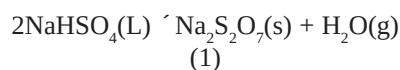


The effect of H_2O on acidic sulfate corrosion in kraft recovery boilers

HONGHI TRAN, NUREZ MAPARA, AND DAVID BARHAM

ACIDIC SULFATES, MAINLY SODIUM bisulfate ($NaHSO_4$) and sodium pyrosulfate ($Na_2S_2O_7$), are thought to be the main cause of fireside fouling and severe tube wastage in the generating bank and economizer regions of kraft recovery boilers (1–3). Due to the important role of acidic sulfates in recovery boiler performance, their formation and stability have been intensively studied (4, 5). $NaHSO_4$ can be formed directly from sodium sulfate or salt cake, under boiler upset conditions that cause the SO_x ($SO_2 + SO_3$) concentration in the flue gas to exceed 150 ppm (4). Once formed, liquid $NaHSO_4$ decomposes to H_2O vapor and solid $Na_2S_2O_7$ according to Reaction 1. The resulting solid $Na_2S_2O_7$, in turn, can be stable under normal boiler operations by forming solid complex compounds with Na_2SO_4 (5).



Severe corrosion has been found in a number of boilers in the generating bank and economizer regions (3, 6, 7). As advanced nondestructive testing technologies for measuring tube thickness have become available in recent years, more boilers have been found with tube wastage near the mud drum (8). The wastage has been attributed to corrosion–erosion, where corrosion is a result of molten acidic sulfate attack and erosion is caused by the removal of the corrosion product layer on the tube by the adjacent sootblower jet. In a recent field study performed by Thompson *et al.* (7) using a conduc-

tivity probe inserted near the mud drum in a boiler where corrosion was found, the conductivity of probe deposits increased when adjacent sootblowers were activated, whereas in a boiler that has no history of near-mud-drum corrosion, the conductivity was low and unaffected by sootblowing.

Thus, the water vapor in the flue gas may have a role in aggravating tube wastage. One explanation may lie in the fact that the equilibrium in Reaction 1 is a function of water vapor pressure. The equilibrium may shift to the left, i.e., solid $Na_2S_2O_7$ (noncorrosive) may revert to liquid $NaHSO_4$ (corrosive) if the H_2O vapor pressure in the flue gas reaches a critical level.

The present study is a continuation of previous studies on the behavior of acidic sulfates (4, 5). The objective was to examine the effect of H_2O vapor pressure on the stability of acidic sulfates, and to determine the temperature for solid $Na_2S_2O_7$ to revert to liquid $NaHSO_4$ and its implications for recovery boiler corrosion.

EXPERIMENTAL APPARATUS

An electrical conductivity measurement method was used in this study to determine whether a liquid phase was present in the sample. The method considered the fact that the electrical conductivity of an ionic solid is low but increases markedly if a liquid phase is present. As is shown in Fig. 1, the sample was placed in an alumina (Al_2O_3) boat heated in a temperature-controlled tubular furnace. A mixture of N_2 gas and H_2O vapor of an appropriate composition

ABSTRACT

Acidic sulfates, mainly $NaHSO_4$ and $Na_2S_2O_7$, are highly corrosive when molten. Liquid $NaHSO_4$ is formed as a result of a direct reaction between Na_2SO_4 in the deposit, and SO_3 and H_2O in the flue gas. Once formed, it decomposes rapidly into solid $Na_2S_2O_7$ and H_2O . Solid $Na_2S_2O_7$, which is noncorrosive, may revert to the corrosive liquid $NaHSO_4$ if the H_2O content in the flue gas exceeds a critical value. This critical H_2O content increases with temperature, which is consistent with the regression relationship $\log P_{H_2O} \text{ (atm)} = 3.598 - 2.300 \times 10^3/T$ suggested by Ingraham and Hotz. The re-formed liquid $NaHSO_4$ causes tube wastage if the deposits at the tube surface do not contain sufficient Na_2CO_3 to neutralize it. The risks of acidic sulfate corrosion are higher for low-pressure boilers, particularly boilers that are operated at low bed temperatures, with low solids firing, high sulfur input, and high sootblowing steam consumption.

Application:

Thinning of recovery boiler generating bank tubes caused by acidic sulfates can be minimized by operating boilers at high bed temperatures and by lowering sootblowing steam consumption in the affected areas.

