Institute of Paper Science and Technology

ANNUAL RESEARCH REVIEW

CORROSION CONTROL

March 26, 1992

Atlanta, Georgia
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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

ANNUAL RESEARCH REVIEW

CORROSION CONTROL

MARCH 26, 1992
CORROSION CONTROL RESEARCH OVERVIEW

MARCH 26, 1992
TECHNICAL PROGRAM REVIEW

Project Title: RECOVERY BOILER CORROSION
Project Code: CORRN
Project Number: 3628
Division: Chemical and Biological Sciences
Project Staff: Jeff Colwell, Greg Fonder
FY 91-92 Budget: $150,000

GOAL:
Improve safety and increase operating life of equipment by proper selection of construction materials and by identifying suitable process conditions.

OBJECTIVE:
To understand the causes of corrosion on the waterwall tubes in the lower furnace of kraft recovery boilers.

SUMMARY:
This project is focused on two main areas of corrosion in the lower furnace of the recovery boiler: fireside corrosion and corrosion due to hydroxide condensation at ports. Our understanding of the gas-solid reactions leading to sulfidation of carbon steel tubes has improved with the knowledge of how initial gas mixtures equilibrate and how reactions between gas and smelt change both the gas and smelt chemistry over time. Moreover, our work here will be integrated with the proposed industry standard test being developed by API.

While the need for sensor development is a necessary part of our efforts at increasing industry knowledge about gas-solid reactions in the recovery boiler, manpower limitations and technical challenges have slowed progress. Work on this task should expand next year to try new concepts.

The initial experiments on determination of long-term corrosion kinetics have shown that the apparatus will be capable of achieving the objectives. The remaining experimental portion of this task will be completed by an incoming Master's student who will begin tests shortly.
By far, most of the progress on this project has come on the port corrosion task. After many different types of experiments were completed, a mechanism for port corrosion has been proposed which is very consistent with the observations. The proposed mechanism is summarized in the paper which is appended to this report. This new mechanism will change the direction of the air port corrosion research in the industry, and probably accelerate the solution to this problem for many mills.
PROJECT 3628

RECOVERY BOILER CORROSION

RESEARCH REVIEW

MARCH 26, 1992

Jeffery A. Colwell
Gregory J. Fonder
INTRODUCTION

The main objective of this project is to understand the causes of corrosion on the waterwall tubes in the lower furnace of the kraft recovery boiler. Once those causes are better understood, preventive measures can be developed. Problems on the fireside and coldside have been observed by many mills, and corrosion has been implicated in several smelt-water explosions over the years. Obviously, safe operation of the boiler is of prime concern, so IPST has been aggressively pursuing research which will contribute to the general, and specific, understanding of recovery boiler corrosion.

This project has been divided into several different tasks to focus our efforts on areas that need the most attention. Figure 1 gives an overview of the structure of the project and how it ties in with other related activities, such as student research and research funded by other agencies. Next to each task is a brief description of the main objective or the question which needs to be answered.

REVIEW OF PAST PROJECT ACTIVITY

Much of the initial work on this project in the past dealt with what is now defined as Task 1, Gas Phase Tests. Experiments have been conducted with different gas chemistries and coupons have also been exposed to powdered smelt to simulate reactions with frozen smelt. The gas that has been primarily used is one of 1% H₂S, 1% O₂, 2% H₂O, 10% CO₂, bal N₂. This composition was found by other researchers to provide maximum corrosion of carbon steel in the laboratory, while being comprised of the same gaseous components found in recovery boilers. Consequently, this allows an acceleration of the corrosion kinetics and allows laboratory tests to be used to rank different materials. Both carbon steel and
stainless steel initially corrode with a parabolic or logarithmic rate law, but after some time, the rate becomes linear.

Sulfur species were added to the powdered smelt in different forms, and in all cases the corrosion kinetics were increased by about the same factor when compared to the base smelt. It was also found that the smelt chemistry changes during the test, i.e., after about 5 hours the sulfide in the smelt is almost gone by reaction with CO₂. Thus, it would be an advantage to develop a gas-only test in which the gas composition simulates the conditions beneath frozen smelt.

The only other task that had a substantial amount of work completed during the previous reporting period was that of Task 4, Port Corrosion. During the last reporting period polarization curves were generated in molten NaOH simultaneously for carbon steel and stainless steel. The results of these tests were not conclusive because sometimes the behavior was opposite from what is generally found in service, i.e., in the laboratory tests sometimes carbon steel was observed to have a higher current (higher corrosion rate) than the stainless steel electrode.

**DISCUSSION OF 1991 RESULTS**

This discussion is divided into parts consistent with the task numbers defined above.

**Task 1. Gas Phase Tests**

**Experimental Procedures**

There are only a few new results in this task because of delays in getting a replacement ceramic tube for the furnace and because of a student project that required the use of this furnace. The tube
was replaced because of excessive sulfur buildup. Also, the stainless steel inlet gas tubing was replaced with ceramic tubes.

After all the physical modifications were completed, tests were run with carbon steel coupons in a pure nitrogen environment to determine a baseline weight loss. Various scenarios were used in an effort to minimize the corrosion due to handling and test start-up conditions. The minimum weight loss occurred using the following procedure:

1) ensure that furnace temperature is 100°C or lower,
2) place coupons (in ceramic boat) in furnace,
3) flush furnace for 10-15 minutes with high flow of nitrogen to remove atmospheric oxygen,
4) reduce nitrogen flow to normal,
5) raise and stabilize furnace temperature to test value, and
6) begin flow of test gas to furnace.

The start-up procedure only made a difference when a very mild environment was used, and low corrosion rates observed. In aggressive environments, the start-up procedure is not as critical. However, the above procedure will now be followed for all future tests.

Another standard procedure has also been implemented. Whenever the test environment is changed from that of a previous run, the furnace is heated in air to 800°C, to oxidize any sulfur deposits in the reaction tube prior to the new run. This is to ensure that the sulfur pressure in the furnace is the desired value, and not the result of the vapor pressure of solid or liquid sulfur deposits.

A schematic representation of the experimental apparatus is given in Figures 2 and 3.
Results

The tests completed in this reporting period were run in a gas-only environment at either 360°C or 440°C. Four different gas mixtures were used.

A. IPST Standard Atmosphere (1% H₂S, 1% O₂, 2% H₂O, 10% CO₂, balance N₂) at 440°C.

This is the same environment that was used in most all of the other previous gas-only tests. During this last reporting period, carbon steel coupons with a pack cementation coating were tested. The coating is a Si-Cr diffusion coating which basically converts the surface of the carbon steel tube to a high performance stainless steel. This coating was conceived at Ohio State University and is still under development, but promising trials in utility boilers are underway. Carbon steel (C1018) coupons were simultaneously chromized and siliconized to give a 25% Cr - 3% Si composition at the coupon surface; a micrograph of the cross-section is given in Figure 4. Also in Figure 4, the concentration profiles and effective depth of the coating, which is about 250 microns, is illustrated. The results of the corrosion tests are shown below in Table 1.

Table 1. Weight-loss and Corrosion Rates for Si-Cr Coated Carbon Steel Coupons.

<table>
<thead>
<tr>
<th>Time</th>
<th>Weight Loss</th>
<th>Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>72 hr</td>
<td>9.9 mg</td>
<td>3 mpy</td>
</tr>
<tr>
<td>168 hr</td>
<td>6.9 mg</td>
<td>&lt;1 mpy</td>
</tr>
</tbody>
</table>
These rates are much less than the rates for uncoated carbon steel or Type 304 stainless steel which are 175 mpy and 10 mpy, respectively. The higher weight loss figures for the shorter run may have been due to surface contamination remaining from the pack cementation process that was not present for the longer run. The same coupon was used for both tests. Thus, this coating should be considered further for kraft recovery boiler applications.

**B. Water Vapor Enriched Atmosphere (1% H₂S, 1% O₂, 9% H₂O, 10% CO₂, balance N₂) at 440°C.**

One test each was run on carbon steel (C1018) and stainless steel (304). The additional water vapor had no effect on the corrosion of carbon steel while the corrosion rate was reduced by a factor of five for stainless steel. The values for the corrosion rates are 170 mpy and 2 mpy, respectively.

