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Corrosion of Composite Tube Air-Ports in Kraft Recovery Boiler:
 Cr_2O_3 , Fe_2O_3 , NiO Solubility in Molten Hydroxide

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CORROSION OF COMPOSITE TUBE AIR-PORTS IN KRAFT RECOVERY BOILER: Cr_2O_3 , Fe_2O_3 , NiO SOLUBILITY IN MOLTEN HYDROXIDE

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ABSTRACT

Composite tubes in Kraft recovery boiler air-ports can experience severe corrosion, thought by most to be caused by molten hydroxide. Molten salt corrosion is often a function of salt basicity. This research measured the solubility of the oxides in stainless steel, (Cr_2O_3 , NiO , and Fe_2O_3), as a function of the basicity of molten NaOH. Understanding the mechanisms of corrosion and a knowledge of the variation of the solubility of oxides with the chemistry of the boiler environment allows measures to be taken to lower the corrosion rate of the composite tube air-port of Kraft recovery boilers.

INTRODUCTION

In recent years, the frequency of corrosion in recovery boiler air-ports has risen dramatically throughout the pulp and paper industry¹⁻¹⁰. The increase coincides with the growing use of composite tubes, which are fabricated with a stainless steel outer shell and carbon steel inner body. Air-port corrosion is unique when compared to other types of corrosion in the Kraft recovery boiler. Stainless steel is preferentially attacked until the carbon steel underneath is exposed. In many cases, complete wastage of the stainless steel layer took only six months to two years to expose the carbon steel^{5,10}. Stainless steel corrosion rates have been measured between 0.76-3.81 mm/year²⁻⁷. After completely consuming the stainless steel, mild corrosion of the carbon steel proceeds at 0.13-0.41 mm/year, similar to rates reported for carbon steel tubes in the recovery boilers of the 1960s¹⁻⁷. There is concern among boiler operators that the exposed carbon steel could be subject to sulfidation corrosion. The preferential corrosion of stainless steel in air-ports of recovery boilers is an unusual and costly phenomenon, and thus warrants more study.

Molten sodium hydroxide has been postulated as a possible cause for corrosion at air-ports¹⁻¹⁰. The severity and uniformity of corrosion are consistent with a molten salt reaction. It has been suggested that sodium hydroxide vaporizing from the smelt bed can migrate to the air-port.

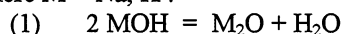
The walls of the air-port at 275 to 500°C are cool relative to the inside of the boiler^{3,5,11} and the sodium hydroxide vapors would condense on the waterwall tube surface as a liquid.

There is evidence that NaOH is present at kraft recovery boiler air-ports. Colwell and Fonder collected deposit samples on a cooled probe and measured the melting point *in situ* inside a kraft recovery boiler¹². The melting point detected by the probe is close to the melting point of sodium.

Laboratory experimentation has shown that molten sodium hydroxide corrodes stainless steel faster than carbon steel^{7,12}. Other corrosive mechanisms in addition to molten NaOH may take place^{11,13}, but they do not explain why stainless steel corrodes faster than carbon steel.

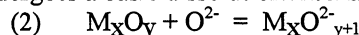
Theory of molten salt reactions

Since solubility of a metal oxide is often a function of the salt basicity; the corrosion rate should also be a function of basicity when solubility is the dominant step in the corrosion mechanism. Basicity of a molten salt is defined by the dissociation of the compound, in the case of hydroxide, MOH, where M = Na, K :

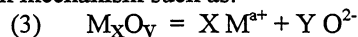


For hydroxide, M_2O is defined as the Brönsted conjugate base because it accepts a proton, and water is defined as the Brönsted conjugate acid because it donates a proton. Basicity is defined by the oxide ion, O^{2-} as $-\log a_{(\text{O}^{2-})}$, analogous to the definition of pH.