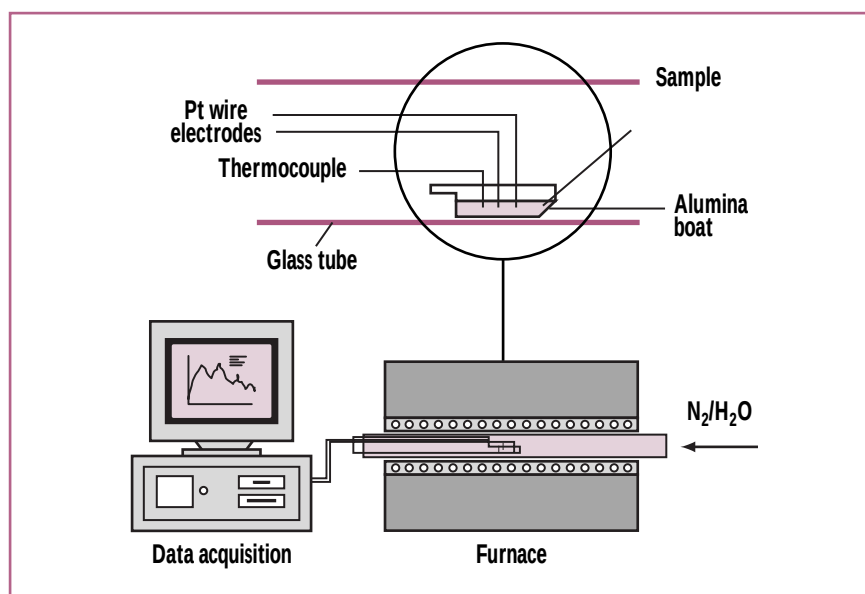
was passed through the furnace. Two platinum (Pt) wires, which served as electrodes, and a thermocouple were submerged in the sample along the sides of the alumina boat. The other ends of the Pt wires were connected to a potentiometer. The sample was heated at a rate of 5–10°C/min. The sample temperature, and the change in voltage across the Pt wires, which is a function of the electrical conductivity of the sample, were monitored using a data acquisition system.

The apparatus was calibrated against analytical-grade sodium nitrate (NaNO_3), which has a melting temperature of 308°C as determined by differential thermal analysis (DTA). As shown in Fig. 2, the electrical conductivity of NaNO_3 increased abruptly at 310°C as it melted and abruptly decreased at 288°C as it solidified. The slightly higher melting temperature obtained with the apparatus was due to the large sample size used in the test, which caused a delay in response to thermal changes. The low freezing temperature obtained was due to supercooling.

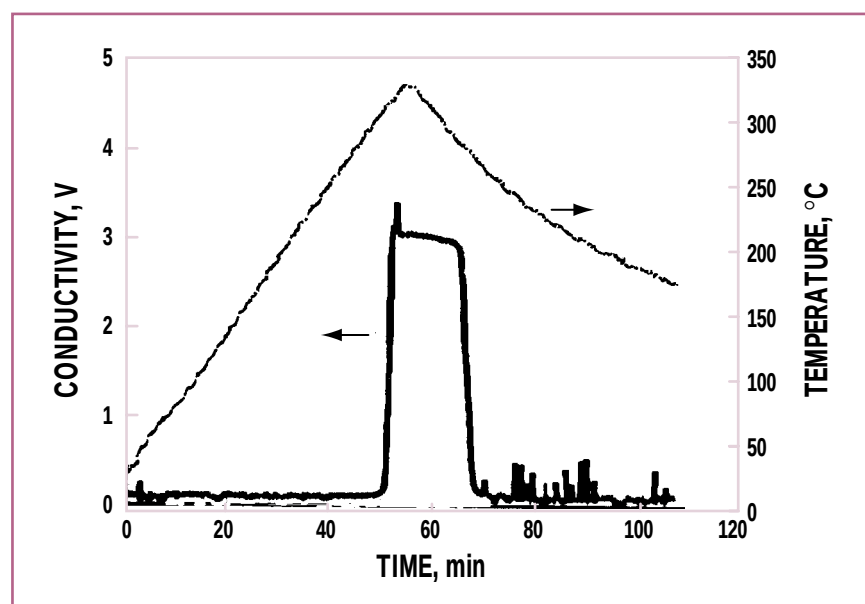
CONDUCTIVITY OF NaHSO_4 AND $\text{Na}_2\text{S}_2\text{O}_7$ IN N_2

NaHSO_4 was prepared by drying an analytical-grade sodium bisulfate monohydrate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$) under vacuum at 60°C for 24 hours. The dehydrated NaHSO_4 was placed in the Al_2O_3 boat sample holder, heated to 300°C , and then kept at this temperature while its electrical conductivity was monitored. During the test, only N_2 was passed through the reactor at a constant flow rate. The results are shown in Fig. 3.

