Understanding low temperature corrosion in Kraft Recovery Boilers – Implications for Increased Energy Recovery

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ABSTRACT

Our measurements in Kraft Recovery boilers, a sodium sulfite boiler and biomass boilers have all shown that there is no sulfuric acid in the stack gases of these boilers. However, hygroscopic salts coat the steel surfaces in boilers. It is absorption of water by these hygroscopic salts that can cause low temperature corrosion. When these salts absorb water, a concentrated salt solution is formed on the surface of the salt. This solution leads to corrosion of the steel surface. In this work we have measured the corrosion of carbon steel coupons under salts, held at different temperatures and different volume % water in the gas. We have tested the salts Na_2SO_4, Na_2CO_3, NaCl, KCl, $NaHSO_4$, salt mixtures and ashes from boilers. By testing at different temperatures and volume% H_2O, we have been able to find a transition from visible corrosion to no visible corrosion. Because corrosion of steel in contact with these electrolyte solutions is quite rapid, we ran corrosion experiments for 4 or 24 hours. The experimental set-up is shown in Figure 1. These results indicate that flue gas temperatures can be lowered significantly without corrosion, resulting in improved efficiency of these boilers.

INTRODUCTION

When black liquor is burned, a significant amount of S is released as reduced sulfur compounds during devolatilization of the black liquor [1]. The reduced sulfur compounds are oxidized to SO_2. It was thought that some of this SO_2 results in the formation of H_2SO_4. Resent measurements have shown that there is no H_2SO_4 in the stacks of kraft recovery boilers [2]. This is because any formed SO_3 or H_2SO_4, will react almost immediately with Na and K to form Na_2SO_4 or K_2SO_4 [unpublished results]. Even in a recovery boiler with high SO_2, such as a sulfite boiler, sodium bisulfate is formed rather than H_2SO_4. The practical implication of this is that the lower limit for the flue gas temperatures is not determined by a sulfuric acid dewpoint. We have hypothesized that the hygroscopic nature of salts sets the temperature where dewpoint corrosion can occur.

Some salts are more hygroscopic than others while mixtures can behave differently than either of the individual salts [3]. One measure of the hygroscopic nature of a salt is the humidity of deliquescence. It is the humidity at a given temperature above which the salt is completely dissolved in the water it absorbs [4]. Sodium carbonate and sodium sulfate have a much lower humidity of deliquescense than for example $NaHSO_4$, Figure 1 [2]. For example, the pure water dewpoint at 20% humidity is 60 °C while the humidity of deliquescence is a few degrees higher for Na_2SO_4, and Na_2CO_3 and about 15 °C higher for $NaHSO_4$.

Yang et al. [5] studied the corrosion of 316 stainless steel under NaCl and KCl in the presences of water vapor. They found that corrosion occurred below the humidity of deliquesence. They termed the humidity at which corrosion occurred to be the critical relative humidity. Thus the salts absorbed some water to which lead to dewpoint corrosion, but not enough water to fully dissolve the salt.

In this work we began mapping the conditions at which corrosion occurred on carbon steel (ST45.8/III) under different sodium salts and salt mixtures as a function of temperature and vol-% H_2O. The objective was to determine at what temperatures no corrosion was seen for salts relevant to precipitator ashes. In addition, 2 precipitator ashes were used.

