

CORROSION PROBES FOR FIRESIDE MONITORING IN COAL-FIRED BOILERS

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ABSTRACT

Electrochemical corrosion rate (ECR) probes were constructed and exposed along with mass loss coupons in a $N_2/O_2/CO_2/H_2O$ environment to determine ECR probe operating characteristics. Temperatures ranged from 450° to 600°C and both ECR probes and mass loss coupons were coated with ash. Results are presented in terms of the probe response to temperature, the measured zero baseline, and the quantitative nature of the probes. The effect of Stern-Geary constant and the choice of electrochemical technique used to measure the corrosion rate are also discussed. ECR probe corrosion rates were a function of time, temperature, and process environment and were found to be quantitative for some test conditions. Measured Stern-Geary constants averaged 0.0141 V/decade and the linear polarization technique was found to be more quantitative than the electrochemical noise technique.

INTRODUCTION

Increasing the efficiency of the Rankine cycle in coal combustors can be accomplished by increasing heat exchanger steam temperatures and pressures, as is done in supercritical and ultra supercritical units. The benefits of increasing energy conversion efficiencies are reduced consumption of fossil fuels (coal, oil, and gas) and reduced emission of greenhouse gases (CO_2). In order to achieve both of these benefits, it is necessary to overcome technological challenges related to materials of construction. New materials or material/coating combinations with adequate strength, creep, fatigue, and corrosion resistance will need to be developed. Additional issues are present when alternate fuels are used. While heat exchanger tubes in a coal-fired plants using clean high quality fuel may last 20 to 30 years, tubes in coal-fired plants using lower quality fuel and in some coal gasification plants last only 3 to 5 years.

Problems occur when equipment designed for either oxidizing or reducing conditions is exposed to alternating oxidizing and reducing conditions. The use of low NO_x burners is becoming more commonplace and can produce reducing environments that accelerate corrosion. Complicating the development of corrosion-resistant materials for fireside applications is the influence of ash deposits and thermal gradients on the corrosion mechanism. Ash deposits and thermal gradients have a synergism that greatly increases the corrosive attack on heat exchanging equipment such as waterwalls, reheaters, and

superheaters. One method of addressing corrosion of these heat exchange surfaces is the use of corrosion sensors to monitor when process changes cause corrosive conditions. In such a case, corrosion rate could become a process control variable that directs the operation of a coal combustion or coal gasification system. Alternatively, corrosion sensors could be used to provide an indication of total metal damage and thus a tool to schedule planned maintenance outages.

A number of research efforts have been aimed at developing high temperature corrosion probes for various industries. The majority of the research has been based on the use of electrochemical noise (EN)¹⁻⁶ techniques. Others have considered the use of electrochemical impedance spectroscopy (EIS)³⁻⁵ and linear polarization resistance (LPR)⁶, zero resistance ammetry (ZRA)⁴, and electrical resistance (ER)⁴. However, only a limited effort has been made to quantify² the operation of corrosion rate probes. For these probes to be accepted routinely in the power generation industries, it will be necessary to determine if they accurately measure corrosion and the changes in corrosion rate that occur in environments of interest, if the sensor materials have an optimum composition for the intended exposure, and if the sensitivity or accuracy of the sensor changes with exposure time in fireside environments. Once this is established, electrochemical corrosion rate sensors can be used extensively and will allow corrosion rate to become a process variable for power plant operators.

Most electrochemical corrosion rate measurement techniques measure a resistance that is representative of the rate of the corrosion reaction. This is true of the LPR, EN, and EIS techniques. These resistances are related to corrosion rate by the Stern-Geary linear approximation to the Butler-Volmer equation,

$$R_p = R_n = \frac{\Delta E}{\Delta i_{applied}} = \frac{\beta_a \beta_c}{2.303(i_{corr})(\beta_a + \beta_c)} = \frac{B}{(i_{corr})} \quad (1)$$

where R_p is a resistance obtained from the LPR and EIS techniques, R_n is a resistance obtained from the EN technique, B is the Stern-Geary constant, β_a and β_c are the anodic and cathodic Tafel constants, respectively, and i_{corr} is the corrosion current density from which a corrosion rate may be calculated. The Stern-Geary constant (determined by the Tafel constants) is the only variable that is normally not measured, but commonly assumed to be a value of 0.020 to 0.030 V/decade. Because B is related to Tafel constants, it can be measured using either standard electrochemical polarization techniques or the harmonic distortion analysis (HDA) technique that is used in this report.

