_2 concentration in the flue gas in this case is not the cause of fouling. Rather, it and the high carryover (fouling) are a result of other boiler operating factors, which may be low bed temperatures, high air flow rates, and high liquor firing temperatures.

These two explanations of recovery boiler fouling behavior involving SO_2 need further investigation to establish which is a better description of field observations. We identified as a key step in this investigation a systematic study to examine whether SO_2 has an effect on fouling. This was the main objective of the M.A.Sc. thesis research project of Brown [5]. In this paper we discuss the key findings of Brown's thesis work, and the implications of the results.

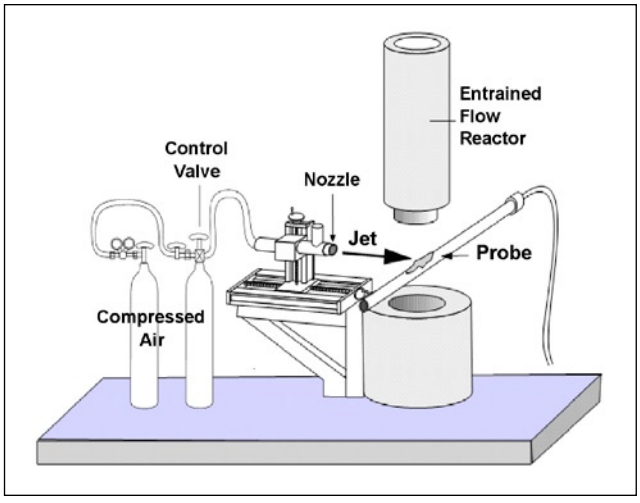


1. Correlation between attemperator flow of a recovery boiler and SO_2 emissions.

EXPERIMENTS

We carried out experiments in an entrained flow reactor (EFR) to determine the deposition rate, composition, and adhesion strength of carryover deposits produced by burning dried black liquor with various SO_2 concentrations in the flue gas. **Figure 2** shows the experimental setup, which coupled the EFR with a jet blow-off apparatus.

Fired black liquor from a kraft pulp mill was completely dried at 130°C (266°F) in an oven, and then cooled, ground, and sieved into the following size ranges: 150-300 µm, 300-425 µm, 425-600 µm and 600-710 µm. For each test, we fed 100 grams of dried black liquor particles at 10 g/min into the EFR from the top. We introduced a 90% N_2-10% SO_2 gas mixture into the EFR at an appropriate flow rate to produce the desired SO_2 concentration. We placed an air-cooled probe, made from stainless steel 304 tubing with an outside diameter



2. EFR coupled with an air jet blow-off apparatus.

of 2.5 cm, horizontally at the EFR exit to collect the carryover particles. The probe surface temperature was controlled at 500°C (930°F). The EFR was controlled at 800°C (1470°F) with a gas exit velocity of about 1.8 m/s. The SO_2 concentration in the EFR atmosphere was varied between 0 and 1200 ppm, and was monitored using a gas analyzer.

We monitored the deposition rate of the carryover particles continuously, using an electromagnetic balance. We determined the adhesion strength of the carryover deposits collected on the probe surface by using the air jet blow-off apparatus mounted beside the probe. Compressed air passed through a brass nozzle with an exit diameter of 7.35 mm to produce an air jet that simulates the fully expanded sootblower jets in a recovery boiler. The air pressure at the nozzle inlet was 5.5 MPa. The peak impact pressure (PIP) of the jet was predetermined, using a Pitot tube, as a function of distance from the nozzle.

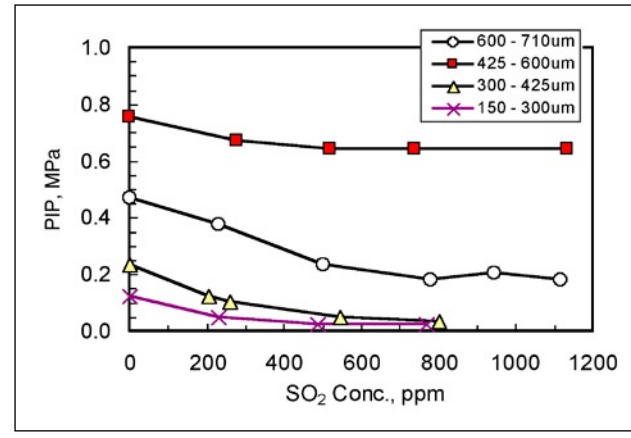
Once the deposit had been collected, we rotated the probe 90° so that the deposit was perpendicular to the nozzle axis while it was still enveloped by the hot flue gas from the EFR. The probe was anchored rigidly to prevent it from moving when blasted by the jet. A blow was then initiated by turning the air valve on for one second. We examined the appearance of the deposit after each blow for any signs of deposit removal. If there was no indication of deposit removal, we moved the nozzle closer to the deposit to increase the PIP. The blowing process was repeated until a piece of deposit was removed from the probe surface. Using the relationship between the PIP value and distance, the minimum PIP required to remove the deposit was determined, and used as an indication of the adhesion strength of the deposit.

