Corrosion in a Temperature Gradient

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ABSTRACT

High temperature corrosion limits the operation of equipment used in the Power Generation Industry. Some of the more destructive corrosive attack occurs on the surfaces of heat exchangers, boilers, and turbines where the alloys are subjected to large temperature gradients that cause a high heat flux through the accumulated ash, the corrosion product, and the alloy. Most current and past corrosion research has, however, been conducted under isothermal conditions. Research on the thermal-gradient-affected corrosion of various metals and alloys is currently being studied at the Albany Research Center's SECERF (Severe Environment Corrosion and Erosion Research Facility) laboratory. The purpose of this research is to verify theoretical models of heat flux effects on corrosion and to quantify the differences between isothermal and thermal gradient corrosion effects.

The effect of a temperature gradient and the resulting heat flux on corrosion of alloys with protective oxide scales is being examined by studying point defect diffusion and corrosion rates. Fick's first law of diffusion was expanded, using irreversible thermodynamics, to include a heat flux term – a Soret effect. Oxide growth rates are being measured for the high temperature corrosion of cobalt at a metal surface temperature of 900ºC. Corrosion rates are also being determined for the high temperature corrosion of carbon steel boiler tubes in a simulated waste combustion environment consisting of O_2, CO_2, N_2, and water vapor. Tests are being conducted both isothermally and in the presence of a temperature gradient to verify the effects of a heat flux and to compare to isothermal oxidation.

INTRODUCTION

Temperature gradients and high heat flux conditions abound in fossil energy and waste incineration power generation systems. In coal-fired boilers, heat fluxes of 400 kW/m^2 are found in furnace section evaporator tube walls and 200 kW/m^2 in superheater walls.[1] Even greater heat fluxes are found in turbine blades. Oxidation and corrosion behavior can be different than in isothermal conditions. As seen in Figure 1, a complex high temperature corrosion process can be made even more complex by the presence of temperature gradients. Under isothermal conditions, corrosion or oxidation of the metal structure can be influenced by the deposition of very corrosive fused salts and relatively thick layers of ash. The composition of the fused salts and of the ash is determined by the material being combusted and can have a significant impact on corrosion. Under thermal gradient conditions, there are other phenomena that can affect corrosion of the structure. Thermal stresses induced by temperature gradients can affect scale adhesion and point defect diffusion within oxide scales can be increased or decreased. Temperature gradients can also change the composition of the ash and fused salt layers when condensed salts are deposited on the relatively cooler surfaces.

Oxide Scale Adhesion, Cracking, and Disbondment

Ash

Fused Salt

Oxide Scale

Metal

Internal Scale

Transport and Chemical Processes Within Ash

Heat Flux

Condensation Effects (eg, Chloride Deposition)

