

Potential Impacts of Oxy-Combustion Retrofit on Boiler Tube Corrosion Rate

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Introduction

Fireside tube corrosion is a topic of great concern for US utility boilers. Some furnaces have experienced local tube metal loss rates on the order of 2.5 mm/yr (100 mil/yr) and EPRI recently estimated that fireside corrosion costs the U.S. electric power industry up to \$590 million per year and is responsible for approximately half of unscheduled outages in steam generation units [Syrett and Gorman, 2003]. During the last twenty years, the introduction of low NO_x firing systems (low NO_x burners and overfire air) and efforts to improve thermal efficiency through the use of higher pressure/temperature steam conditions have resulted in growing concern with fireside corrosion and have led to increasing pressure to improve materials technology. Recent focus has been on the introduction of oxy-fuel combustion, which has the advantage of reducing the volume of exhaust combustion gases, thereby simplifying the approach to reducing CO₂ emissions. Oxy-fuel combustion will also change the heat balance within the boiler, especially when applied within existing boiler units. Additionally, the prospect of combusting coal with oxygen and flue gas recycle has the potential to affect corrosion behavior in a number of different ways.

REI and Corrosion Management Ltd. have performed pilot-scale experimentation to elucidate the potential impacts of oxy-coal combustion retrofit of utility boilers on corrosion. The goals of these tests were two-fold:

1. To demonstrate differences, if any, in corrosion behavior of materials typically implemented in US utility boilers between air-coal and oxy-coal combustion conditions.
2. To develop a data set suitable for validation of mechanisms developed to predict the corrosion rate of heat transfer surfaces under air- and oxy-fired coal combustion conditions.

Experimental

In order to obtain a real-time indication of corrosion, a measurement system based on electrochemical noise sensing was utilized [Bakker et al., 1992]. This sensing technique was performed on corrosion probes with sensor elements fabricated from materials representative of heat transfer surfaces in high temperature combustion applications. One waterwall material and three superheater tube materials were chosen that are typical of those used in US utility boilers. The specifications of the materials chosen are presented in Table 1.

Table 1. Specification of the materials used for corrosion probe sensor elements

Material	SA 210	T22	P91	347H
HT Surface	Waterwall	Superheater	Superheater	Superheater
C, %	0.07	0.11	0.10	0.048
Si, %	0.23	0.2	0.32	0.40
Mn, %	0.42	0.44	0.47	1.32
Ni, %	-	-	0.15	9.73
Cr, %	-	2.21	8.52	17.45
Mo, %	-	0.95	0.93	-
S, %	0.002	0.003	0.002	0.008
P, %	0.009	0.01	0.018	0.026
Cu, %	-	-	0.11	-
Al, %	-	-	0.01	0.005
Nb/Cb, %	-	-	0.07	0.63
V, %	-	-	0.22	0.078
N, %	-	-	0.044	-
Ta, %	-	-	-	0.02

The materials shown in Table 1 are arranged in order of increasing alloy content from left to right. The SA210 material is a low-carbon steel that is commonly used to fabricate waterwall tubes in utility boilers and was used for the waterwall sensor element in this investigation. The remaining three materials, T22, P91 and 347H, are commonly used in the construction of superheater tubing and each of these was used to create the sensor elements for superheater probes. The waterwall and superheater probes differ in their physical construction. The sensor elements of the waterwall probe are at the tip of the probe on the flat surface of the probe. When installed in a furnace, the probe is positioned so that the front face of the probe is flush with the plane of the wall of the furnace. The elements of the superheater probe are rings of tubing that are cut from actual boiler tube. The corrosion surface of these elements has the standard mill finish. The superheater sensor elements are situated at the end of a long, cooled stainless steel lance. When inserted into the furnace, the orientation of the sensor elements is that of a tube in cross flow, precisely simulating the condition of a typical superheater tube in a utility boiler. The four probes used for this investigation are pictured in Figure 1.