A considerable volume of work has been reported in the literature showing the solubility of different metal ions plotted as function of basicity^{14,15}. These plots can be used to locate the basicity conditions that minimize solubility for a particular metal oxide. Under basic conditions, the metal oxide undergoes a basic dissolution mechanism such as:



Under acidic conditions, the metal oxide undergoes an acidic dissolution mechanism such as:



Thus, the location on the solubility curve provides information about which type of dissolution is occurring.

In addition, the dependence of the solubility of a particular ion on basicity can be related to the slope of the curve. A hypothetical basic and acidic dissolution would be:

$$(4) \quad \left(\frac{-\log M_x \text{O}_a^{p-}}{-\log \text{O}^{2-}} \right) = \frac{Z}{X}$$

$$(5) \quad \left(\frac{-\log M^{a+}}{-\log \text{O}^{2-}} \right) = \frac{Y}{X}$$

Agreement between the experimental slopes and the theoretical slopes based on the stoichiometric equations can be used to confirm the identity of the soluble ion.

EQUIPMENT

Equipment, which has been described previously, uses electrodes to measure basicity^{16,17}. The electrode system consisted of a combination of a β -alumina probe with a sodium reference and a zirconia probe with air as the reference^{18,19}. The Nernst equation gives the relationship between the cell potential and the concentrations of the cell components.

$$(6) \quad \varepsilon = \varepsilon^\circ - \frac{RT}{2F} \ln a_{(\text{Na}_2\text{O})} + \frac{RT}{4F} \ln P(\text{O}_2)$$

For the experiments, temperature was held constant at 500°C, and ϵ° was calculated by experimentation to be 0.567.

Sodium oxide pellets were used to make the NaOH more basic. To make NaOH more acidic water vapor was added by bubbling the carrier gas through a water column fitted with a polyurethane frit. The vapor pressure was determined by fixing the water column temperature and assuming saturation²⁰.

Samples for chemical analysis were collected by inserting a ceramic rod through a ball valve on the top. The sample was then quickly scraped off with ceramic tweezers into a volumetric flask partially filled with deionized water. Four replicate salt samples were taken at each basicity. Chromium concentration was measured using a Perkin Elmer Optima 3000 Dual View Inductively Coupled Plasma (ICP) Spectrometer. Standards were prepared, values loaded into the computer, and then compared with unknown samples using EPA guidelines for solid waste²¹.

RESULTS AND DISCUSSION

Chromium Oxide Solubility Curve

The data averages for solubility of Cr_2O_3 are plotted in Figure 1.

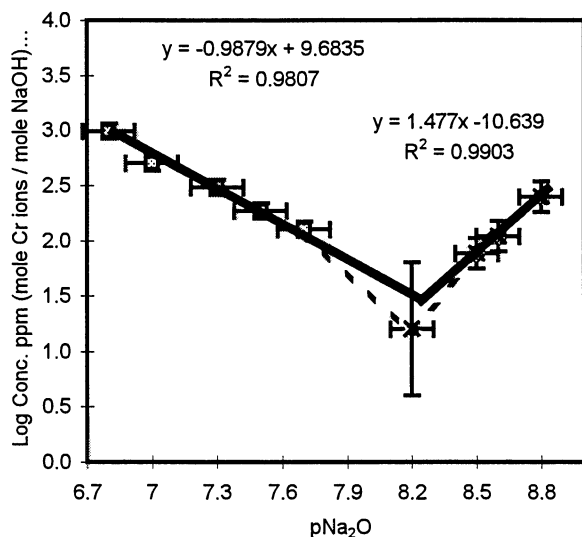


Figure 1: Solubility curve for Cr_2O_3 at 500°C.

Chromium oxide has a minimum solubility at a pNa_2O of 8.2. The solid line represents the least-squares best fit of the data. Basicity error bars were estimated at $\text{pNa}_2\text{O} \pm 0.1$, based upon fluctuations in the voltage readings. Error bars for chromium concentration show \pm one standard deviation.

