Electrochemical Corrosion Rate Probes for High Temperature Energy Applications

Bernard S. Covino, Jr., Sophie J. Bullard, Stephen D. Cramer, Gordon R. Holcomb, Margaret Ziomek-Moroz
Albany Research Center, U. S. Dept of Energy, 1450 Queen Ave, S. W., Albany, OR 97321

Michael S. Cayard and David A. Eden
InterCorr International Inc., 14503 Bammel North Houston, Suite 300, Houston, TX 77014

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 450º to 800ºC 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 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.

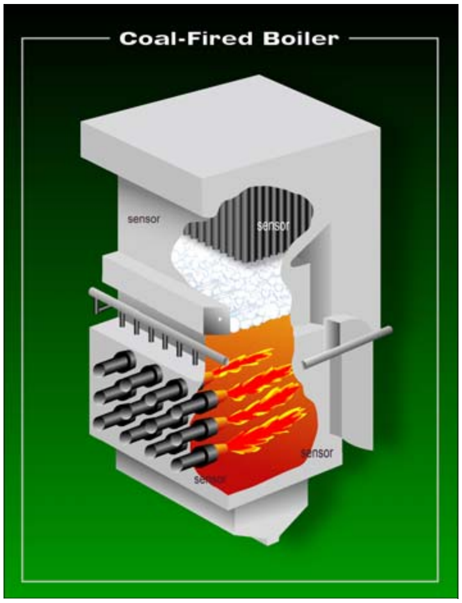

Figure 1- Possible locations for corrosion sensors in boilers.

Problems occur when equipment designed for either oxidizing or reducing conditions is exposed to alternating oxidizing and reducing conditions. This can happen especially near the burners pictured in Figure 1. 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, as pictured in Figure 1, 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 quantify[2] 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,

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

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 a mild carbon steel (CS), 304L stainless steel (SS), and 316L SS sensors or electrodes, Table 1.

Table 1 – Compositions of alloys used to make ECR probes.

Alloy	Concentration, wt %						
	Fe	Cr	Ni	Mo	Cu	Si	Mn
Mild Steel	97.8	0.13	0.14	0.024	0.35	0.22	0.82
304L SS	69.5	18.43	9.7	0.14	0.21	0.53	1.2
316L SS	67.8	16.84	11.1	2.1	0.12	0.47	1.3

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 800ºC. 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.

Figure 2 – A completed high temperature corrosion rate probe and the components of construction.

Three-sensor electrochemical corrosion rate probes were fabricated using the components shown in Figure 2. 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 first using an alumina cement and later using Ceramcast 586, a zirconia/magnesia potting compound. After curing at room temperature for 12 to 18 hours, the ECR probe was cured at 93ºC for 4 hours and then at 121ºC for 3 hours. Final preparation included hand polishing the sensors to a 9 µm finish. The finished probe is shown in Figure 2.

Experiments were conducted using an ash coating and a mixed gas environment identical to those reported previously[7]. 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% N_2, 15 vol% H_2O, 9 vol% O_2, and 8 vol% CO_2. Temperatures ranged from 450 to 600ºC. Uncoated probes were tested to 800ºC. Typical test periods were 100 to 180 hours.

Figure 3 – 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 3 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. The CS mass loss coupons were cleaned at 60ºC in a 12 vol% H_2SO_4 plus 0.25 vol% Rodine 95 (inhibitor) solution; the 304L and 316L SS mass loss coupons were cleaned at 25ºC in a 10 vol% HNO_3 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