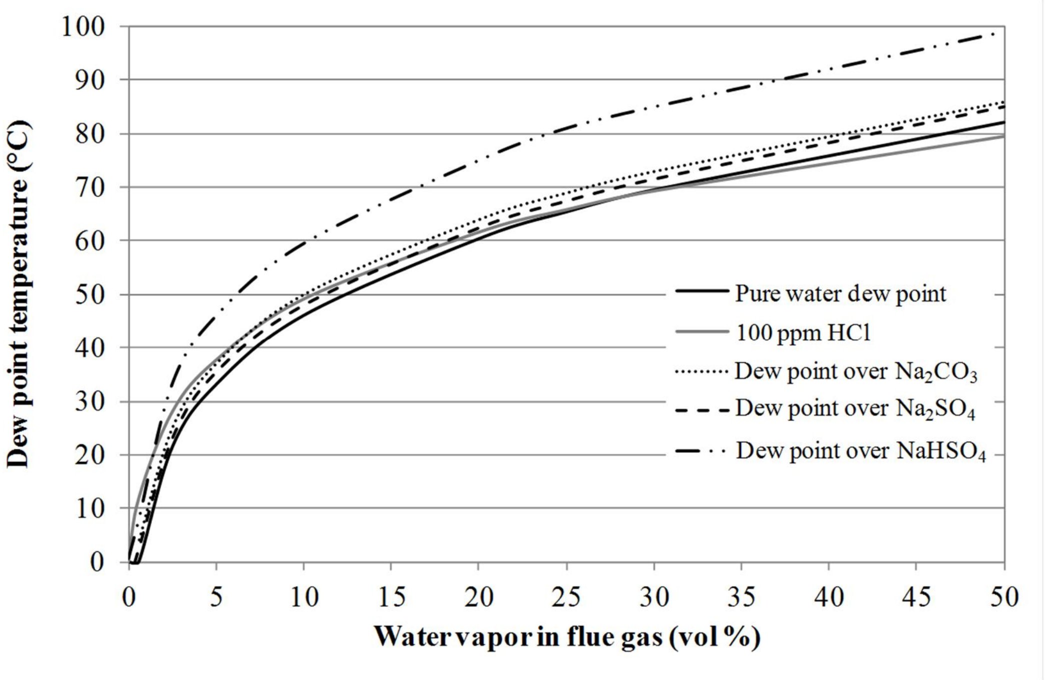

Figure 1. Pure water dew point, and humidity of deliquescence for the hygroscopic salts (Na_2CO_3, Na_2SO_4 and $NaHSO_4$) as a function of water vapor concentration. Adapted from [2].

METHODS

For this work, 100 mg of salt was packed onto a steel surface. The steel used was ST45.8/III, Table 1. Salt mixtures were physically mixed. The precipitator ashes were both taken from the same Nordic mill. Precipitator ash 1 was from the firing of softwood black liquor and the precipitator ash 2 sample was pulled during a hardwood campaign, Table 2. The salt matrix tested is given in Table 3.

The steel coupons were placed on a tray and the temperature at the tray was measured by a thermocouple connected to the tray. The temperature profiles for two runs with NaCl are given in Figure 2. The tray was inserted into the reactor. The reactor was then heated to the test temperature in 100% N_2. Once the reactor temperature was stabilized, the gas composition was changed to the target composition, and the coupons were then held at that temperature for 4 or 24h. While there is a difference in the extent of corrosion between 4 and 24 hours, corrosion was visible after 4 hours, Figure 3.

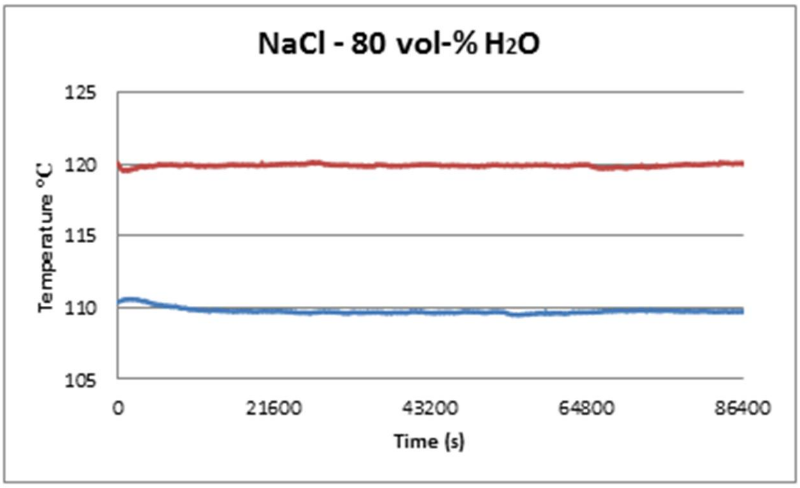

Figure 2. Temperature profiles for the experiments with NaCl at 110°C and 120°C, 24h run with 80 vol% H_2O.

