Final Report

Materials for Industrial Heat Recovery Systems

Materials for Mid Furnace Environments of Kraft Recovery Boilers

Preet M. Singh

School of Materials Science and Engineering

Georgia Institute of Technology,

Atlanta, GA, 30332

ABSTRACT

Kraft recovery boilers experience localized accelerated corrosion in mid furnace areas. Corrosion patterns may vary from one boiler to other depending upon the operation parameters and general design of the boiler. Local gaseous environments were characterized in areas with corrosion and equivalent areas without accelerated corrosion in a selected boiler over the period of two years. Results from this study indicated that in the areas with accelerated corrosion there was a large variation in the local gas composition at the waterwall surface. Reducing and sulfidizing gases were found in the areas with accelerated corrosion whereas the gas compositions were more oxidizing in the low corrosion areas. Observations during field tests have indicated that the local waterwall temperature may also vary in the mid furnace due to localized combustion and air flow patterns. Mid-furnace environments were simulated in laboratory to evaluate the effect of gas composition and fluctuations on corrosion kinetics of carbon steel tube material. Laboratory tests with SA-210 carbon steel samples with gas composition cycling between oxidizing and reducing/sulfidizing led to an unstable scale formation on the surface. Extent of accelerated corrosion was found to depend upon the extreme partial pressure values of sulfur and oxygen. Carbon steel samples were coated with chromized or aluminized diffusion coatings in the laboratory and were tested under sulfidizing conditions. Both type of diffusion coatings had superior performance compared to the carbon steel samples under similar conditions. Mid-furnace corrosion can be controlled by making gaseous environments in the mid furnace more stable. However, more practical solution seems to be to use waterwall tubes with protective outer layer. This may be done by using composite tubes (stainless steel outer layer), thermal spray coatings of resistant alloys or diffusion barrier coatings like chromizing or aluminizing treatment.

Key Words: Kraft Recovery Boilers, Mid-furnace, Corrosion, Carbon steel, Coatings, Gas sampling, Gas Chromatography, Oxidation, Sulfidation

INTRODUCTION

Water leak in kraft recovery boiler furnace can potentially lead to water-smelt explosion. One of the possible causes for the water leak in recovery boilers is the corrosion of waterwall tubes in the lower and mid furnace areas. Lower furnace area of the kraft recovery boiler has reducing and sulfidizing environment which is known to cause accelerated corrosion of carbon steel waterwall tubes due to high temperature sulfidation. To protect waterwall tubes in the lower furnace from high corrosion rates, composite tubes, with an outer layer of stainless steel, were introduced. Stainless steel layer of composite tubes have generally performed well against the general sulfidation attack in the lower furnace area. However, composite tubes are typically only used in the waterwalls till the last air-port level, which may be secondary in two-level boilers or tertiary air-port in most of newer boilers. Carbon steel tubes are used in the mid and upper furnace areas as the environment in these areas was considered to be oxidizing and far less corrosive than the lower furnace areas.

In recent years, there have been many reports of accelerated corrosion of carbon steel tubes in mid-furnace areas. This is generally attributed to significant changes in the boiler operation parameters like decrease in the air supply at the lower furnace levels and firing high-solids black liquor, which may also raise the gas temperatures in the furnace. Mid-furnace corrosion of boiler waterwalls is prominent above the "cut-line" where the stainless steel waterwall is welded to the carbon steel sections. Due to the appearance of corrosion on waterwall near weld, sometimes this type of mid-furnace corrosion phenomenon is also referred to as cut-line corrosion in the pulp and paper industry.

Our previous work on mid furnace corrosion has shown that the changes in the boiler operation parameters seem to have resulted into changed local environments in the mid furnace of boilers. These changes vary from one boiler to another or within one boiler from one location to another. Based on our field study and limited laboratory data it can be postulated that the recent operational changes in boilers to increase boiler efficiency and to control pollution might have led to the changes causing corrosion rates of waterwall tubes in mid furnace areas to increase significantly. However, what these changes were was not known.

In last few years we have done a number of field studies in different mills to characterize and understand the local environmental changes in the mid furnace area that are responsible for accelerated corrosion of carbon steel tubes in these areas. Typically these studies were short term studies where samples were taken for a few days and our conclusions were made on these observations. Although, a large amount of data was gathered which gave us information on different corrosion mechanisms in the mid-furnace area but long term changes could not be captured by these studies. Results from our previous work have shown that recent changes in the boiler operations seem to be responsible for the changes in local environments in the mid furnace of kraft recovery boilers. Environmental changes vary from boiler to boiler or within one boiler from one location to another. In the present study, a boiler was selected and environmental characterization was done over a two year period, without any operation changes in the boiler or the pulp mill.

Mid-furnace corrosion is forcing longer inspection times during annual shutdowns. Loss of productions along with panel replacement costs can cost millions of dollars to the boiler owners. Main aim of this task of the project is to understand the mechanisms responsible for this recent problem in kraft recovery boilers so that mitigation strategies could be recommended based on results.

EXPERIMENTAL PROCEDURES

Project related to the mid-furnace was divided into two main tasks where in the first task (task 3.2 of initial project proposal) we characterized gaseous environment in a selected boiler whereas in the second task we carried out controlled experiment (task 3.4 of initial project proposal) in representative environments to quantify and confirm the reasons for high corrosion rates of boiler tubes in mid furnace of a boiler.

Characterization of Mid Furnace Environments in Kraft Recovery Boilers

This task was related to characterization of local gaseous environments, in areas with high and low rates of corrosion of carbon steel waterwalls, to understand the reasons behind these differences. Previous work on gaseous environment characterization had shown that the areas with high corrosion rates in the mid furnace generally had higher concentrations of sulfur-bearing gases like hydrogen sulfide and reducing gases like hydrogen and carbon monoxide compared to the low corrosion areas at similar elevation in the boiler. In some boilers, the upper part of the mid furnace (~10 to 30 ft above tertiary airports) had cyclic environments in the high corrosion areas where the environments changed frequently from reducing-sulfidizing to oxidizing (without sulfur-bearing gases).

Long time environment characterization study was planned so that any changes in the environment with time could be evaluated. A boiler with mid-furnace corrosion problem was selected for this study. Selected boiler was a retrofitted B&W boiler with three air levels. Boiler pressure was 10.3 MPa (1500 psig) with the steam temperature around 320°C. Composite tubes were used till the tertiary airport elevation. This boiler experienced a significant corrosion of the carbon steel in three corners of the boiler. The front-wall and the rear-wall had accelerated corrosion on the carbon steel tubes extending almost 12 feet above the cutline, as is shown in Figure 1. Mid-furnace areas with high and low corrosion rates were selected based on the waterwall thickness data from their annual inspection. Identified areas for the environment characterization in the selected boiler were above tertiary airport levels, as shown in Figure 1. Air-tight, stainless steel gas-sampling ports were welded through the web membrane, during a shutdown, to support the ceramic tubes that were used to take samples of boiler gases. Gas sampling ports were designed to eliminate any air leaks into the sample and were accessible from the cold side of the boiler. Gas samples were taken from the waterwall tube surface by keeping the sampling tube flush with the waterwall surface. Gas samples were collected in specially designed glass sampling containers with a composite septum seal. During each visit, multiple gas samples were collected from each port to get the information on the variation in the gas composition. Gas samples were analyzed in the laboratory using a Perkin-Elmer Gas Chromatograph. Two thermal conductivity detectors (TCD), for the light gases and a flame

photometric detector (FPD) for the sulfur-bearing gases were used to analyze the recovery boiler gases. The chromatographic equipment was calibrated using standard gases.
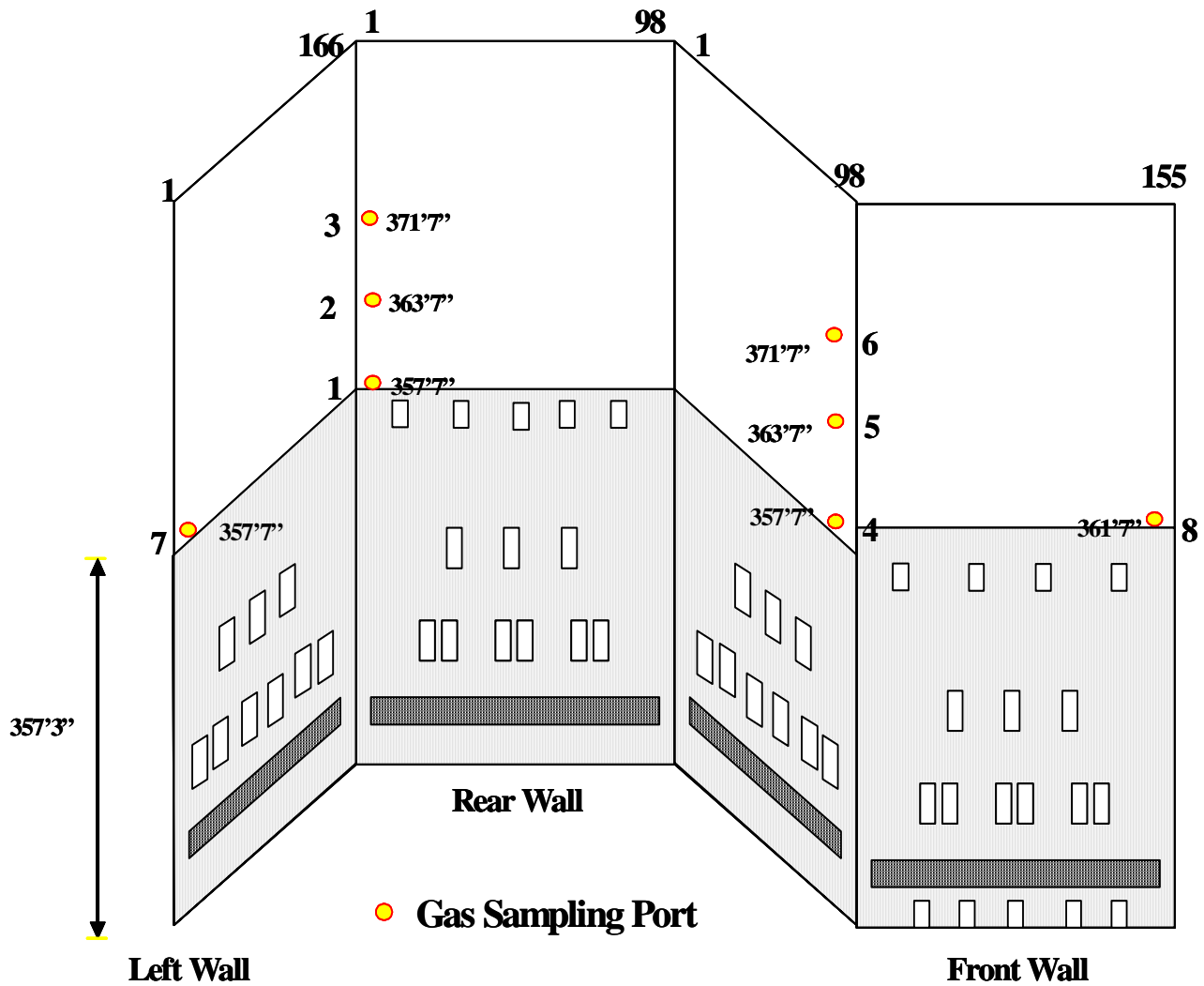

Figure 1. Schematic of the boiler showing port location in mid-furnace area (above the cut-line).