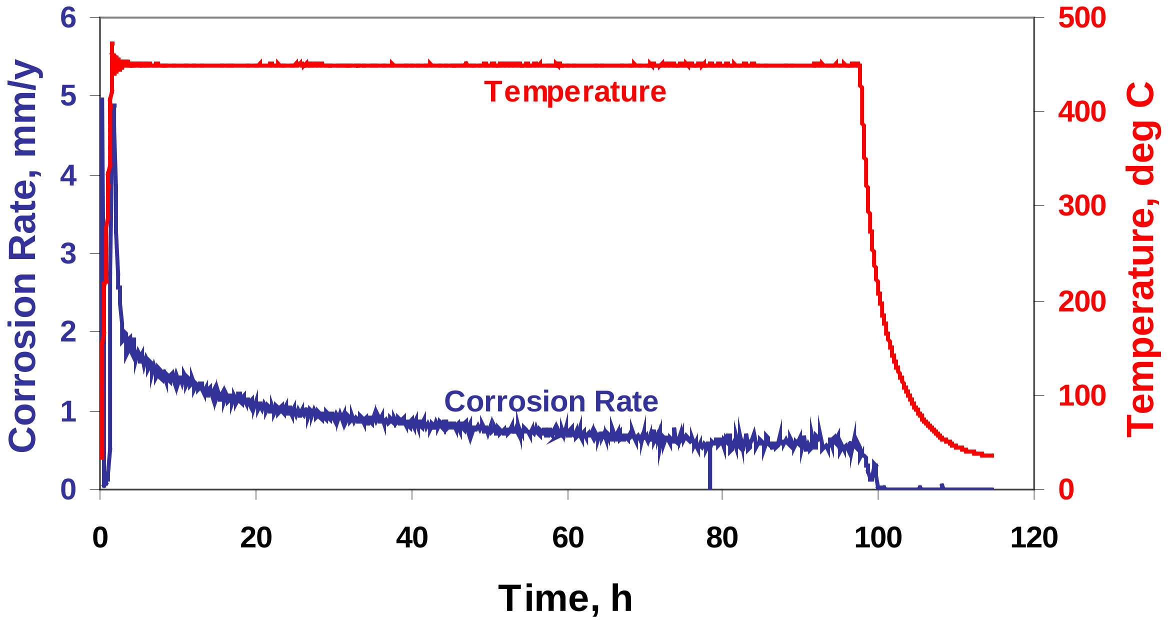

Figure 4 – Typical response of corrosion rate to time and temperature

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 2, and also an electrolyte that electrically connects the three electrodes. Other investigators[8] 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 4 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. 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 plus 100-hour exposure period, Figure 4. 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.

ECR PROBES -- 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 zero baseline response, a test was run in which an 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 5 shows the results of a zero baseline test in which the temperature was raised stepwise from 500 to 800ºC. The corrosion rate was zero during part of the heat-up phase of the experiment but started increasing as the temperature exceeded 400ºC and then increased to an average value of 0.9 mm/y (36 mpy). After approximately 20 hours at 500ºC the corrosion rate decreased to near zero and stayed there as the temperature was stepped from 500 to 800ºC.