**C. Simplified Atmosphere (1% H₂S, balance N₂) at 360°C.**

This atmosphere was selected to compare results with those obtained by PAPRICAN in work funded by API. The test was run with C1018 coupons and yielded a corrosion rate of 4 mpy for a 10 day trial. This value is close to the 7 mpy reported by PAPRICAN, even though the test setup is not exactly the same. However, this result is very much lower than our previous 14 day runs using the IPST Standard Test Gas, which yielded 175 mpy.

**D. Equilibrium Atmosphere (50% H₂, 1.7% H₂O, 1.4% H₂S, balance N₂) at 360°C and 440°C.**

The results of previous tests in the horizontal tube furnace reveal that there is usually a difference in weight loss between two duplicate coupons. In almost all cases the upstream coupon has the
higher weight loss. Temperature differences are not likely because the coupons are placed in the center of the furnace and the experimentally determined furnace temperature profile shows that it is essentially constant. All the coupons are manufactured from the same heat of steel, so compositional differences between coupons should be very small.

The other variable in the test is the gas environment. The difference in weight loss that each coupon experiences is probably because the coupons are exposed to slightly different gas environments. The composition of the gas could change for two primary reasons; the sulfur in the gas is reacting with the metal and being consumed, the composition changes because the initial gas mixture (non-equilibrium) requires some unknown length of time to reach equilibrium. It is also possible that a combination of the two reasons controls the corrosion kinetics of the two coupons.

In order to reduce the number of experimental variables an initial gas which is already close to equilibrium was used. A commercial thermochemical equilibrium program (TEQWORKS©) was used to determine the equilibrium concentrations of test gases present when a certain combination of inlet gases was used. The test gas was selected as a combination of $\text{H}_2\text{S}$, $\text{H}_2\text{O}$ and $\text{H}_2$, to fix the $\text{P}_2\text{O}_2$ and $\text{PS}_2$. The composition of the atmosphere described below shows very small changes in composition when equilibrium is reached, so little change in the gas occurs as it enters the furnace and reaches the specimens. The equilibrium gas composition and the results of the tests are given in Tables 2 and 3, respectively.

These results are opposite from the previous tests because in this case, the downstream coupon suffered more weight change than the upstream coupon. This needs further investigation before the reasons are clear.
Task 2. Local S and O Activities

The local thermodynamic conditions beneath a frozen smelt layer obviously control the kinetics of scale growth more than the bulk gas chemistry in the furnace. While it may be possible to develop models to predict these conditions, it is always better if a direct measurement can be made.

The objective of this task is to develop a technique using solid electrolytes. Solid electrolytes are typically ionic conductors which can be used to measure a thermodynamic quantity, relative to the conducting species, on one side of the electrolyte if the value on the other side is known. Thus, if that value is fixed in an experiment, the device becomes a probe capable of determining instantaneous values for the thermodynamic potential of interest. For this case, we are primarily interested in knowing what the local sulfur and oxygen activities are beneath the smelt. There are published reports on the use of sulfate electrolytes for measuring SO₃ partial pressure at the temperatures of interest in kraft recovery boilers. But, to obtain the sulfur partial pressure, an oxygen probe is also needed for an independent measurement of oxygen partial pressure. The experimentation in this task was designed to determine whether a standard zirconia oxygen gauge could be used for this purpose.

Experimental Procedures

An oxygen probe was built as part of this effort to determine local activities of oxygen and sulfur below the frozen smelt layer on recovery boiler waterwall tubes. A schematic drawing of the probe is shown in Figure 5.

A stabilized zirconia tube (McDanel Refractory Company) was used as the solid electrolyte because of its exclusive oxygen ion conductivity. The end of the tube was platinized to ensure that
equilibrium is attained on the surface, and provide good electrical contact to measure the potential difference between the inside and outside of the tube. The procedure for constructing the probe is as follows:

1) clean the zirconia tube; if any grease present, heat to 700°C in air (heating and cooling should be slow, not more than 100°C/hour)
2) thin platinum paste (Engelhard Corp. part #6082) using toluene
3) use small brush to apply a very thin layer of platinum paste to surface of zirconia tube
4) heat the oxide electrolyte with platinum paste to 850°C, hold at this temperature for 1 hour and then cool to room temperature
5) repeat application of paste and sintering until resistance of platinized surface is several pico-ohms, where measuring electrodes are 1 inch apart.

It may also be necessary to apply the platinum paste to the bottom inside of the tube. The same procedure outlined above is followed if good electrical contact cannot be obtained with the inner surface of the tube.

A thin platinum wire was wound tightly around the platinized section of the tube OD and secured using another short piece of platinum wire. The free end of the wire was fed through a ceramic tube to prevent electrical contact with the zirconia tube, and the tube sealed. Another piece of platinum wire was crumpled into a ball, fed through another single bore ceramic tube, and the wire and ceramic tube inserted into the zirconia tube. A small clamp held the inner ceramic tube in place to maintain good contact between the platinum wire and the inside of the zirconia tube. Both the ceramic outer tube and the zirconia tube were routed through a gas-tight flange and sealed using ULTRA-TORR® o-ring fittings.
The entire probe assembly was then inserted into the furnace and sealed. The inside of the zirconia was left open to the air which fixed the oxygen activity at the inside electrode. Thus, the measurement of the unknown oxygen activity is made inside the furnace tube on the outside surface of the zirconia tube end. Ultra-pure nitrogen was then flowed into the furnace for 15 minutes before the test began. The temperature of the furnace was slowly raised to 800°C to avoid thermal shocking the zirconia, and the potential difference across the zirconia probe wall was recorded.

The relationship between oxygen pressure and potential difference is given by the formula:

\[ E(\text{volts}) = \frac{RT}{4F} \ln \frac{P_i}{P_0} \]

where

- \( R = 8.314 \ \text{J/mol K} \)
- \( T = \text{gas temperature in K} \)
- \( F = 96,500 \ \text{C/mol} \)
- \( P_i = \text{oxygen pressure inside tube} \)
- \( P_0 = \text{oxygen pressure outside tube} \)

After several tests it became apparent that the probe did not give reliable results below 500°C. One result that was useful was that above 500°C an oxygen partial pressure of \( 2 \times 10^{-9} \ \text{atm} \) was recorded over the 300°C range from 800 down to 500°C. This partial pressure measurement helped to explain a result from Task 1; it was not possible to lower the corrosion rate below some minimum level in a pure nitrogen atmosphere due to this small amount of oxygen.

The development of a sulfur probe hinges on the development of a method to measure the oxygen activity independently at lower temperatures. Additional effort will be made to determine alternatives. Moreover, the \( \text{SO}_3 \) probe needs further consideration.
to determine whether the knowledge of the local $\text{SO}_3$ partial pressure would be beneficial in itself to some degree.

**Task 3. Long-Term Kinetics**

Boilers are designed to operate for many thousands of hours without replacing waterwall tubes. Indeed, even between scheduled shutdowns, the boiler must operate for 4,000 to 8,000 hours, depending upon the interval. Most of our laboratory tests are at most a few hundred hours and usually much less than that. From the laboratory data, an estimate of remaining life is made based on these short-term kinetic experiments, and material rankings result. An implicit assumption in this approach is that the kinetics do not change and the rate laws developed are constant. This has not been demonstrated for this application. In other industries a phenomenon known as breakaway corrosion has been reported for stainless steels. Breakaway corrosion occurs as a result of depletion of the scale-forming element and causes the kinetics to change from parabolic to linear with a higher rate constant. This task is designed to determine whether this phenomenon is likely to occur in the recovery boiler environment.

**Experimental Procedures**

The previous technique for establishing kinetics has been by determining weight loss of an individual coupon after a specific time of exposure. In this task a different approach will be used. A continuously recording thermobalance will allow the weight of the specimen to be recorded so that any changes in the rate constant will be immediately apparent.

The system is shown schematically in Figure 6. The balance is placed on top of a frame which holds a vertical tube furnace. A platinum wire is used to support the test specimen from the balance
and is adjusted so that the specimen is located at the furnace hot zone. Gas is admitted into the furnace through the bottom and exits above the furnace but below the balance. Provisions for an inert gas purge of the balance will also be made for runs containing hydrogen sulfide. The balance provides a voltage output which is recorded on a strip chart.