Chemical analysis of the deposit obtained from each test was performed to examine how the deposit composition changed with SO_2 concentration.

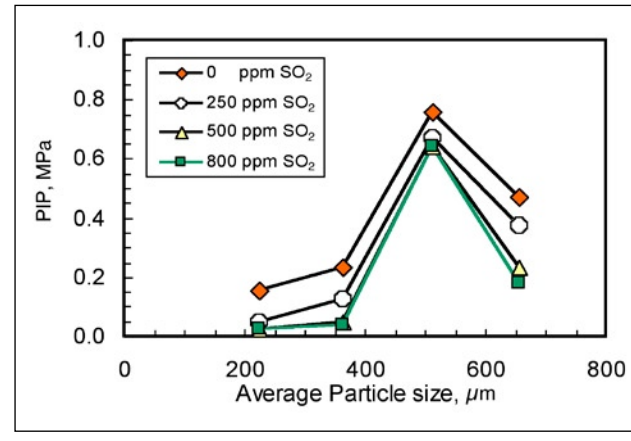
RESULTS AND DISCUSSION

Effect of SO_2 on deposit adhesion strength

Figure 3 shows the effect of SO_2 concentration in the flue gas on the minimum PIP required to remove the deposit produced by burning dried black liquor particles of different sizes in the EFR. For all particle size ranges examined, the results were consistent, showing a decrease in PIP with an increase in SO_2 concentration. This implies that the presence of SO_2 in the flue gas would make deposits easier to remove.



3. Effect of SO_2 concentrations on PIP for deposits produced by burning dried black liquor particles of different sizes.

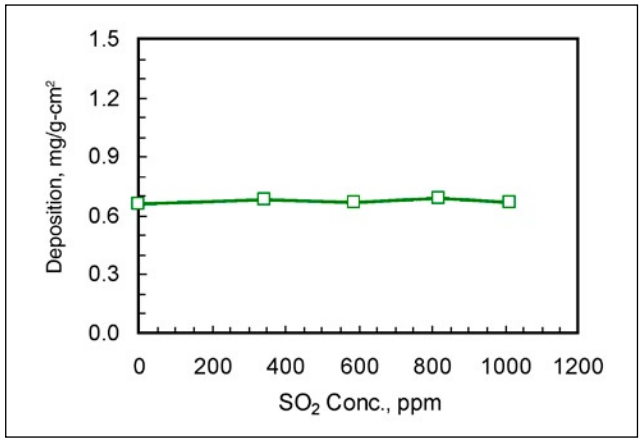


4. Effect of dried black liquor particle size on PIP required to remove deposits in different SO_2 concentrations.

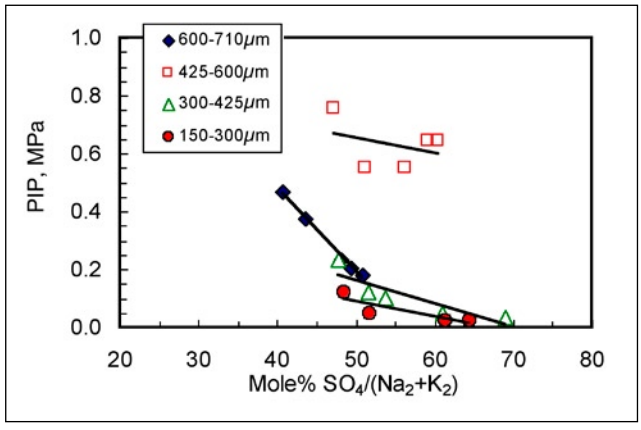
The effect of dried black liquor particle size on PIP at various SO_2 concentrations is shown in **Fig. 4**. At a given SO_2 concentration, increasing the particle size up to 425-600 μm resulted in a significant increase in the minimum PIP required to remove the deposit. However, the PIP requirement decreased for larger particles, 600-710 μm. A possible explanation of this trend is that larger particles cool much more slowly than smaller particles before striking the probe, and consequently, they deposit at a higher temperature, contain more liquid phase, and are more tenacious than smaller particles. However, since large particles require more time to burn, 600-710 μm particles could not completely burn before they exited the EFR. As a result, they contained more char and formed deposits that were less tenacious, requiring a lower PIP to remove them.