The electrical conductivity of NaHSO_4 was initially low, 0.2 V at low temperatures. It started to increase at about 190°C and reached a high value at temperatures above 195°C , which is close to the melting temperature of NaHSO_4 [about 180°C as determined by DTA (5)]. The conductivity increased further with temperature and became relatively constant at 4 V at 300°C . After being held at this temperature for 25 min, the conductivity suddenly decreased, implying that the sample might have become solid and thus less conductive. Our results were consistent with previous results (5), which showed that, in the temperature range of 180 – 380°C , NaHSO_4 melts and decomposes into solid $\text{Na}_2\text{S}_2\text{O}_7$ and H_2O vapor according to Reaction 1.



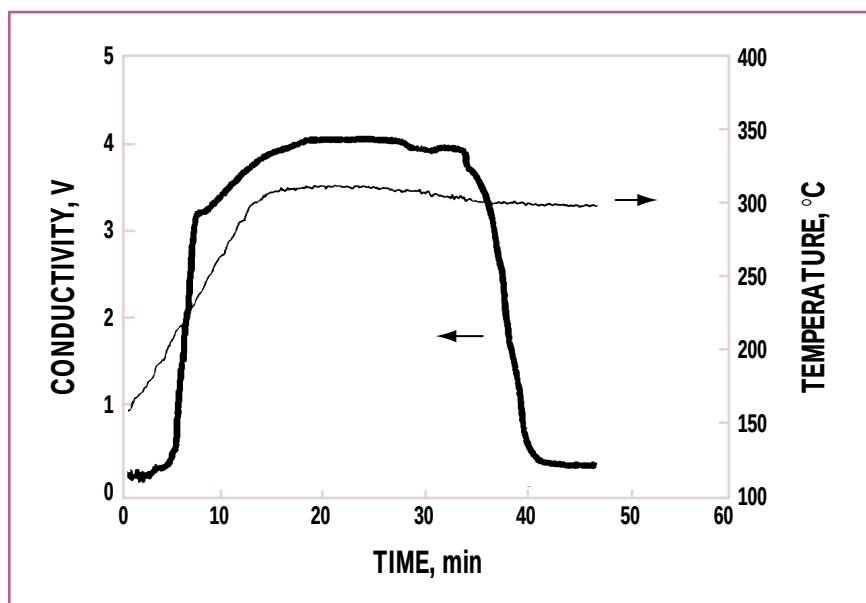
1. Electrical conductivity apparatus schematic



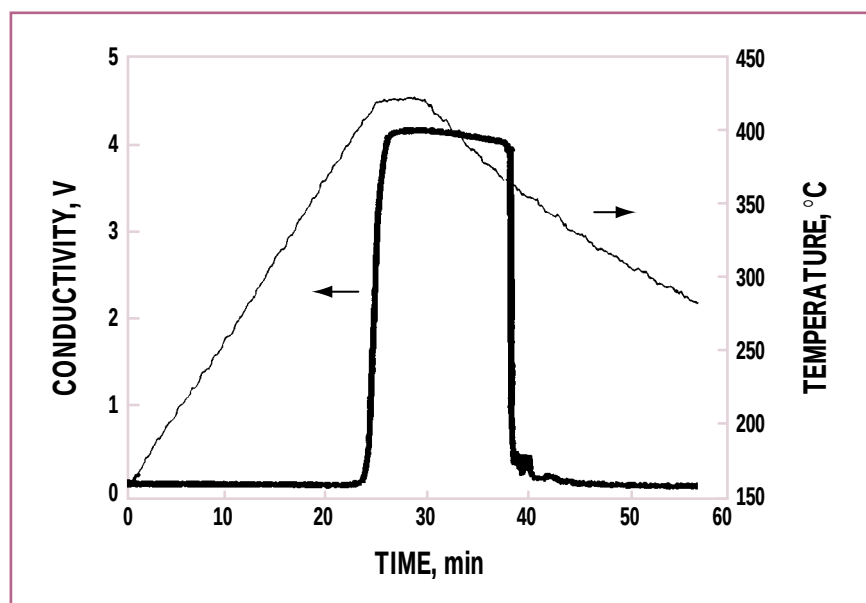
2. Calibration of the apparatus with pure NaNO_3