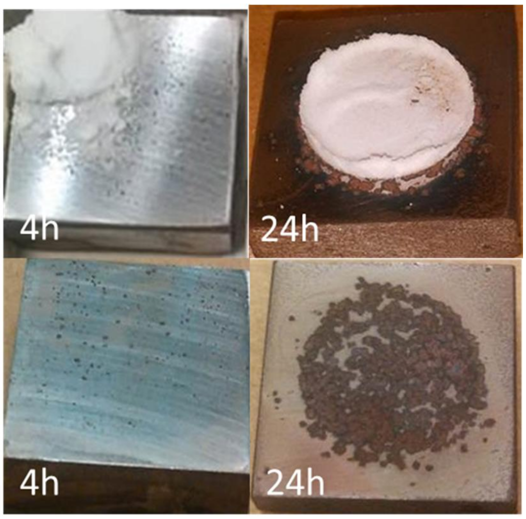

Figure 3. Samples under Na_2SO_4 at 60% H_2O and 100 °C for 4h or 24h.

The experimental set-up is shown in Figure 4. The flow of N_2, O_2 and CO_2 was controlled by mass flow meters. The flow of water was controlled by a peristaltic pump. The flow rate was kept constant at 2 Nl/min so the concentration of N_2, CO_2 and O_2 changed with changes in H_2O. The ratio of N_2, CO_2, O_2 in the gas was 15.5:3.5:1. Steam was generated by pumping water with a peristaltic pump into a thin stainless steel tube that was electrically heated at 200 °C to generate steam. The generated steam was picked up by the dry gases N_2, CO_2 and O_2. These moist gases were carried through a tube wound in the oven to both allow for the equilibration of the gases and to start adjusting the temperature towards the reactor temperature. The humidified gases then passed through another heated tube connecting the tube from the preheater to the oven in which the samples were placed. The back end of the quartz tube in the oven was well insulated to minimize condensation and avoid water flowing back to the samples.