Deviation from the minimum solubility

The data appear to have more scatter at the minimum basicity of 8.2. This is partially an artifact of plotting against the log scale. Also, chromate and chromium ions can act as a weak acid or base in molten hydroxide, which will affect the results near the minimum. Pourbaix found that substances can act as a weak acid or base in water.²² For our system at equilibrium,

(7) $\text{Log } C = [\text{Cr}_2\text{O}_3] / [\text{Cr}^{3+}] = \text{pNa}_2\text{O} - \text{pK}$, where $\text{pK} = 8.2$. The quantity of acidic form, Cr^{3+} , existing in the resulting solution is equal to the quantity of O^{2-} ions formed by autoprolysis less the quantity of Na_2O previously present in

pure NaOH, i.e., $10^{-8.2}$. The hypothesized deviation caused by these secondary reactions is calculated in Figure 2.

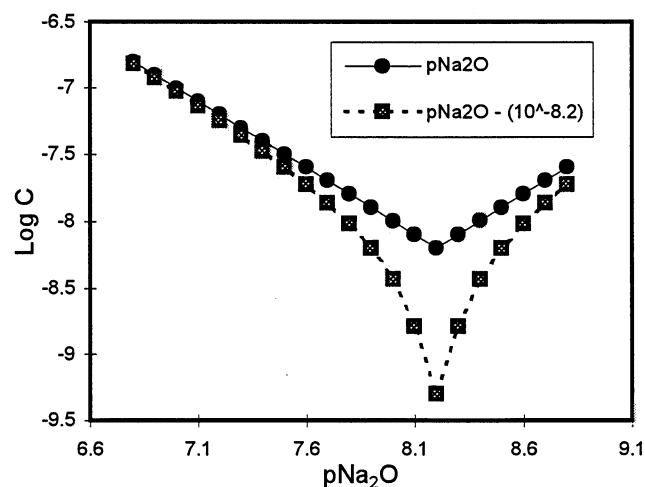
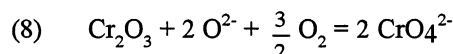


Figure 2. Weak acid/base, deviation from minimum solubility.

The deviation from the slope at the minimum appears to correspond to chromium behaving as a weak acid that affects the overall concentration of chromium. Therefore, it was decided to ignore the average at the minimum and determine the slopes of the line outside the minimum.

If the dissolution reaction for basic conditions is assumed to be:

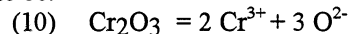


At constant $P(\text{O}_2)$, the theoretical slope for the reaction is given by:

$$(9) \quad \left(\frac{-\log \text{CrO}_4^{2-}}{-\log \text{O}^{2-}} \right) = -1$$

The measured value of -0.9879 is in very good agreement with theory. Also, the melt was yellow in color, which is consistent with the formation of chromate¹⁵.

If the dissolution reaction for acidic conditions is assumed to be:



The theoretical slope for the reaction is given by:

$$(11) \quad \left(\frac{-\log \text{Cr}^{3+}}{-\log \text{O}^{2-}} \right) = \frac{3}{2}$$

The measured value of 1.477 is in very good agreement with theory. Also, the melt was green in color, which is consistent with the formation of chromium ion¹⁵.

Potassium Hydroxide Solubility Curve with Cr_2O_3

A solubility curve of Cr_2O_3 in KOH has also been constructed. Potassium hydroxide was studied because laboratory experiments on type 304L stainless steels have shown an approximate 200% increase in the corrosion rate with the addition of 25% KOH over a 30-day period²³.

Experiments with KOH were carried out using the same environmental conditions as were used with NaOH tests. Because the β -alumina conducts sodium exclusively, pK_2O measurements could not be made for KOH tests. The data was plotted at the same environmental conditions.

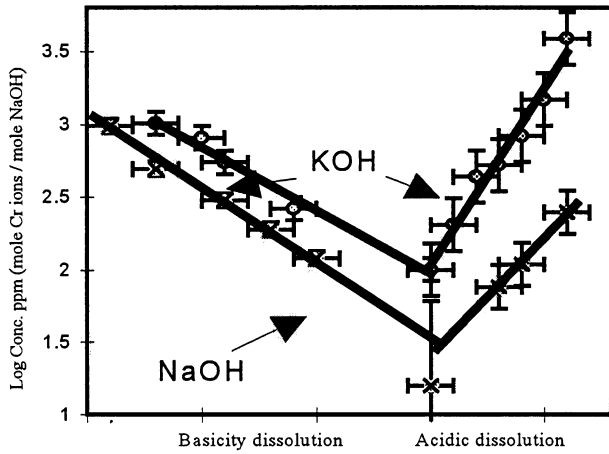


Figure 3. Solubility curves of Cr_2O_3 with KOH and NaOH at 500°C .