Point Defect Diffusion in Oxide Scale - Soret and Heat of Transport Effects
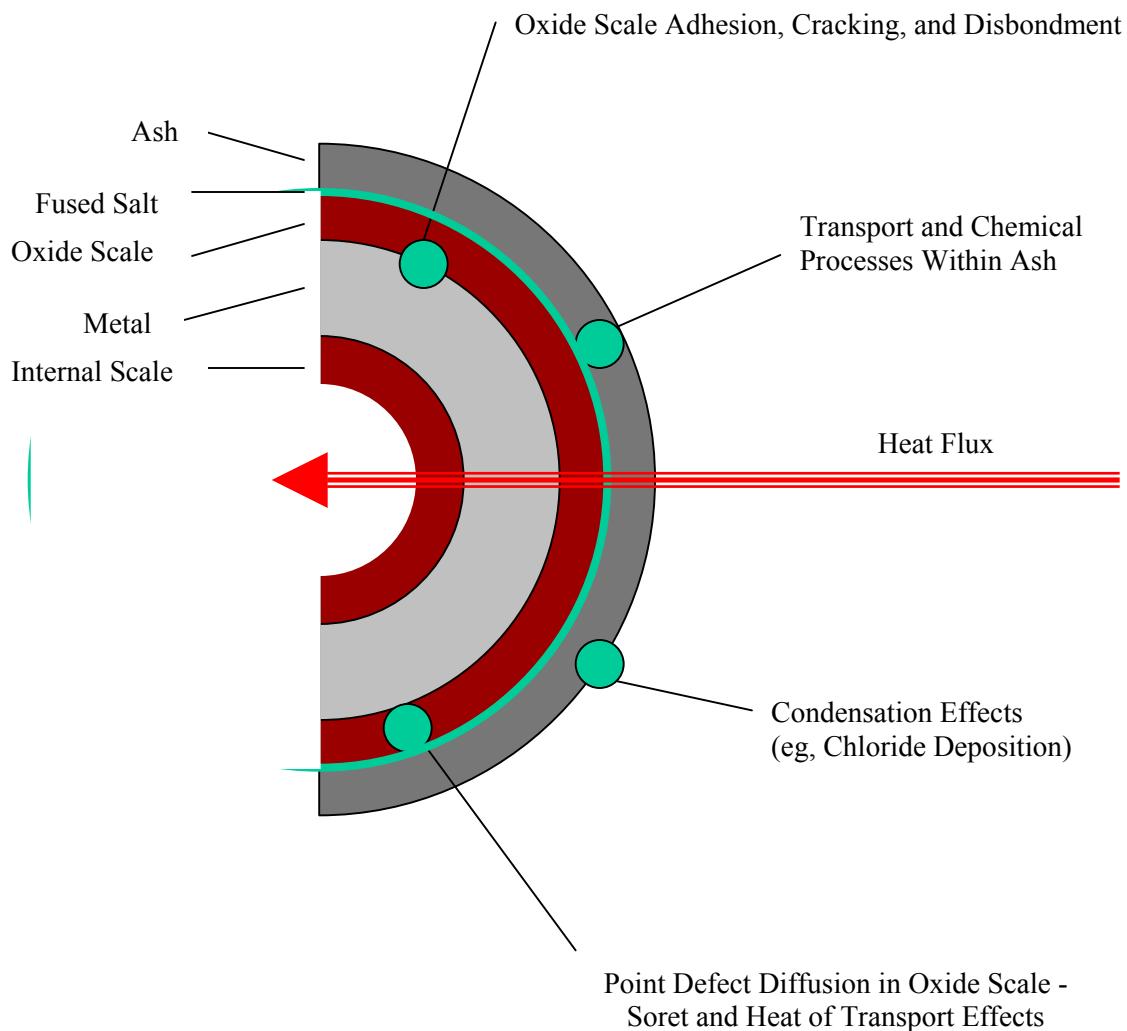
Figure 1 - Heat Flux Considerations due to Fireside Corrosion.

An area of interest in this report is the effect that temperature gradients in a solid oxide have on diffusion within the oxide. Equilibrium concentrations of point defects are a function of temperature. A temperature gradient can create a gradient in point defect concentration within the oxide. More vacancies are expected at higher temperatures. An allied phenomena is the heat carried with each diffusion jump of an atom. Since each jump results in a transport of heat, the presence of a temperature gradient biases the jumps. This transport of heat is described by the heat of transport, Q*, and is the heat carried from the initial site to the final site. A similar term found in the literature is the reduced heat of transport, Q*', and is the portion of Q* in excess of the partial molar enthalpy, h. Thus Q*' = Q* - h.

Both Glover[2] and Malik[3-4] have used non-equilibrium thermodynamics[5] to develop general flux equations that can be combined with point defect information of specific oxides to predict oxidation rates. The general flux equation, from Malik[3-4] is

$$J_i = -\frac{N c_i D_i}{kT}\left\{(1-t_i)\left[\frac{d\mu_i}{dx}+\frac{Q_i^* dT}{T dx}\right] - q_i \sum_{k \neq i}\frac{t_k}{q_k}\left(\frac{d\mu_k}{dx}+\frac{Q_k^* dT}{T dx}\right)\right\} \qquad (1)$$

where J_i is the flux of species i in the oxide, N is the number of lattice sites available to species i per unit volume, c_i is the concentration of species i, D_i is the diffusion coefficient of species i, k is Boltzmann's constant, T is temperature, t_i is the transport number of species i, μ_i is the chemical potential of species i, x is the distance into the oxide from the metal, and q_i is the effective charge of species i. . Equation 1 differs from Glover[2] by including the consequences of effective charge on the diffusion process (t_i and the $q_i\Sigma(\ )$ term). When the temperature gradient is zero and effects of effective charge are neglected, then Equation 1 simplifies to Fick's first law of diffusion.