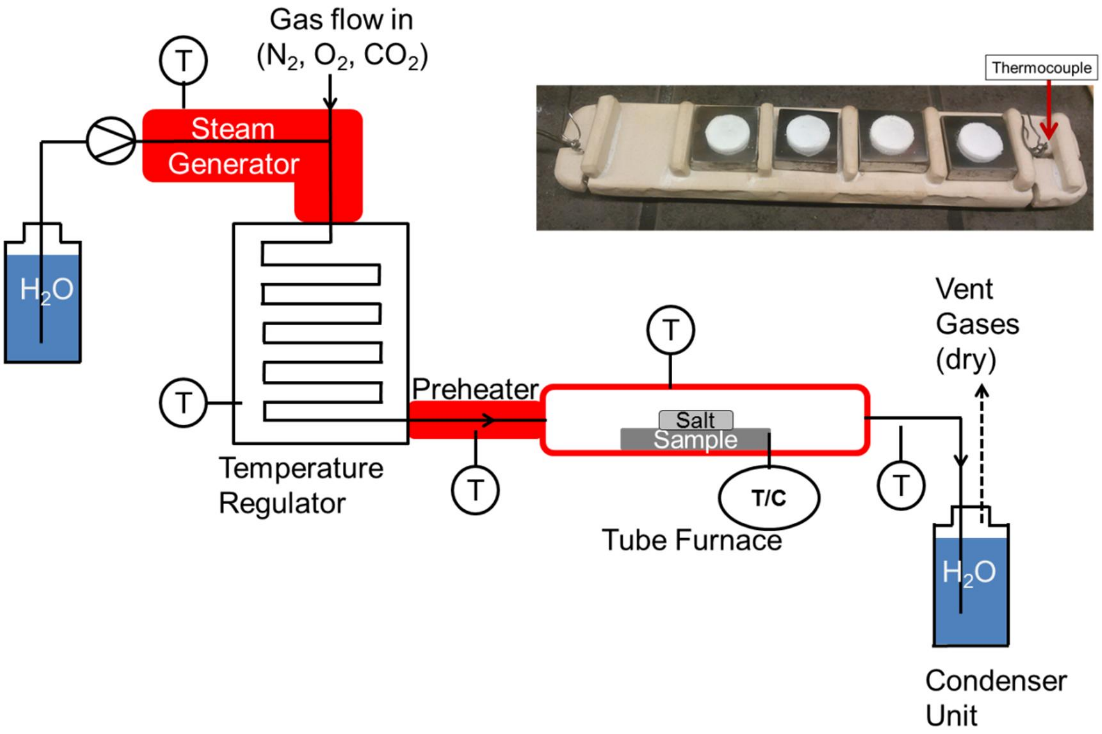

Figure 4. Experimental set-up used in this work.

Table 1. ST45.8/III composition on a C free basis based on SEM-EDX analysis.

Fe (wt-%)	Cr (wt-%)	Mn (wt-%)	Si (wt-%)	Al (wt-%)
98.76	0.12	0.74	0.28	0.09

Table 2. Composition of precipitator ashes used. CO_3 determined as difference.

	Na (wt-%)	K (wt-%)	SO_4 (wt-%)	Cl (wt-%)	CO_3 (wt-%)
PA1	30.3	4.6	58.4	0.9	5.8
PA2	29.8	4.8	61	1	3.6

Table 3. Salts and corrosion conditions.

Salts	H2O (vol-%)	Temp (°C)	Time (h)
Na_2SO_4	27%	80	4
		90	4
	60%	100	4
		100	24
		110	24
Na_2CO_3	80%	90	4
		100	4
		110	24
		120	24
Na_2SO_4-Na_2CO_3 (90:10)	27	80	24
NaCl	80	110	24
		120	24
PA1	27	70	24
		80	24
		90	24
		100	24
		110	24
	60	100	4
		110	4
		120	4
	80	110	24
PA2	27	100	4
		110	4
	60	100	4
		110	4
NaHSO4	0	150	4
	27	80	4
		90	4
	60	120	4
		130	4
		140	4
		150	4

RESULTS

Na_2SO_4. Experiments with Na_2SO_4 were carried out at 27 and 60 vol-% water. At 27 vol-% water, corrosion was visible at 80 °C, but not at 90 °C, Figure 5. At 80 °C, the salt clearly absorbed some water, but not enough to dissolve the salt. At 90 °C, the salt looked as though it might have absorbed some water, but no corrosion was seen. At 27 vol-% H_2O, the deliquescent temperature is about 70 °C. Thus, as with the findings of Yang [2003], deliquescence does not describe the absorption of water by a salt so that it describes the condition at which corrosion occurs. At 60 vol-% water the transition from corrosive to non-corrosive conditions occurs between 100 and 110 °C.