Laboratory Studies in Simulated Environments

To confirm the effect of gas compositions and instability on corrosion rates, simulations tests were planned in laboratory. These tests involved quantification of corrosion kinetics for carbon steel (SA-210) and other selected alternate materials in simulated boiler environments in laboratory. Various factors included in corrosion kinetic study in simulated environment were

- Gas composition
  - oxidation and sulfidation potential of gas environments
- Temperature
- Cyclic gas composition

Environments used in this laboratory study included typical mid-furnace waterwall environments as well as extreme environments found in high corrosion areas. Coupons of SA210 carbon steel (30mm x 20mm x 5mm) were cut from unused boiler tubes and used as a substrate for diffusion coatings. Composition of SA210 carbon steel in listed in Table 1. These test coupons were ground through 100-grit paper, polished to 5nm Al_2O_3, ultrasonically degreased in acetone, and dried before weighing.

In first series of tests SA-210 carbon steel samples were exposed to 1% H_2S in N_2 in TGA with Cahn D101 microbalance, with an accuracy of 10^{-6} g, to study corrosion kinetics of different surfaces in sulfidizing environment at 300°C. Weight change was normalized to exposed surface area to compare different samples. In another series of tests, carbon steel samples were exposed to alternating environments. Two different types of cyclic environments were simulated, one with extreme sulfidizing and oxidizing environments analyzed in our field tests, and another where environments were cycled between the compositions where the gases were either oxidizing with sulfur-bearing gases or without the presence of any sulfur bearing gases. Theses results were used to understand the effect of cycling gas composition on overall corrosion kinetics of carbon steel tubes in local areas of mid furnace. Scale composition and morphology was characterized by mounting and sectioning the scale and examining it using Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometer (EDS).

Evaluation of Alternate Materials for Mid Furnace
Although 304L stainless steel layered composite tubes have been used in a large number of recovery boilers to mitigate waterwall corrosion but a number of boilers still use carbon steel or chromized tubes for their waterwalls. To evaluate the effect of cycling in the mid furnace areas, chromized carbon steel tubes were included in this study. Other similar coating that has been considered for different combustion and gasifier environments is aluminide coatings on carbon steel. Pack cementation process was used to form surface layer rich in chromium or aluminum. These coatings were developed in laboratory to be able to control their properties and thickness. Carbon steel samples were heat treated in a chemically reactive environment to alter the surface composition, to one which can form a protective oxide on the surface when exposed to aggressive gases. Carbon steel coupons were placed in alumina crucible with pack of composition 75%Al_2O_3 + 20%(Al or Cr) + 5% NH_4Cl for aluminizing and chromizing. The crucible was sealed with alumina cap using high temperature cement and placed in a horizontal tube furnace purged with Ar for 2 hours. A hole (~1mm diameter) was also drilled in carbon steel coupons before cementation process to get an even coating on any surface exposed to sulfidizing environments during thermo-gravimetric analysis (TGA) measurements. Argon was used throughout coating process to prevent any oxidation. After cooling in the furnace under

argon, coated surface was cleaned ultrasonically and reweighed. Surface and cross-section of coated samples was characterized using X-Ray Diffraction (XRD) and SEM with EDS to get the concentration profile of the coated surface.

Table 1: Chemical composition of carbon steel tube (SA210) in this study

C	Mn	Si	S	P	Fe
0.27	0.93	0.1	0.058	0.048	Balance

RESULTS AND DISCUSSION

Gas samples were collected from the sampling ports installed in the mid furnace area of the kraft recovery seven times, over a two-year period. Location of these gas sampling ports is shown in Figure 1. During this time period, the boiler operation parameters were not changed, so the data in this report was taken under the "normal boiler operation" conditions, unless otherwise indicated. Multiple samples were taken from each port during each visit. Gas species and their concentrations were determined by gas chromatography method. Typical sample included light gases like oxygen, nitrogen, hydrogen, carbon dioxide, methane, carbon monoxide and sulfur-bearing gases like hydrogen sulfide, carbonyl sulfide, methyl mercaptan, di-methyl sulfide, sulfur dioxide, etc. H_2S and other sulfur bearing gases were detected in almost all selected areas near the cut-line, but the concentration of oxidizing gases were higher in the low-corrosion area as well as at the elevation of about 10 feet above the cut-line on both walls. Gases in the samples taken from the high-corrosion areas on both walls were generally sulfidizing and reducing with higher concentrations of hydrogen and carbon monoxide gases. Results indicated that there was sample to sample variation among samples taken on a particular day from the same location. However, this difference was smaller than the difference in average gas compositions at the same location on different days. Average gas composition at a given location for one particular day was used to see day to day variation in the boiler.

Some researchers have considered the environment at the waterwall to be similar to the bulk gas environments in the boiler[19, 26]. However, for corrosion reactions, local environment at the tube surface are more important to characterize than the bulk environment. Recent changes in the operating process like limited air supply at the lower level seem to have caused significant change in the local environment at the tube surface. Thermodynamics calculations indicate that at pyrolysis temperature of $700^{o}C$ (>waterwall surface temperature) or lower, the reactions to form Na_2S and K_2S do not occur appreciably, thus CH_3SH and H_2S are more stable and are likely to be higher in concentration in the vicinity of the tubes than in the bulk of the flue gas, particularly away from the airports[2]. Recent studies [28] have shown that the thermal and the chemical environments at the surface of tubes may vary with the local environmental conditions like combustion of partially burnt black liquor at the waterwall surface[11].

During heating and combustion reaction of black liquor, oxygen is consumed and pyrolysis gases like hydrogen, methane, and carbon monoxide are released. There are other gases like nitrogen

which do not participate much in this process. By analyzing gas compositions at each location, one can determine if pyrolysis and combustion reactions are going on at the waterwall surface in these areas or not. For corrosion, environments at the waterwall surface are more important than the bulk environments. Data in Figure 2 shows hydrogen in collected gas samples at the waterwall surface in different areas of the boiler on different days. It can be seen that, in-general, the amount of hydrogen decreases at higher elevations. This is due to more pyrolysis and combustion at lower levels due to availability of black liquor fuel closer to the point of firing or liquor guns. At each wall the amount of reducing gases is different. This shows that the reactions and flow is different near different waterwalls at roughly similar elevation in a boiler.

In cases where the black liquor was sprayed on the tube surface and undergoes pyrolysis at the waterwall surface, the reduced sulfur gases remains in their reduced form in sampled gases because of the low temperature and the low oxygen partial pressures. This can lead to a change in the ratio of methyl mercaptans and dimethyl sulphates to hydrogen sulphide [32]. This can further change the oxygen to sulfur ratio locally and favor a sulfide corrosion product rather than an oxide. Small variations in the sulfur partial pressure can result into catastrophic corrosion conditions [33].

Figure 2a shows hydrogen sulfide concentration in each sample taken from every port over 2 year period, whereas Figure 2b shows hydrogen from the same locations during same times. It is clear from this data that the hydrogen sulfide and hydrogen in port # 1 varied significantly. Both, hydrogen and hydrogen sulfide are produced during pyrolysis of black liquor and therefore their concentrations in the sampled gas follow the same trend. Presence of these gases signifies a reducing and sulfidizing environment. For hydrogen sulfide, concentration changed from ~3500 ppm to 0 ppm whereas at the higher elevation, in the same corner of rear wall of boiler, at port #s 2 and 3, the variation was smaller and maximum concentrations were significantly lower than port#1. Similarly on the right wall, port # 4 at the cutline had more variation in the gas composition along with generally higher concentrations of H_2S compared to the gas samples collected from equivalent locations at higher elevations in the boiler. Results clearly show that at the lower elevation in the mid furnace, near tertiary air port, gas compositions were more instable than at the higher elevations. Overall gas compositions in the high corrosion areas near cutline fluctuate between the oxidizing to reducing and sulfidizing.
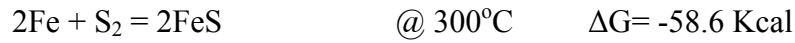
Figure 3 shows the oxygen concentration in gas samples taken from different ports. Results in Figure 3 show a large difference in concentration of oxygen in gases at the waterwall surface from one sample to another. On right wall, the amount of oxygen in the areas above tertiary airport is higher at the lower levels as the air is supplied from these ports and the air/oxygen is consumed at higher levels. However, on the rear wall (ports 4, 5, 6) this is not apparent. This difference may result into different oxygen partial pressures on two walls at similar elevation.

Gas sampling data from different mill visits show clear evidence of differences in gas composition where the areas with high corrosion rates for the waterwall had higher concentrations of sulfur bearing gases like hydrogen sulfide and reducing gases like hydrogen compared to the low corrosion areas at the same wall and elevation. Variation in gas composition on a particular day was not as significant as between samples taken during different visits. Another important conclusion from field tests results is that the gaseous environment the mid
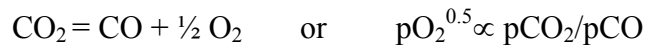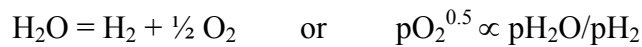
furnace area is not stable. It is not clear if there is any cyclic pattern over days or not. Initial efforts to correlate gas compositions with the boiler operations parameters did not yield any clear patterns. Boiler operation records for the boiler were compared with our gas composition data to see if there were any changes in the liquor temperature, liquor pressure, air temperature, air distribution to explain the variation in local gas composition. No correlation was found between the changes in the local gaseous environment in the mid-furnace and the boiler operating parameters.