**Results**

The initial experiments with this apparatus were made to calibrate and determine the sensitivity of the measurements. Carbon steel (C1018) was reacted in air at 400°C for 115 hours. The weight change as recorded is shown in Figure 7. The plot shows that the kinetics are parabolic with time which indicates diffusion control through the oxide scale, as would be expected. The rate constant was determined from a \( \Delta W^2 \) vs. time plot to be \( 1.25 \times 10^{-12} \) mg²/cm⁴/sec. Comparison of the weight change from the recording balance with the coupon weight change (final - initial) from another balance showed that the weight change from the recording balance was about 0.7 mg higher. This difference still needs to be reconciled and is not in the direction expected if scale spallation occurred on cooling.

Because stainless steels will be tested in the apparatus, another run was made with Type 304 stainless steel to determine if the balance would be sensitive enough to read small but significant changes in the weight change of alloys with low corrosion rates. The rate constant for corrosion of Type 310 stainless steel has been reported at 500°C to be about \( 1 \times 10^{-16} \) g²/cm⁴/sec (Wright and Colwell, DOE Report ORNL/Sub/86-57444/02, pg. 26, 1990). Assuming that the rate constant of Type 304 stainless steel is about the same as that of 310, the experiment at 400°C should have produced a weight gain of about 0.1 mg. However, the balance showed a weight increase of about 1 mg. A run at room temperature for six days indicated that the balance had a baseline drift of about 0.5 mg over that period of time. Consequently, the apparatus has an
accuracy limitation of recording weight changes of probably about 5 mg, if 10 percent error is acceptable. The difference in the weight from the balance compared to the actual weight change for the first carbon steel experiment is probably due to this drift.

The use of this thermobalance appears to be promising for tests in corrosive environments with reasonably high weight changes. However, modifications will need to be made to the laboratory to allow ventilation should the furnace tube break during an $H_2S$ test.

Task 4. Port Corrosion

Because of excessive fireside sulfidation corrosion of carbon steel waterwall tubes, boiler manufacturers began offering composite tubes for lower furnace applications. Composite tubes are manufactured with a carbon steel inner tube for corrosion protection on the waterside, and a stainless steel outer tube which protects from fireside corrosion. This combination has provided a good compromise in performance and has allowed boilers to be operated at higher pressures.

As boiler operating pressures continue to rise, a problem of corrosion at air ports is occasionally observed. This has also been seen at other ports, too. Corrosion of the stainless steel outer layer occurs very rapidly (150 mpy) until it is completely consumed. Then, when the carbon steel becomes exposed, the corrosion of the tube slows and is minimal thereafter. Because the stainless steel was used to prevent corrosion of the carbon steel tubes, there is an obvious concern when carbon steel is exposed. Most researchers believe that port corrosion occurs because of the condensation of NaOH in stagnant flow areas. The mechanism for this attack is under investigation because the industry needs to know how to prevent or control this situation. So far, this type of attack has not resulted in any tube ruptures, but the severity of corrosion justifies work to solve the problem.
A. Field Tests

A field probe had been designed previously to make in-situ measurements in an operating boiler. The probe will collect deposit samples near the cold side of the waterwall tubes and be able to determine the melting point of the deposit before removing the probe from the furnace.

Experimental Procedures

The air port corrosion probes were slightly modified (Figure 8) and then bench tested to insure proper temperature control. The temperature was controllable to within a $\Delta T$ of $\pm 1^\circ F$. The ability of the probe to determine the melting point of any deposit was also tested and it was found to depend slightly on the rate of temperature change. An estimated accuracy of $\Delta T$ of $\pm 5^\circ F$ in determining the melting point is expected. After all bench testing was completed new coupons were weighed and installed. Final arrangements were made with the mill to install two probes.

Upon arrival at the mill it was discovered that one of the probe ports was damaged during the previous shutdown period. A decision was made to install one probe in the location at the secondary air ports. All the necessary electrical and air supply connections were made and the probe was inserted. The temperature setpoint for all tests was $536^\circ F$ and this temperature was maintained within $\pm 1^\circ F$ as had been seen during bench testing.

Results

The first test was conducted for a period of 24 hours. There were insufficient deposits accumulated during this time to get an accurate melting point temperature or to collect deposits for analysis. The first probe was damaged during the melting point determination and was returned to IPST for repairs. The coupon
from the 24 hour test was removed from the probe, cleaned, and reweighed. The corrosion rate was calculated to be 2 mpy over the 24 hour time period, but deposit had not covered the entire surface, so this is not indicative of the local corrosion rate.

The second unused probe was installed for a longer and unattended test. The second test lasted for 22 days and this time there was sufficient deposition to enable a sample to be taken. The coupon showed little evidence of corrosion and was not removed. Also, it was possible to determine a melting point temperature in-situ. The temperature of the probe was slowly raised while resistance between the platinum electrodes was continuously monitored using a Keithley Model 610C Electrometer. At 562°F the resistance dropped rapidly to 0 Ω, indicating that the deposit had melted. The probe was reinstalled and the weight loss trial continued. The deposits were returned to IPST for analysis. The following results were determined:

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>15.3%</td>
</tr>
<tr>
<td>K</td>
<td>2.6%</td>
</tr>
</tbody>
</table>

The K/Na ratio yields a theoretical melting point value close to that measured, if the same ratio of hydroxide is assumed.

No results were obtained for the third test because the air supply line connector was damaged and the probe was left installed with electrical power still on. Without air flow the cartridge heater attempted to maintain temperature and blew the fuse in the temperature controller. There were no deposits present and no accurate knowledge of when the probe failed. The probe was removed and returned to IPST for repairs.
B. Laboratory Tests

Experimental Procedures

The laboratory work went through several modifications to develop repeatable quantitative results. The prior work used a quasi-potentiostatic method (Figure 9). However, that method gave results that were very difficult to repeat. The results from this method when performed in Appleton could not be reliably repeated in Atlanta; in Appleton stainless steel always had a higher corrosion current than carbon steel, while the reverse was found most of the time during our recent tests in Atlanta.

The next method attempted was to use a zero-resistance ammeter (ZRA) to measure the galvanic current between the stainless steel and carbon steel electrodes in molten NaOH. A Wenking potentiostat was used as the zero-resistance ammeter (Figure 10). The same four-electrode probe as used in the initial series of tests (Figure 11) was used for these galvanic current measurements. But, only the stainless steel and carbon steel electrodes were used. The NaOH was raised to the test temperature, 320°C, where it was molten. The probe was inserted partway into the retort for about 5 minutes in order to prevent the molten NaOH from freezing when the probe was inserted. The test leads from the ZRA were attached to the steel electrodes and the output of the ammeter was directed to a strip chart recorder. The length of each test was from 2-3 days. This test did not yield all the information needed to completely explain rapid corrosion of stainless steel at air ports so another method was needed.

The next method chosen was a simple weight loss experiment. Short pieces of wire (2-3 cm) were weighed and placed in alumina crucibles. Sodium hydroxide (20 g) and any additions were then added to the crucible, which was then placed in the retort and raised to the test temperature. Tests of various duration were performed. At the end of the test the furnace was turned off and
the retort removed and allowed to cool. The crucible was then removed from the retort and the frozen NaOH dissolved using water. The wires were dried and weighed. The wires were then chemically cleaned and reweighed. This step was repeated until no further weight loss was measured.

**Results**

As mentioned in the laboratory procedures section, the results obtained using the simultaneous polarization method yielded results which contradicted previous findings. Some typical results are shown in Figures 12 through 15. They reveal that carbon steel has a higher corrosion current than stainless steel, which is not what was observed in service. In Figure 15, the data is for Type 316 stainless steel rather than 304, but the behavior of both of these alloys is very similar in the weight loss tests, so this should be representative.

Before this line of inquiry was abandoned, it was decided to make galvanic current measurements between stainless and carbon steel in the same environment. The results of these tests were much more encouraging. A typical curve is shown in Figure 16. Note that the test begins with current flowing from the carbon steel to the stainless steel. But after 4 to 6 hours, the situation reverses and current begins to flow from the stainless to the carbon steel. Similar results were obtained in every case except where there was a large CO₂ percentage in the gas, where it is likely that the hydroxide was converted to carbonate. In that case the stainless steel had a lower current for the entire duration of the test. Since this only gave qualitative results, and were at least in the right direction, additional tests were necessary.