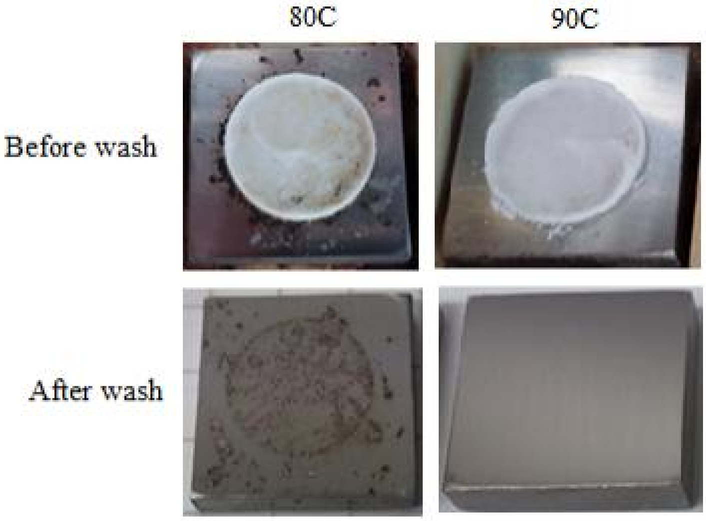

Figure 5. Na_2SO_4 on carbon steel after 4h exposure with 27 vol% H_2O.

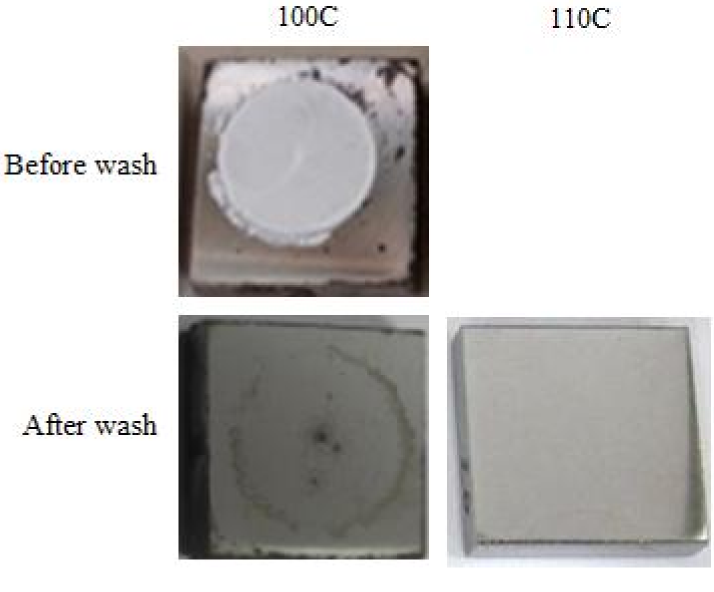

Figure 6. Na_2SO_4 on carbon steel after 24h exposure with 60 vol% H_2O.

Na_2CO_3. Sodium carbonate is more hygroscopic than Na_2SO_4 and so the salt was totally dissolved during the experiment at 90 °C, Figure 7. However, no corrosion was seen in any of the experiments. This is consistent with tests of carbon steel in saturated solutions of sodium carbonate [6].

