

FIRESIDE CORROSION PROBES – AN UPDATE

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ABSTRACT

The ability to monitor the corrosion degradation of key metallic components in fossil fuel power plants will become increasingly important for FutureGen and ultra-supercritical power plants. A number of factors (ash deposition, coal composition changes, thermal gradients, and low NO_x conditions, among others) which occur in the high temperature sections of energy production facilities, will contribute to fireside corrosion. Several years of research have shown that high temperature corrosion rate probes need to be better understood before corrosion rate can be used as a process variable by power plant operators. Our recent research has shown that electrochemical corrosion probes typically measure lower corrosion rates than those measured by standard mass loss techniques. While still useful for monitoring changes in corrosion rates, absolute probe corrosion rates will need a calibration factor to be useful. Continuing research is targeted to help resolve these issues.

INTRODUCTION

Corrosion of metals and alloys is a natural occurrence in high temperature energy conversion systems. Thermodynamic calculations predict that elements such as Fe, Ni, and Cr (which make up the majority of alloys used in this industry) will always seek their lowest energy state, that of an oxide, sulfide, or chloride. It is then the stability of this compound that will determine the long term corrosion rate. Successful coatings or alloying additions can help slow down or in some cases eliminate the corrosion process. When this is not possible, it is necessary to observe corrosion damage after the fact during plant shutdowns or to seek ways to monitor the corrosion of key components during operation.

Monitoring of corrosion during power plant operation has, up to the present, consisted primarily of inserting and removing metal coupons on a periodic basis. While this can give plant operators an early warning of accumulated corrosion damage, it usually has a minimum time period of months and can not give an instantaneous measure of corrosion that can sometimes be correlated to changes in process. If instantaneous reading corrosion rate probes were available, power plant operators would then have the ability to make changes in their processes to reduce the corrosion of their assets.

There have been a number of research efforts aimed at developing high temperature corrosion probes for various industries, such as Pulverized Coal-Fired (PC) plants using lower quality fuel and in Waste-to-Energy (WTE) plants¹. The majority of this research has been based on the use of electrochemical noise (EN)²⁻⁷ techniques. Others have considered the use of electrochemical

impedance spectroscopy (EIS)^{4,6} and linear polarization resistance (LPR)⁷, zero resistance ammetry (ZRA)⁵, and electrical resistance (ER)⁵. There has been, however, only a limited effort reported to quantify³ the operation of corrosion rate probes.

This paper will discuss some of the results and problems encountered in research to develop electrochemical corrosion rate probes for high temperature ash-covered conditions common to waterwalls and superheaters. Previous research⁸⁻¹¹ has addressed the issues of response and zero baseline as well as the quantitative nature of the corrosion probes in these environments. The state of this research as well as questions to be answered and suggestions for future research will be presented.

EXPERIMENTAL DETAILS

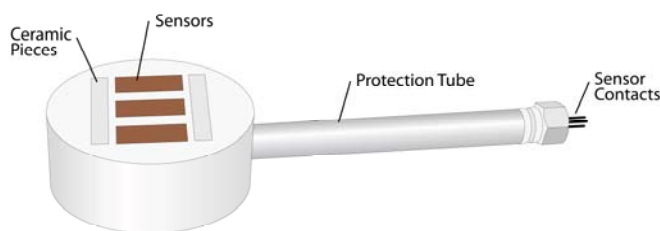


Figure 1: Schematic representation of a typical ECR probe

The two outer sensors in Figure 1 are the working and counter electrodes and the inner sensor is the reference electrode. Sensors were embedded within a plastic removable form using Ceramcast 586, a zirconia/magnesia potting compound. The ceramic pieces shown in Figure 1 were used as reference surfaces for optical profilometry measurements (not discussed in this paper). After curing the potting compound, the probes were covered with ash and then exposed to high temperature gaseous conditions, along with ash-covered mass loss coupons made from the same material as the sensors.

A single three-sensor isothermal electrochemical corrosion rate (ECR) probe, shown schematically in Figure 1, was designed and constructed for laboratory experiments using either mild carbon steel (CS), 304L stainless steel (SS), or 316L SS sensors (sensors are the same as electrodes used in a typical electrochemical cell). Wires were welded to each sensor and a protection tube allowed the wires to exit the furnace and not be corroded.

Table 1
Composition (wt %) of major corrosion-causing elements in 2 combustion ashes used in ECR probe research.

