

Synergistic air-port corrosion in Kraft recovery boilers

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ABSTRACT: Localized hot corrosion can occur on the cold-side of air-ports in Kraft recovery boilers. Depending on the basicity of the molten salt, either acidic or basic fluxing takes place, with a solubility minima at the transition between the two reactions. For stainless steel, if the basicity of the fused salt is between the iron and chromium oxide solubility minima, then a synergistic effect can occur that leads to rapid corrosion. The products of one reaction are the reactants of the other, which eliminates the need for rate-controlling diffusion. This effect can explain why stainless steel is attacked more readily than carbon steel.

KEYWORDS: Air-ports, boiler, fused salt, hot corrosion, hydroxides, Kraft, molten salt, stainless steel.

Corrosion of boiler tubes at air-ports is a chronic problem in Kraft recovery boilers (1-7). The Kraft recovery boiler is a steam boiler with the fuel being spent liquor from the digester, and the air-ports are where air is introduced into the boiler through water-cooled walls. Localized corrosion occurs on the outside (cold side) of the furnace walls, not on the fireside.

The primary corrosion mechanism (1-7) involves the migration of sodium hydroxide (NaOH) and potassium hydroxide (KOH) vapor through the furnace wall at the air-ports (where an air-tight seal is not maintained on the cold side of the furnace wall) and their subsequent condensation. When the conditions (primarily temperature and condensate composition) are such that the condensation products are molten, then the molten salt attacks the metal heat exchanger tubes. It is reported that stainless steel is attacked much faster than carbon steel in composite tubes (2-7) and that under the wrong conditions, nickel overlays can also be attacked (5). It has also been observed that carbon steel tubing, when used with a lower chromium refractory, does not exhibit this type of corrosion (2).

Hot corrosion reactions

The corrosion attack by the (Na,K)OH-based molten salt is termed hot corrosion, and has been extensively studied (8-11) in sodium sulfate (NaSO₄)-based molten salts in boilers and turbines. Hot corrosion is defined as the accelerated corrosion some metals and alloys have when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures (8).

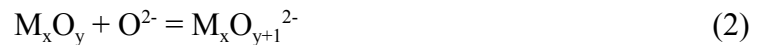
One of the main hot corrosion mechanisms is the dissolution, or “fluxing”, of protective metal oxides and the subsequent exposure of the metal to the aggressive fused salt. Fluxing can proceed unabated if there is a negative solubility gradient within the fused salt away from the metal oxide (the Rapp-Goto criterion (9)). With a negative solubility gradient, metal oxides precipitate out within the fused salt, which acts as a sink for metal oxides and allows further dissolution of the protective oxide. With a positive solubility gradient, metal oxides build up in the fused salt and

limit further dissolution of the protective oxide. Thus the solubility behavior of the metal oxide in the fused salt is important in describing hot corrosion behavior.

Oxyanion melts of sulfates and hydroxides exhibit an acid/base character analogous to aqueous solutions (6-8). In the case of the hydroxide, MOH, where M equals Na or K, the dissociation is described by:

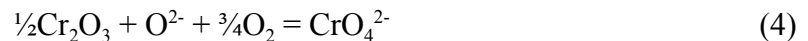


where M_2O is the base component and H_2O is the acid component. Metal oxide fluxing can occur as either basic Eq. (2), or acidic Eq. (3) dissolution:



When the solubility of metal oxides are plotted as a function of basicity ($-\log a_{\text{M}_2\text{O}}$), and both basic and acidic dissolutions takes place, then a solubility minima occurs. This is illustrated in Fig. 1 with data at 500°C from Estes *et al.* (6-7) for Cr_2O_3 . The data for Fe_2O_3 and NiO are also shown. In Fig. 1, the solubility axis is log concentration (ppm) of the moles of metal ions/moles of NaOH. For Cr_2O_3 , the solubility minima is at a pNa_2O of 8.2. No acidic dissolution was reported (6-7) for Fe_2O_3 in the basicity range tested. However, one would expect an acidic reaction at higher basicities. For NiO , no nickel was found in the melt below a pNa_2O of 8.3.