The purpose of the research presented here is to address some of the issues that impact the understanding and the use of ECR probes. This report is part of an effort to characterize the long-term stability and performance of probes, and to optimize the choice of sensor materials.

EXPERIMENTAL DETAILS

Electrochemical corrosion rate (ECR) probes were designed and constructed for laboratory experiments using 4130 carbon steel (CS), 304L stainless steel (SS), and 316L SS sensors or electrodes. The probes were covered with ash and exposed, along with mass loss coupons made from the same material, to a mixed gas environment and temperatures that ranged from 450 to 600°C. The purpose was to determine the operating characteristics of probes and to compare integrated or average corrosion rates obtained from ECR probes to those obtained from mass loss coupons.

Three-sensor electrochemical corrosion rate probes were fabricated using the components shown in Figure 1. The cylindrical piece of ceramic served as the form to contain the sensors. The stainless steel tubing served to isolate the wires from the test environment and provided a path for the wires to exit the high temperature environment. Sensors were embedded within the ceramic form using a water-based high-alumina cement. Final preparation included hand polishing the sensors to a 600 grit finish. The finished probe is shown in Figure 1.

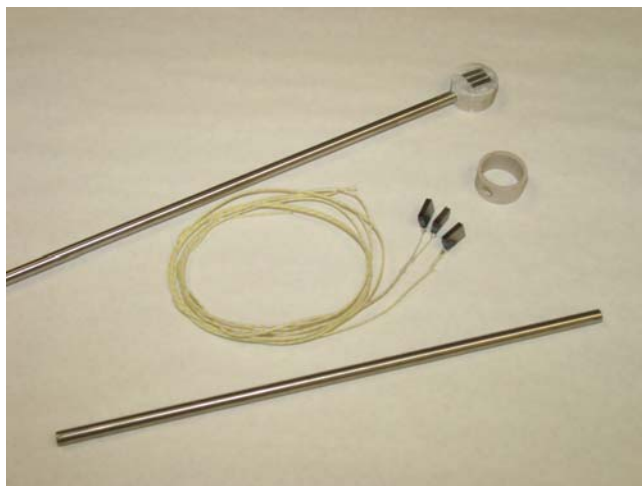


Figure 1 – A completed high temperature corrosion rate probe and the components of construction.

Experiments were conducted using an ash coating and a mixed gas environment identical to those reported previously⁷. The ash was obtained from a municipal incinerator and analyses showed high concentrations of corrosion-causing elements such as S, Cl, Pb, and K. The gas mixture consisted of 68 vol% N₂, 15 vol% H₂O, 9 vol% O₂, and 8 vol% CO₂. Temperatures ranged from 450 to 600°C. Typical test periods were 100 to 120 hours.



Figure 2 – Electrochemical corrosion rate probe and mass loss coupons prior to testing but after the application of a layer of ash. One coupon (far right) intentionally ash free.

Tests designed to determine the quantitative nature of ECR probes involved exposing four mass loss coupons and the probe to the corrosive environment. Three of the four mass loss coupons were coated with ash on one side while one was left ash free. A slurry of the ash was applied to each of the ash-covered coupons and to the probe. Water was originally used to make the ash slurry; however, methanol was used for later tests. Two of the ash-covered coupons were used to determine the mass loss corrosion rate for comparison to the ECR probe corrosion rate. The third ash-covered coupon was cross-sectioned for analyses to provide mechanistic information. Figure 2 shows the ash-covered probe and ash-covered and ash-free mass loss coupons.