Average gas composition at each location was used to calculate partial pressures of oxygen and sulfur by assuming equilibrium. This was further used to predict the type of scale that may be stable at the tube surface under those gas environments at a given temperature.
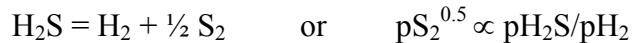
Main competing reactions for sulfidation and oxidation of carbon steel at high temperatures are given in the following equations.

$$2Fe + S_2 = 2FeS \qquad @\ 300^oC \qquad \Delta G = -58.6\ Kcal$$

$$2Fe + 1.5O_2 = Fe_2O_3 \qquad @\ 300^oC \qquad \Delta G = -159.5\ Kcal$$

The partial pressures of sulfur and oxygen in a given gas mixture and at a given temperature was calculated by assuming a thermodynamic equilibrium, which is a good assumption at higher temperatures. Average gas composition data from each port was used to calculate the partial pressure of oxygen and sulfur. Figures 4 and 5 show calculated partial pressures of oxygen and sulfur at each port during different days. Amount or partial pressure of S_2 or O_2 for these competing reactions depends upon gas composition of the mixture. For example ratio of H_2O and H_2, or CO_2 and CO will contribute to O_2 potential of gas. Similarly ratios of H_2S and H_2, or CH_3SH and CH_4 will contribute to the partial pressure of S_2 at a given temperature.

$$H_2O = H_2 + \tfrac{1}{2}\ O_2 \qquad or \qquad pO_2^{0.5} \propto pH_2O/pH_2$$

$$CO_2 = CO + \tfrac{1}{2}\ O_2 \qquad or \qquad pO_2^{0.5} \propto pCO_2/pCO$$

Similarly

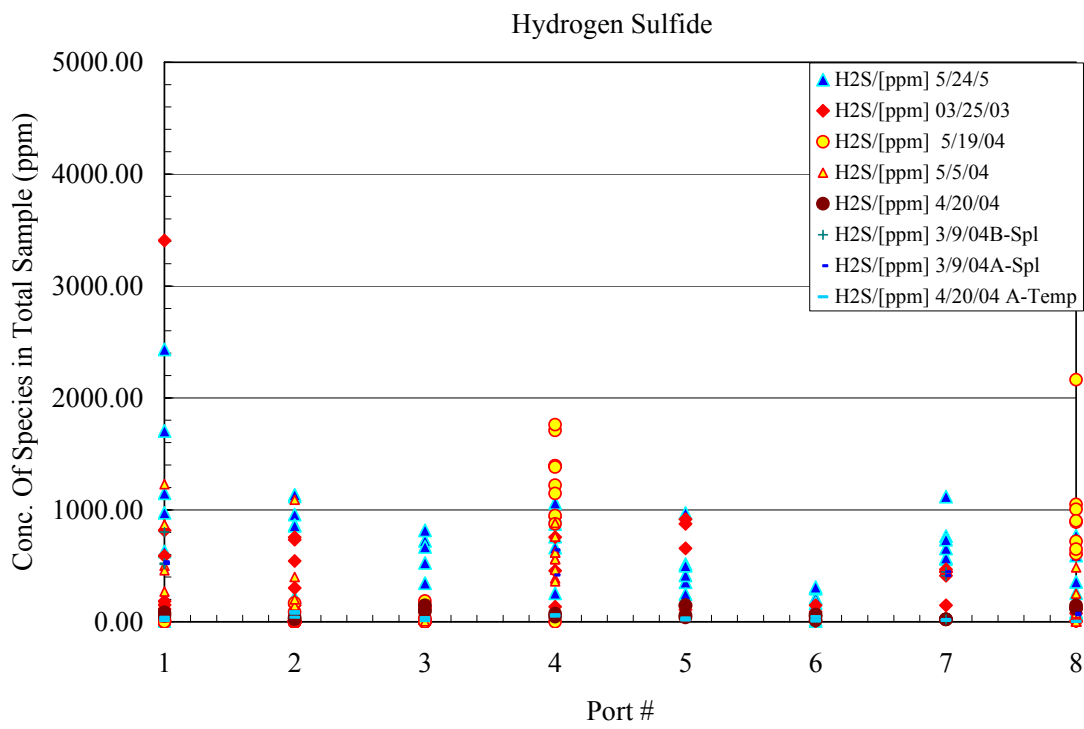$$H_2S = H_2 + \tfrac{1}{2}\ S_2 \qquad or \qquad pS_2^{0.5} \propto pH_2S/pH_2$$

A number of other possible reactions between different gas constituents were considered under assumption of equilibrium to calculate overall partial pressure of sulfur or oxygen in a given gas sample.
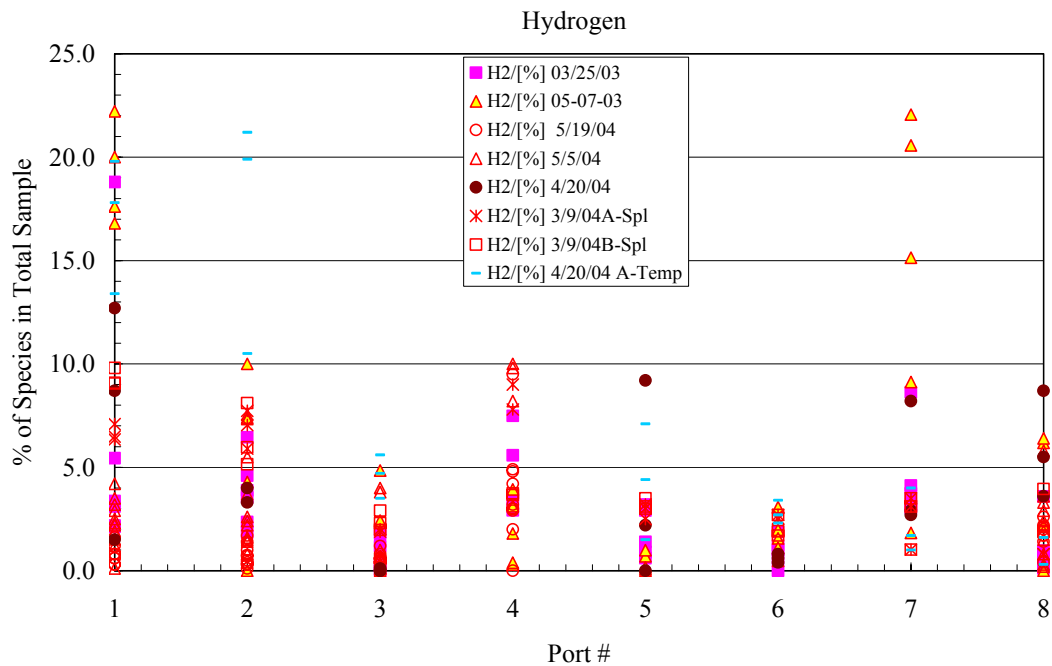
Hydrogen Sulfide

(a)

Hydrogen

Figure 2. Variation in the concentration of a) hydrogen sulfide and b) hydrogen in gas samples, during a 2-year period, taken from different ports in the mid-furnace, shown in Figure 1.
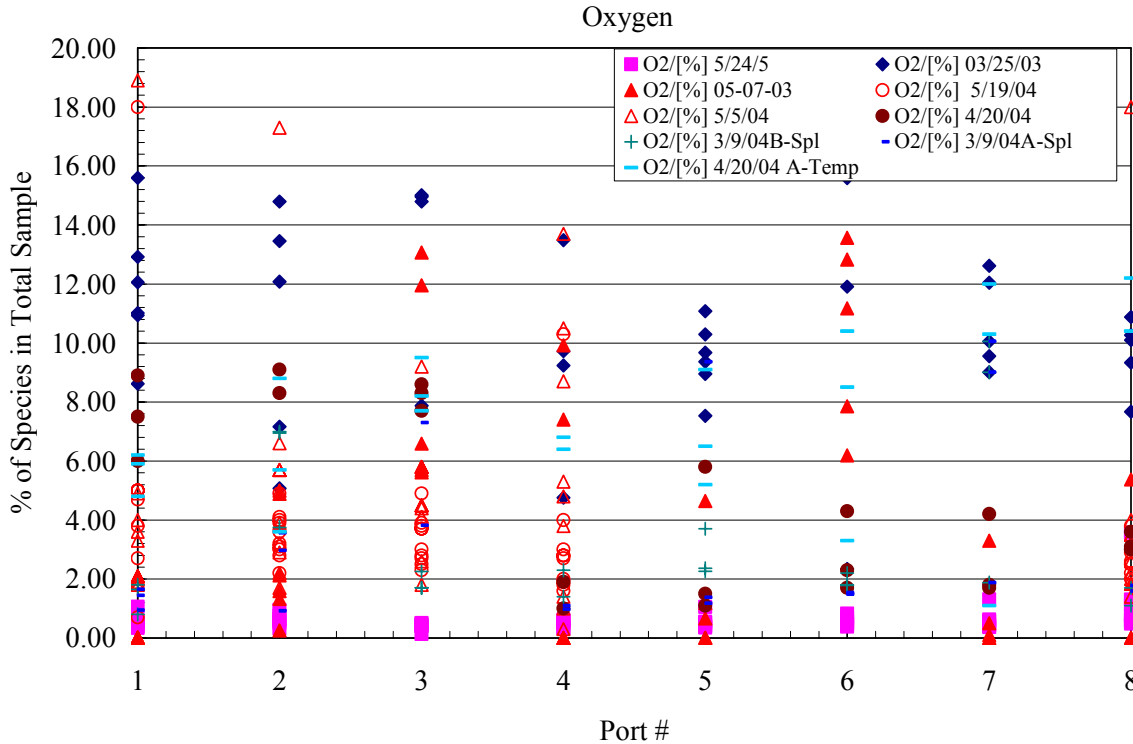
Figure 3.   Variation in the concentration of oxygen in gas samples, during a 2-year period, taken from different ports in the mid-furnace, shown in Figure 1.