The solubility of chromium was much higher in KOH than NaOH. At the solubility minimum the concentration of chromium was 1024 ppm, which is 1700% higher than the solubility minimum for NaOH at 58 ppm. The solubility increase ranged from 200 to 5600% and could account for the 200% increase in the weight loss observed in the lab.

Iron Oxide Solubility Curve

The solubility relationship of Fe_2O_3 is plotted in Figure 4.

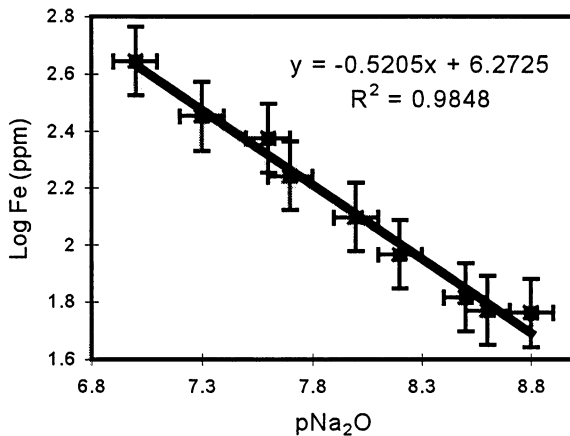
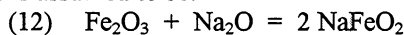


Figure 4. Fe_2O_3 in NaOH at 500°C .

The trend is a decrease in iron concentration as the melt becomes more acidic. If the dissolution reaction for acidic conditions is assumed to be:



The theoretical slope for the reaction is

$$(13) \quad \left(\frac{-\log \text{NaFeO}_2}{-\log \text{Na}_2\text{O}} \right) = \frac{1}{2}$$

The measured value of -0.5133 is in very good agreement with theory. The red color of the melt is consistent with the formation of sodium ferrite. Acidic dissolution of Fe_2O_3 was not observed. The minimum solubility and acidic dissolution are probably beyond the experimental limits. The basic dissolution forming NaFeO_2 is consistent with findings of NaFeO_2 by X-ray diffraction in air-port boiler deposits¹.

Nickel Oxide Solubility Curve

Figure 5 shows the basicity and solubility relationship of NiO.

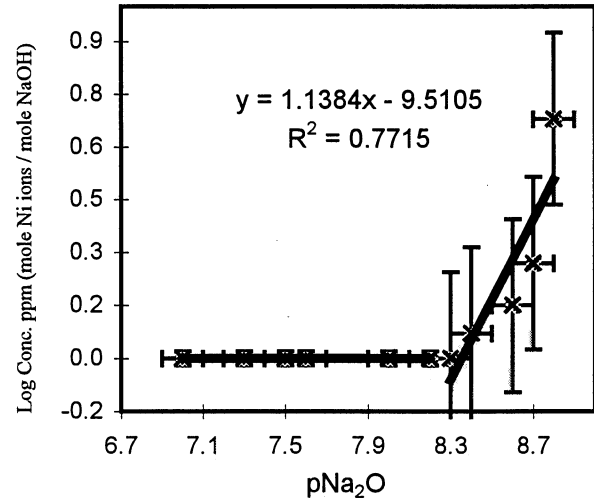
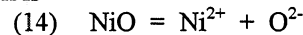


Figure 5. NiO in NaOH at 500°C .

Nickel ions were not detected in the melt under conditions more basic than pNa_2O of 8.3. Since nickel is known to be stable in molten NaOH, this is to be expected.