Effect of SO_2 on deposition rate and deposit composition

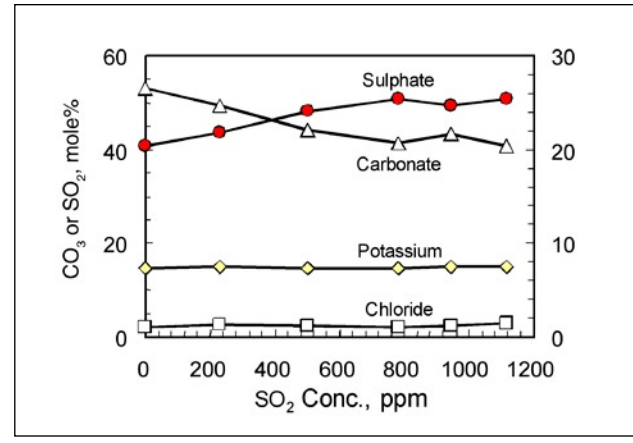
Figure 5 shows that SO_2 had no appreciable effect on the amount of deposits formed from burning 425--600 μm dried



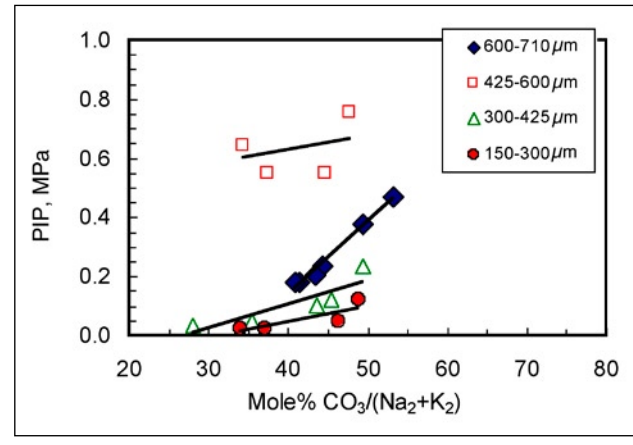
5. Effect of SO_2 concentration on deposition. Particle size 425 to 600 µm, probe surface temperature 500°C.



7. Effect of sulfate content on the minimum PIP for various particle size ranges.



6. Effect of SO_2 on sulfate, carbonate, potassium, and chloride contents of deposits produced by burning 600-710 µm dried black liquor particles.



8. Effect of carbonate content on minimum PIP for various particle size ranges.

black liquor particles. Similar results were also obtained for other particle sizes. The results are not surprising, since increasing the SO_2 concentration would affect only the carbonate and sulfate contents of deposits, and the potassium and chloride contents remain the same (**Fig. 6**). Hence, the deposition tendency of the particles would remain unchanged.

The composition is expressed in terms of mole%, i.e: mole% Cl/(Na+K) for chloride, mole% K/(Na+K) for potassium, mole% $CO_3/(Na_2+K_2)$ for carbonate, mole% $SO_4/(Na_2+K_2)$ for sulfate, and mole% $S_2/(Na_2+K_2)$ for sulfite. Figure 6 shows the effect of SO_2 on the composition of deposits produced by burning 600–710 µm dried black liquor particles. We observed no significant difference in chloride and potassium contents with an increase in SO_2 concentration. However, the sulfate content of the deposits increased from 40 mole% to about 50 mole% $SO_4/(Na_2+K_2)$ as the SO_2 concentration increased from 0 ppm to 800 ppm. The carbonate content changed in the opposite direction, decreasing with an increase in SO_2 concentration by about the same amount gained by the sulfate. This suggests that increase in sulfate content was due mainly to the sulfation reaction between carbonate, SO_2 and O_2 (Reaction 1).