Superheat Probes



Water Wall Probe



Figure 1. Waterwall and superheater sensor probes used for real-time corrosion monitoring

The platform for this corrosion investigation was the University of Utah's 1.5 MW furnace, the L1500. The corrosion sensor probe and furnace configuration for these tests is presented in Figure 2. The sensor elements of the waterwall probe were typically maintained at 720°F and the probe was installed in section 2 of the L1500 with gas temperatures about 2300°F. The sensor elements on the superheater probes typically were controlled at 910°F and were installed at a gas temperature of about 1800°F. To target this gas temperature, the superheater sensor probes were installed in section 10 of the L1500. The superheater probes were typically installed with the P91 probe on top, the 347H probe in the center and the T22 probe on bottom. For all of these tests, the firing rate was 3.5 MBtu/hr. For the majority of these tests, the burner was staged with a stoichiometric ratio of 0.9. The overall stoichiometric ratio was sufficient to produce 3.0% O₂ (dry) in the flue gas and the concentration is dependent on air or oxy-fired conditions. The over-fire air was introduced in section 6 of the furnace. This configuration and typical operating conditions result in reducing conditions at the waterwall probe and oxidizing conditions at the superheater probes.

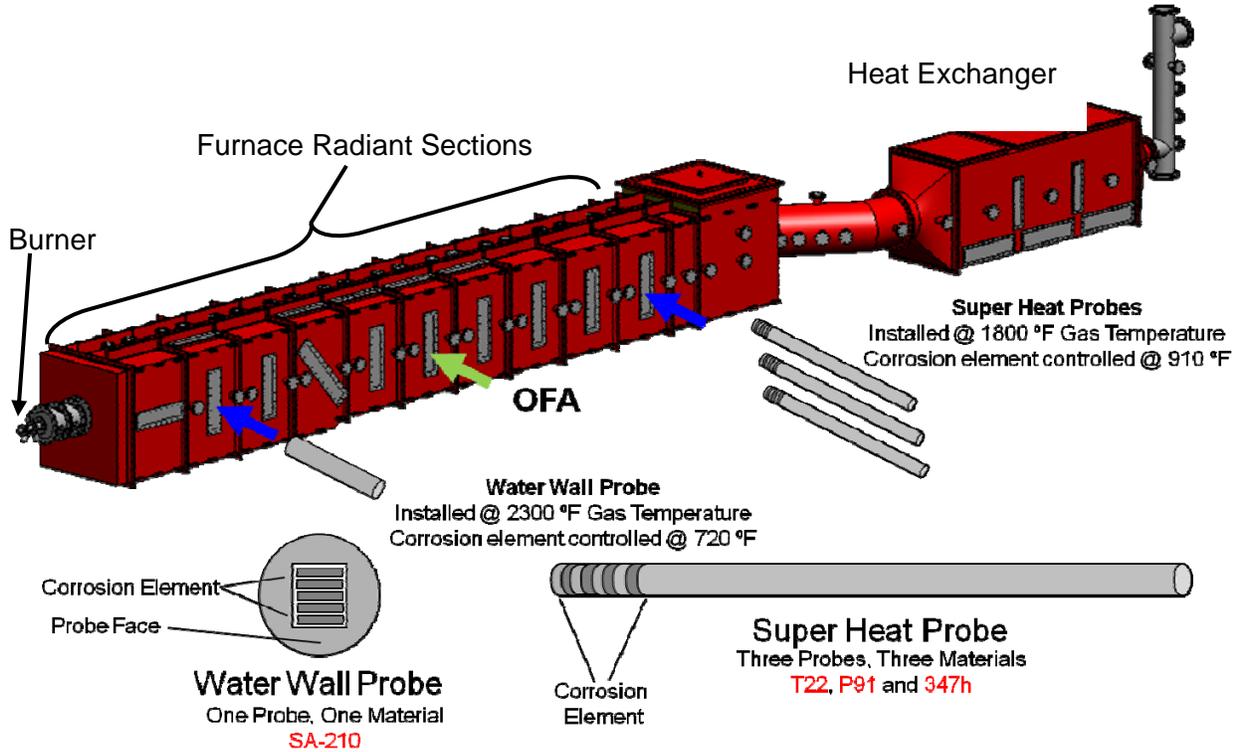


Figure 2. Pilot-scale furnace and corrosion sensor probe configuration

Three different coals were used for this experimental program. The Utah coal was from the Skyline mine and is a western bituminous, low-sulfur coal. The PRB coal was from the North Antelope mine and is also low sulfur. The Illinois coal was from the Shay #1 mine and has very high sulfur content. The analyses of the coals and of the mineral matter are presented in Table 2.