Thermodynamics indicate that only insoluble NiO or an acidic dissolution forming Ni^{2+} is possible. Nickel ions become soluble at $\text{pNa}_2\text{O} > 8.3$ and assuming the acidic dissolution is



The theoretical slope for the reaction is

$$(15) \quad \left(\frac{-\log \text{Ni}^{2+}}{-\log \text{O}^{2-}} \right) = 1$$

The observed slope of the acidic dissolution is 1.1. The proposed reaction is plausible since the theoretical and measured slopes are similar. The melt with NiO was colorless for $\text{pNa}_2\text{O} < 8.3$. At $\text{pNa}_2\text{O} > 8.3$ the melt was gray-greenish, consistent with Ni^{2+} . In conclusion, a mechanism exists to dissolve the nickel in molten NaOH with sufficient water vapor. This could be one possible explanation why thermal spray nickel coatings corrode in the air-port¹¹

WEIGHT LOSS EXPERIMENTS

Chromium metal weight loss

Weight loss experiments were performed using 98% chromium metal at pNa_2O of 6.8, 8.2, and 8.8. The three pNa_2O values represented basic dissolution, the solubility minimum, and an acidic dissolution for the Cr_2O_3 , respectively, as shown in Figure 6. The correlation coefficient for the relationship between solubility and weight loss was 0.998. The weight loss of chromium metal was at the lowest value at the same pNa_2O where the solubility minimum occurred. At pNa_2O of 6.8 and 8.8 the solubilities were much higher, which led to a higher weight loss. Furthermore, the weight loss at a pNa_2O of 6.8 was higher than at 8.8, as predicted by the solubility curve. The weight loss was a function of basicity. Therefore, basicity and oxide solubility appear to control corrosion under the conditions tested.

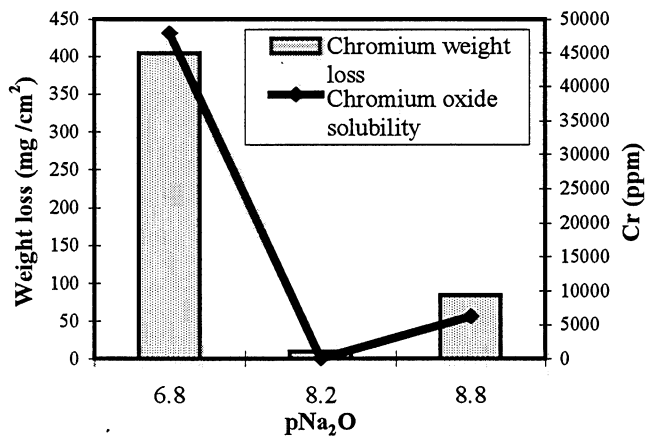


Figure 6: Correlation between weight loss and solubility at 500°C.

Carbon steel weight loss

Weight loss experiments were performed on carbon steel 1010 with 99.4% iron. The results shown in Figure 7 indicate that the weight loss of carbon steel 1010 was not controlled by the solubility of Fe₂O₃, particularly at a pNa₂O of 8.8.

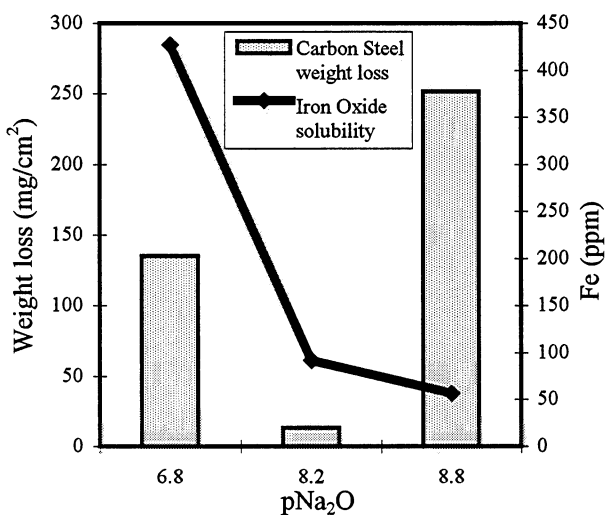


Figure 7. Correlation between iron solubility and carbon steel weight loss.