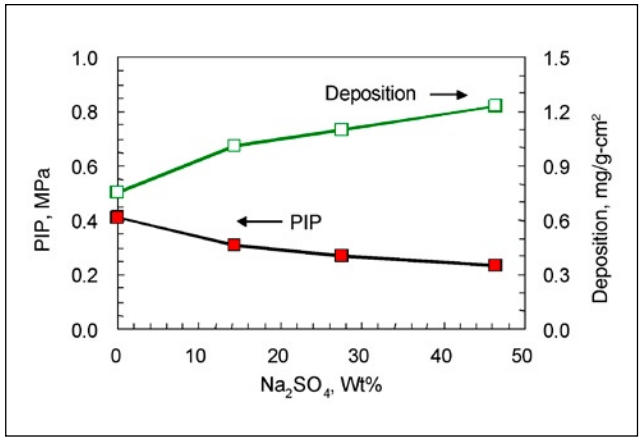
Deposit composition vs. PIP

Figure 7 shows the correlation between the minimum PIP required to remove the deposits and the sulfate content of the deposits produced from burning dried black liquor of different particle size ranges. For each particle size range, the difference in sulfate content was due to the deposits being produced at different SO_2 concentrations.

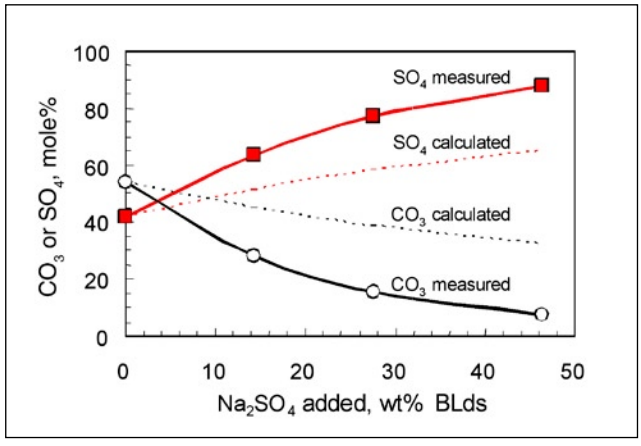
The results show that deposits with higher sulfate contents are easier to remove, as they require a lower PIP. Conversely, deposits with higher carbonate contents are more difficult to remove, as they require a higher PIP (**Fig. 8**). This confirms results of an earlier study using synthetic carryover deposits [6], which showed that deposits with a high carbonate content are more difficult to remove than deposits with a low carbonate content.

Effect of adding Na_2SO_4 to black liquor

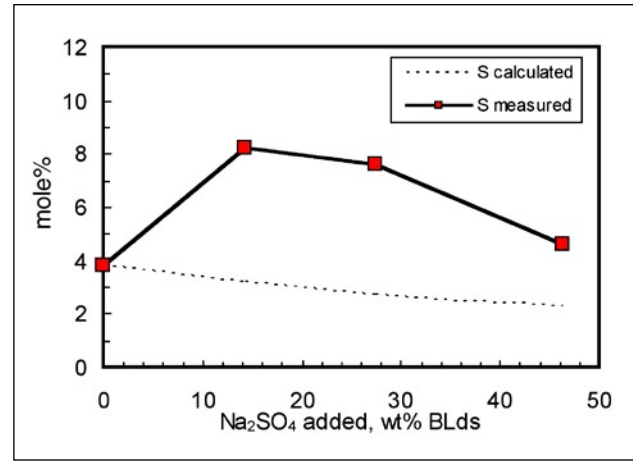
In the previous experiments, the sulfate in the deposits was formed in situ, and we altered its content by changing the SO_2 concentration in the EFR. It is not known whether the effect on PIP would be the same if the sulfate originated from make-up salt cake or from recycled precipitator ash. In this study we examined the effect of added sulfate by adding various amounts of pure Na_2SO_4 to the original black liquor. The ex-



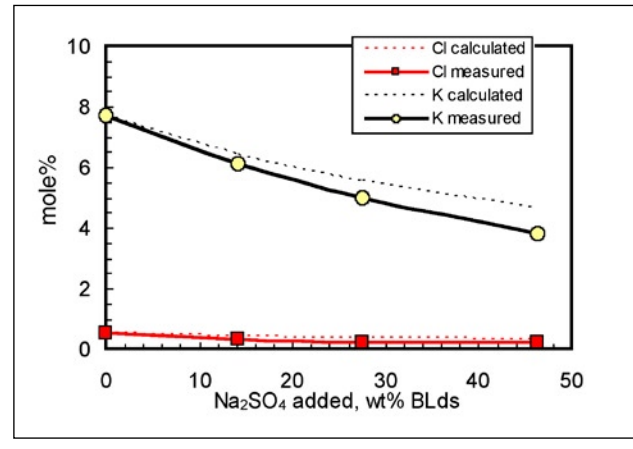
9. Effect of Na_2SO_4 content on the PIP and deposition. Particle size 600-710 µm.