Weight loss tests were carried out with a number of alloys and pure metals. The composition of the various metals and alloys are given in Table 4. All samples, except CA-15 which was washer-shaped,
were wire specimens. All tests were performed with a dry air (dew point of 200 K) gas atmosphere. The results are summarized in Tables 5 through 7 and 8 through 10, which have units of mg/cm² and mpy, respectively.

The base composition of the melt is pure NaOH, to which various additions were made. Initially carbon steel corrodes faster than stainless steel, but after 24 hours the weight loss for carbon steel remains fairly constant while that for stainless steel continues to increase linearly. The basicity of the pure NaOH melt was unknown so Na₂O₂ was added to make the melt more basic. With a 5% Na₂O₂ addition, all the peroxide was gone at the end of a test, so the basicity was still unknown. The amount added was then increased to 10%, and there was still peroxide present at the end of the test. In the basic melt, stainless steel always corroded faster than carbon steel. The results are summarized in Figure 17.

Most mills have potassium present in the recovery boiler deposits so the effect of potassium additions was tested. The addition of KOH reduces the melting point of NaOH with increasing amounts until the system reaches a eutectic composition. The corrosion of both carbon and stainless steel were accelerated by the addition of KOH. For a 20% addition the weight loss was doubled for both steels; the 50% addition resulted in a weight loss increase directly proportional to the increase in KOH for carbon steel, while the weight loss for stainless steel remained fairly constant, but very high.

The other additions represent possible corrosion products present in the molten deposit near the corroding metal surface. The addition of Na₂CrO₄ had little affect on the corrosion of stainless steel while the corrosion rate of carbon steel was reduced by a factor of three. The addition of Na₂CrO₄ and Na₂O₂ to the NaOH doubled the corrosion of stainless steel and increased that of carbon steel by 40%.
The addition of Cr$_2$O$_3$ to NaOH drastically reduced the corrosion of stainless steel while only a small decrease was seen for carbon steel. Chromium oxide is only slightly soluble in molten NaOH as was seen by the fact that most of the 5% addition was still present at the end of the test. Thus, the saturation of the NaOH deposit with the Cr$_2$O$_3$ addition may prevent the NaOH from fluxing the corrosion products from the surface of the stainless steel wire.

Two pure metals, Co and Ni, and an iron-chromium alloy, CA-15 were also tested. Cobalt was tested because its Pourbaix diagram for aqueous systems indicated that at high potentials, an oxide should be stable. This was not the case, and a highly soluble ion is actually stable. The high weight loss observed also proved that the oxide was not protective. The CA-15 alloy was selected because carbon steel does not show rapid corrosion, but 304 stainless steel does, so the idea was to test an alloy which might be a compromise between passivity and rapid corrosion. But, this alloy also had a very high weight loss which shows that the presence of chromium alone (no Ni) in an alloy does not provide adequate protection in this environment.

The weight losses observed for pure nickel show that it should provide protection in a molten hydroxide environment. Tests using nickel coatings are being conducted by several mills but no detailed results have been published yet.

Tests were also made to rate the effectiveness of several different stainless steel grades. The tests were performed with a dry air gas environment at 320°C in pure NaOH and NaOH with a 10% Na$_2$O$_2$ addition. Based on corrosion resistance, the results are (from best to worst):

NaOH \quad 309 > 316 \approx 304

NaOH + 10\% Na$_2$O$_2$ \quad 309 > 304 \approx 316.

After reflecting on the results obtained thus far, several new tests were conducted. These were designed to determine whether
galvanic corrosion effects would be significant when using a Ni coating on either Type 309 stainless steel or carbon steel. The first series of tests measured the galvanic current between two electrodes in molten hydroxide.

1. Nickel vs. 309 Stainless Steel
The galvanic current direction slowly oscillated over time. The oscillations were not symmetric, the amount of time that nickel was polarized in an anodic direction was greater than that for 309. The same type of behavior was seen in both plain NaOH and in NaOH with a 10% Na₂O₂ addition but the peroxide tests showed gentler current swings than those in plain NaOH.

2. Nickel vs. C1010 Carbon Steel
Initially, the C1010 had a very high corrosion current which quickly fell to a low level, and after approximately 18 hours the current direction changed. The current eventually reached a higher level than was seen when the nickel was polarized anodically versus 309 SS. In order to see if this meant that nickel actually corroded more than C1010 in this environment weight loss coupons were placed in the crucible and the galvanic test repeated. The same galvanic current behavior was observed, but the weight loss coupons showed that C1010 had actually corroded more (37 mpy vs. 7 mpy for Ni). Please note, however, that this corrosion rate for C1010 is much less than seen when nickel is not present.

Because the galvanic corrosion current of 304 stainless steel becomes greater than that of the C1010 after 24 hours during the galvanic corrosion tests, individual potentiodynamic polarization scans were conducted. The tests were conducted after the electrodes were aged in the melt for 1, 5, and 72 hours. The results are shown in Figures 18 through 20. After 1 hour, the current for carbon steel is significantly higher than that for stainless steel and there is a very pronounced active-passive peak in the curve. After 5 hours the two curves lie virtually on top of
one another, which is about the same time as the current crossover. After 72 hours, at high potentials, where the corrosion potential lies, the stainless steel curve is above that of the carbon steel (higher current). These curves reflect very well the behavior seen in the galvanic corrosion tests where the anodic current reverses from being from the carbon steel to being from the stainless steel. Thus, the initial potential of the electrode is critical to the electrochemical test behavior observed; it is variable, and is probably an indication of why the simultaneous polarization tests were difficult to repeat reliably.

During the course of conducting the weight loss experiments it was noticed that the NaOH melt was green when the crucible was removed from the retort at the completion of a test. Several tests were conducted to see what was causing the color change (NaOH melt is white). These tests only used a single wire coupon. When only C1010 carbon steel was placed in the crucible and a test conducted the melt was white with a small rust colored area adjacent to the coupon on the surface of the frozen smelt. When stainless steel was used the melt turned green. In both cases the test duration was 24 hours in plain NaOH and the corrosion rate was 10% lower for C1010 and 15% higher for 304 compared with the results of Tables 7 and 8.

As a result of all the experimental work completed thus far, a proposed mechanism for corrosion at ports has been developed. The work is described in the attached paper which will be submitted to an appropriate journal. During the course of the model development, a few additional critical experiments were conducted which were used to determine whether certain features of the model were correct, or at least consistent with the theory. The results of those experiments are best considered in the context of the model and are not repeated here.
CONCLUSIONS AND RECOMMENDATIONS

This project is focused on two main areas of corrosion in the lower furnace of the recovery boiler: fireside corrosion and corrosion due to hydroxide condensation at ports. Our understanding of the gas-solid reactions leading to sulfidation of carbon steel tubes has improved with the knowledge of how initial gas mixtures equilibrate and how reactions between gas and smelt change both the gas and smelt chemistry over time. Moreover, our work here will be integrated with the proposed industry standard test being developed by API.

While the need for sensor development is a necessary part of our efforts at increasing industry knowledge about gas-solid reactions in the recovery boiler, manpower limitations and technical challenges have slowed progress. Work on this task should expand next year to try new concepts.

The initial experiments on determination of long-term corrosion kinetics have shown that the apparatus will be capable of achieving the objectives. The remaining experimental portion of this task will be completed by an incoming Master's student who will begin tests shortly.

By far, most of the progress on this project has come on the port corrosion task. After many different types of experiments were completed, a mechanism for port corrosion has been proposed which is very consistent with the observations. The proposes mechanism is summarized in the paper which is appended to this report. This new mechanism will change the direction of the air port corrosion research in the industry, and probably accelerate the solution to this problem for many mills.
FUTURE ACTIVITY

1. Continue gas-solid reaction studies and link with API-funded test development.

2. Make use of student research to answer the question about the long-term kinetic rate laws for corrosion in the lower furnace.

3. Focus on new concepts for oxygen sensors which can be used in conjunction with a new sulfur probe.

4. Based on the newly proposed mechanism for air port corrosion, revise the research direction and develop a program to determine controlling variables and potential mitigation methods.
Table 2. Results of Chemical Equilibrium Calculations.