In an attempt to verify the theory of oxidation in a temperature gradient, Malik[3-4] examined the oxidation of nickel at 600 to 900ºC. The results were inconclusive. Besides the inherent

1. Tipping Floor
2. Refuse Holding Pit
3. Feed Crane
4. Feed Chute
5. Martin Stoker Grate
6. Combustion Air Fan
7. Martin Residue Discharger and Handling System
8. Combustion Chamber
9. Radiant Zone (furnace)
10. Convection Zone
11. Superheater
12. Economizer
13. Dry Gas Scrubber
14. Baghouse
15. Fly Ash Handling System
16. Induced Draft Fan
17. Stack
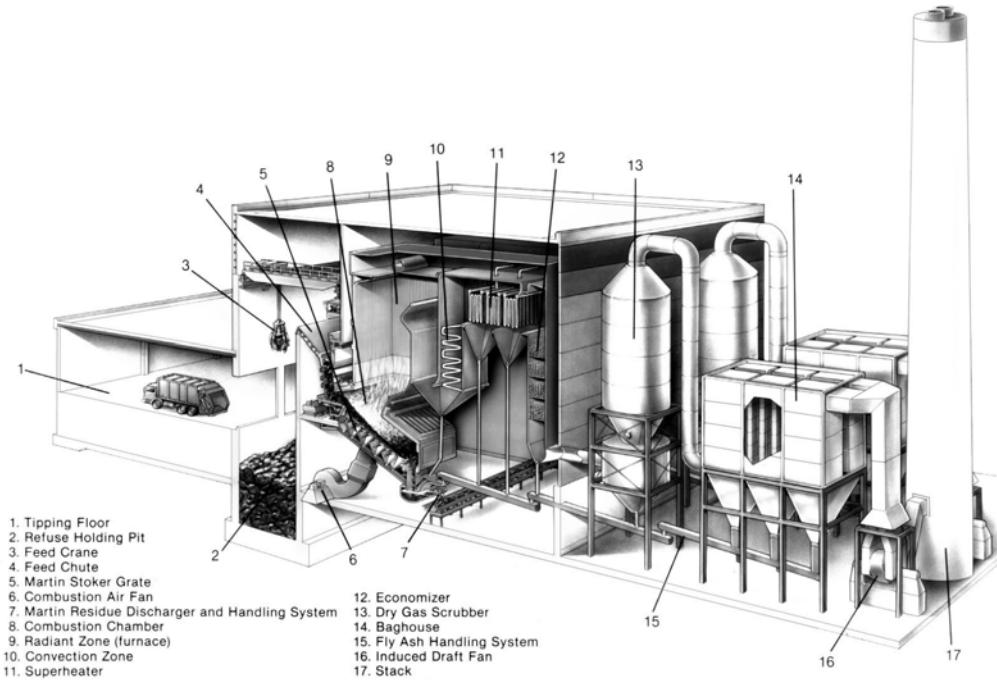
Figure 2 - Schematic of a typical waste incineration facility.

difficulty in measuring what may be a small effect, there were other factors that could have masked the effect. One factor was that the defect structure of NiO is very dependant upon impurity levels, which are difficult to control. A second factor is that most of the temperature range was below 800ºC, where grain boundary diffusion becomes more predominant than lattice diffusion. In the present investigation, cobalt oxidation at a metal surface temperature of 900ºC was selected because: 1) the defect structure of CoO is much less susceptible to impurity effects; 2) lattice diffusion should predominate over grain boundary diffusion at temperatures above 800ºC; and 3) model parameters for the oxidation of cobalt are well known. Also, CoO forms a dense and adherent scale, which is needed for the temperature cycling inherent in periodic measurements of scale thickness.