10. Change in sulfate and carbonate content of deposits as a result of Na_2SO_4 addition to black liquor. Particle size 600-710 µm.



11. Change in sulfite content of deposits as a result of Na_2SO_4 addition to black liquor. Particle size 600-710 µm.



12. Change in chloride and potassium contents of deposits as a result of Na_2SO_4 addition to black liquor. Particle size 600-710 µm.

perimental procedure was the same as in the previous case, except that tests were carried out with no SO_2 injection, and only 600-710 µm dried black liquor particles were used.

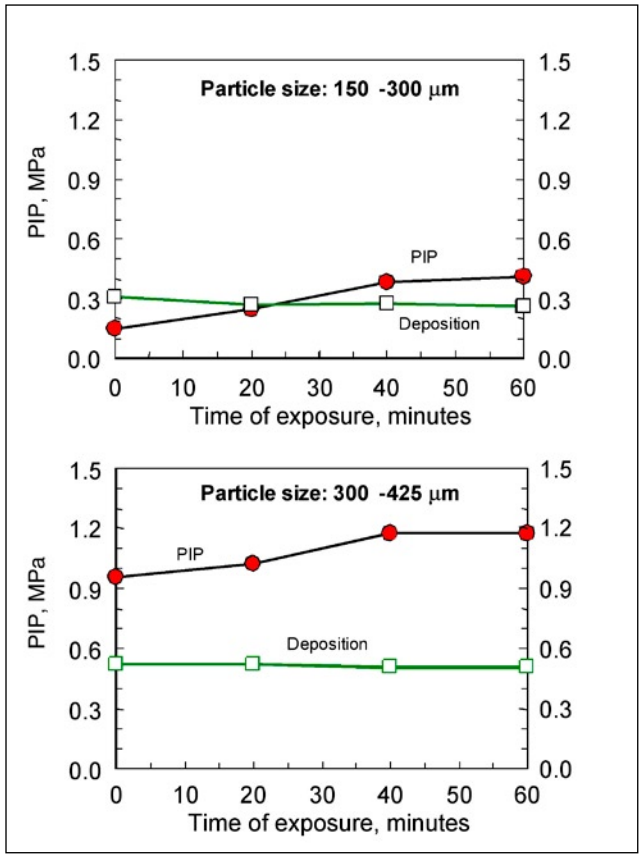
As shown in **Fig. 9**, the amount of carry-over deposition increased as the amount of Na_2SO_4 added to the black liquor increased. This is likely due to the increase in ash content of the black liquor as a result of Na_2SO_4 addition. The deposits, however, were weaker, having a PIP value which decreased with an increase in Na_2SO_4 addition. This is consistent with the results obtained with SO_2 injection (Fig. 7).

Figure 10 shows the sulfate and carbonate contents in deposits as a function of Na_2SO_4 addition. The sulfate content increased markedly from about 42 mole% $SO_4/(Na_2+K_2)$ with no Na_2SO_4 to 88 mole% $SO_4/(Na_2+K_2)$ with 46 wt% Na_2SO_4 added to the dried black liquor. The carbonate content changed in the opposite direction, decreasing from 54 mole% $CO_3/(Na_2+K_2)$ to 7.4 mole% $CO_3/(Na_2+K_2)$ for the same amount of Na_2SO_4 added.

The sulfate and carbonate contents can also be calculated as a function of Na_2SO_4 addition, by assuming that the Na_2SO_4 was well mixed with the dried black liquor and that there was no interaction between the added Na_2SO_4 and the black liquor during the combustion. As shown in Fig. 10 (broken curves), the calculated sulfate and carbonate contents, respectively, were lower and higher than the experimental data. The discrepancy was greater as more Na_2SO4 was added.