Thermodynamic stability of scale on the surface will depend upon the partial pressure of oxidizing and sulfidizing gases, as is shown in the phase stability or predominance diagram in Figures 6 and 7. Oxide scales are typically more protective due to lesser density of point defects compared to in the sulfide scales. Due to large amount of lattice defects, sulfide scales allow faster diffusion of reactants and generally result into much higher corrosion rates. This example shows how the gas composition data collected from different parts of boiler was analyzed to determine the scale composition and its protective nature. Data from the gas composition at different ports correlates fairly well with the observed corrosion pattern in those locations.
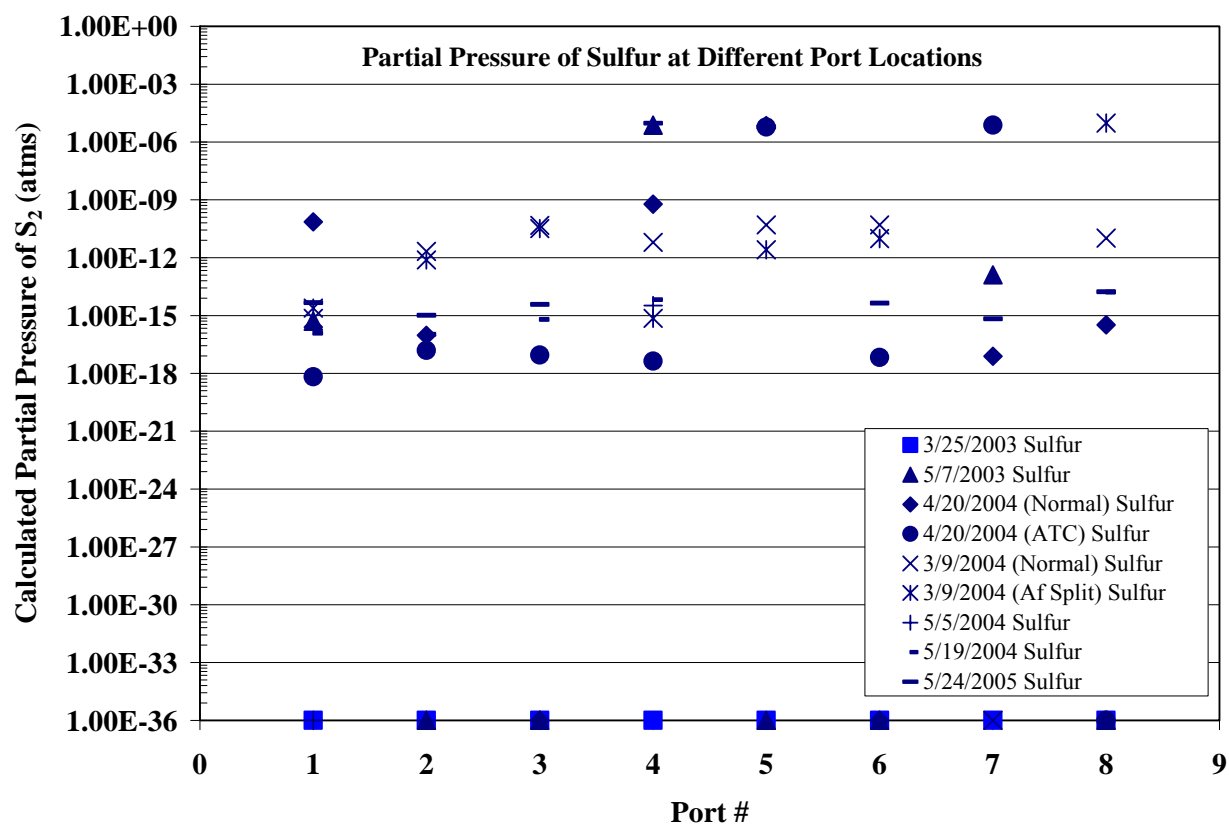
Figure 4. Variation in the calculated partial pressure of sulfur for gases collected during a 2-year period from different ports in the mid-furnace.
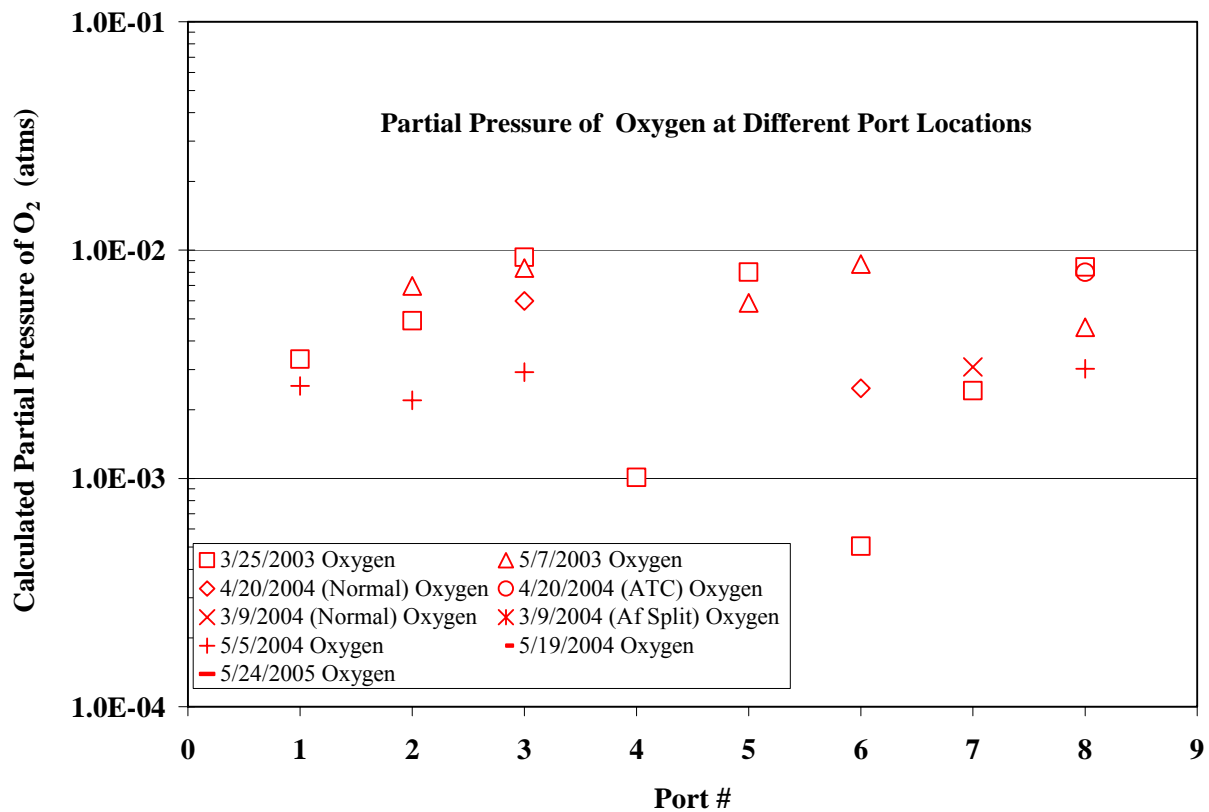
Figure 5.   Variation in the calculated partial pressure of oxygen for gases collected during a 2-year period from different ports in the mid-furnace.
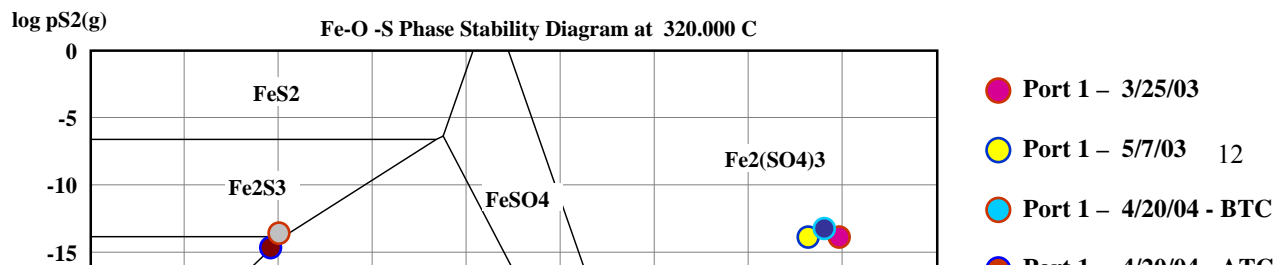
Figure 6.   Phase Stability diagram for Fe-O-S system at 320°C. Diagram shows partial stability regions for different possible scale compositions as a function of oxygen and sulfur partial pressure in contact with iron. Calculated average partial pressures of oxygen and sulfur from port #1 from different days were superposed on this equilibrium diagram, as indicated by different symbols.
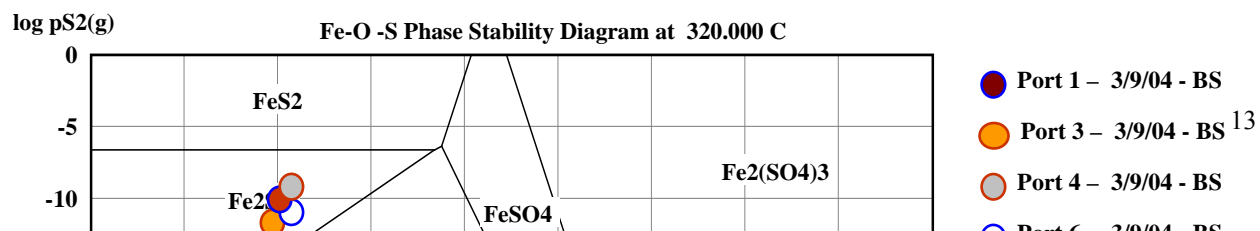
log pS2(g)

Fe-O -S Phase Stability Diagram at 320.000 C

- Port 1 – 3/9/04 - BS
- Port 3 – 3/9/04 - BS
- Port 4 – 3/9/04 - BS

Figure 7. Phase Stability diagram for Fe-O-S system at 320°C. Diagram shows partial stability regions for different possible scale compositions as a function of oxygen and sulfur partial pressure in contact with iron. Calculated average partial pressures of oxygen and sulfur for all ports during our visit on 3/9/04 were superposed on this equilibrium diagram, as indicated by different symbols.

Although thermodynamic data, shown in the figures 6 and 7, describes the difference in possible scale compositions but the real compositions as well as rate of corrosion is determined by kinetics of competing reactions. Kinetics of corrosion reactions needs to be determined experimentally in simulated tests. Work in this project will be concentrated to evaluate corrosion kinetics of SA210 carbon steel in the mid furnace area environments. Test matrix for the gas mixtures will cover range of partial pressures of sulfur and oxygen calculated from the real gas samples taken from the mid furnace areas.