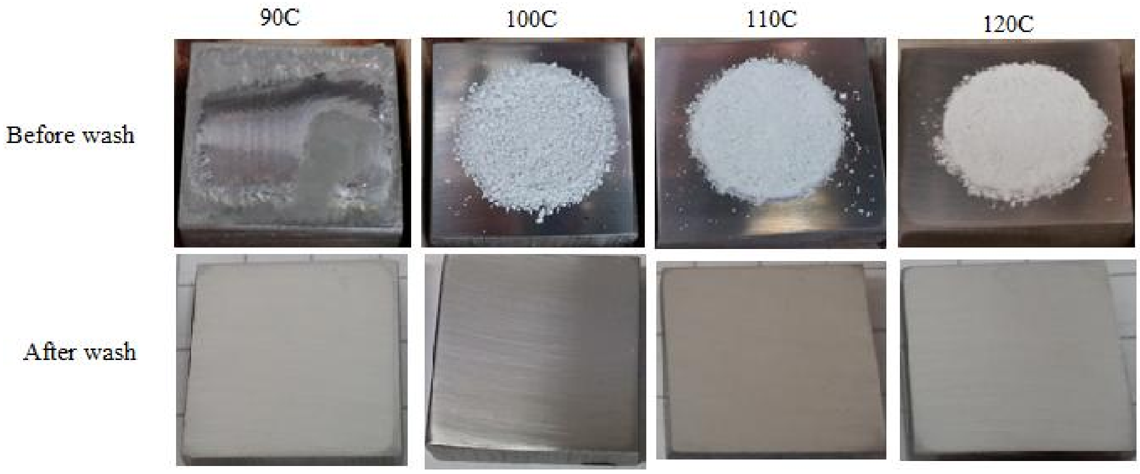

Figure 7. Na_2CO_3 on carbon steel coupons after 4h (90°C and 100°C) and 24h (110°C and 120°C) exposure with 80 vol% H_2O. Sodium carbonate dissolved in absorbed water after 4h exposure at 90°C with 80 vol% H_2O.

NaCl. For NaCl the transition was between 110 and 120 °C for a gas with 80 vol-% H_2O, Figure 8.

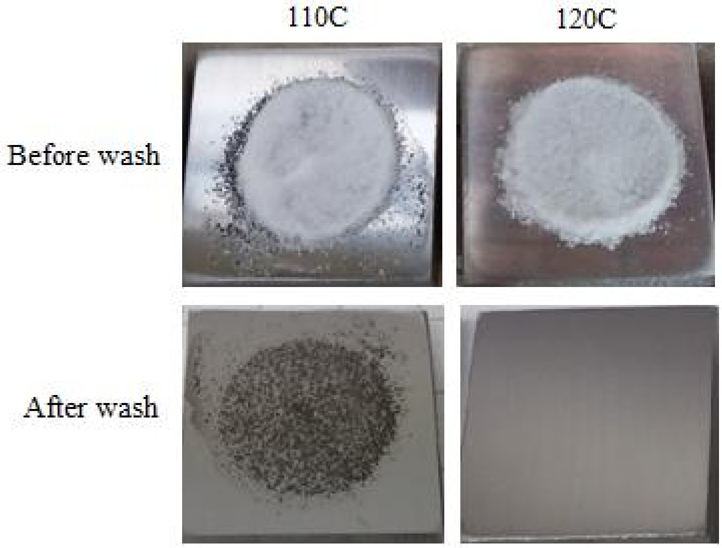

Figure 8. NaCl on carbon steel after 24h exposure with 80 vol% H_2O.

Precipitator Ashes. The corrosion under precipitator ash 1at 27 and 60 vol-% H_2O are shown in Figures 9 and 10 respectively. At 27 vol-% H_2O, the salt is fully dissolved at 70 and 80 °C, while corrosion was seen up to 100 °C, but not at 110 °C. Interestingly, corrosion was mild at 80 C, but extensive at 70 °C. At 80 °C, it appears that the salt was fully dissolve, but not fully washed off of the coupon. The carbonate concentration of the ash was 5.8 %, so the pH of the solution would be slightly over 10 for a saturated solution and this might have led to the observed reduced corrosion compared to the run at 70 °C, where enough water was absorbed that the solution appears to have run off the steel coupon. However, at 90 °C, not enough water was absorbed to dissolve the salt, but corrosion appears to have been more severe than the 80 °C case.

At 60 vol-% water, the transition between observed corrosion and no corrosion occurs between 100 and 110 °C. This is the same as for the case with 27% H_2O. This is in contrast to the runs with Na_2SO_4 where there was a 20 °C difference between 27 and 60 vol-% water. There is some drop in the transition temperature seen when the H_2O is increased to 80 vol-%. Then corrosion was still seen at 110 °C. A run at 120 °C was not made, but given that 2 of the four coupons showed corrosion and 2 did not, it is probable that corrosion would not be seen at 120 °C.