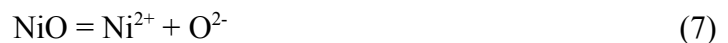
For the basic dissolution of Cr_2O_3 at a constant oxygen partial pressure, the reaction



is predicted to have a slope of -1 in Fig. 1 ($\log [\text{CrO}_4^{2-}] \propto \log [\text{O}^{2-}] \propto -\text{pNa}_2\text{O}$). This is quite close to the experimental value of -0.99 (6-7). For the acidic dissolution of Cr_2O_3 at a constant oxygen partial pressure, the reaction



is predicted to have a slope of $3/2$ in Fig. 1 ($\log [\text{Cr}^{3+}] \propto -3/2 \log [\text{O}^{2-}] \propto 3/2 \text{ pNa}_2\text{O}$), which is quite close to the experimental value of 1.48 (6-7). Similar agreements between experiment and theory (6-7) support the following reactions for the basic dissolution of Fe_2O_3 (slope of $-1/2$) and the acidic dissolution of NiO (slope of 1):



Additional support for Eq. (6) is that NaFeO_2 was found by x-ray diffraction in air-port boiler deposits (1,6-7).

Synergistic hot corrosion

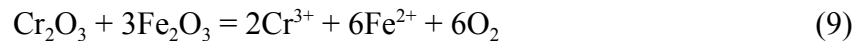
Studies (8, 10) of hot corrosion in Na_2SO_4 have shown that the reaction rate, when the Rapp-Goto criterion is satisfied (9), is controlled by the diffusion of oxygen in the form of $\text{S}_2\text{O}_7^{2-}$. In basic solutions, it is diffusion to the protective oxide. In acidic solutions, it is diffusion away from the protective oxide.

When two metals together undergo hot corrosion, and the basicity is such that it is between the solubility minima of the two metal oxides, the kinetics can greatly increase (10). This is because the products of one dissolution reaction are the reactants of the other, thus largely eliminating diffusion of oxygen as controlling the kinetics.

In the case of stainless steel in NaOH, when the basicity is above the Cr_2O_3 solubility minima and below the Fe_2O_3 minima (beyond the basicity range in Fig 1), a coupled reaction can be written that eliminates the need for the diffusion of O^{2-} . If Eq. (6) is rewritten as



with a subsequent reaction with Na_2O to form NaFeO_2 , then Eqs. (5) and (8) can be combined to form the coupled reaction:



The O_2 subsequently combines with Na_2O to form NaFeO_2 . This coupled reaction, without the need for the kinetics to be limited by O^{2-} diffusion, would explain the rapid localized attack of stainless steel at air-ports (2-7). It would also explain the observation that carbon steel is attacked much less when used with a lower chromium refractory (2).

Controlling the basicity

It would appear that if one could control the basicity of the environment, then hot corrosion could also be slowed. If the basicity is moved away from between solubility minima, then synergistic effects would be eliminated. However, it is not at all certain that controlling the atmospheric environment will change the local environment at the fused salt-protective oxide interface. For example, when pre-oxidized nickel was placed under a thin film of Na_2SO_4 in an acidic O_2 -0.1% SO_2 gas environment at 900°C , simultaneous measurements of the sodium and oxygen activities have shown that the local environment changes to basic conditions within 15 minutes (8,11). Thus it was the local reactions at the fused salt-protective oxide interface that determined the basicity, not the overall environmental basicity. So further investigation is needed to determine if environmental control can be effective in reducing hot corrosion at air-ports. For example, in the case of corrosion in Na_2SO_4 -based fused salts, low temperature "Type 2" hot corrosion is very sensitive to the environmental basicity, while high temperature "Type 1" hot corrosion is much less sensitive (12).

Conclusions

Hot corrosion theory can explain the localized corrosion on the cold-side of air-ports in Kraft recovery boilers. Hot corrosion can occur by the dissolution, or fluxing, of the metal into the fused salt. Depending on the basicity, either acidic or basic fluxing takes place. There is a solubility minima at the transition between the two reactions.

For the hot corrosion of alloys, if the basicity of the fused salt is such that it is between two metal oxide solubility minima, then a synergistic effect can occur that leads to rapid hot corrosion attack. This is due to the products of one reaction being the reactants of the other, which eliminates the need for rate-controlling diffusion of either one. This synergistic effect can explain why stainless steel is attacked more readily than carbon steel, and why carbon steel is not attacked in the presence of low chromium refractory.

The local reactions at the fused salt-protective oxide interface are likely to control the basicity, and not just the atmospheric conditions. Therefore simply changing the environment might not significantly change the local basicity (and thus the rate of hot corrosion).

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Figure caption

1. Measured oxide solubilities in fused NaOH at 500°C (6-7).