Figure 6 and 7 shows regions of thermodynamically stable phases as a function of oxygen and sulfur partial pressures in a Fe-O-S system at 320°C. The calculated partial pressures of oxygen and sulfur were plotted on the phase-stability diagram for the Iron-Oxygen-Sulfur system at 320°C. Gas samples for Figure 6 were taken from the same port location (i.e. port#1) in the boiler, but on seven different days over the 2-year period. Average gas composition for samples taken from this port on each day was used to plot the data in Figure 6. Data indicates that the gaseous environment varies from being very oxidizing to sulfidizing in this area under the so-called "normal boiler operation" conditions during different time periods. Similarly, when gas

composition data between different ports on the same day is compared, as shown in Figure 7, a significant variation in gas composition was found. This clearly indicates that the gaseous environment cycles in the mid-furnace of this boiler. However, the cycling frequency could not be determined from this study. Subtle changes in the gas composition may favor one scale composition over the other. Difference in the local gas composition and the waterwall temperature will affect the kinetics of corrosion reactions on the carbon steel surface and the resulting scale composition. Data in Figures 6 and 7 supports the notion that there is instability in the boiler gas-flow in the mid-furnace area, which may explain the difference in the local gas composition at different times under otherwise similar operating conditions.

It is known that the oxide scale on the iron surface, in the boiler tube temperature range, is much more protective than the sulfide scale. If the gas composition cycles between the sulfidizing to the oxidizing compositions, the resulting scale may not be very protective and can result into a higher corrosion rate [19]. Previous work on the lower furnace corrosion has shown that the higher corrosion rate of carbon steel may result from following; the presence of organo-sulfur compounds in gases; alternating oxidizing/reducing conditions; cyclic temperatures; and higher temperatures [19, 20]. The differences in corrosion rates in the high and the low corrosion areas will largely depend upon the stability of the scale. Conditions favoring the sulfide scale or an unstable scale will lead to accelerated waterwall corrosion.

Results from our data in Figures 2 to 6 show that gaseous environment in local areas can change from completely oxidizing to completely reducing. This was found to be more prominent in the lower areas, near cut-line, and generally associates with areas with higher corrosion rates.

A computational fluid dynamics (CFD) model was developed for this particular boiler by PSL. Results from this model have predicted that some liquor could end up on the waterwall surface in certain areas of the mid-furnace, depending upon the air flow pattern as well as liquor spray parameters and properties. Due to liquor on the waterwall surface, the local environments in these areas can be very different. Release of sulfur bearing and reducing gases during pyrolysis can lead to higher partial pressures of sulfur in these areas. Data in figures 8 and 9 show some of the predictions for the model run with a set of normal boiler parameters. Model also calculates local heat flux differences in the mid furnace, near waterwall surface. Local environment near waterwall will change locally if the boiler operations are altered. Model is capable of calculating these effects, but this model needs to be validated with the real data from the boiler. Laboratory tests have shown that the temperature has very significant role in corrosion rates of carbon steel in recovery boiler environments. An increase in test temperature from 320°C to 400°C increased the corrosion rate of carbon steel SA210 from 0.320 mm/year to 14.66 mm/year in gaseous environment simulating lower-furnace area with low corrosion areas. Local heating due to fireside events or due to waterside scaling may increase local tube surface temperatures and lead to local high corrosion rates on waterwall tubes in the mid furnace areas.
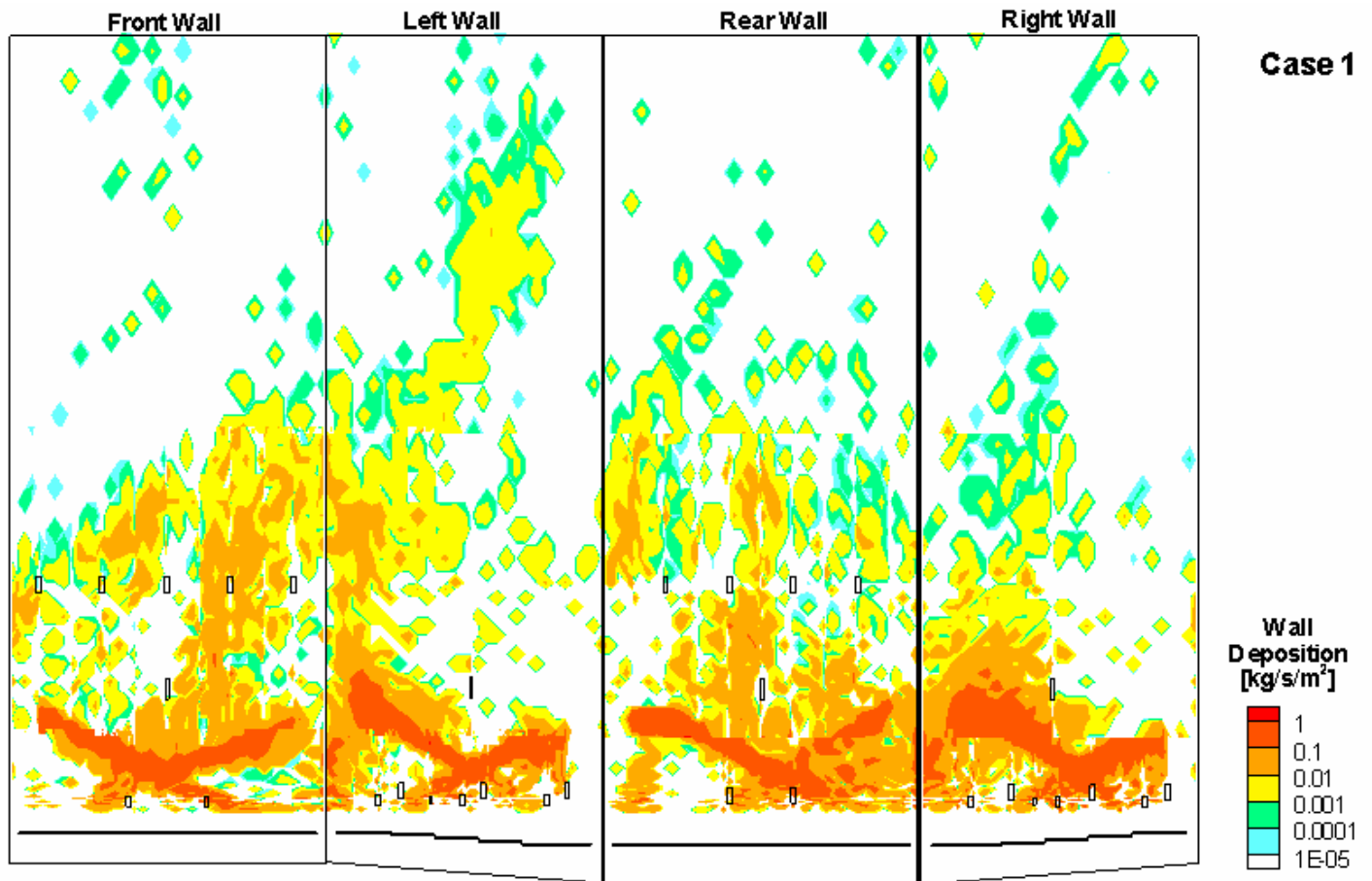
Figure 8 CFD model results showing black liquor spray pattern on waterwall surface in the mid furnace. Notice differences on the same wall and on different walls.
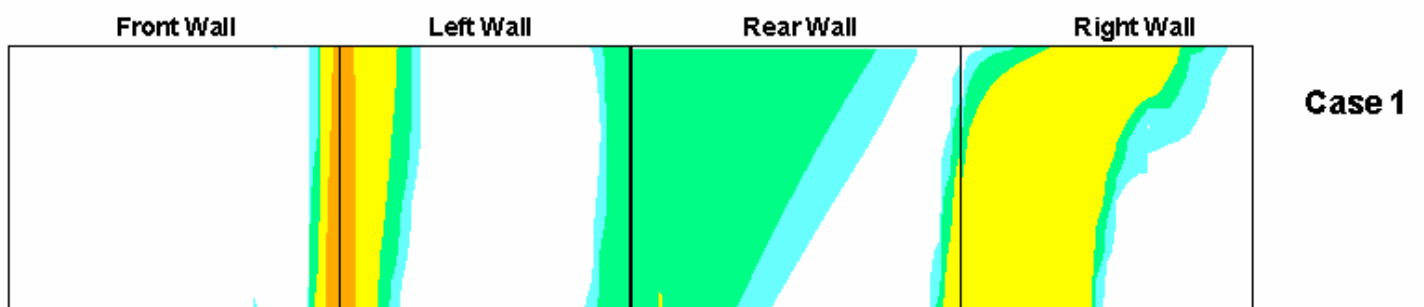
Figure 9   CFD model results showing H_2S concentration on the waterwall surface in boiler furnace. Some areas of the mid furnace waterwall have higher concentration of sulfur bearing and reducing gases compared to others at the same boiler elevation. These trends match with the general corrosion patterns found in this boiler

Carbon Steel Corrosion Kinetics –Laboratory Simulations

Data from the boiler study was used to carry out a series of laboratory tests. SA-210 carbon steel samples were tested in simulated mid-furnace environments in the selected recovery boiler. Cyclic gaseous environments found in the corrosive and non-corrosive area of the mid-furnace were used in these tests. Tests were carried out at temperatures, representative of the maximum

and minimum detected at the waterwall surface. Scales developed under different conditions were analyzed using X-ray diffraction and EDS analysis. Thermal balance setup at GTech/IPST is shown in Figure 10. Surface scales developed under different conditions were analyzed using X-ray diffraction and EDS analysis and compared with the calculated phase stability diagrams
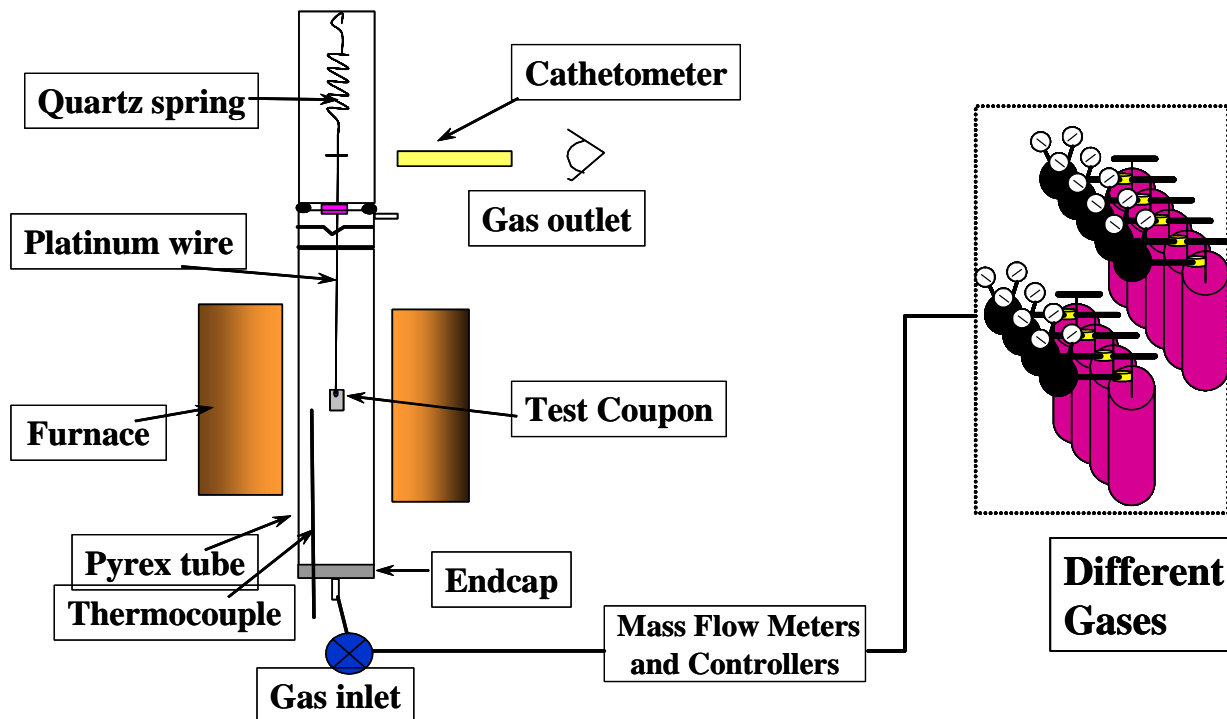
Figure 10.   Experimental setup to simulate recovery boiler gaseous environments for corrosion kinetics tests