<table>
<thead>
<tr>
<th>Initial Gas Composition (mole fraction)</th>
<th>Equilibrium Gas Composition (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>H₂</td>
<td>0.4998</td>
</tr>
<tr>
<td>N₂</td>
<td>0.4688</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0170</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.0145</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.0</td>
</tr>
<tr>
<td>S₂</td>
<td>0.0</td>
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<tr>
<td>SH</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 3. Weight Loss and Corrosion Rates for Carbon Steel (C1018) Coupons in the Equilibrium Gas of Table 2.

<table>
<thead>
<tr>
<th>Coupon</th>
<th>Corrosion Rate, mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>320°C</td>
</tr>
<tr>
<td>upstream</td>
<td>6</td>
</tr>
<tr>
<td>downstream</td>
<td>5</td>
</tr>
<tr>
<td>average</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Table 4. Composition of wire materials used as electrodes and weight loss specimens.

<table>
<thead>
<tr>
<th></th>
<th>C1010</th>
<th>304</th>
<th>316</th>
<th>309</th>
<th>Cobalt</th>
<th>Nickel</th>
<th>CA-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.10</td>
<td>0.04</td>
<td>0.06</td>
<td>0.018</td>
<td></td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td>5*</td>
<td>0.06</td>
</tr>
<tr>
<td>Fe</td>
<td>BAL</td>
<td>BAL</td>
<td>BAL</td>
<td>BAL</td>
<td>3*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.49</td>
<td>1.07</td>
<td>1.80</td>
<td>1.79</td>
<td></td>
<td></td>
<td>0.44</td>
</tr>
<tr>
<td>Mo</td>
<td>2.20</td>
<td></td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td>Ni</td>
<td>9.05</td>
<td>12.5</td>
<td>13.8</td>
<td></td>
<td>99.995</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99.995</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.02</td>
<td>0.03</td>
<td>0.020</td>
<td>0.016</td>
<td></td>
<td></td>
<td>0.027</td>
</tr>
<tr>
<td>S</td>
<td>0.02</td>
<td>0.006</td>
<td>0.01</td>
<td>0.002</td>
<td></td>
<td></td>
<td>0.03</td>
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<tr>
<td>Si</td>
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<td>0.34</td>
<td>0.40</td>
<td>0.41</td>
<td></td>
<td>20*</td>
<td>0.3</td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*ppm
Table 5. Weight loss data in mg/cm² for carbon steel in molten NaOH at 320°C.

| Additives     | C1010 |               |               |               |               |               |               |
|---------------|-------|---------------|---------------|---------------|---------------|---------------|
| Hrs NaOH KOH | KOH   | Na₂O₂ Na₂O₂   | Na₂CrO₄ + Na₂O₂ | Na₂CrO₄      | Cr₂O₃         |
| 20% 50% 5%   | 10%   | 5%            | 5%            | 5 & 10%       | <5%           |
| 5 11.6       |       | 1.2           |               |               |               |
| 24 13.9      | 31.0  | 74.0          | 5.1           |               | 8.1           |
| 72 13.2      | 9.0   | 25.7          | 4.1           | 35.1          |
| 168 15.2     |       | 30.3          |               |               |               |

Table 6. Weight loss data in mg/cm² for stainless steel in molten NaOH at 320°C.

<table>
<thead>
<tr>
<th>Additives</th>
<th>304</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hrs NaOH KOH</td>
<td>KOH</td>
<td>Na₂O₂ Na₂O₂</td>
<td>Na₂CrO₄ + Na₂O₂</td>
<td>Na₂CrO₄</td>
<td>Cr₂O₃</td>
<td></td>
</tr>
<tr>
<td>20% 50% 5%</td>
<td>10%</td>
<td>5%</td>
<td>5%</td>
<td>5 &amp; 10%</td>
<td>&lt;5%</td>
<td></td>
</tr>
<tr>
<td>5 0.62</td>
<td></td>
<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 7.2</td>
<td>19.3</td>
<td>17.6</td>
<td>31.6</td>
<td></td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>72 26.2</td>
<td>18.9</td>
<td>43.2</td>
<td>22.1</td>
<td>82.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>168 79.5</td>
<td></td>
<td>85.5</td>
<td></td>
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</table>

Table 7. Weight loss data in mg/cm² for various pure metals and alloys at 320°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>Cobalt</th>
<th>Nickel</th>
<th>CA-15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10% Na₂O₂</td>
<td>NaOH</td>
<td>10% Na₂O₂</td>
</tr>
<tr>
<td>24</td>
<td>21.9</td>
<td>0.90</td>
<td>0.60</td>
</tr>
<tr>
<td>72</td>
<td></td>
<td>0.90</td>
<td>0.30</td>
</tr>
</tbody>
</table>

¹ dew point = -70°C
Table 8. Weight loss data in mpy for carbon steel in molten NaOH at 320°C.

<table>
<thead>
<tr>
<th>Hrs</th>
<th>NaOH</th>
<th>KOH</th>
<th>KOH</th>
<th>Na₂O₂</th>
<th>Na₂O₂</th>
<th>Na₂CrO₄</th>
<th>Na₂CrO₄ + Na₂O₂</th>
<th>Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10%</td>
<td>50%</td>
<td>5%</td>
<td>10%</td>
<td>5%</td>
<td>5 &amp; 10%</td>
<td>&lt;5%</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>567</td>
<td>1353</td>
<td>93</td>
<td>146</td>
<td>23</td>
<td>214</td>
<td></td>
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</tr>
<tr>
<td>72</td>
<td>51</td>
<td>146</td>
<td>23</td>
<td>214</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>168</td>
<td>40</td>
<td></td>
<td></td>
<td>79</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9. Weight loss data in mpy for stainless steel in molten NaOH at 320°C.

<table>
<thead>
<tr>
<th>Hrs</th>
<th>NaOH</th>
<th>KOH</th>
<th>KOH</th>
<th>Na₂O₂</th>
<th>Na₂O₂</th>
<th>Na₂CrO₄</th>
<th>Na₂CrO₄ + Na₂O₂</th>
<th>Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>54</td>
<td></td>
<td></td>
<td>611</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>133</td>
<td>350</td>
<td>318</td>
<td>572</td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>72</td>
<td>158</td>
<td></td>
<td></td>
<td>114</td>
<td>279</td>
<td>133</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>168</td>
<td>205</td>
<td></td>
<td></td>
<td>221</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10. Weight loss data in mpy for various pure metals and alloys at 320°C.

<table>
<thead>
<tr>
<th>Time</th>
<th>Cobalt</th>
<th>Nickel</th>
<th>CA-15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hrs</td>
<td>10% Na₂O₂</td>
<td>NaOH</td>
<td>10% Na₂O₂</td>
</tr>
<tr>
<td>24</td>
<td>353</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>72</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

¹ dew point = -70°C
RECOVERY BOILER CORROSION

Task 1  
Gas Phase Tests

Develop Suitable Test Gas
With Controlled C,O,S Potentials

Task 2  
Determine Local S,O

Develop Sensor for O and S
Under Frozen Smelt

Task 3  
Determine Long-Term Behavior

Can the Kinetics be Extrapolated
to Predict Service Performance?

Task 4  
Port Corrosion

Determine Mechanism and Mitigate
Composite Tube Wastage

Figure 1. Overall Organization of Recovery Boiler Corrosion Project.
EXPERIMENTAL ARRANGEMENT

Experimental Arrangement for Gas Phase Tests.

Gas cylinder contents:
#1 3% O₂, 30% CO₂, bal. N₂
#2 3% H₂S, bal. N₂
#3 N₂

Flow gages

Heated line

Fume hood

Scrubber (NaOH solution)

Water vapor addition

Gas cylinders

Figure 2.
Figure 3. Schematic of Gas Phase Test Furnace Showing Coupon Placement.
Figure 4. Optical Photomicrograph Showing Cr-Si Coating Morphology and Concentration Profiles.
Schematic Representation of Zirconia Oxygen Gauge.

- OXYGEN PROBE
- Platinized Surface
- Stabilized Zirconia Tube
- Ceramic Tubes
- Ceramic Cement
- Platinum Wires

Figure 5.
Figure 6. Schematic Representation of Thermobalance Apparatus.
Continuous Weight measurements

Figure 7. *Kinetics Obtained for Carbon Steel in Air at 400°C with Thermobalance.*
Figure 8. Field Probe Used to Collect Air Port Deposits and Measure Deposit Melting Temperature In-situ.
Molten Sodium Hydroxide Studies
Electrical Connections

Meaning of Current Values
AMEL = -I_{ss}
Wenking = I_{ss} + I_{cs}

Operation
Wenking supplies the current to polarize both electrodes. AMEL supplies current to keep potential between electrodes at 0 V.