Waste incinerators have more severe thermal gradient influenced corrosion problems than most coal combustors because the ash deposited in waste-to-energy (WTE) plants typically contains low melting fused salts and eutectic mixtures that can accelerate corrosion. A schematic of a typical WTE incinerator in Figure 2 shows some of the areas that are of concern due to corrosion. The most corrosion susceptible areas are the first pass waterwall (area 9 in Figure 2), the second pass waterwall (between areas 9 and 10 in Figure 2) where gas is traveling in a downward direction, and the superheater (area 11, Figure 2). All of these environments have substantial temperature gradients across the ash-corrosion product-metal structure.

Carbon steel boiler tubes in the waterwall can experience corrosive conditions that will cause them to fail in as little as 3-5 years in a WTE incinerator compared to 10's of years before failure occurs in some coal combustors.

Because of these problems, research was conducted to better understand the corrosion process on carbon steel tubes. One goal was to find a solution to the observed corrosion that is more economically feasible than replacing the tubes with higher alloy boiler tubes or applying weld overlays. One of several successful outcomes of this research project would be to alter the WTE process to minimize corrosion.

The research reported here shows some initial effects of temperature and thermal gradients on the high temperature corrosion of cobalt and carbon steel.

EXPERIMENTAL PROCEDURES

High Temperature Corrosion of Cobalt

The assembly used to study the effect of thermal gradients on the oxidation of cobalt is shown at the top of Figure 3. It consists of a 1 in (2.5 cm) diameter cobalt disk machined so that two thermocouples can be inserted in the side at two distances from the exposed surface. Six small bolts are used to attach it to the stainless steel air-cooled chamber. The rest of the sample assembly, shown at the bottom of Figure 3, is wrapped in insulation and inserted into a tube furnace. The insulation wrap covers the outer circumference of the sample to promote one-dimensional heat flow within the sample.

Three variations on the same type of experiment were used. The test conditions consisted of a metal surface temperature of 900ºC and an atmosphere of $N_2 + 1\%$ O_2 for all three types of experiments. The first experiment was designed to closely follow the procedure that Malik[3-4] used. It consists of oxidizing one side of a piece of cobalt, while cooling the other side and measuring the temperature gradient across the sample. For this experiment, a piece of 50 mesh stainless steel screen was placed between the cobalt sample and the cooling chamber. Cooling air was flowed at up to 1 to 20 L/min to produce heat fluxes of 15 to 53 kW/m^2. This establishes a known temperature gradient across the metal sample from which the heat flux is calculated using the thermal conductivity of cobalt. After exposure to oxygen at temperature, the sample is removed from the furnace, the oxide scale nicked with a drill bit at a 45º angle, and the thickness of the scale measured with scanning electron microscopy (SEM) of the nick.

Heat Flux of 40-50 kW/m^2

Tube Furnace Insert

Figure 3 - Tube furnace insert for one-sided cooling of sample with compressed air.

Scale thickness, sample heat flux, sample temperature gradient, and CoO thermal conductivity are used to calculate the temperature gradient across the oxide scale. These samples were then cycled through the oxidation and scale measurement procedures two or more times to develop data for longer exposure times on the same sample. These were called cyclic tests because the oxide film was allowed to remain intact when the samples were re-exposed to the high temperature corrosion. The second experiment was identical to the first but samples were oxidized and the oxide thickness measured only once. The third experiment was again identical to the first

except that an alumina disk was placed between the C sample and the cooling chamber. Cooling air was flowed at only 2 L/min which produced heat fluxes of only 1-3 kW/m^2. In other words, these were isothermal tests.