Ash	Al	K	Pb	Na	Cl	Fe	S
Waste	3.6	3.7	2.7	3.5	6.7	5	6.5
Coal	4.0	Trace	0	trace	0	4.5	6

Two different types of ash were used in this research. The first was an ash from the Lee #1 Municipal Incinerator supplied by Covanta Energy, Inc. The second was a coal ash described as AEP TIDD (American Electric Power TIDD Coal Plant in Brilliant, OH) ash derived from Illinois #8 coal, and supplied by EERC, the University of North Dakota Energy and

Environmental Research Center. Table 1 compares the composition of the two types of ash. Waste ash was used for the majority of the experiments discussed in this report because it provided a more corrosive environment. This ash shows high concentrations of corrosion-causing elements such as S, Cl, Pb, and K, all of which are able to form low melting point compounds and eutectic mixtures. The gas mixture consisted of 68 vol% N₂, 15 vol% H₂O, 9 vol% O₂, and 8 vol% CO₂. The temperature used was 500°C and typical test periods were 100 to 500 hours. Coal ash was used for several experiments. In these experiments, the gas mixture consisted of 69 vol% N₂, 15 vol% CO₂, 10 vol% H₂O, 5 vol% O₂, and 1 vol% SO₂.



Figure 2 – Data displayed during an ECR probe test.

Figure 2. Most of the corrosion rates in this report were taken from the LPR measurements modified using the measured B values from each experiment. The default ECR probe corrosion rates were determined by integrating the LPR corrosion rates to calculate the mass loss, which was then converted to a penetration rate with units of millimeters per year (mm/y).

All experiments were conducted in a three-zone tube furnace containing a 2 in diameter alumina tube. Each zone was controlled with a separate temperature controller. Set temperatures for each zone were determined for each test temperature using an external calibration thermocouple and taking measurements at 1 cm intervals. For example, settings of 490, 510, and 400°C for zones 1, 2, and 3, respectively, gave an internal temperature of 500°C with a flat profile over 12 in (30.5 cm) of the 24 in (61 cm) heated zone. An alumina D-tube was inserted in the furnace tube to provide a platform for mass loss coupons. Measurement and control thermocouples were inserted in a 316 SS sheath that was then inserted in the D-tube.

Gas flows, and thus gas mixture compositions, were controlled using digital mass flow controllers that were controlled using Lab-view programs. Water vapor was added through an air-powered metering pump that pumped a specific quantity of water into a heated chamber where the water vapor was picked up by the test gas mixture.

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RESULTS AND DISCUSSION

The goal of this research was to show that electrochemical corrosion rate probes can be used to monitor corrosion in high temperature environments where ash is deposited on metallic surfaces. The optimal result of this research would be that probes are able to quantitatively measure corrosion rates (that is, electrochemical corrosion rates = mass loss corrosion rates). In the case where the probes are not quantitative, but semi-quantitative, it is necessary to determine if a calibration factor can be established to make the probes appear to act quantitatively. In order for a semi-quantitative probe to work for the many different environments (ash compositions, temperature, gas compositions, etc.) encountered in energy production, it will also be necessary to understand the operation of the probes.

Semiquantitative Probe Nature

Electrochemical corrosion rate probes based on either LPR or EN measurements have been reported to be semi-quantitative for measurements made on mild and stainless steels in high temperature gaseous ash-depositing environments¹¹. This conclusion is based on a comparison of mass loss measurements to electrochemical measurements which has shown that for a large

Table 2
Real-Time Corrosion Monitoring Corrosion rate ratios with ML corrosion rates for select experiments.

Alloy	Ash	ML/LPR	ML/EN
CS	Waste	9.6	19.9
304 SS	Waste	4.2	9.7
304 SS	Waste	6.5	8.5
316 SS	Waste	1.4	3.2
316 SS	Waste	12.9	7.6
304 SS	Coal	0.35	0.31
316 SS	Coal + FeS	0.05	0.08
ML = mass loss corrosion rates, LPR = LPR probe corrosion rates, and EN = electrochemical noise probe corrosion rates			

number of measurements in waste ash, the corrosion rates are under-reported (that is, the sensors measure less of the corrosion than actually occurs). For a smaller number of tests in coal ash, the measurements are over-reported (that is, the sensors measure more of the corrosion reaction than actually occurs). In the former case, the electrochemical sensors “see” only a part of the corrosion process. In the latter case, the electrochemical sensors apparently measure other electrochemical reactions. Some of these data are shown in Table 2 along with a comparison of the mass loss (ML) to the electrochemical corrosion rates based on LPR and EN.