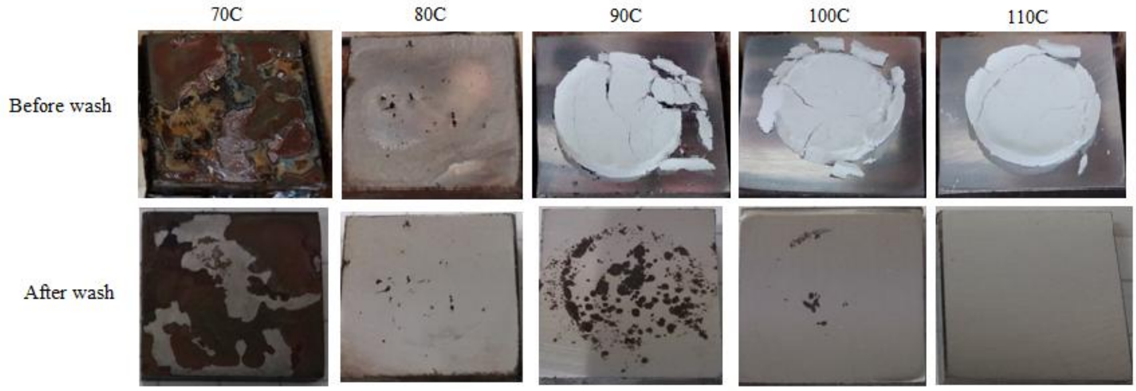

Figure 9. Precipitator ash 1, on carbon steel coupons after 24h exposure at 70°C to 110°C with 27 vol% H_2O. The ash is dissolved in absorbed water at 70°C and 80°C.

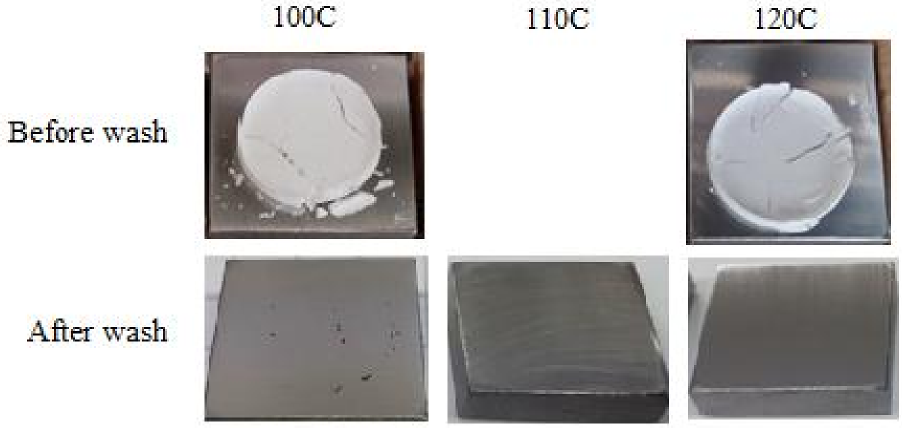

Figure 10. Precipitator ash 1 on carbon steel coupons after 4h exposure at 100°C to 120°C with 60 vol% H_2O.

Figure 11. Precipitator ash 1 on carbon steel coupons after 24h exposure at 110 °C with 80 vol-% H_2O.

Precipitator ash 2 was also run at 27 and 60 vol-% H_2O. At 27 vol-% H_2O, no corrosion was seen at 100 °C and at 60 vol-% H_2O, no corrosion was seen at 110 °C. The results at 60 vol-% H_2O agree with the precipitator ash 1 results while the 27 vol-% H_2O results are different. At 27 vol-% H_2O, corrosion was seen at 100 °C for precipitator ash 1, but not for precipitator ash 2. The reason for this is not clear. One possibility is that the temperature between corrosion occurring and not occurring is close to 100 °C and that a small difference in composition lead to the absorption of some water at 100 °C for precipitator ash 1, but not 2. The temperature of the samples as measured at the tray did not vary from the target temperature by more than 1.5 °C, thus a temperature fluctuation does not seem to be the cause.

$NaHSO_4$. Sodium bisulfate can form when all of the sodium is sulfated and there is an excess of SO_2. Thus older boilers operating at lower dry solids and with high sulfidity could expect the formation of some $NaHSO_4$.