SA-210 carbon steel samples were exposed in the cyclic environments and the weight change was recorded continuously. Results from these tests are shown in Figure 11. Figure 11 has alternating 12-hours zones marked as A and B which represent different gas compositions during that time, as indicated in the figure caption.

For Test#1 there was a sharp mass loss seen after each environmental cycle which indicates spallation of scale. Scanning electron micrograph in Figure 12 shows cross-section of surface scale after 100 hours of exposure under Test#1 conditions at 300°C. Scale shows a layered structure due to the formation of different oxides/sulfides on each cycle of gas change. During first sulfidizing cycle, sulfide scale forms as most stable corrosion product. As atmosphere changes to oxidizing, oxide scale formation causes layered structure with large mismatch between corrosion products, which seem to cause scale to crack and spall exposing the metal to corrosive gases. Weight change during each environment was used to determine if the reaction rate was linear or parabolic during that stage of test. During first two sulfidation cycles, corrosion showed linear behavior and oxidation showed parabolic behavior as comparable to

fresh alloy. As the scale grows, sulfidation behavior showed dependence on diffusion of sulfur species through unspalled/adherent scale indicating transition to parabolic behavior. The qualitative composition of different layers of the surface scale was determined by EDS line spectra. A sulfur peak indicated a sulfide layer whereas lack of sulfur peak was assumed to be oxide layer, as is labeled in Figure 12 and 13. These results indicate that even a small amount of oxygen introduced during environmental cycling can form stable oxide layer and provide protection.

For Test#2, sulfide scales on SA210 did not show any significant spallation as evident from TGA plot in Figure 11. The scale was adherent to the substrate after removal from the TGA apparatus. Results show that the sample tested in Test#2 showed lower mass gain than Test #1 as the scale was adherent and the reaction kinetics was primarily governed by the diffusion of gaseous species through the scale with parabolic rate constant of $0.25mg^2/cm^4.sec$. Scanning electron micrograph in Figure 13 shows the cross-section of scale after 100 hours of exposure at 300^oC in Test#2. Morphology of this scale suggests the formation of laminated structure of oxides/sulfides. Although the scale looks continuous through thickness, but some cracking was observed at the scale/alloy interface due to a large CTE mismatch between the scale and the steel. Scale thickness was roughly 60-80 μm with an outer dense layer#1 of ~50-60μm thick, which consists primarily of sulfides, and a highly porous layer#2, ~10-20μm thick, which consists primarily of oxide at the scale/alloy interface. Perhaps the presence of thin oxide layer and its interdiffusion in the sulfide layer provides good adherence to the scale in Test#2 conditions.
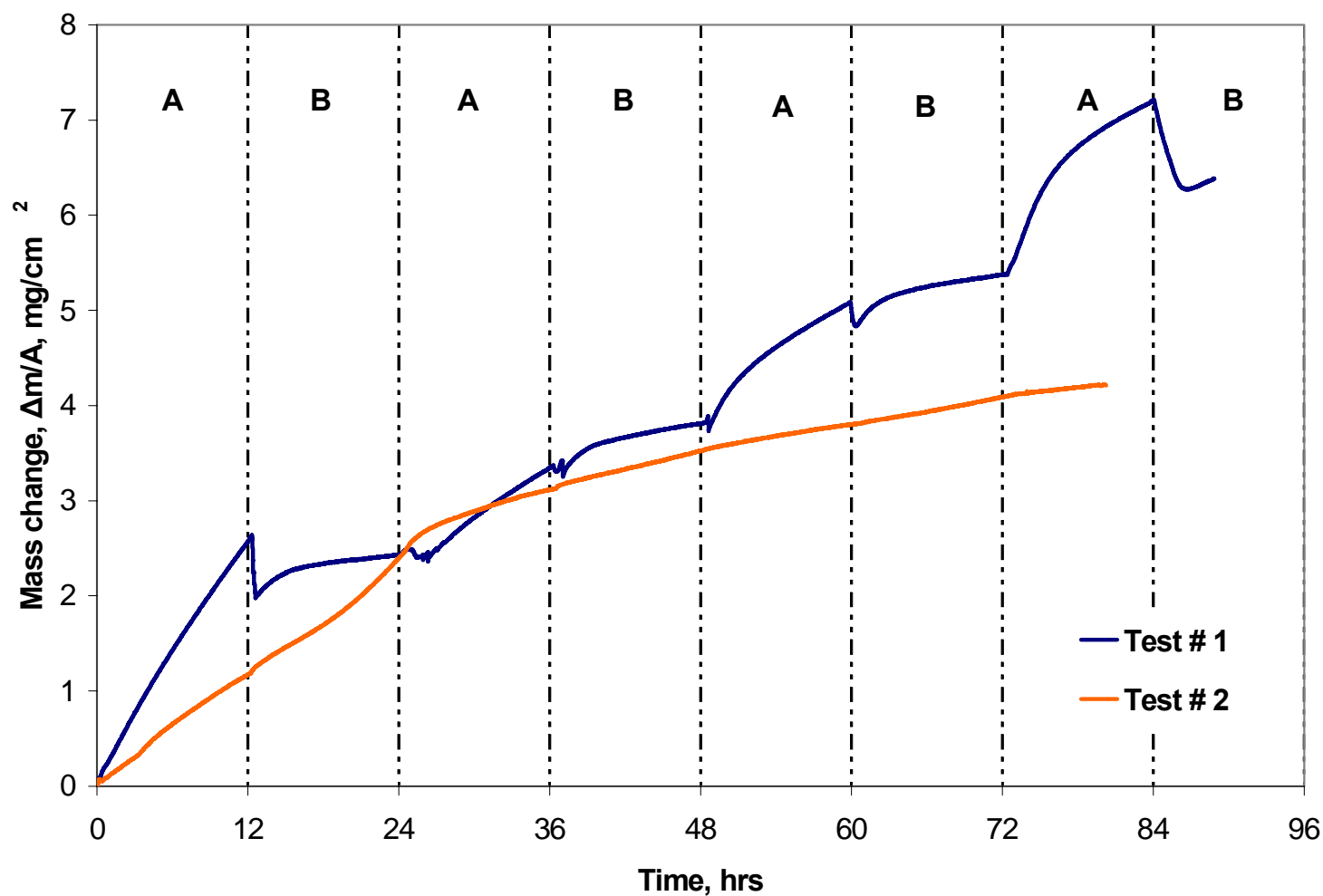
Figure 11: Effect of fluctuating sulfidizing/oxidizing atmosphere on corrosion behavior of SA210, A and B denotes gas atmosphere as follows: Test # 1: (A) 1% H_2S in N_2, (B) 1% O_2 in N_2, Test # 2: (A) (1%H_2S +1%O_2) in N2, (B) 1% H_2S in N_2

Results from Tests# 1 and 2 show that the local corrosion behavior depends on the stability of scale formation in the mid-furnace areas. Extreme changes in the local environment is one major reason for accelerated corrosion in the mid-furnace areas due to the formation of a non-protective scale like in Test#1 whereas in case where the oxygen may be available intermittently in a sulfidizing area, the scale can be more protective compared to the continuous sulfidizing environment.
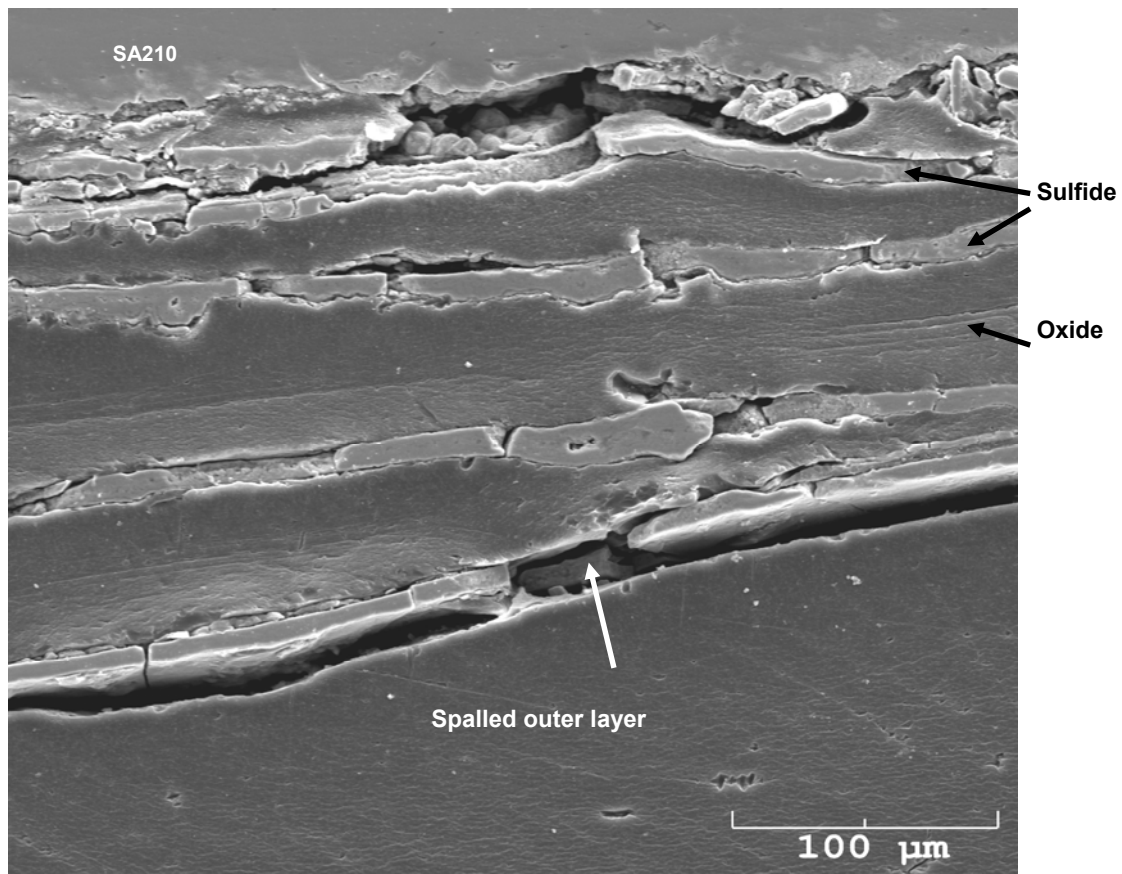