Probe Sensitivity

Tables 3-5 show the response of the electrochemical corrosion rate probes based on LPR measurements. In general, the data show that LPR measurements are sensitive to changes in alloy composition, ash composition, and temperature and water vapor content of the environment, despite the fact that the measurements are not quantitative. Table 3 shows that for carbon steel and 316 SS in the same environment, higher temperatures result in higher corrosion rates. Secondly, at the same temperature, the corrosion rate is higher for carbon steel.

Table 3
Effect of alloy and temperature on Real-Time Corrosion Monitoring corrosion rate measurements

Alloy	Temp, °C	ECR, mm/y
Carbon Steel	450	0.89
Carbon Steel	500	2.74
316 SS	500	0.28
316 SS	600	3.73

Table 4 shows that the waste ash causes higher corrosion rates than the coal ash. As seen in Table 1, the waste ash has a higher concentration of elements, such as chlorine, lead, sodium, and potassium, elements that are known to accelerate corrosion. Also, the addition of iron sulfide, as shown in Table 4, increased the corrosion rate in the coal ash. Table 5 shows that increased water vapor content in the environment leads also to higher corrosion rates. It has also been reported¹¹ that these measurements are sensitive to changes in gas phase composition, such as O₂ and CO₂ content.

Table 4
Effect of ash type on Real-Time Corrosion Monitoring corrosion rate measurements

Alloy	Ash	ECR, mm/y
316 SS	Waste	0.28
316 SS	Coal	0.005
316 SS	Coal + FeS	1.44

Field Use of Corrosion Rate Probe

The probe sensitivity measurements reported above suggest that, at the very least, electrochemical corrosion rate probes can be used as qualitative indicators of the corrosivity of the environment (a function of ash, gas, and alloy composition). Research indicates that the corrosion rate probe can be successfully used in energy conversion power plants, if information about the corrosivity of the operating environment is desired. However, the probe will give indications of levels of corrosion that may not equal the actual corrosion rate. If corrosion rate measurements are made in a WTE facility, they could be multiplied by 7 (the approximate average of the ML/LPR values for waste ash in Table 2), which should give a fair approximation of the corrosion rate. The probe will also indicate changes (increases and decreases) in corrosion rate that plant operators may choose to try to link to changes or upsets in the energy conversion process.

Table 5
Effect of water content on Real-Time Corrosion Monitoring corrosion rate measurements

Alloy	% H ₂ O	ECR, mm/y
304 SS	0	0.563
304 SS	14	1.1

On this basis, a six-month field test in a commercial WTE boiler has been scheduled to begin during October 2006. This test will include four probes at distinctly different positions in the WTE power plant boiler. The data to be collected will include corrosion rates from LPR, HDA, and EN measurements, localized corrosion factors, Stern-Geary factors, and temperature. Attempts will be made to adjust the probe temperature to that of the waterwall tubes using an air-cooling technique. Ultrasonic transducer (UT) measurements will be made in the areas of the probes both before and after the field trial to provide a secondary measurement of corrosion, and for comparison to the ECR probe corrosion rates.

Questions that Need to Be Answered

Because the nature of the current probe system appears to be qualitative to semi-quantitative, and because the ML/LPR ratio is as varied as shown in Table 2, there is a need to find a means to make the probe act more quantitatively if it is to develop wide-spread industrial acceptance. To do that, it is important that the complexity of the system be better understood. The corrosion system involves at least three solid phases (the metal, the corrosion product, and the ash) and a multi-component mixed gas phase. As a further complication, the ash is heterogeneous, consisting not only of many chemical compounds, but multiple physical forms of these compounds (powder, rock, slag). Also these compounds can react with each other, with different

components of the alloy, and/or with different components of the gaseous phase to form other compounds, some of which could have melting points below the process temperature. In addition, all of these components can behave differently, depending on ash and gas composition, both of which can vary from location to location within the same power plant, and from plant to plant.

Listed below are several thoughts or questions that, if explored, may provide a path toward more quantitative operation of the ECR probe:

1. How does the ash contribute to the electrochemical corrosion reactions? Do low melting eutectic mixtures form and cause molten salt chemical attack?
2. Does corrosion in the presence of ash occur in the same manner as in high temperature oxidation?
3. How important is a physically stable probe in making accurate corrosion rate measurements?
4. Is there significant intergranular corrosion (IGC) that can account for the higher ML corrosion rate?
5. Are the electrochemical corrosion reactions limited by the cathodic reaction, as occurs frequently in aqueous environments?
6. What role does the ash resistivity play in the electrochemical measurements?
7. Can unburned carbon in the ash short-circuit the electrochemical measurements?