Bisulfate is very hygroscopic. In this work we ran experiments with at 60 vol-% H_2O up to 150 °C and still saw that the salt had at least mostly dissolved and corrosion had occurred, Figure 12.

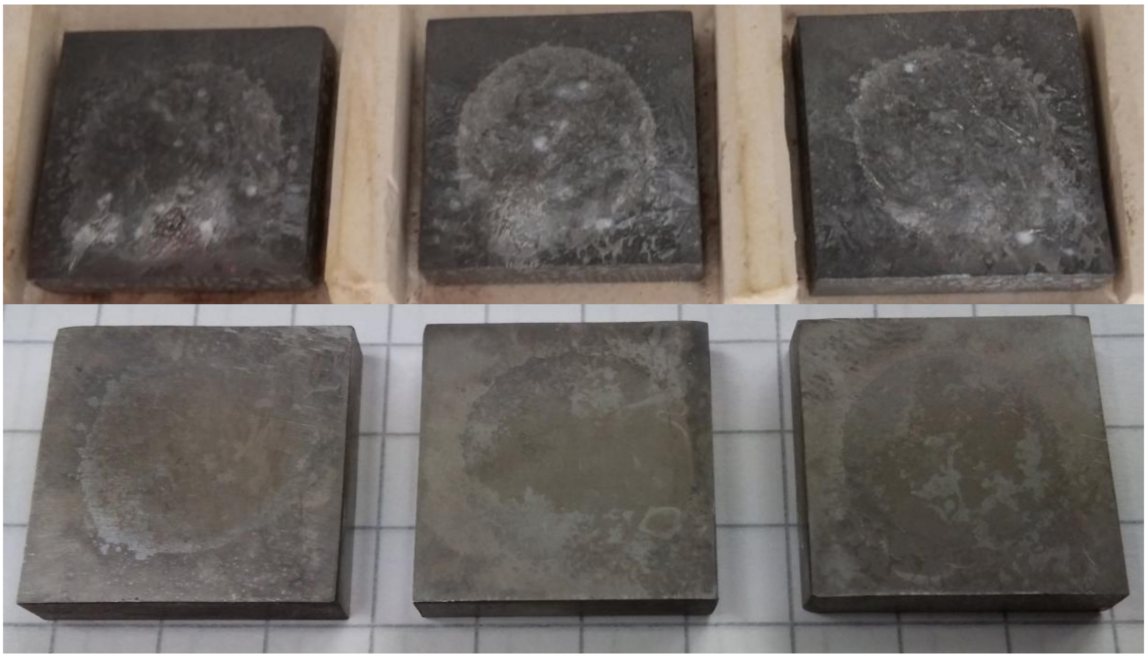

Figure 12. Unwashed coupons above and washed coupons below after 4h exposure to $NaHSO_4$ at 150°C and 60 vol%-H_2O.

CONCLUSIONS

The results of this study support the hypothesis that hygroscopic salts effectively limit the lowest flue gas temperature that can be achieved without dew point corrosion. They also indicate that mills could lower the flue gas temperature closer to 110 °C if the recovery boiler runs hot enough to result in sufficient alkali release that the precipitator ash that has some carbonate in it. This would be a significant improvement in thermal effieciency if the heat can be utilized. If the steel experiences soot blowing or is close to a soot blower, this temperature may need to be 5-10 °C higher to avoid corrosion completely as increasing the vol-% H_2O in some cases resulted in corrosion occurring where it otherwise had not.

Additional work is planned with additional precipitator ashes, as well as with ash mixtures containing bisulfate. Work is also planned with ashes and salts relevant to biomass boilers. It has been found that H_2SO_4 is not found in biomass boilers, so the absorption of water by salt deposits in biomass combustion is thought to control the lowest temperature the flue gas can be lowered in these units as well. However, the salts are different and so the minimum flue gas temperature may also be different.

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