Figure 12:   SE micrographs of laminated scale after test # 1.(A) Alternative   oxide/sulfide
            scale corresponding to each cycle, (B) Extensive cracking evident in sulfide scale.
            Oxide scale is relatively continuous   and free from cracking.
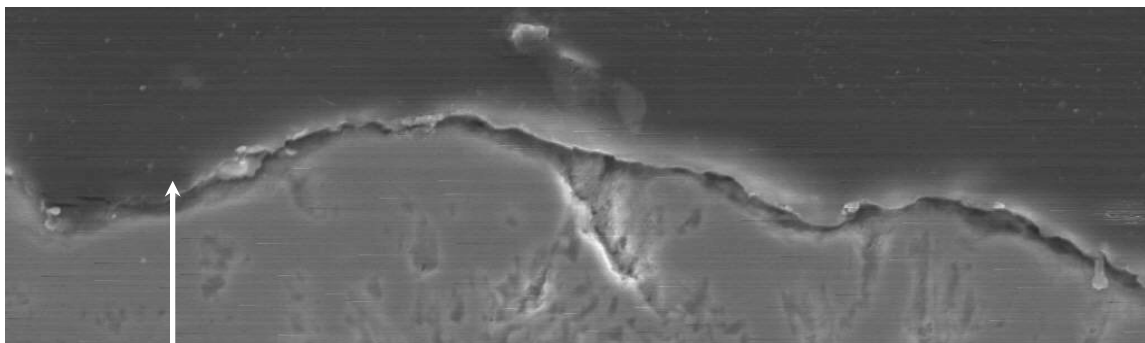
Figure 13:   Cross-sectional SE micrographs of scale after Test # 2. Laminated
              structure is evident due to cycling of gaseous atmosphere between
              oxidizing and sulfidizing.

**Performance of Diffusion Coatings in Mid-Furnace Areas**

Composite tubes have been used in the mid furnace areas of some boilers and have generally performed well. However, there are other alternatives to protect carbon steel tubes from sulfidizing environments. One such method is to use tubes with diffusion coatings like chromized of aluminized tubes in the mid furnace areas. These tubes have generally not been tried in the mid furnace so we tested two different types of diffusion coatings on SA210 carbon steel samples (i.e. chromium and aluminum rich diffusion coatings).

To coat carbon steel samples, pack cementation was carried out at 800°C to form alumnized and chromized surfaces. Resulting coatings were characterized using XRD and SEM. Chromized layer on SA210 was ~60-70 μm thick (Figure 14A) and consisted of $(Cr,Fe)_{23}C_6$ and $(Cr,Fe)_7C_3$ as major phases, whereas, aluminized layer was ~ 70-80 μm thick (Figure 14B) with FeAl as the major phase after 8 hours of pack cementation. The chromium carbide formed in the process due to outward diffusion of carbon and strong affinity of Cr towards carbon.

Chromized and aluminized SA210 samples were tested for 100 hours in 1% H_2S in N_2 mixture to compare their sulfidization resistance to uncoated carbon steel samples. Figure 15 shows weight change vs time curves of chromized and aluminized steel as compared to uncoated SA210 at 300°C. Both diffusion coatings provided excellent resistance to the carbon steel sample in sulfidation environment as compared to uncoated sample. Aluminized sample was tested at 600°C and showed overall mass gain of ~1 mg/cm^2. Whereas, chromized steel showed total mass gain of ~0.5mg/cm^2 at 300°C. Uncoated steel showed much higher mass gain (~8mg/cm^2) at 300°C than coated samples with formation of highly porous, non adherent scale. XRD revealed that the sulfide scale had a non stochiometric ($Fe_{1-x}S$) composition. XRD results indicated that aluminized steel had a Al_2O_3 scale even after 100 hours of sulfidation at 600°C. On the other hand chromized steel had undergone some reaction and was mostly chromium sulfide with minor amount of Cr_2O_3 on the surface. These results clearly indicated that the diffusion coatings, like chromized or aluminized coatings could be used to protect the carbon steel tubes in sulfidizing environments. These coatings are also being tested in cyclic environments of mid-furnace to compare their performance against carbon steel performance.

Table 2: Corrosion rates of SA210 as compared to coated samples

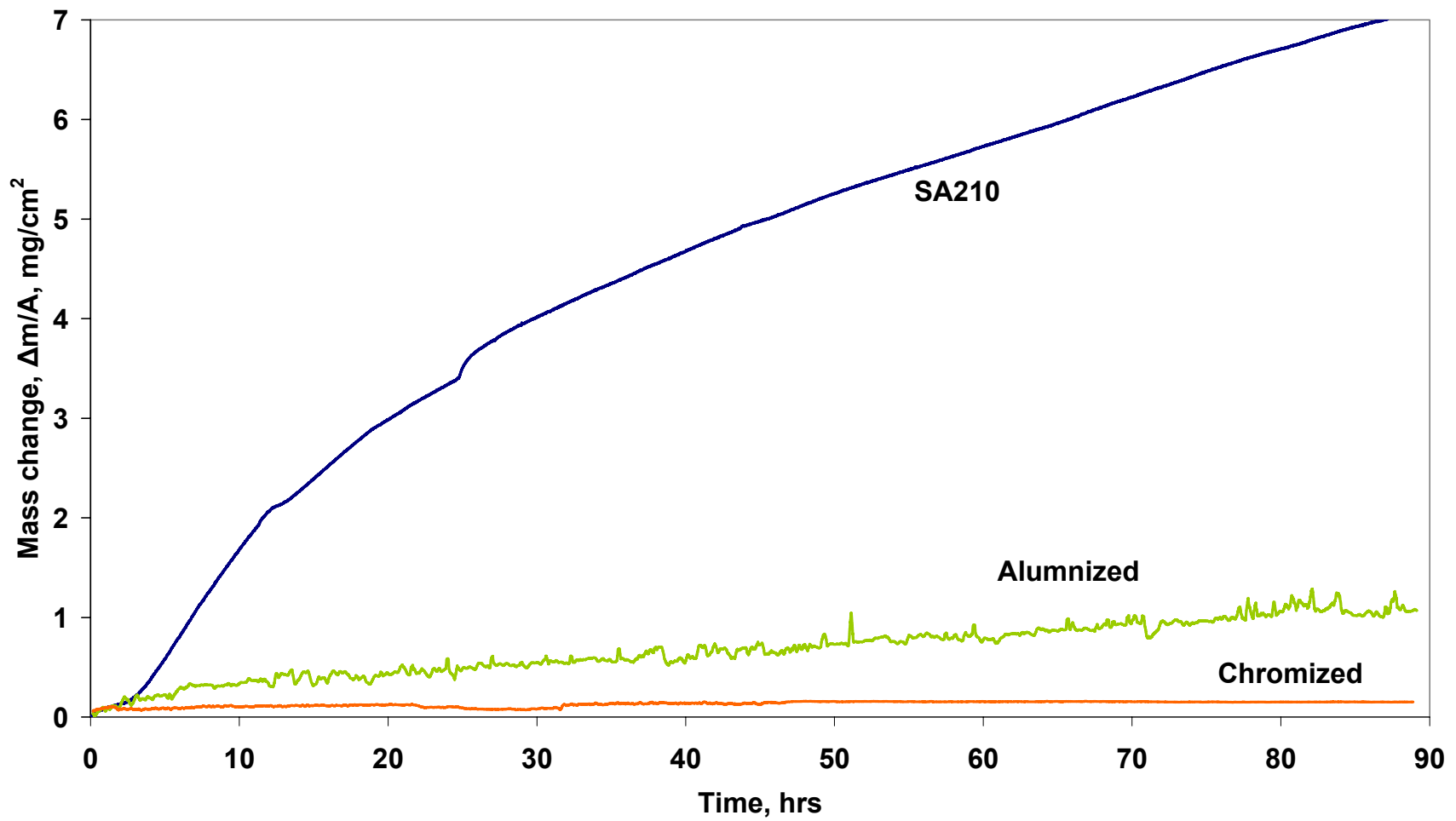| Sample	K_p (mg^4/cm^2.sec)
SA210	0.59
Aluminized - SA210	0.01
Chromized - SA210	0.002
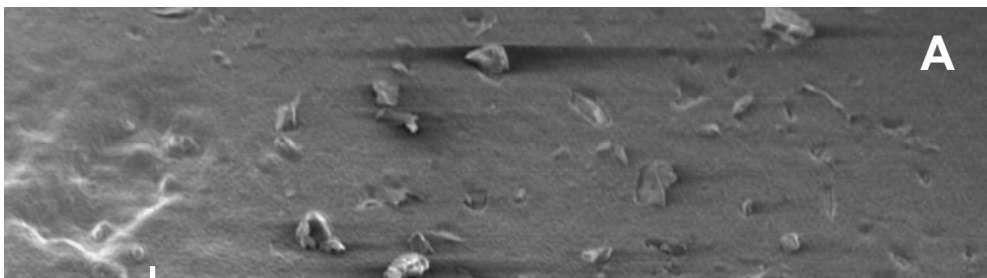
Figure 15 : Thermogravemetric analysis of alumnized and chromized SA210 as compared to uncoated steel in 1% H_2S in N_2 at 300°C. Parabolic rates are tabulated in Table # 2.