Following exposure to the corrosive environment, ash was scraped from the surface of the mass loss coupons in preparation for chemical cleaning. 4130 CS mass loss coupons were cleaned at 60°C in a 12 vol% H₂SO₄ plus 0.25 vol% Rodine 95 (inhibitor) solution; the 304L and 316L SS mass loss coupons were cleaned at 25°C in a 10 vol% HNO₃ solution containing 2 vol% HF.

The corrosion measurement equipment used for this research was the SmartCET system. This system

applies three techniques, EN, LPR, and HDA, to the measurement of corrosion. The application of the three techniques and the appropriate data analysis produces a set of corrosion measurements approximately every 7 minutes. Data, which include EN, LPR, and HDA corrosion rates, an EN pitting factor, and Tafel and Stern-Geary constants from the HDA technique, are collected, displayed, and stored using FieldCET software. A number of other variables, such as solution resistance, skew, and kurtosis, are collected and available for use. The ECR probe corrosion rates were determined by integrating the corrosion rates measured every 7 minutes to calculate the mass loss which was then divided by exposure time and converted to units of a penetration rate of mm/y.

RESULTS AND DISCUSSION

The major emphasis of the research presented here is to evaluate the quantitative nature of ECR probes. In doing so, it became apparent that there were a number of variables that could affect that evaluation. Some of the variables that were considered, electrolyte, zero baseline, electrochemical technique, and Stern-Geary factor, are discussed below.

ECR PROBE RESPONSE AND ELECTROLYTE

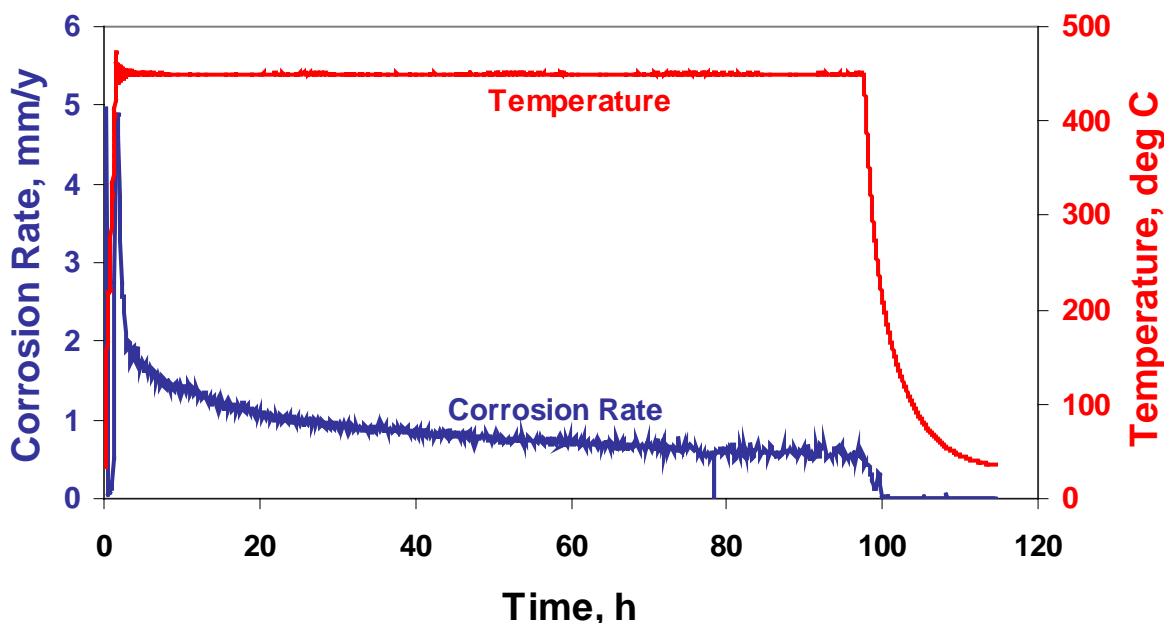


Figure 3 – Typical response of corrosion rate to time and temperature

Because an ECR probe is electrochemical in nature, all parts of an electrochemical cell must be present in order for the technique to work. For the probes used here, that includes the working, counter, and reference electrodes shown in Figure 1, and also an electrolyte that electrically connects the three electrodes. Other investigators⁸ have applied salt films to act as the initial electrolyte. In the research presented here, it is the ash layer and then possibly the ash plus corrosion film layers that act as the electrolyte as the corrosion reaction progresses. Figure 3 shows the response of an ECR probe with mild steel sensors to time and temperature. This was the type of behavior that was observed for most of the