Figure 9. Electrochemical Equipment Used to Develop Simultaneous Polarization Curves for Carbon Steel and Stainless Steel in Molten NaOH.
Figure 10. Apparatus Used to Make Galvanic Corrosion Measurements.
Molten NaOH Studies
Experimental Arrangement

Figure 11. Furnace Arrangement for Molten NaOH Studies.
**Molten Sodium Hydroxide Studies**

Nitrogen Atmosphere (20 hr)

![Graph showing simultaneous polarization curves for 304 SS and Carbon Steel in NaOH with Nitrogen Cover Gas.](image)

**Figure 12.** Simultaneous Polarization Curves for 304 SS and Carbon Steel in NaOH with Nitrogen Cover Gas.

Corrosion Potentials:
- SS = -0.345 V
- CS = -0.440 V
- Mixed = -0.420 V
Molten Sodium Hydroxide Studies
Nitrogen Atmosphere (1 hr)
Approx. 200 cu. mm Na metal added

Figure 13. Simultaneous Polarization Curves for 304 SS and Carbon Steel in NaOH with Na added to melt.
Molten Sodium Hydroxide Studies
"Building" Air Atmosphere (1 hr)

Corrosion Potentials
SS = -0.477 V
CS = -0.568 V
Mixed = -0.561 V

Figure 14. Simultaneous Polarization Curves for 304 SS and Carbon Steel in NaOH with Air Cover Gas.
Molten Sodium Hydroxide Studies
"Building" Air Atmosphere (1 hr)

316 SS
C1018 CS

Corrosion Potentials
SS = -0.601 V
CS = -0.647 V
Mixed = -0.631 V

Figure 15. Example of Polarization Curves when 316 SS has Higher Current Than Carbon Steel.
Molten NaOH Studies
Galvanic Current Measurements

Figure 16. Galvanic Current Trace for Couple Between 304 SS and Carbon Steel.
Molten Sodium Hydroxide Studies
Plain NaOH and NaOH + Peroxide

Weight Loss (mg/cm²)

Time (hours)

CS Plain  SS Plain  CS Peroxide  SS Peroxide

Figure 17. Weight-loss vs. Time Plot for Carbon Steel and Stainless Steel. Note that Peroxide Additions Make Melt More Basic.
Molten Sodium Hydroxide Studies

Single electrode scans in plain NaOH

Electrodes in melt 1 hour before test

Figure 18. Individual Polarization Curves When Electrodes Aged in Melt for 1 Hour Before Scan.
Individual Polarization Curves When Electrodes Aged in Melt for 5 Hours Before Scan.
Molten Sodium Hydroxide Studies

Single electrode scans in plain NaOH

Figure 20. Individual Polarization Curves when Electrodes Aged in Melt for 72 Hours Before Scan.
ON THE MECHANISM OF CORROSION OF COMPOSITE TUBES AT PORTS IN KRAFT RECOVERY BOILERS

Jeffery A. Colwell
ON THE MECHANISM OF CORROSION OF COMPOSITE TUBES
AT PORTS IN KRAFT RECOVERY BOILERS

J. A. Colwell
Institute of Paper Science and Technology
575 14th Street, N.W.
Atlanta, GA 30318

INTRODUCTION

The problem of corrosion at air ports in recovery boilers using composite tubes is well-documented (1,2). While most of the attention has been focused on air ports, similar corrosive attack has also been observed at other locations such as inspection ports. The corrosion of the stainless steel outer layer is extremely rapid and continues until the stainless steel is completely consumed in these localized areas. Usually, once the carbon steel part of the composite tube is exposed, corrosion slows and is then minimal. There is concern that if the environmental conditions should change near the area where the stainless steel is depleted, rapid sulfidation of the carbon steel may occur. However, in the highly oxidizing area of the air port, reducing conditions would not be expected. But, in any case, it is desirable to understand the corrosion mechanism in these areas so that life of the waterwall tubes can be estimated with some degree of accuracy. Currently, the mechanism of air port corrosion is not completely understood, but it has been suggested that condensation of NaOH is responsible (3). Several different mechanisms have been postulated, including galvanic effects between the stainless steel outer layer and the carbon steel inner layer.

In gas turbines, especially those operated over seawater, a phenomenon was discovered in the late 1960's in which rapid corrosion of Ni-base super alloys was caused by continued sulfidation of the alloy (4,5). The mechanism has been studied for some time and it is generally agreed that the presence of a thin molten Na$_2$SO$_4$ salt film initiates and propagates the attack (6). The same effect is also observed in molten sodium carbonate fuel cells with Ni (7). Because it is believed that the corrosion of stainless steel at air ports is also initiated by a molten salt, i.e., NaOH, it is at least possible, and most likely, that the same mechanism is responsible.
Thermodynamics and Salt Chemistry

Much of the hot corrosion research on molten sulfates has been conducted and reviewed by Rapp (8,9); it will be highlighted here to aid the reader.

Oxyanion melts of alkali nitrates, carbonates, hydroxides and sulfates exhibit an acid-base behavior where the acid component is NO$_2^-$, CO$_2^-$, H$_2$O, or SO$_3^-$, respectively. The basic component can be chosen as the oxide ion in all of these cases. Consequently, for molten Na$_2$SO$_4$,

\[ \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{O} + \text{SO}_3^- \]

where the basic component is Na$_2$O and the acid component is SO$_3^-$. For the pure salt, the specification of either acidity or basicity is sufficient, because of the above equilibrium. For mixed melts, if only a single cation is present, e.g., Na$^+$, and mixed anions, then basicity is the parameter which is to be chosen to describe the melt. However, when mixed cations are present with a single anion, the acidity parameter is more appropriate.

Phase stability diagrams can be used in describing the thermodynamics of the system, completely analogous to the techniques pioneered by Pourbaix for aqueous corrosion (10). Plots of electrode potential (oxidizing potential or oxygen activity) vs. basicity ($-\log a_{\text{Na}_2\text{O}}$) are useful in the molten salt case. During the course of the development of these diagrams a convention opposite to aqueous systems resulted in acidity increasing to the right rather than the left. Figure 1 gives the Na-S-O phase stability diagram at 900 C (9). In addition to the major phase fields, within the sodium sulfate field, the regions of predominance for the minority ionic species are also given. This allows relatively quick explanations for chemical and electrochemical reactions using the criterion that spontaneous reactions involve the consumption of unstable species and the formation of stable products for the local conditions.

Oxide Solubilities

From a knowledge of the Na-metal-S-O phase stability diagram, and independent measurement of basicity, and oxygen activity, the solubilities of various oxides have been determined at 1 atm $P_{O_2}$ at 1200 K (11). The phase stability diagrams for Na-Fe-S-O and Na-Cr-S-O are given in Figures 2 and 3, respectively. The corresponding solubility curves are given in Figures 4 and 5. Based on assumed soluble ions, the dependence of the solubility of a particular ion
on basicity can be compared to the experimental slope of the curve. Agreement between the experimental and theoretical slopes indicates the identity of the soluble ion. The agreement of the data is remarkable and validates the approach.

Figure 6 represents a compilation of measured solubilities for typical oxides used in high temperature alloys. As can be seen, the stability of various oxides depends upon the local basicity of the melt. At high basicities, the stability of Co and Ni oxides is greater than Cr oxide, but the situation is reversed at much lower basicities.

**Fluxing Mechanisms**

Early studies (12) on hot corrosion indicated that the gradient in the solubility of the protective oxide (either as a basic or acidic solute) in the salt film is negative at the oxide salt interface:

\[
\frac{d(\text{oxide solubility})}{dx} < 0 \Big|_{x=0}
\]

Then, from Figure 7, the oxide scale would dissolve according to its saturation concentration at the scale/salt interface. The solute ions would then diffuse down the concentration gradient in the salt film and reprecipitate as nonprotective oxide particles where the oxide solubility is lower.