The correlation factor of -0.075 further supports this conclusion.

The carbon steel samples were covered by a thick, red-brown product, which could be removed by rinsing and ultrasonic cleaning. For carbon steel, a large portion of the products did not dissolve into the melt, but stayed loosely attached to the surface of the metal. The reaction to form iron oxide occurs much faster than the dissolution of the iron oxide. As a result, a higher weight loss was found than solubility would predict.

The results indicate that solubility of Fe₂O₃ is not critical to the weight loss of carbon steel. The carbon steel probably has Fe₃O₄ formed underneath Fe₂O₃. The dissolution rate of Fe₃O₄ may be what is important to determine the weight loss of carbon steel.

Nickel weight loss

Weight loss experiments were performed with nickel. As shown in Figure 8, the solubility curve for NiO in NaOH matches the weight loss results from experiments performed on nickel metal in molten NaOH.

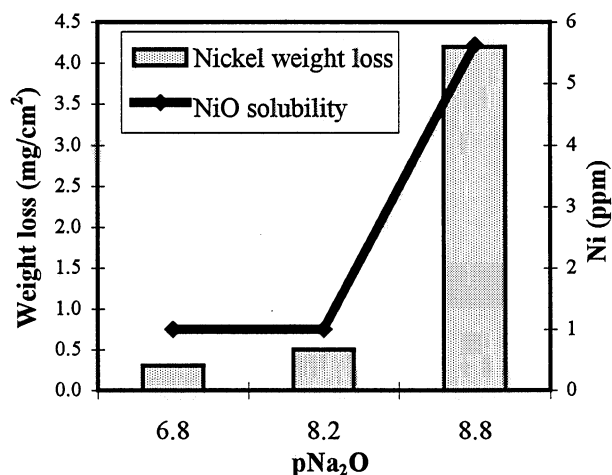


Figure 8. Correlation between solubility and weight loss of nickel at 500°C.

The correlation coefficient of 0.998 indicates that the oxide solubility appears to be the controlling mechanism of corrosion under the test conditions. Similar weight loss experiments performed by Colwell showed an increase in weight loss under air and 80% water vapor⁷. His results corresponded closely to weight loss observed in these experiments. Overall results show that nickel is resistant to NaOH over much of the basicity region, but confirm that nickel can corrode under acidic conditions.

CONCLUSION

Several solubility plots were completed on chromium, iron, and nickel oxides in molten hydroxide providing an understanding of the dissolution reactions. In summary, this work proved the following points:

- Cr₂O₃ can undergo basic or acidic dissolution in molten hydroxides with a minimum solubility at pNa₂O of 8.2.
- Potassium increases the solubility of Cr₂O₃, which leads to higher corrosion rates. Mills considering closure that leads to higher potassium levels should carefully consider possible corrosion effects. Increased potassium levels could cause an order of magnitude or greater increase in the corrosion rates.
- Nickel oxide has a very low solubility until pNa₂O < 8.3 giving an acidic dissolution, indicating nickel should not be chosen for recovery boilers under acidic conditions.
- Iron oxide undergoes basic dissolution under the tested conditions.
- Chromium and nickel oxide solubility curves corresponded to respective weight loss supporting the hypothesis that solubility has a dominant role in the corrosion.
- Iron oxide showed basic dissolution with a slope of -0.513, consistent with the formation of NaFeO₂. The results are consistent with NaFeO₂ found in air-ports. Carbon steel weight loss experiments, however, did not correspond to Fe₂O₃ solubility.

Controlling conditions in the kraft recovery boiler air-ports that establish a minimum solubility condition should lead to a lower corrosion rate of composite tubes. The basicity of a NaOH deposit in a kraft recovery boiler could be controlled by the amount of water vapor in the incoming air, reducing the corrosion rate and providing significant cost savings. The practicality of such an approach would have to be demonstrated. Addition factors, such as the presence of and effect of other metal oxides and chemical species should be investigated further.

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