High Temperature Corrosion of Carbon Steel

These high temperature corrosion experiments were conducted on a mild steel boiler tube, ASME SA-178A steel (UNS K01200), of nominal dimensions: 1.9 cm (0.75 in) outer diameter by 1.4 cm (0.56 in) inner diameter. The composition of the steel tube is listed in Table 1. All samples of the tube were either hand sanded or sandblasted to remove a black manufacturer-applied coating on the outside of the tube and to provide a uniform surface finish. Ash for the experiments was obtained from a Covanta Municipal incinerator, Lee W#1, specifically from the

Table 1 - ASME SA-178A steel (UNS K01200) Boiler Tube Composition.[1]

Weight %														
C	Mn	P	S	Si	Ni	Cr	Mo	Cu	Al	Ca	Nb	N	Ti	V
0.07	0.47	0.01	0.004	0.06	0.054	0.016	0.01	0.119	0.026	0.001	0.002	0.008	0.003	0.002

[1]The balance of the alloy is Fe

sidewalls and the rear of the second pass at the top. The ash composition is given in Table 2. The ash contains high concentrations of corrosion-causing elements, such as S, Cl, Pb, and K. The loss of 26.6 wt% of the sample on ignition under argon (LOI) represents the loss of water and other volatile elements or compounds.

Table 2 – Lee W#1 Ash Composition.

Weight %											
Al	Ca	K	Pb	Na	Cl	LOI	H$_2$O	Fe	Si	S	Mg
3.63	9.97	3.69	2.7	3.53	6.71	26.6	6.74	5.00	8.00	6.47	0.734
mg/kg (ppm by weight)											
Mn	As	Cr	Ag	Ba	Ti	P	Cd	Se	C	N$_2$	
631	107	482	<20	697	5,140	2,130	883	<50	1350	1710	

LOI = Loss on Ignition under argon at 1000ºC

Corrosion tests were performed in a three-zone furnace with an upper temperature limit of 1100ºC. The furnace had a constant temperature zone of 30 cm (12 in) for exposing the test samples. Tests were conducted either isothermally, where the gas and samples were at approximately the same temperature, or non-isothermally, where the gas was at a higher temperature than the metal. Gas compositions were maintained using computer-controlled digital mass flow controllers. Water vapor was added using a metering pump to deliver water at a preset rate through a heated chamber and allowing the water vapor to combine with the flowing gas mixtures prior to entering the furnace.

Gas compositions used in both the isothermal and thermal gradient tests consisted of 9 vol % O$_2$, 8 vol % CO$_2$, 68 vol % N$_2$, and 15 vol % water vapor at a gas flow rate of 0.5 L/min. Future tests will include 1000-2500 ppmv (parts per million by volume) HCl and up to 200 ppmv SO$_2$. Gas mixtures were used once, cleaned of hazardous components, and then released.

Isothermal Corrosion Tests - Corrosion coupons for the isothermal tests consisted of 2.5 cm (1 in) long half cylinders cut from the original boiler tubes. All sides and edges were hand polished using 120 grit paper to produce a uniform surface finish. After cleaning and weighing, the concave surface of the samples was filled with ash. Ash-covered and bare samples were placed in ceramic trays and inserted into the furnace. Heating to test temperature was done with nitrogen flowing at 0.34 L/min. Once at temperature, the gas composition was adjusted to 9 vol % O$_2$, 8 vol % CO$_2$, 68 vol % N$_2$, and 15 vol % water vapor at a flow rate of 0.5 L/min. Tests

were run for 5-7 days at constant temperature. Tests were stopped by initiating the furnace cool-down cycle, stopping the production of water vapor, and switching to a flow of nitrogen. Total test time was the time at temperature during which the test gas composition was present.