experiments conducted here. This type of response suggests that an electrolyte was present because electrochemical techniques were able to measure corrosion rates and changes in corrosion rates. Except for the initial start up time, ECR probe corrosion rates decreased with time to the end of the 100-hour exposure period, Figure 3. This decrease in corrosion rate is the type of response that is typical of materials that form semi-protective corrosion films where the corrosion reaction may be dependant on diffusion of reactants or corrosion products.

ZERO BASELINE

An important property of ECR probes is to have a relatively low baseline corrosion rate when there is no corrosion occurring or when there is no electrolyte present. In order to measure the

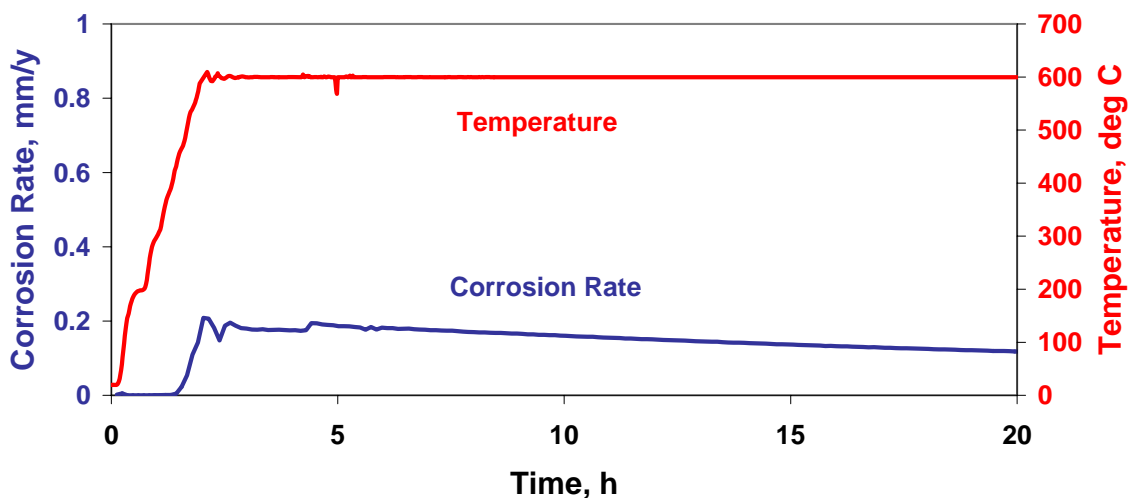


Figure 4 – Zero baseline measured on a 316L SS ECR probe with no ash

zero baseline response, a test was run in which a 316L SS ECR probe was inserted in a nitrogen-filled furnace without any ash or salt film to act as electrolyte. Ideally, the corrosion rates should be zero because there is no electrolyte and no gaseous species to cause corrosion. This was not, however, the case. Figure 4 shows the results of a zero baseline test in which the corrosion rates were not zero. Corrosion rates were zero during part of the heat-up phase of the experiment but started increasing as the temperature exceeded 430°C and then increased to an average value of 0.16 mm/y as the test environment was changed, at the time that the temperature reached 600°C, from nitrogen to the N₂/CO₂/O₂/H₂O mixture.

There are two possible reasons for these non-zero corrosion rates. The first would be the formation of some type of film, such as a corrosion product, that covered and electrically connected the three sensor electrodes. For the results presented here, this does not seem likely because there was no visible corrosion product on the ECR probe surface after removing it from the test. A second and more likely possibility is that, at the test temperature, the potting compound surrounding the sensor electrodes was sufficiently electrically conductive to act as the electrolyte for the electrochemical measurement of corrosion rate. Additional zero baseline tests are planned using more resistive potting compounds.