Table 2. Coal and mineral matter analyses

	Skyline	PRB	Illinois
Coal Analyses			
C	70.60	53.72	64.67
H	5.05	3.57	5.59
N	1.42	0.78	1.12
S	0.53	0.23	3.98
O	10.39	13.07	16.65
Ash	8.38	4.94	7.99
Moisture	3.18	23.69	9.65
Volatile Matter	38.60	33.36	36.78
Fixed Carbon	49.39	38.01	45.58
HHV, Btu/lb	12,606	9,078	11,598

Mineral Matter Analyses			
Al	14.52	14.78	17.66
Ca	6.11	22.19	1.87
Fe	5.09	5.20	14.57
Mg	1.39	5.17	0.98
Mn	0.02	0.01	0.02
P	0.59	1.07	0.11
K	0.57	0.35	2.26
Si	60.89	30.46	49.28
Na	1.41	1.94	1.51
S	2.33	8.83	2.22
Ti	0.88	1.30	0.85

* all values in mass % unless otherwise specified

Results & Discussion

In order to determine the dependence of corrosion rate, several parameters were varied in these experiments. These parameters included: air- vs. oxy-fired conditions, coal sulfur concentration, corrosion sensor element temperatures and oxidizing vs. reducing conditions. However, over the six week period of in-furnace testing the conditions detailed in Figure 2, while firing with a burner stoichiometric ratio of 0.9, were maintained for a majority of the test program in order to confidently compare corrosion rate for air- and oxy-combustion.

The average corrosion rates calculated and reported here assume that the metal loss occurs uniformly over the surface of the corrosion sensor element. In reality, the loss of material is more likely to occur in discrete locations on the sensor element associated with deposit and flow characteristics. For the superheater probes this discrete area is probably limited to about a third of the overall surface on the leading and trailing sides of the tube in cross flow. Therefore peak corrosion rates for the superheat probes are likely to be approximately 3 times higher than the overall average rates reported here. However, as this is a pilot-scale facility which was operated only during an eight to ten hour period each day, and the corrosion probes were removed each night, the relative corrosion rate values were more relevant for comparison purposes than were the absolute rate values. The average corrosion rates measured for the baseline conditions described in Figure 2 are presented in Figure 3 on a large scale and in Figure 4 on a small scale.

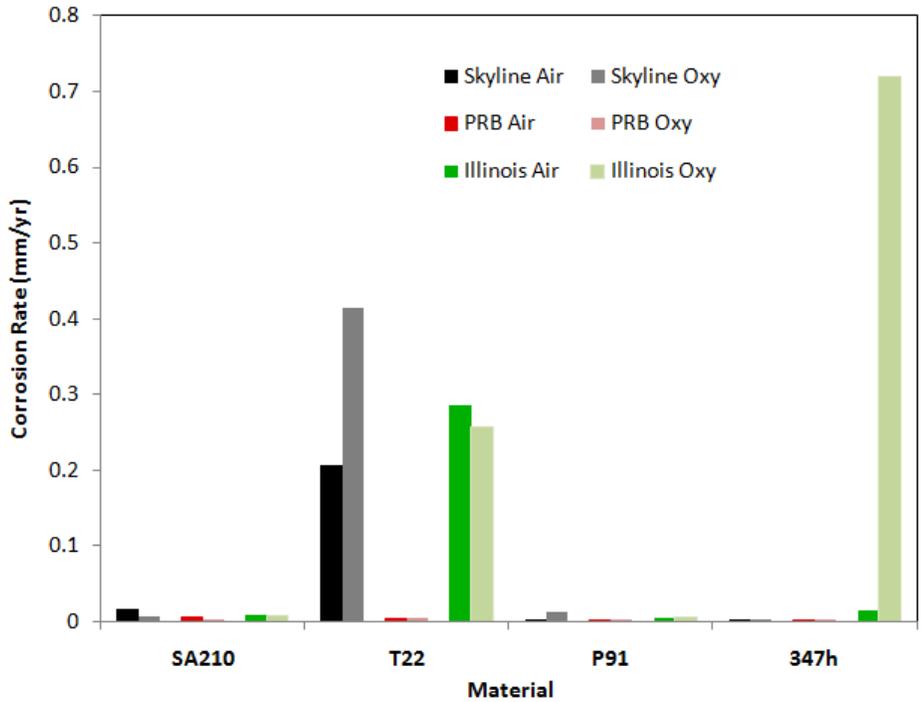


Figure 3. Summary of average corrosion rates for the baseline sensor element temperatures, probe locations and staging conditions (large scale)