To determine if the resulting solid material was actually $\text{Na}_2\text{S}_2\text{O}_7$, the material was cooled to room temperature and reheated to 400°C while its conductivity was monitored. As shown in Fig. 4, the jump in voltage at 195°C shown in Fig. 3 was no longer observed, implying that the material was no longer NaHSO_4 . The conductivity remained

low at its baseline but increased abruptly at 405°C and remained relatively constant at this temperature. After holding the temperature at about 440°C for 10 min, the furnace was turned off to allow the sample to cool. As the temperature dropped below 365°C , the conductivity dropped rapidly to its baseline voltage. This sudden increase and



3. Conductivity of dehydrated NaHSO_4 in N_2



4. Conductivity of $\text{Na}_2\text{S}_2\text{O}_7$ in N_2

decrease in electrical conductivity corresponds well with the melting and freezing behavior of $\text{Na}_2\text{S}_2\text{O}_7$ at about 380°C . The tests were repeated numerous times, and similar results were obtained. In all tests, the melting temperature on heating was $20\text{--}40^\circ\text{C}$ higher than the freezing temperature on cooling, presum-

ably due to the large sample size, the dynamic nature of the test apparatus, and supercooling of the liquid sample.

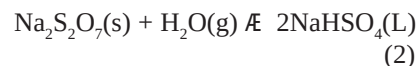
EFFECT OF WATER VAPOR

Water vapor was injected into the apparatus by bubbling N_2 through a water bath. The H_2O vapor concentration was controlled by adjusting

the bath temperature and the N_2 flow rate. The injection time was fixed at 5 min to simulate the typical sootblowing time of 3–5 min in the actual boiler. Figure 5 shows the effect of 33 vol.% water vapor on the conductivity of $\text{Na}_2\text{S}_2\text{O}_7$ at 300°C . The conductivity increased rapidly at the moment H_2O was injected and remained high during the time in which H_2O was injected. This increase implies the regeneration of liquid NaHSO_4 from $\text{Na}_2\text{S}_2\text{O}_7$.

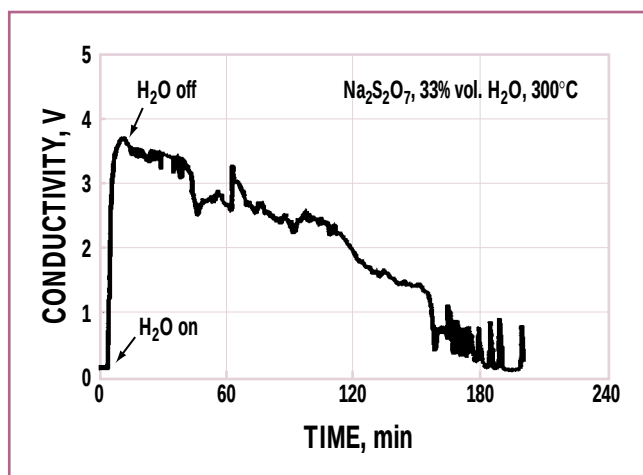
Separate tests were conducted to determine if NaHSO_4 had actually been re-formed. During the tests, at the point where the conductivity increased to above 3.5V as a result of water injection, the water was turned off and the apparatus was quickly cooled to ambient temperature. It was then reheated to 300°C in the absence of water vapor while the conductivity of the sample was monitored. The conductivity curve obtained resembled Fig. 3, showing a marked increase at about 190°C , the melting temperature of NaHSO_4 .

These results clearly indicate that Reaction 1 is reversible and that $\text{Na}_2\text{S}_2\text{O}_7$ is solid at 300°C , but reverts rapidly to liquid NaHSO_4 in the presence of 33 vol.% H_2O :