The results are puzzling, since they cannot explain the origin of the extra sulfate. If the added Na_2SO_4 did react with the black liquor during the combustion, the results should have been the other way around. Adding Na_2SO_4 would have lowered the black liquor heating value, making it burn at a lower temperature. This, in turn, would have caused more sulfur to be released from the burning particles, and less sulfur to be retained in the carryover. As a result, the experimental values should have been lower in sulfate and higher in carbonate than the calculated values. The only explanation we deemed likely for the opposite results obtained in this study is that the added Na_2SO_4 preferentially deposited on the probe, making the sulfate content higher (carbonate content lower) than expected.

Figure 11 shows the sulfite content as a function of Na_2SO_4 addition. Despite the possible lower burning particle temperature caused by the lowered heating value, the sulfite content in the deposits increased with an increase in Na_2SO_4



13. Effect of time of exposure of deposit to the flue gas without SO_2 on the PIP of the deposits, particle sizes: 150-300 µm and 300-425 µm.

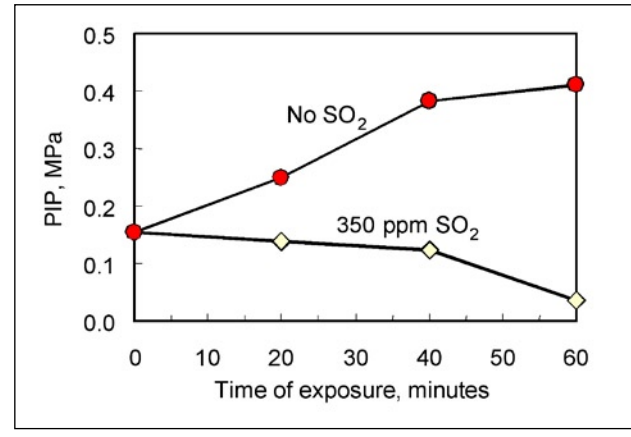
addition up to 30 wt% Na_2SO_4. The results clearly suggest that the added Na_2SO_4 was partially reduced to Na_2S. At a higher amount of Na_2SO_4 addition, the Na_2S content decreased, presumably due to a lower rate of sulfate-to-sulfite reduction caused by a low temperature of the burning particles.

Both chloride and potassium contents in the deposits decreased with an increase in Na_2SO_4 addition (**Fig.12**). This was due to the dilution effect and possibly the preferential deposition of the added Na_2SO_4.

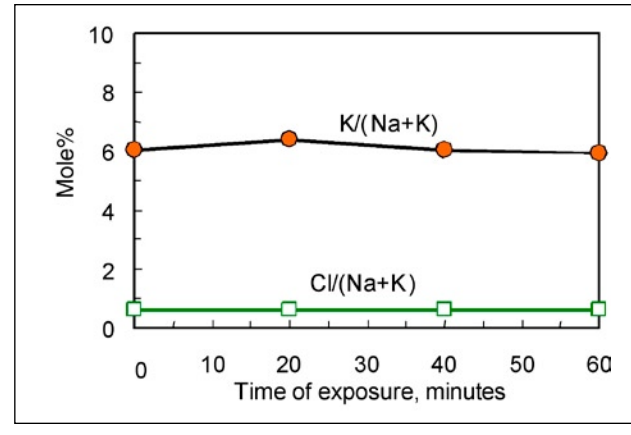
Effect of thermal sintering

Carryover deposits in the superheater region of recovery boilers are constantly exposed to hot flue gases that contain H_2O vapor, O_2 and some SO_2. Upon deposition, deposits consolidate and become stronger with time due to thermal sintering. In this study, the effect of thermal sintering in the hot flue gas, with and without the presence of 350 ppm SO_2, on the deposit adhesion strength was examined. The experimental procedure was similar to that described earlier, except that only 150-300 µm and 300-425 µm size ranges of dried black liquor particles were used.

After the deposits had been collected on the probe, they were exposed further to the hot gas produced by burning natural gas in the combustion chamber at the top of the EFR. The gas contained mainly O_2, N_2, CO_2 and H_2O, and had an average temperature of about 590°C near the probe surface. The exposure time was varied from 20 to 60 minutes. After



14. Effect of time of exposure of deposit to the flue gas with SO_2 on the PIP of the deposits, particle size 150-300 µm.