QUANTITATIVE NATURE OF ECR PROBES

Experiments were conducted to compare ECR probe corrosion rates with actual mass loss corrosion rates for coupons and probes exposed in exactly the same environment. Mass loss coupons were cleaned of all ash and scale and corrosion rates were calculated. Data similar to that in Figure 3, for all of the alloys tested, was integrated to determine a cumulative mass loss. This was then used to calculate a corrosion rate for the ECR probe. The corrosion rates in Figure 4 show a good comparison between the ECR and the mass loss corrosion rates for all of the alloys except for the mild steel. Some possible explanations are differences between the ECR probe and the mass loss coupons, corrosion attack that is

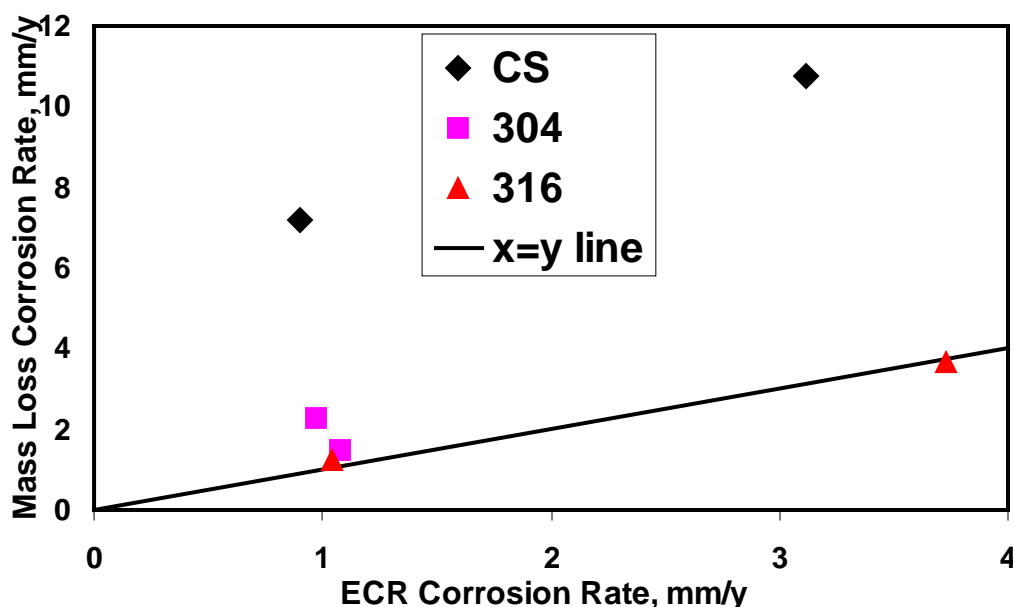


Figure 5 – Comparison of ECR probe to mass loss corrosion rates

non-electrochemical in nature (eg, internal corrosion that can remove whole grains from the matrix without reacting the material) among others. Studies⁸ conducted using different conditions (probe construction, coating, and gaseous environment) but with the same SmartCET equipment had good agreement between ECR probe and mass loss corrosion rates. Research is being conducted to determine the reasons for such differences. One change being considered is the use of a profilometer to measure the actual material lost from the ECR probe electrodes rather than relying on mass loss coupons.

EFFECT OF ELECTROCHEMICAL TECHNIQUE

There are a number of electrochemical techniques that can be used to measure the corrosion rates of ECR probes. All of the currently significant techniques were mentioned earlier in this report. Of those, data from the LPR technique was compared to data from the EN technique because the current research equipment generates both types of data. This comparison is shown in Figure 6 for all of the materials and test conditions used in this research. EN corrosion rates were consistently lower than LPR corrosion rates by an average factor of 6-7. Thus if EN corrosion rates were plotted instead of LPR corrosion rates in