Figure 8 provides a schematic oxide solubility plot with the superposition of different basicities at the oxide/salt interface, I, and the salt/gas interface, II. These conditions set up and maintain continuous hot corrosion according to the model. If the basicities are reversed, then the entire salt film becomes saturated, and hot corrosion stops. This plot is key to understanding when hot corrosion continues and when conditions are such that it stops.

The electrochemical model for the hot corrosion of an initially passivated metal is shown in Figure 9. Two cases are considered, one where the concentration of transition metal ions is small and the reduction step occurs at the oxide/salt interface. Consequently, the basicity is high at that interface because of the locally high concentration of oxide ions. The other case occurs when an appreciable concentration of transition metal ions is present which allows the reduction step to occur at the salt/gas interface, where the basicity would be higher there. In either case, acidic or basic solutes will form based on the oxide solubility plot, i.e., the overall basicity. It would be expected that the shift of the reduction reaction to the salt/gas interface would accelerate oxide dissolution because the need for oxidant diffusion through the salt film to the oxide surface would not be required.
APPLICATION TO AIR PORT CORROSION

The application of the above concepts to air port corrosion begins with the molten salt equilibrium reaction, i.e.,

\[ 2\text{NaOH} \rightleftharpoons \text{Na}_2\text{O} + \text{H}_2\text{O} \]

The basic component is \( \text{Na}_2\text{O} \) and the acidic component is \( \text{H}_2\text{O} \). While it is likely that KOH is also present in the NaOH, the initial treatment will consider only the presence of NaOH.

To consider corrosion of composite waterwall tubes (stainless steel outer tube and carbon steel inner tube), the dissolution of the two oxides which are normally present on the surface, namely \( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \), will be used initially to describe the corrosion of the stainless steel and carbon steel, respectively. We know that the corrosion rate of stainless steel is much more rapid than that of carbon steel. This is observed in service and in the laboratory. Corrosion rate differences of more than an order of magnitude can be observed. Measurements of galvanic currents (13) show that Type 304 stainless steel corrodes preferentially over carbon steel, but the magnitude of those currents do not justify the higher weight losses of the stainless steel. Consequently, even though galvanic corrosion contributes, it is not the controlling mechanism.

If we begin with the schematic solubility curves of Figure 10, it is assumed that the shape and position in NaOH at temperatures just above its melting point are similar to those measured in sodium sulfate at 1200 K (9). The only basicities where the solubility (corrosion) of Cr (stainless steel) would be more than that of Fe (carbon steel), is to the left of point 'a'. Thus, corrosion of Cr would be greater than that of Fe only in melts where the basicity was greater than 'a'. In fact, because of the differences in the corrosion rates, one would expect that the actual basicity would be far from 'a' and be much further to the left on the diagram.

\textbf{Cr}_2\text{O}_3 \text{ Dissolution}

Because the basicity is to the left of the chromia minimum, it is apparent that it dissolves as a basic solute, and because of the relatively high \( P_{\text{O}_2} \) in the air, probably as \( \text{CrO}_4^{2-} \), by the following reaction:

\[ \text{Cr}_2\text{O}_3 + 2 \text{O}^{2-} + 3/2 \text{O}_2 \rightleftharpoons 2\text{CrO}_4^{2-} \]

This is borne out by the laboratory observation that in our tests when chromia powder is added to the melt for the Type 304 stainless steel corrosion tests, the corrosion rate decreases and the melt turns yellow, which is the color of chromate.
Figure 11 gives the schematic electrochemical model for the chromia dissolution case. The reduction step is most likely oxygen reduction by diffusion of oxygen through the salt film and arrival at the oxide/salt interface. Thus, the basicity is locally high at that location, and Figure 12 summarizes the local solubilities at both interfaces. Because the solubility is higher at the oxide/salt interface, dissolution will readily occur and oxide reprecipitation will occur toward the salt/gas interface. Thus, continued hot corrosion will be observed, giving high corrosion rates.

Fe₂O₃ Dissolution

For the dissolution of Fe₂O₃, two cases need to be considered depending on which side of the minimum in the solubility curve is the actual basicity.

Basic Dissolution

In this case the basicity is to the left of the minimum in the solubility curve and the oxide ion reacts with hematite to form ferrite ion or ferrate ion depending on the oxidizing power of the solution:

- reducing: \( \text{Fe}_2\text{O}_3 + O^{2-} \rightarrow 2\text{FeO}^{2-} \)
- oxidizing: \( \text{Fe}_2\text{O}_3 + 3O^{2-} \rightarrow 2\text{FeO}_3^{3-} \)

It is known that NaFeO₂ has a very low solubility in NaOH, so the reaction would tend to be slow, but the gradient in solubility would be negative (like previous discussion on chromia) and the tendency would be for the reaction to continue as a hot corrosion reaction.

Acid Dissolution

In this case oxide ions would be generated by the acid dissolution of Fe₂O₃:

\( \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}^{3+} + 3O^{2-} \)

The basicity would again be higher at the oxide/salt interface, but because the overall basicity is on the acid side of the curve, this means this area has a lower solubility. Thus, the solubility gradient is positive, and the reaction would reach some equilibrium where the solution is saturated with the solute and the reaction essentially stops.
Basic Dissolution with Transport of Transition Metal Ions

This case is shown in Figure 13, where the reduction step shifts to the salt/gas interface as well as the oxide/salt. At the oxide/salt, hematite complexes with the oxide ion to form ferrite ion which diffuses down its concentration gradient. Also, ferric ion is reduced to ferrous ion, causing transport of ferrous ions to the salt/gas interface where they react with oxygen. This causes the reduction of oxygen to oxide ion and the oxidation of ferrous to ferric again. Thus, the basicity increases at the salt/gas and decreases at the oxide/salt (by consumption to form ferrite). So, the solubility is higher at the gas/salt interface, and a positive solubility gradient exists, which should limit hot corrosion. Note that in this case diffusion of the oxidant through the salt is not required.

Therefore, there are two mechanisms which would allow a low corrosion rate for iron. Normal acidic dissolution and basic dissolution with ferrous ion transport are both possible. Our limited laboratory work and field measurements indicate that the corrosion rate of carbon steel is extremely low, so one of these mechanisms is probable.

Corrosion of Alloys

In the recovery boiler both stainless steel and carbon steel are present, rather than pure Cr and Fe, so pure oxides of Cr and Fe will not be present. One important question that needs to be resolved is if Fe (i.e., carbon steel) has such a low corrosion rate and Type 304 stainless steel is nominally 74 percent Fe, why is the stainless steel completely corroded away leaving no hematite film (or NiO, for that matter) which would protect the remainder of the stainless steel because of its lower solubility.

Acidic dissolution of Fe$_2$O$_3$ and NiO (the Fe and Ni from the stainless steel) could be used to explain this phenomena. The production of oxide ions from the dissolution of both the Fe$_2$O$_3$ and the NiO would be consumed by the basic dissolution of Cr$_2$O$_3$. The normally protective film is likely composed of Fe, Ni and Cr cations in close proximity on the M$_2$O$_3$ lattice so the dissolution and transfer of oxide ions from the Fe- and Ni-oxygen clusters to the Cr-oxygen clusters near the oxide/salt interface could occur extremely rapidly. Oxygen transport to that interface allows the reduction reaction to oxide ions which adds to the supply generated by the acid dissolution of Fe$_2$O$_3$ and NiO. Because of the consumption of the oxide ions by the chromia, the solubility gradient is negative, instead of being positive when dissolution of the individual Fe- and Ni-oxides occur. The salt never becomes saturated in Fe and Ni oxides, so the reaction continues until the stainless steel is consumed.
So, in the case of stainless steel corrosion, the reaction does not stop until the stainless steel is consumed, and then the slower reactions involving Fe$_2$O$_3$ only (the carbon steel inner part of the composite tube) take over, and the corrosion essentially stops due to the saturation of solute as a result of the positive solubility gradient.

MODEL VALIDATION FROM LABORATORY EXPERIMENTS

To test some of the features of this proposed mechanism, a few experiments were conducted to determine whether the data would support the main points of the theory.