15. Effect of time of exposure to the chloride and potassium contents of deposits formed from 150-300 µm particle size in 350 ppm SO2.

each exposure, the minimum PIP required to remove the deposit was determined. In order to examine the effect of SO_2, a 90% N_2-10% SO_2 gas mixture was introduced into the EFR during the exposure time, to produce a 350 ppm SO_2 gas atmosphere near the probe.

Effect on deposition and removal

Figure 13 shows the effect of exposure time, with no SO_2, on the deposition rate of the deposits produced from burning 150-300 µm and 300-425µm dried black liquor particles, and on the minimum PIP required to remove the deposits. Larger size ranges were not examined in this study due to an inadequate amount of black liquor sample. For these size ranges, the deposition did not change, while the PIP value increased with time. **Figure 14** shows a comparison of PIP values of the deposits produced from burning 150-300 µm dried black liquor particles, and exposed for different times with no SO_2 and with 350 ppm SO_2. The results clearly show that in the presence of SO_2, the PIP or the deposit adhesion strength decreased with time of exposure. A possible explanation for the lowered PIP value is that the CO_2 released as the result of sulphation of carbonate (Reaction 1) may disrupt the inter-par-

ticle bonding and make the deposit weaker.

Effect on deposit composition

Both chloride and potassium contents remained unchanged at 0.6 mole% Cl/(Na+K) and 6.4 mole% K/(Na+K) respectively after the deposits had been exposed to a 350 ppm SO_2 gas atmosphere for up to 1 hour (**Fig. 15**). The increase in sulfate content and the corresponding decrease in carbonate content suggest that the sulfation of carbonate occurred after deposition (**Fig. 16**).

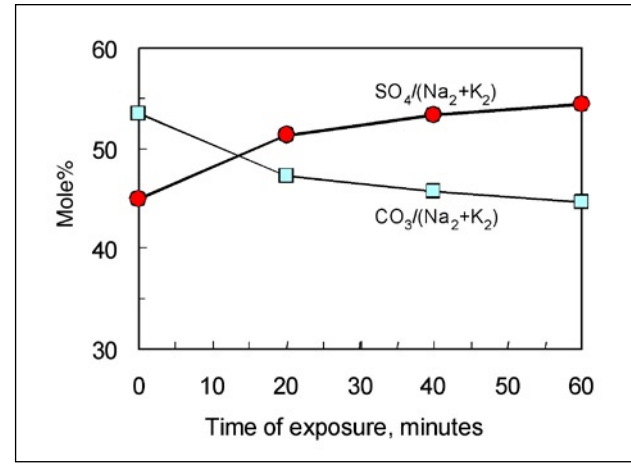
IMPLICATIONS

Results of this study show that by increasing the SO_2 concentration in the flue gas, or by adding Na_2SO_4 in the black liquor, carryover deposits contain more sulfate and less carbonate. This must have an effect on the deposit sticky temperature.

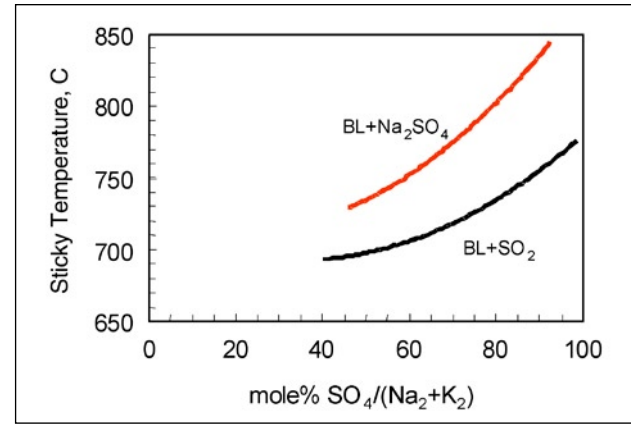
Using Meltcalc, a deposit melting temperature calculator jointly developed by our group at the University of Toronto and Dr. Mikko Hupa's group at Åbo Akademi University in Finland, it is possible to calculate the sticky temperatures of deposits produced in this study, as a function of sulfate contents. As shown in **Fig. 17**, in both cases (burning black liquor in a high SO_2 atmosphere, and burning black liquor mixed with Na_2SO_4), the calculated sticky temperature increases with an increase in sulfate content, suggesting that deposits are less sticky or less tenacious, and hence, more likely to be removed by a sootblower. The high sticky temperature obtained for the case of black liquor mixed with Na_2SO_4 compared to the other case is due to the lowered Cl and K contents of the deposits caused by a dilution effect. The increase in sticky temperature as a result of increased sulfate content makes deposits adhere less tenaciously to the tube surface, and thus, a lower sootblower PIP is required to remove them.