Insight into Question 2

Past research¹¹ has verified that there is an electrochemical nature to the corrosion reaction on stainless steel in ash-covered high temperature gaseous environments.

Often the electrochemical nature of these high temperature reactions is ignored, because the reaction rate is controlled by diffusion and not electrochemistry. It has also been verified that measurements made using standard laboratory potentiostats produce the same values of corrosion rate as produced by the SmartCET® Realtime Corrosion Monitoring System.

Keeping in mind from Table 2 that these same electrochemical techniques measure only a small part of the actual corrosion reaction, begs the question of WHY? What part of the corrosion reaction is not being measured? As discussed below, it may not be a question of which reactions occur, but rather where these reactions occur.

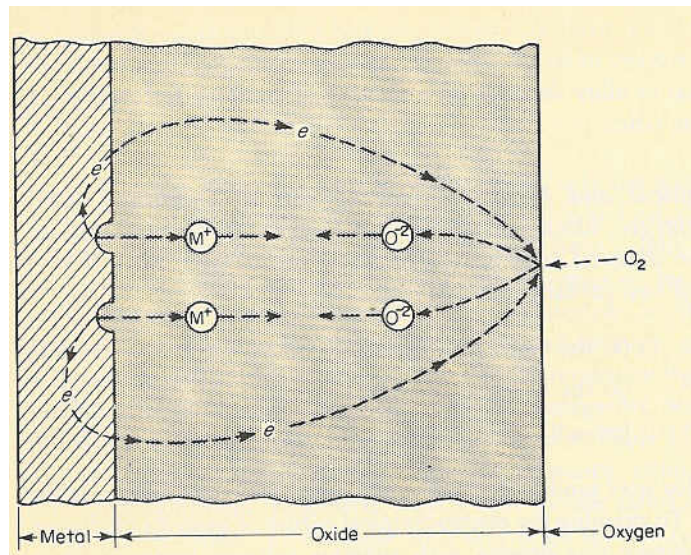


Figure 3 – Schematic illustration of electrochemical processes occurring during gaseous oxidation¹²

Figure 3 is a schematic¹² of the electrochemical processes that occur in the high temperature oxidation of a metal. Note that even though metal ions are generated at the metal-oxide interface, and electrons travel through the metal, the cathodic reaction does not occur at the metal surface, as happens in lower temperature gaseous and aqueous corrosion. The reduction of oxygen occurs at the oxide-oxygen interface, partly because of the enhanced electron conductivity of the oxide at high temperatures.

For ash-covered metals, the ash is on the outer surface of the oxide and it is likely that this reduction reaction may occur at the ash-oxygen interface. The problem this presents for the electrochemical measurement of corrosion rate is considerable, because the probe's sensors are at the physical level of the metal in Figure 3, and not at the oxide- or ash-oxygen interface where the cathodic reaction is occurring. It may be that the electrochemical probe will measure a corrosion reaction based only on whatever part of the oxygen is able to diffuse to the metal (sensor) surface. It is known that scales on Fe, Ni, Cu, Cr, Co, and others do grow principally at the scale-gas interface¹². It has also been suggested¹² that some of the oxide in the middle of the scale dissociates, sending cations outward and oxygen molecules inward (towards the sensors). If this occurs, it could account for the observation that a smaller part of the corrosion reaction is detected by the electrochemical corrosion rate probe, especially in the WTE environment.

SUMMARY AND CONCLUSIONS

- Electrochemical corrosion rate probes have been shown to be sensitive to changes in the alloy (composition) and in the environment (temperature, gas phase composition, and ash composition).
- Standard electrochemical techniques have measured electrochemical polarization diagrams that are typical of actively corroding metals.
- Electrochemical corrosion rate probes appear at this time to be either qualitative or semi-quantitative in nature. Electrochemical corrosion rate probes measure less of the corrosion reaction than measured by the mass loss technique.
- Corrosion in high temperature gaseous environments is different than at lower temperatures because of the increased electron conductivity of oxides at high temperatures. The reduction reaction generally occurs at the oxide-gas interface rather than at the metal surface where electrons are generated from the oxidation of metal atoms.
- Several questions were posed to help stimulate discussion/research to gain insight about electrochemical corrosion rate measurements in high temperature ash covered gaseous environments.

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