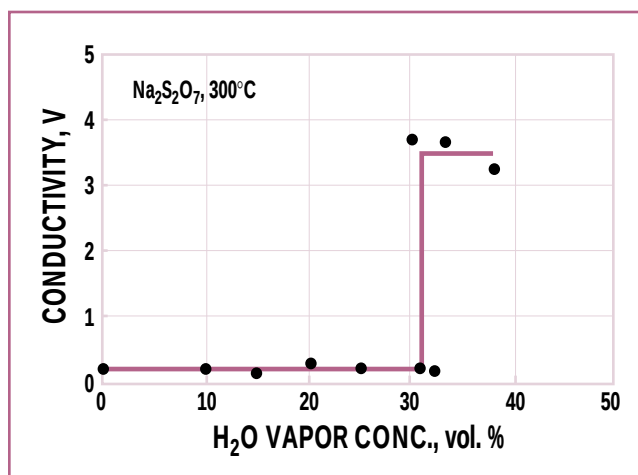


Note from Fig. 5 that, after the water vapor had been turned off, the conductivity started decreasing but did not immediately return to the baseline level. Instead, it remained high for more than 2 hours. It is not known why this happened, but results were reproducible in all tests. This pseudo-stability of the re-formed NaHSO_4 has a significant implication regarding corrosion; this is discussed later.

Figure 6 shows the effect of injecting various H_2O concentrations on the conductivity of $\text{Na}_2\text{S}_2\text{O}_7$ at 300°C . The increase in conductivity



5. Effect of H₂O injection on conductivity of Na₂S₂O₇ at 300°C



6. Effect of various H₂O concentrations on Na₂S₂O₇ conductivity at 300°C

occurred only when the H₂O vapor concentration exceeded about 30 vol.%. This means that for Reaction 2 to occur at 300°C, a minimum of about 30 vol.% of H₂O vapor is required.

At lower temperatures, the critical H₂O vapor content required was lower. Figure 7 shows whether a liquid phase was present during tests at various temperatures. The open circles represent tests in which the sample was nonconductive (or solid), whereas the black circles are tests in which the sample was conductive, or somewhat conductive (>0.5 V), due to the presence of liquid NaHSO₄. Note that most of the black circles (liquid or partially liquid) fall within the region in which liquid NaHSO₄ is stable. This region was constructed based on the NaHSO₄ – Na₂S₂O₇ – H₂O phase equilibrium data provided by Ingraham and Hotz (9). The solid curve represents the experimental data, whereas the broken curve is the extrapolation of the solid curve based on the following regression relationship:

$$\log P_{\text{H}_2\text{O}} = 3.598 - 2.300 \times 10^3/T \quad (3)$$

where $P_{\text{H}_2\text{O}}$ is vapor pressure of H₂O (atm) and T is absolute temperature

(°K). From Fig. 7, it is clear that the critical H₂O vapor concentration required for solid Na₂S₂O₇ to revert to liquid NaHSO₄ increases with temperature. At 200°C, for instance, the minimum amount of H₂O required under equilibrium is 0.054 atm (or 5.4 vol.%) compared to a much higher value, 0.38 atm or 38.4 vol.%, at 300°C. The kinetics of the reaction, however, are expected to be slow at 200°C. The slow reaction kinetic at low temperatures was particularly apparent in this study since the water injection time was only 5 min to simulate average sootblowing time in the actual boiler. The magnitude of increase in conductivity was small at low temperatures.

CONDUCTIVITY OF OTHER COMPOUNDS

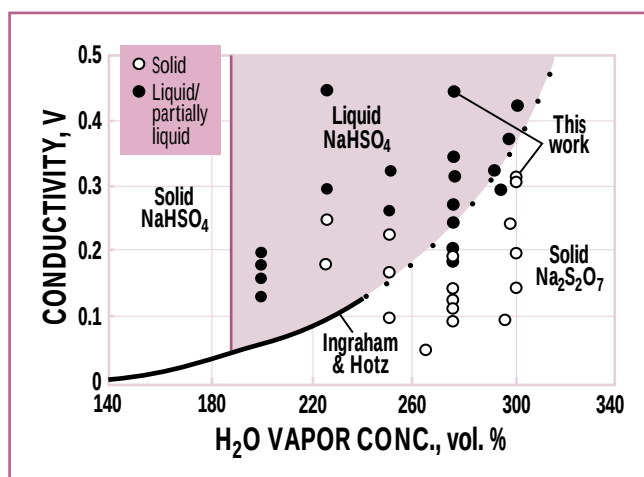
Limited tests were performed to examine the effect of water vapor on the stability of potassium pyrosulfate (K₂S₂O₇). The results were similar to the Na₂S₂O₇ described above, suggesting that solid K₂S₂O₇ also reverts to liquid KHSO₄ if the H₂O vapor concentration exceeds a critical value.