The increase in sticky temperature should have resulted in a lower deposition rate, particularly in tests where dried black liquor was burned in the EFR with a high SO_2 concentration in the gas. However, the results show no change in deposition with increased SO_2 (Fig. 5). This was probably because in these tests, carryover particles were at a higher temperature than the sticky temperature at the moment they struck the probe. The decrease in PIP value with an increase in SO_2 in these tests implies that the minimum amount of liquid phase needed to make deposits sticky (15% to 20%) is likely smaller than that required to make deposits difficult to remove.

The SO_2 concentration in the flue gas is usually higher for boilers that operate at a low bed temperature, as well as for boilers with a high sulfur input, i.e., boilers that burn black liquor with high-solidity, or black liquor with a large amount of make-up saltcake/recycled precipitator ash, or elemental sulfur as makeup sulfur, or non-condensable gases (NCG). The results imply that for such boilers, carryover deposits in the superheater region may contain more sulfate, less carbonate, and thus, be easier to be removed by sootblowers, if they contain the same levels of chloride, potassium, and sulfite.



16. Effect of time of exposure on the carbonate and sulfate contents of deposits formed from 150-300 µm particle size.



17. Effect of sulfate content on calculated sticky temperatures of deposits formed from burning 600-710 µm dried black liquor particles mixed with Na_2SO_4 or in various SO_2 concentrations in the EFR.

It is important to point out that in boilers that burn high-sulfidity black liquor, the carryover particles in the superheater region usually also contain more sulfite than in boilers that burn low-sulfidity black liquor. The resulting carryover deposits will likely be stickier and more difficult to be removed by sootblowers. Such an effect of high-sulfidity on superheater fouling is caused by high sulfite content in carryover, not by high SO_2 concentration in the flue gas.

The results imply that high SO_2 is not a direct cause of fouling in the superheater region of recovery boilers. It may even be beneficial, as it helps facilitate deposit removal in this region. In recovery boilers where both high SO_2 and carryover (fouling) are observed at the same time, it is likely that they are a result of other boiler operating factors.

SUMMARY

We performed a systematic study using an entrained flow reactor (EFR) coupled with a jet blow apparatus to determine how SO_2 may affect the deposition rate, composition, and adhesion strength of carryover deposits produced by burning

dried black liquor. The results show that:

1. Increasing the SO_2 concentration in the flue gas had little effect on the amount of carryover deposited, but made deposits easier to remove.

2. Increasing the SO_2 concentration in the flue gas increased the sulfate content of the deposits at the expense of the carbonate content. However, it had no effect on chloride and potassium contents.

3. Adding Na_2SO_4 to the black liquor increased the deposition and made deposits easier to remove.

4. In the absence of SO_2, thermal sintering made deposits stronger and more resistant to sootblowing with time. However, in a high (350 ppm) SO_2 atmosphere, the sulfation of carbonate had a greater effect than thermal sintering, weakening deposits with time and making them easier to remove.

The results suggest that high SO_2 is not a cause of fouling, and that it may even be beneficial and help facilitate deposit removal in the superheater region.

ACKNOWLEDGEMENTS

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INSIGHTS FROM THE AUTHORS

We were asked by several kraft pulp mills to look into the problems of fouling. The observation of rapid accumulation of deposits in the superheater region when the concentration of sulfur dioxide (SO_2) in the flue gas was high had led to a general belief that the SO_2 was a cause of fouling. However, it has also been observed that during an upset in the lower furnace, high SO_2 emissions often coincided with high carryover, which is the main cause of rapid deposit accumulation on superheater tubes. Thus, the high SO_2 concentration in the flue gas was not necessarily the cause of fouling.

Our research helped to significantly improve the understanding of the role of SO_2 in fouling. The most difficult aspect of our research was simulating the recovery boiler firing environment in the laboratory. Fortunately, we could do it our large-scale entrained flow reactor.

The most interesting and surprising discovery from our findings was that SO_2 actually makes carryover deposit easier to remove. We had thought that it would hinder deposit removal. Mills may now understand that a high level of SO_2 may be related to superheater fouling, but is not the cause of it. High SO_2 may even be beneficial, as it helps to produce deposits that are more easily removed by soot blowers.


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