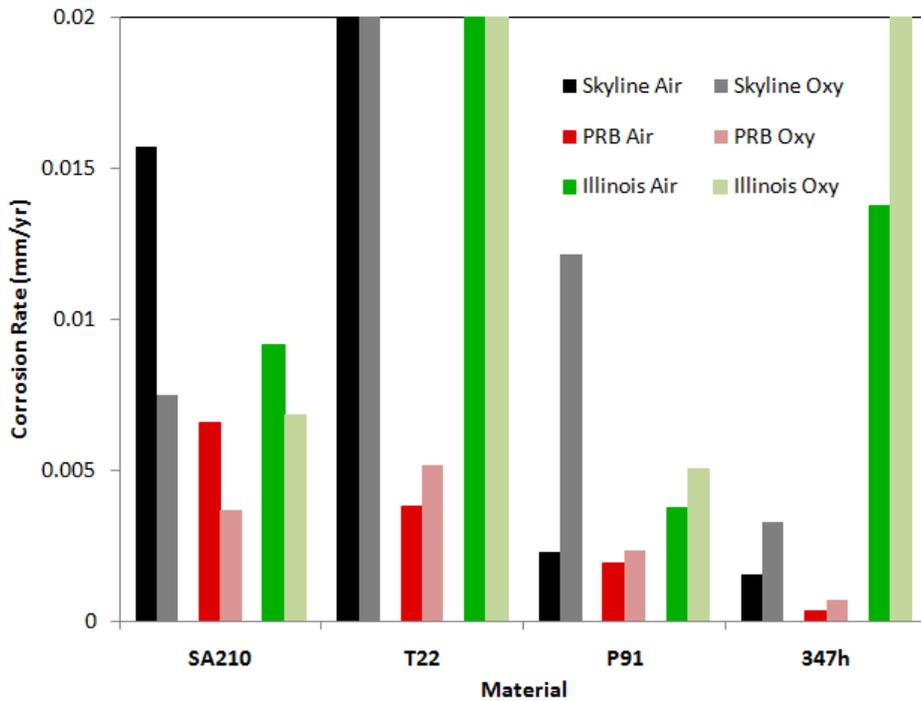


Figure 4. Summary of average corrosion rates for the baseline sensor element temperatures, probe locations and staging conditions (small scale)

Figure 3 and Figure 4 indicate very low corrosion rates for all of the materials, coals and air and oxy-firing, with the exception of five conditions. These conditions included the T22 material with Skyline and Illinois coals and for both air and oxy-fired conditions and the 347H material under Illinois/Oxy conditions. These five conditions and material combinations produced rates on the order of 0.21 to 0.72 mm/yr (8.3 to 28.3 mils/year), which are significant. While firing the Illinois coal, the flue gas SO₂ concentrations were approximately 3,200 ppmv (wet) for air-fired conditions and 17,600 ppmv (wet) for oxy-fired conditions. Later experiments suggested that at these high SO₂ concentration conditions, condensation of trisulphate species may be responsible for the high corrosion rate at the baseline probe setpoint temperatures. The corrosion rate of the 347H probe was significantly lower for the Illinois/Oxy conditions and an elevated probe setpoint temperature of 1150 °F.

More important than the absolute corrosion rates is the trend between the air and oxy-fired conditions. For the waterwall probe (SA210), the corrosion rate decreased when the combustion conditions were changed from air- to oxy-firing for all conditions tested. By contrast, for all of the superheater probes (T22, P91 and 347H) the corrosion rate increased when combustion conditions in the furnace were changed from air- to oxy-firing for all but one condition tested. To examine these trends in more detail it is useful to look at the plot of the increase in corrosion rate when converting from air- to oxy-firing for all materials and conditions. This plot is presented in Figure 2.9.