The effect of water vapor at three different concentrations (26, 35, and 47 vol.%) on the conductiv-

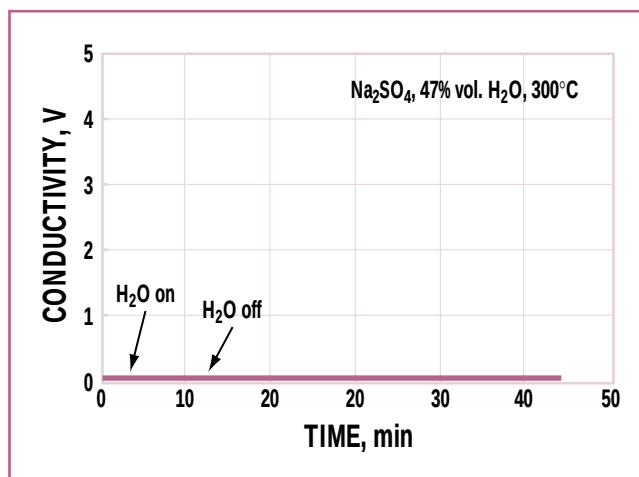
ity of sodium sulfate (Na₂SO₄) was examined at 300°C. As shown in Fig. 8, no effect was observed, even at 47 vol.% H₂O injection. Tests, in which up to 58% H₂O was injected, were also carried out at 300°C on Na₂CO₃, boiler bank deposit, and precipitator dust. Again, no appreciable change in conductivity was observed. These results are understandable, because Na₂SO₄ and Na₂CO₃ are unlikely to react with water vapor, and because the boiler bank deposit and the precipitator dust used did not contain acidic sulfates.

IMPLICATIONS

The results of this work clearly suggest that the re-formation of liquid NaHSO₄ from solid Na₂S₂O₇ occurs rapidly as the H₂O vapor content in the flue gas reaches a critical value. This critical H₂O vapor pressure increases with temperature, consistent with Ingraham and Hotz's regression relationship. Once re-formed, liquid NaHSO₄ takes some time (2 hours) to decompose to solid Na₂S₂O₇, even after the H₂O content has returned to a subcritical level. During such time, corrosion of tubes may result if the deposits do not contain sufficient Na₂CO₃ to neutralize the re-formed liquid NaHSO₄.



7. Effect of H_2O vapor on $\text{Na}_2\text{S}_2\text{O}_7$ - NaHSO_4 conversion at various temperatures



8. Effect of 47 vol.% H_2O injection on conductivity of Na_2SO_4 at 300°C

Water vapor in the flue gas is derived mainly from water in the black liquor, from the combustion of hydrogen-containing organic material in the black liquor, and from sootblowing steam. It also comes, to a lesser extent, from the moisture in the combustion air. For a typical black liquor composition, the water vapor content in the flue gas decreases with an increase in the percent black liquor dry solids (BL d.s.): about 29 vol.% at 60% BL d.s., 24 vol.% at 70% BL d.s., and 19 vol.% at 80% BL d.s.

Figure 9 shows the relationship between %BL d.s. and calculated flue gas water vapor content (horizontal lines), superimposed on the critical water vapor content vs. temperature relationship for Reaction 2 shown in Fig. 7. The vertical lines in Fig. 9 represent saturated steam temperatures at various boiler pressures. If the horizontal line intercepts the vertical line at a point inside the liquid NaHSO_4 region, a boiler operating at such conditions may experience near-mud-drum corrosion associated with molten bisulfate. If the interception point lies outside the liquid NaHSO_4 region, it is considered to be safe.

An example of this is given in Fig. 9. The horizontal line at 70% BL d.s.

intercepts the four vertical lines at points A, B, C, and D. Point A lies inside the liquid NaHSO_4 region, while Points C and D lie outside. This means that low-pressure boilers [41 bar (600 psi)] may experience molten bisulfate corrosion in the generating bank, while higher-pressure boilers [83 bar (1200 psi) and 103 bar (1500 psi)] may not. However, because of the lower temperature at Point A, the kinetics of the corrosion reaction are likely to be low.

Point B, on the other hand, lies near the borderline. This means that intermediate-pressure boilers [62 bar (900 psi)] may experience molten bisulfate corrosion at locations near sootblowers. Note that, for a sootblower that consumes 5% of the total steam production, there is an estimated increase of 3.5 vol.% H_2O vapor as the sootblower is activated. This additional vapor from sootblowing may be sufficient to shift Point B inside the liquid NaHSO_4 region, and corrosion may result. Thus, for 62-bar (900-psi)-pressure boilers, the location of sootblowers near the mud drum and the amount of sootblowing steam used can be critically important from a corrosion point of view.