Thermal Gradient Corrosion Tests - A schematic of a cross section through the thermal gradient apparatus is given in Figure 4 to aid in the discussion that follows. Sections of boiler tube 1.4 m (54 in) in length were used for thermal gradient corrosion test samples. The tubes were cleaned by sandblasting the black factory-applied coating from a 30 cm (12 in) length in the center of the tube. Two type K thermocouples were then welded approximately 25 cm (10 in) apart in the sand blasted region. These thermocouples were used to measure the temperature at the outer surface of the boiler tube. Five separate thermocouples were contained in a stainless steel sheath and used to measure the gas temperature.
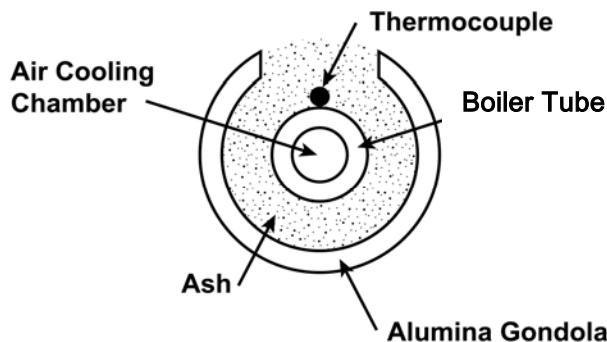
Figure 4 - Thermal Gradient Test Apparatus used for Waste Incinerator Tests.

An alumina "gondola" was slid over the boiler tube and then filled with ash as pictured in Figure 4. Ceramic fiber wool plugs at the ends of the gondola were used to keep the ash in the gondola. The ash covered the entire surface of the boiler tube including the attached thermocouples.

The instrumented boiler tube was inserted into the tube furnace and tests were started in a manner similar to the isothermal tests. Heating to the desired gas temperature occurred in flowing nitrogen. Once at the desired gas temperature, cooling air was passed through the tube to reduce the boiler tube surface temperature with respect to the gas temperature. Two additional thermocouples in the air stream were used to facilitate control of the boiler tube surface temperature. Because the cooling air reduced both the tube and the gas temperatures, gas temperature and cooling air flow rate were incrementally adjusted to give the final test conditions. Gas composition was then changed to 9 vol % O_2, 8 vol % CO_2, 68 vol % N_2, and 15 vol % water vapor at a gas flow rate of 0.5 L/min. At the end of the test period, furnace cool down was initiated, gas composition was changed to nitrogen, and the cooling air allowed to continue flowing.

After cooling, the boiler tube was removed from the tube furnace and the ash-containing gondola was removed. The loose ash was brushed off of the tube and then the tube was coated with a lacquer to stabilize the corrosion product and the remaining ash. Several coats of epoxy were then applied prior to cutting cross-sections from the tube. These cross sections were mounted, polished, etched, and then examined metallographically to measure the minimum wall thickness for the cross sections.

Mass Loss (ML) Corrosion Rate Measurements. - Corroded mass loss samples from the isothermal tests were cleaned chemically by pickling in a 60ºC solution of 12 vol % H_2SO_4 plus 2.5 mL/L Rodine 95 inhibitor. Sample cleaning times ranged from 2 to 19 minutes. Final sample weights were measured to the nearest 0.01 mg and adjusted for blank weight losses in the cleaning solution. Corrosion rates for the bare samples were calculated using mass loss, exposed area, steel density, and test duration.

Metallographic (MET) Corrosion Rate Measurements - Cross-section thickness was measured metallographically at the points of greatest metal loss of both the isothermal and temperature gradient test samples. These measurements did not, however, include any regions of intergranular attack, even if that type of attack was present. Measurements were made on polished and etched cross sections using an optical microscope .

High Temperature Corrosion of Cobalt

The relationship of CoO thickness to exposure time at a metal surface temperature temperature of 900ºC is shown in Figure 5 for isothermal and thermal gradient (heat flux) samples. Also shown is a line predicted for isothermal corrosion from results presented by Kofstad.[6] The first two data points near 50 h represent samples that were oxidized only once. The group of four data points above the solid line at 100 h in Figure 5 represent the cyclic corrosion samples. These were reoxidized after their initial exposure. The heat flux point at 500 h was not cyclic.

All of the points appear to lie on a line that would be distinctly different from the isothermal line predicted from Kofstad.[6] The cause of this difference is unknown at this time. The isothermal and thermal gradient data are similar. This suggests that for the oxidation of cobalt, the effect of heat flux may be minimal.