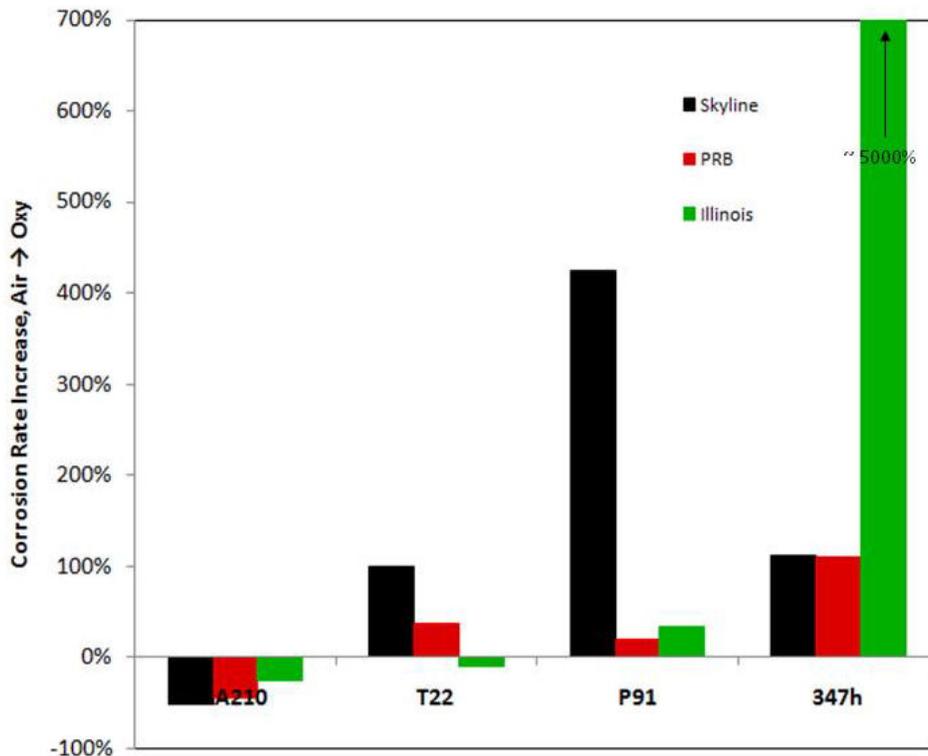


Figure 5. Measured increase in corrosion rate when converting from air- to oxy-firing

Figure 5 clearly indicates the difference in behavior between the waterwall and the superheater probes. The only material and coal that exhibited behavior that was contrary to the general trend was the T22 material with Illinois coal. The decrease in waterwall corrosion rate when converting from air to oxy-fired conditions, although involving minor corrosion rates, could be a significant circumstance. An expected decrease in corrosion rate to these heat transfer surfaces when retrofitting for oxy-combustion could be a facilitating result for the technology. The difference in behavior between the waterwall and superheater probes may be explained by the difference between oxidizing and reducing conditions. For these data, the waterwall probe was installed in a region with stoichiometry of 0.9, whereas the superheater probes experienced superstoichiometric conditions. The behavior of the superheater probes was un concerning for most of the materials and coals tested. The increase in corrosion rates was small, compounding an already small corrosion rate. The results here that may be concerning and warrant further investigation are the P91 material with Skyline coal and again the 347H material with Illinois coal.

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References

1. Bakker, W. T., Mok, W. Y., and Cox, W. M., "High-Temperature Fireside Corrosion Monitoring in the Superheater Section of a Pulverised-Coal-Fired Boiler", EPRI, Palo Alto, CA: 1992, TR-101799.
2. French, D. N., "Creep and Creep Failures", Bulletin of the National Board of Boiler and Pressure Vessel Inspectors, July, 1991.
3. Syrett, B. C., and Gorman, J. A., "Cost of Corrosion in the Electric Power Industry – An Update", *Materials Performance*, **42** (2), 32-38, 2003.
4. Viswanathan, R, and Bakker, W. T., "Materials for Boilers in Ultra Supercritical Power Plants", Proceedings of the International Joint Power Generation Conference, Miami Beach, Fl., July 23-26, 2000.