Weight loss corrosion tests on several different materials were conducted in pure NaOH at 320°C for various times. Alloy wires were placed in an alumina crucible containing the molten NaOH for the specified time. A summary of the weight loss for each is shown in Table 1. The top part of the table covers experiments which were conducted with a cover gas of flowing dry air. From these data it can be seen that the weight loss of carbon steel remains approximately constant at exposure times between 5 and 168 hours. In contrast, the Type 304 stainless steel continues to lose weight at about the same rate over the same time period. This result is consistent with the model presented here, i.e., chromia dissolution is occurring via a hot corrosion mechanism. Also, the fact that the weight loss of hematite remains essentially constant indicates that dissolution is either by the acidic mechanism or the basic dissolution with transition metal ion transport mechanism. Either of these two mechanisms predict that the salt film will eventually become saturated with solute and the reaction will then essentially stop, which is observed when the weight loss is constant.

Because the model requires that both oxidation and reduction reactions occur to generate the high rates of corrosion of stainless steel, a set of experiments was conducted to stifle the reduction reaction by limiting oxygen transport to the oxide/salt interface. This was accomplished by changing the cover gas to nitrogen with a very low oxygen content. The corrosion data for this case is shown in the last two entries in Table 1. Note that reducing oxygen had very little effect on the corrosion of carbon steel, as would be predicted, because that reaction is controlled by solute saturation due to its positive solubility gradient. In contrast, note that the corrosion of 304 stainless steel was essentially stopped, even up to 139 hours. Another test was devised to determine if the reaction could be slowed by removing the oxidation step, so pure Cr$_2$O$_3$ was used to remove the possibility of the formation of Cr$^{3+}$. These results are also given in Table 1, and as can be seen, the weight loss is much less than that of the 304 stainless steel. Consequently, the model appears to be valid relative to the oxidation and reduction steps.
Another feature of the model is concerned with the acceleration of corrosion of Cr in a stainless steel because dissolution of Fe- and Ni-oxides supply oxide ions which complex with chromia. An experiment was completed where pure Cr metal was compared to the rate of corrosion of 304 stainless steel. The model would predict that the corrosion of pure Cr would be less than that of stainless steel, and that is what was observed, as given in Table 1. The corrosion rate of pure Cr is still greater than that of Fe, by virtue of the position of the two solubility curves, but is smaller than 304 stainless steel by about a factor of two.

A series of experiments was conducted to examine the effect of basicity when the melt is equilibrated in an air cover gas. The data for the "normal" basicity of the melt is again given for comparison, along with data for corrosion in more basic as well as more acidic melts. The more basic melts were achieved by the addition of Na$_2$O$_2$, and the acidic melts were obtained by equilibration with a large fraction of H$_2$O vapor in the flowing air cover gas. The data are summarized in Table 2. The corrosion rate of the carbon steel is at a minimum in the normal melt, and it is accelerated when the basicity is made either more acidic or more basic. Thus, the basicity of the normal melt must be near the solubility minimum for Fe$_2$O$_3$, with changes to more basic melts causing basic dissolution at a higher rate. Modifications which cause the melt to become more acidic must change the dissolution mechanism to that of an acidic solute. In contrast, the 304 stainless steel data show that the corrosion rate continues to decrease as basicity decreases, so the basicity must remain on the basic side of the Cr$_2$O$_3$ minimum.

Thus, the limited number of experiments conducted thus far seem to favor the proposed mechanism. Much work remains to be completed to confirm all the details. For example, areas that need attention are determining the effect of melt chemistry on solubilities, and developing a technique for the reliable measure of basicity.

**SUMMARY**

The corrosion of composite waterwall tubes in the lower furnace of kraft recovery boilers has been explained on the basis of previous work which investigated the hot corrosion of gas turbines. In the case of gas turbines, a molten salt of Na$_2$SO$_4$ caused rapid attack of Ni-base alloys. In recovery boilers the salt is NaOH, or a eutectic mixture with K, and the stainless steel outer layer of the tube is subjected to the rapid wastage.

The corrosion mechanism of the stainless steel (Fe-Cr-Ni alloy) can be summarized as basic dissolution of Cr$_2$O$_3$, with acidic dissolution of Fe$_2$O$_3$ and NiO, which promotes the synergistic dissolution of all components in the alloy. Once the stainless steel has dissolved, the model predicts that the remaining carbon steel is not susceptible to the same rapid corrosion rates observed for
stainless steel because the solute becomes saturated in the molten salt.

Experiments conducted to determine the effect of melt basicity show that corrosion of stainless steel can be reduced (to about 70 mpy) by decreasing melt basicity, i.e., by increasing water content of the gas above the molten NaOH. However, at the same time, the corrosion of carbon steel is increased to unacceptable levels (about 900 mpy). Consequently, because the corrosion of the carbon steel inner layer is the controlling factor in pressure containment, modifying melt basicity will need to be carefully considered before it is a viable method for corrosion control.
REFERENCES


Table 1. Weight-loss of Various Materials in Molten NaOH at 320 C.

<table>
<thead>
<tr>
<th>Time, hr</th>
<th>Environment</th>
<th>Carbon Steel</th>
<th>304 SS</th>
<th>Pure Cr</th>
<th>Pure Cr₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>NaOH (air)</td>
<td>11.6</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>NaOH (air)</td>
<td>13.9</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>72</td>
<td>NaOH (air)</td>
<td>13.2</td>
<td>26.2</td>
<td>-</td>
<td>6.2</td>
</tr>
<tr>
<td>168</td>
<td>NaOH (air)</td>
<td>15.2</td>
<td>79.5</td>
<td>36.2</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>NaOH (N₂)</td>
<td>10.2</td>
<td>0.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>139</td>
<td>NaOH (N₂)</td>
<td>11.3</td>
<td>0.41</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2. Effect of Basicity Changes on the Corrosion of Carbon Steel and Stainless Steel in NaOH at 320 °C for 72 hours. Cover Gas is Dry Air Except for the Water Vapor Case.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Weight-loss, mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon Steel</td>
</tr>
<tr>
<td>NaOH + 10%Na₂O₂ (basic)</td>
<td>25.7</td>
</tr>
<tr>
<td>NaOH</td>
<td>13.2</td>
</tr>
<tr>
<td>NaOH + 80%H₂O(v) (acidic)</td>
<td>145.7</td>
</tr>
</tbody>
</table>
Figure 1. Na-S-O phase stability diagram for 900 C. After Rapp (9).
Figure 2. Na-Cr-S-O phase stability diagram for 1200 K. After Rapp (9).
Figure 3. *Na-Fe-S-O phase stability diagram for 1200 K. After Rapp (9).*
Figure 4. Measured and calculated solubilities of Cr$_2$O$_3$ in fused Na$_2$SO$_4$ at 1200 K for several oxygen activities. After Rapp (9).
Figure 5. Measured and calculated solubilities of $\alpha$-$\text{Fe}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$ in fused $\text{Na}_2\text{SO}_4$ at 1200 K for several oxygen activities. After Rapp (9).
Figure 6. Measured oxide solubilities in fused Na$_2$SO$_4$ at 1200 K and 1 atm O$_2$. After Rapp (9).
Figure 7. Cathodic reduction of $SO_3$ (as $S_2O_7^{2-}$) or molecular oxygen for (a) a high permeability of $SO_3$ or $O_2$ in thin salt film, (b) high concentrations and diffusivities of $M^{2+}$ and $M^{3+}$, or electronic conduction, in the salt film. After Rapp (9).
Figure 8. Cases of Continuous Hot Corrosion of a Pure Metal (I is the oxide/salt interface, and II is the salt/gas interface). After Rapp and Goto (12).
Figure 9. Reprecipitation of a porous MO oxide supported by the solubility gradient in a fused salt film. After Rapp and Goto (12).
Figure 10. *Schematic Solubility Curves for Fe$_2$O$_3$ and Cr$_2$O$_3$. Point "a" indicates basicity where Cr$_2$O$_3$ solubility is greater than Fe$_2$O$_3.*
Figure 11.  Electrochemical Model for the Corrosion of Cr in Molten NaOH in an Oxygen Containing Gas. Negative Solubility Gradient Allows Continuation of Hot Corrosion.
Figure 12. Local Solubilities at Oxide/Salt (I) and Salt/Gas (II) Interfaces for Continued Hot Corrosion of CR in NaOH.
Figure 13. **Electrochemical Model for Hot Corrosion of Fe in NaOH.** Transition Metal Ion Transport Allows Reduction Reaction to Occur at Two Locations. Positive Solubility Gradient Would Limit Hot Corrosion.