The tendency for acidic sulfates to form in recovery boilers increases with SO_x content in the flue gas (4, 5). If molten bisulfate is responsible for the thinning of the generating bank tubes near the mud drum, the tendency for corrosion to occur is high if the flue gas contains high concentrations of both SO_x and H_2O . Such conditions are likely to prevail in boilers that are operated at/with the following conditions:

- Low saturated steam pressure (i.e., low critical H_2O vapor value)
- Low bed temperature (i.e., high SO_x content in the flue gas)
- Low solids firing (i.e., high H_2O content in the flue gas)
- Unstable operation with frequent boiler upsets (i.e., high SO_x content in the flue gas)
- High-sulfidity liquor (i.e., high SO_x content in the flue gas)
- High-steam-consumption sootblowing (i.e., high H_2O content in the flue gas).

In the economizer, the tube temperatures vary between the feedwater temperature (typically about 200°C) and near 300°C , depending on the boiler pressure. Acidic sul-

KEYWORDS

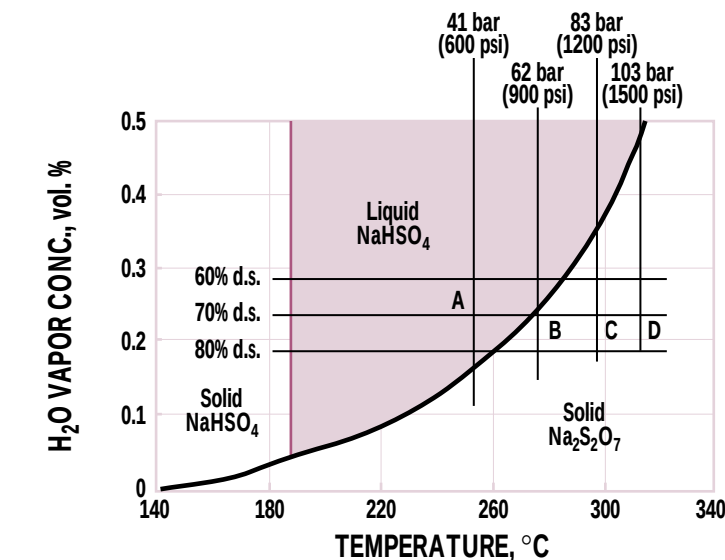
Acidity, alkali metal compounds, bisulfates, chemical properties, corrosion, furnaces, recovery furnaces, sodium bisulfate, sodium compounds, sulfates, sulfur compounds, temperature, water.

fates, if formed, must be present as liquid bisulfate at the tube surface and hence are corrosive. In this case, the addition of sootblower steam is not required to promote corrosion.

CONCLUSIONS

The effect of H_2O vapor on the stability of acidic sulfates was studied. The results suggest that:

- The re-formation of liquid NaHSO_4 from solid $\text{Na}_2\text{S}_2\text{O}_7$ occurs rapidly as the H_2O content in the flue gas reaches a critical value. This critical H_2O vapor pressure increases with temperature, consistent with Ingraham and Hotz's regression relationship.
- Once re-formed, liquid NaHSO_4 takes some time to decompose to solid $\text{Na}_2\text{S}_2\text{O}_7$, even after the H_2O content of the flue gas has returned to a subcritical level.
- The effects of water vapor on the stability of $\text{K}_2\text{S}_2\text{O}_7$ were similar to $\text{Na}_2\text{S}_2\text{O}_7$. No effect was found on Na_2SO_4 , Na_2CO_3 , a boiler bank deposit, and a precipitator dust.
- If the deposits at the metal surface do not contain sufficient Na_2CO_3 , the resulting liquid NaHSO_4 is not neutralized; hence, corrosion of tubes may result.
- For 62-bar (900-psi)-pressure boilers, the location of sootblowers near the mud drum plays an important role in the generating bank tube thinning problem.
- If the liquid NaHSO_4 is responsible for the tube thinning near the mud drum surface, the tendency



9. Implications for corrosion by acidic sulfates in generating bank and economizer regions

for this type of corrosion to occur is higher in boilers that are operated at/with low saturated steam pressure, low bed temperature, low solids firing, high-sulfidity liquor, and high-steam-consumption sootblowing. TJ

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