Conclusions from Field and Laboratory Study

- Areas with higher corrosion rates in the mid-furnace had higher concentrations of reducing gases and sulfur-containing gases at the waterwall surface, than in the low-corrosion areas of the same boiler.

- Field data over last two years indicates that the cyclic *(Oxidizing/Reducing)* environments in the mid-furnace results from the gas-flow instability and can cause an unstable or less protective scale on the tube surface, depending upon the extent of environmental change.

- Increase in the concentration of sulfur-bearing gases like hydrogen sulfide and methyl mercaptans on waterwall surfaces in certain areas of mid furnace as the black liquor may get sprayed on waterwall tubes in these areas due to air flow patterns.

- Local heat flux at the waterwall tube surface may increase due to higher gas temperatures in the mid-furnace areas because of the availability of excess oxygen in this area due to changes in boiler operations and thereby increasing the corrosion rate.

- In areas where the gaseous environments are not always completely reducing or oxidizing but cycles between the two due air circulation instability. The corrosion rates of carbon steel tubes in cyclic environment can be higher than any of the two extreme stable conditions due to the formation of non-protective scale.

- If there are thermal excursions in a local area of waterwall due to fireside or waterside phenomenon, the surface scale may crack and become non-protective due to the thermal shock and may result into higher corrosion rates. This effect will depend upon the extent or magnitude of thermal excursion.

- Chromized and aluminized SA210 showed excellent sulfidation resistance as compared with uncoated SA210.

- Effect of frequent environmental changes on corrosion kinetics of carbon steel and chromized and aluminized steels need to be evaluated to confirm our conclusions based on the field study.

Recommendations for Mid-Furnace Corrosion Mitigation

Based on the results from this study, main reasons for accelerated mid-furnace corrosion in local areas are higher concentrations of reducing gases and sulfur-containing gases at the waterwall surface in these areas than in the low-corrosion areas of the same boiler. Other major reason, that is specific to the mid furnace area is the instability in gas composition due to gas flow patterns. There are some indications of differences in the heat flux in the mid-furnace areas, generally due to local combustion of black liquor near waterwall surfaces.

Combustion of black liquor at the waterwall surface in the mid-furnace is one of the reasons for higher concentrations of reducing and sulfidizing gases like hydrogen and hydrogen sulfide in these areas. One way to mitigate local accelerated corrosion will be to avoid any liquor spray on the waterwall surface. It may not be always possible to predict gas flow in boilers, which may affect possibility of liquor droplets falling on waterwall surface.

Other way to mitigate local accelerated corrosion in the mid furnace areas is to control local corrosive environmental conditions. However, it is very difficult to control gas flow and instability.

Easiest way to control mid-furnace corrosion is to use corrosion resistant materials, which for protective oxides on the surface under kraft recovery boiler operating conditions. Composite tubes with 304L stainless steel layer or equivalent materials are expected to perform well under these conditions. Thermal spray coatings with high chromium should perform well in mid-furnace areas. However, performance of thermal spray coatings will depend upon their physical integrity, which depends upon the surface preparation and coating procedures used. Most of failures in thermal spray coatings in kraft recovery boilers can be attributed to poor adhesion rather that corrosion resistance.

Chromized carbon steel tubes were found to have very good resistance to mid-furnace environments. Aluminide coatings also showed very good resistance under both static and fluctuating mid-furnace environments. However, due to less experience with aluminide coatings, chromized tubes are expected to be selected for mid-furnace applications. Inconsistent coating quality was reported to be a concern in the lower furnace areas. Similar concerns are expected unless better production controls are applied in coatings and welding chromized tubes.

In conclusion, mechanisms of accelerated corrosion the mid-furnace are very similar to the ones operating in the lower furnace. Therefore, mitigation strategies applied in the lower furnace areas are applicable in the mid-furnace areas. Only major difference in the two areas is the fluctuating gaseous compositions due gas flow and that can be controlled by boiler design and operation. CFD model can be useful in determining the effect of boiler design or operation change on local gaseous environments.

REFERENCES

1. Dykstra, Harry, Recovery Boiler Waterwall Tube Failure Analysis with Implications for Furnace Replacement and New Construction, Proceedings TAPPI Engineering Conference, Nashville, Vol. 2 p. 431 (1998).
2. Preet M. Singh, Vikas R. Behrani, Fireside corrosion of carbon steel tubes in Kraft Recovery boiler mid-furnace, NACE Corrosion/2005, Paper # 05197, Houston, TX
3. B. Gleeson, Alloy degradation under oxidizing-sulfidizing conditions at elevated temperatures", Mat. Res., vol.7, No.1, 61-69.
4. F. Gesmundo, D. J. Young, S. K. Roy, The high-temperature corrosion of metals in sulfidizing-oxidizing environments: a critical review, High Temp. Mater. Proc., vol.. 8, 149-90.
5. M. F. Stroosnijder , W. J. Quadakkers Review of high temperature corrosion of metals and alloys in sulfidizing/oxidizing environments. II. Corrosion of alloys", , High Temp. Technol., v. 4, n. 141, 1986.
6. J. Stringer, Mixed oxidant corrosion in coal combustion and conversion systems: manifestations and mechanisms", High-Temperature Oxidation and Sulphidation Processes, J.D. Embury (Ed.), Pergamon Press, New York, . 257-275.
7. H. J. Grabke, R. Lobnig, P. Papaiacovou, Johannesen and A.G. Andersen (Eds.), Selected Topics in High Temperature Chemistry: Defect Chemistry of Solids, Elsevier, New York, 263-289.
8. P. M. Singh, S. J. Al-Hassan, S. Stalder, and G. Fonder, Corrosion in Lower Furnace of Kraft Recovery Boilers-in situ Characterization of Corrosive Environments", TAPPI Journal, Vol. 3:No. 2, 21-26.
9. D. L. Douglass, P. Kofstad, A. Rahmel and G. C. Wood, International Workshop on High Temperature Corrosion", Edited by Oxidation of Metals, 45 (5-6), 529-620.
10. V. Sricharoenchaikul, W.J. Frederick and T. M. Grace, Journal of Pulp and Paper Sci. Vol. 23, No. 8, J394-J399, Aug. 1997.
11. H. Tran, Kraft Recovery Boilers, (eds T.N. Adams, W.J. Frederick, T.M. grace, M. Hupa, K. Iisa, A.K. Jones, H. Tran), TAPPI Press, Atlanta, GA (1998).
12. J. Li, and A. R. P. Van Heiningen, Tappi J., 74, No. 3, 237-239, 1991.
13. Preet M. Singh and Safaa J. Al-Hassan, Corrosion in Lower Furnace of Kraft Recovery Boilers-*In-situ* Characterization of Corrosive Environments, TAPPI Journal. Vol. 87, No. 2, 2003.
14. P.M. Singh, S.J. Al-Hassan, S. Stalder, G.J. Fonder, NACE Corrosion-2000, FL, Paper # 00237 (2000).
15. D.L. Feuerstein, J.F. Thomas, D.L. Brink, Tappi J., 50, No. 6, 258 (1967).
16. R. G. Tallent and A. L. Plumley, Tappi J., 52, No. 10, 1955-1959, 1969.
17. A. L. Plumley, E. C. Lewis, and R. G. Tallent, Tappi J, 49, No. 1, 72A, 1966.
18. A. L. Plumley, W. R. Roczniak, Tappi J, 58, No. 9, 118. 1975.
19. D. Singbeil, L. Frederick, N. Stead, J. Colwell, G. Fonder, Proceedings of TAPPI Engineering Conference, TAPPI Press, Atlanta, 649-680, 1996.
20. Preet M. Singh, Jorge Perdomo, Jamshad Mahmood, *Mid-furnace Corrosion in Kraft Recovery Boiler,* Proceedings of the 11th International Symposium on Corrosion in the Pulp and Paper Industry, Charleston, USA, June 7-11, 2004.
21. A. Hendry, The oxidation resistance of nitrided mild steel, Corrosion Science (1978), 18(6), 555-71.

22. S. F. Chou, P. L. Daniel,Hydrogen sulfide corrosion in low nitrogen oxide (NO_x) combustion systems, High Temperature Corrosion in Energy Systems, Symposium Proceedings, 327-43.

23. M. Schulte and M. Schutze, The Role of Scale Stresses in the Sulfidation of Steels, Oxidation of Metals, Vol. 51, No. 1/2, 55-77.

24. S. Osgerby, Oxide scale damage and spallation in P92 martensitic steel, materials at high temperatures 17(2), 307–310.

25. A. L. Plumley, W. R. Roczniak, Tappi J, 58, No. 9, 118. 1975.

26. D. Singbeil, L. Frederick, N. Stead, J. Colwell, G. Fonder, Proceedings of TAPPI Engineering Conference, TAPPI Press, Atlanta, 649-680, 1996.

27. S. J. Al-Hassan, G. J. Fonder, P. M. Singh, The Effect of Temperature Excursion on Sulfidation of Carbon Steel in 1% H_2S Environment", Pulp & Paper Canada (1999), 100(10), 40-43

28. Preet M. Singh, Jorge Perdomo, Jamshad Mahmood, *Mid-furnace Corrosion in Kraft Recovery Boiler,* Proceedings of the 11th International Symposium on Corrosion in the Pulp and Paper Industry, Charleston, USA, June 7-11, 2004.

29. A. Hendry, The oxidation resistance of nitrided mild steel, Corrosion Science (1978), 18(6), 555-71.

30. D. L. Singbeil, L. Frederick, N. Stead, J. Colwell and G. Fonder, Testing the Effects of Operating Conditions on Corrosion of Water Wall Materials in Kraft Recovery Boilers", TAPPI 1996 Engineering Conference, Vol. 2, 649-680.

31. P. McKeough, M. Kurkela, H. Kyllonen, and E. Tapola, New Insights into the Release of Sodium, Sulphur, Potassium and Chlorine During Black-Liquor Combustion and Gasification", LIEKKI 2, Technical review 1993–1998. Vol 2. Edited by M. Hupa, Abo Akademi University, Abo, 1998. 855–873.

32. M. Mäkipää, M. Oksa and P. Pohjanne, Corrosion Testing of High-Nickel Alloy Composite Tube Materials in Simulated Recovery Boiler Lower Furnace Conditions", Proceedings of 10th International Symposium on Corrosion in Pulp and Paper Industry, Vol. 1, 73-87.

33. P. J. Ficalora, T. G. Godfrey, Technique to Study Corrosion in Fluctuating Gaseous Atmospheres", Oak Ridge Natl. Lab., Oak Ridge, TN, USA. Report (1983), ORNL/TM-8734; DE83014565).