High Temperature Corrosion of Carbon Steel Boiler Tubes

Isothermal Tests - ML corrosion rates for the bare samples and ML and MET corrosion rates for the ash-covered samples are

Figure 5 - Effect of exposure time and thermal gradients (heat flux) on the growth of CoO on Co at 900ºC in N_2 + 1% O_2.
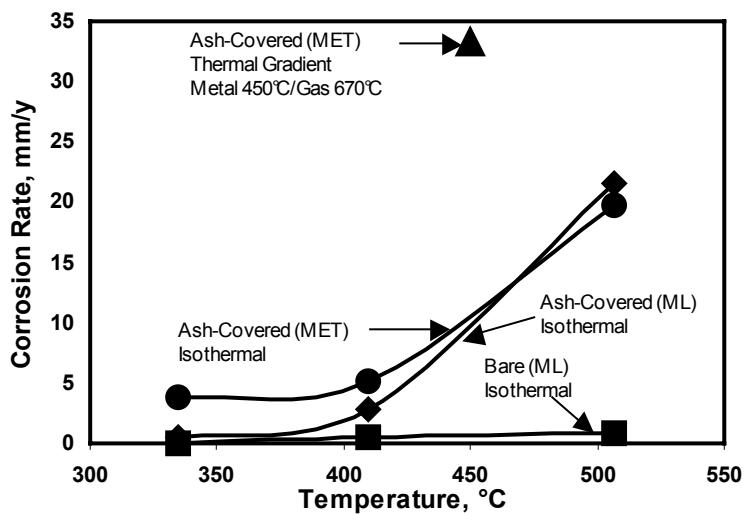
Figure 6 - Effect of temperature and thermal gradients on the high temperature corrosion of carbon steel boiler tubes.

shown plotted versus temperature in Figure 6. ML corrosion rates for the bare samples increase slightly with temperature and are significantly lower than the ash-covered samples at test temperatures greater than 400ºC. ML and MET corrosion rates for the ash-covered samples are similar at temperatures greater than 400ºC and show a more pronounced increase as temperature increased. In fact, corrosion rates for the ash-covered samples were as high as 20 mm/y at 510ºC. This rapid increase in corrosion rate at temperatures greater than 400ºC has been

reported previously for an in-plant test[7] of carbon steel and has been attributed to the formation of volatile $FeCl_3$ compared to the less volatile $FeCl_2$ at lower temperatures. 10-hour ML corrosion rates during the in-plant tests[7] were as high as 90 mm/y, which is significantly higher than those reported in Figure 6.

Thermal Gradient Tests - The MET corrosion rate for the thermal gradient test plotted in Figure 6 is 33 mm/y, about a factor of 2 higher than what would be predicted from the data for an isothermal test at 450ºC, Figure 6. These differences suggest that there are other factors operating besides the temperature difference between the gas phase and the metal surface. As shown in Figure 1, corrosion can be affected by scale adhesion problems and by the deposition of volatile and corrosive chemical species.

Analysis of the corroded thermal gradient samples showed that some of the ash was very firmly attached to the scale, the scale formed in layers, the tube was corroded uniformly around the circumference, and the scale was not tightly adhered to the metal. This non-adherent scale may have been the result of breakaway corrosion as Spiegel and Warnecke suggested[8] occurs at metal temperatures greater than 427ºC. Metallographic analysis also showed the presence of extensive intergranular attack in the layer beneath the scale.

CONCLUSIONS

The oxidation of Co at 900ºC in N_2 + 1% O_2 proceeded at approximately the same rate regardless of the presence of a thermal gradient or cyclic exposures. This suggests that for Co, the effect of thermal grqdients is minimal to the oxidation process

Increasing temperature greatly affects the isothermal corrosion rate of an ash-covered low carbon steel in an O_2/CO_2/N_2/H_2O environment. Mass loss (ML) and metallographically-determined (MET) measurements produced similar corrosion rates for the ash-covered samples. The presence of the ash covering causes a large increase in corrosion rate compared to bare corrosion rates. A thermal gradient test is a more severe, and perhaps more realistic, test of corrosion resistance than an isothermal test.

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