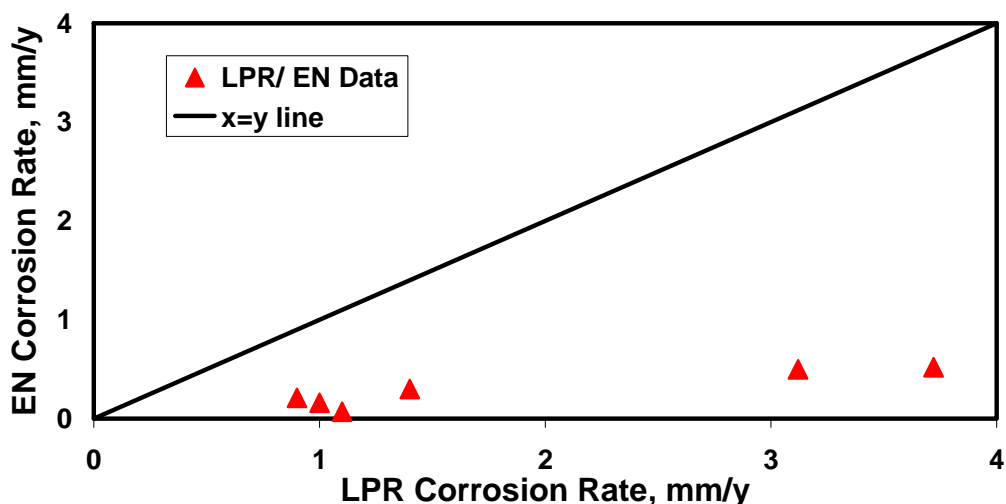


Figure 6 – Comparison of electrochemical noise to linear polarization corrosion rates.

Figure 5, the comparison to mass loss corrosion rates would have been worse. For the equipment used here, it is concluded that LPR corrosion rates better represent the actual corrosion reaction. Other researchers² have used EN probe data and profilometry to measure the corrosion penetration rate of their probe surfaces in an effort to quantify their electrochemical corrosion rates. Still others⁴ have used EIS data for the probe measurement and the SEM to measure the metal lost from the actual probe. Both of these research groups generated mass loss and electrochemical probe corrosion rates that differed by only about 50%.

EFFECT OF CHOICE OF STERN GEARY CONSTANT

The choice of the Stern-Geary (B) constant may be the most powerful factor affecting reported electrochemical corrosion rates. As can be seen in equation 1, corrosion rate is directly proportional to B. Within reason, a B value could be chosen to make the ECR probe corrosion rates coincide with mass loss corrosion rates. This was not done in this report; rather the B values measured using the HDA technique were used to calculate the corrosion rates. Other studies^{1,2} of ECR probes did not report the method used to calculate corrosion rates or the value of B used

The Stern-Geary constants measured for all of the experiments ranged from 0.0117 to 0.0182 V/decade with an average value of 0.0141V/decade. This average is significantly lower than the normally assumed values of 0.020 to 0.030 V/decade. The actual values, and not the average value, were used to calculate the LPR and EN corrosion rates that are shown in Figures 5 and 6. One use for this measured value of B is to allow a more accurate calculation of corrosion rate when using equation (1). The Stern-Geary constant and the Tafel constants that are used to calculate B can also be coupled with other information, such as scale analyses and electrochemical data from other techniques, to help explain corrosion mechanisms.

SUMMARY

Results presented here show that validation of ECR probes for use in high temperature fossil energy applications requires an understanding of: probe construction and how that affects the zero baseline response, the correlation between mass loss and ECR probe corrosion rates, the measurement and use of the most representative value of the Stern-Geary constant, and the choice of the most appropriate electrochemical technique to use with the ECR probes.

CONCLUSIONS

- LPR-based ECR probes are able to measure corrosion rates that are sensitive to temperature and process changes.
- The HDA technique is able to measure a unique value of the Stern-Geary constant that averaged 0.0141 V/decade in the high temperature corrosion environments considered here.
- Both 304L and 316L SS produced ECR probe corrosion rates that were similar to their mass loss corrosion rates.
- There were relatively large differences between the mass loss and ECR probe corrosion rates for the 4130 CS coupons and probes.
- A relatively low but steady baseline corrosion rate was measured when no electrolyte was present. Conductivity in the potting compound is suspected.
- For the hardware/software combination used here, LPR corrosion rates appeared to measure more accurate (compared to mass loss corrosion rates) corrosion rates than the EN technique.

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