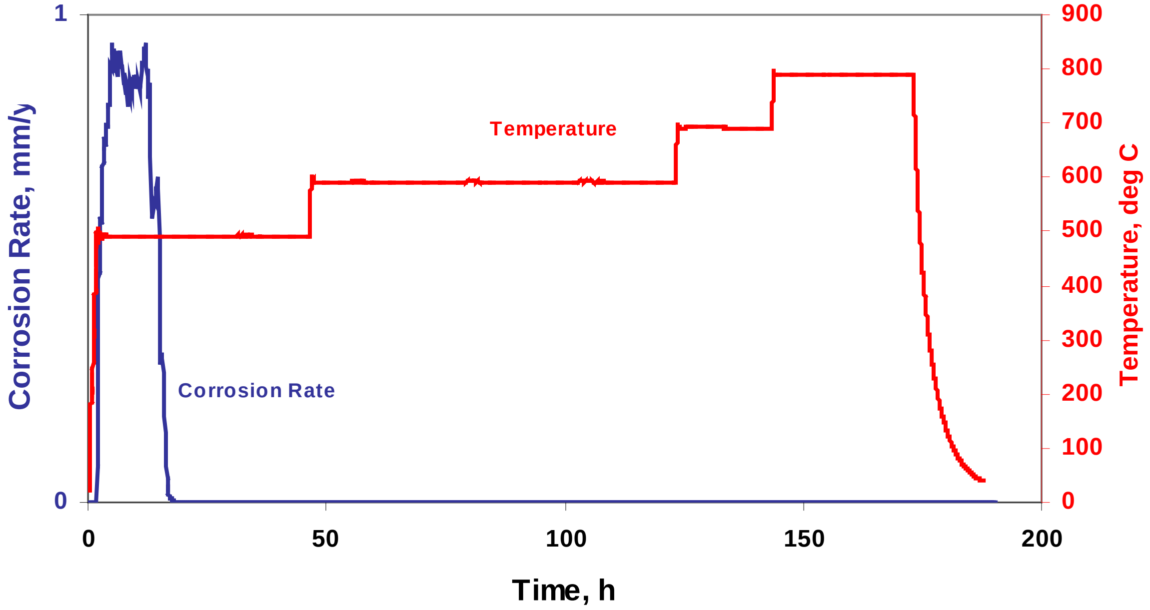

Figure 5 – Zero baseline measured on a 316L SS ECR probe with no ash

There are two possible reasons for these non-zero corrosion rates. The first is the formation of 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 ceramic potting compound surrounding the sensor electrodes was sufficiently electrically conductive to act as the electrolyte for the electrochemical measurement of corrosion rate. Additionally, the species responsible for the corrosion rate peak either dissipated or became depleted over the approximately 20 hour exposure at 500ºC. This suggests than an additional curing step should be added to the ECR fabrication process.

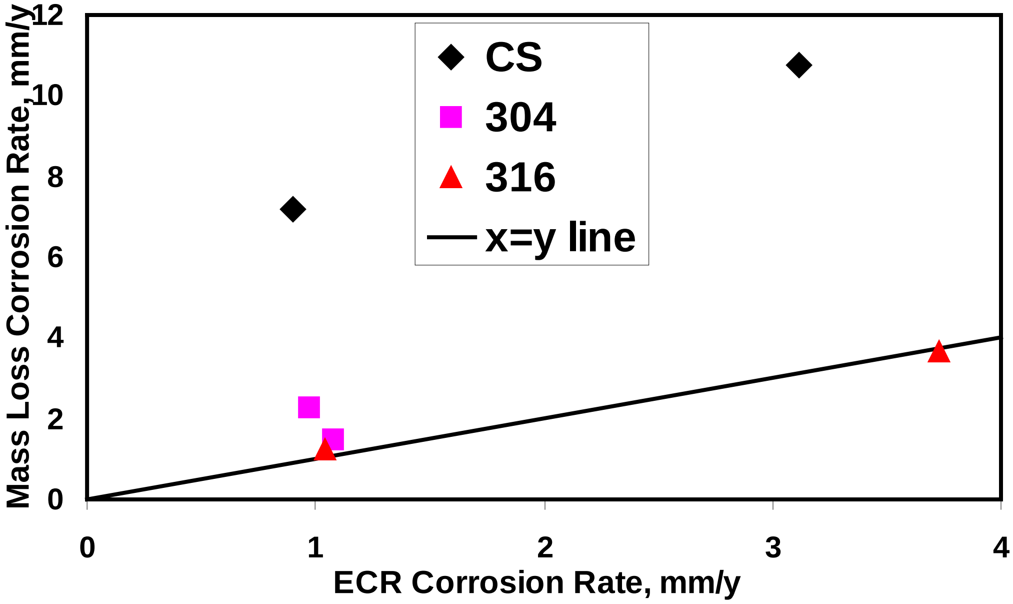

Figure 6 – Comparison of ECR probe to mass loss corrosion rates

ECR PROBES -- QUANTITATIVE NATURE

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 4, 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 6 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 non-electrochemical in nature (eg, internal corrosion that can remove whole grains from the matrix without reacting the material) among others. Studies[8] 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.

ECR PROBES -- 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 and makes the comparison possible. The comparison is shown in Figure 7 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, 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 researchers[2] 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 others[4] 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%.

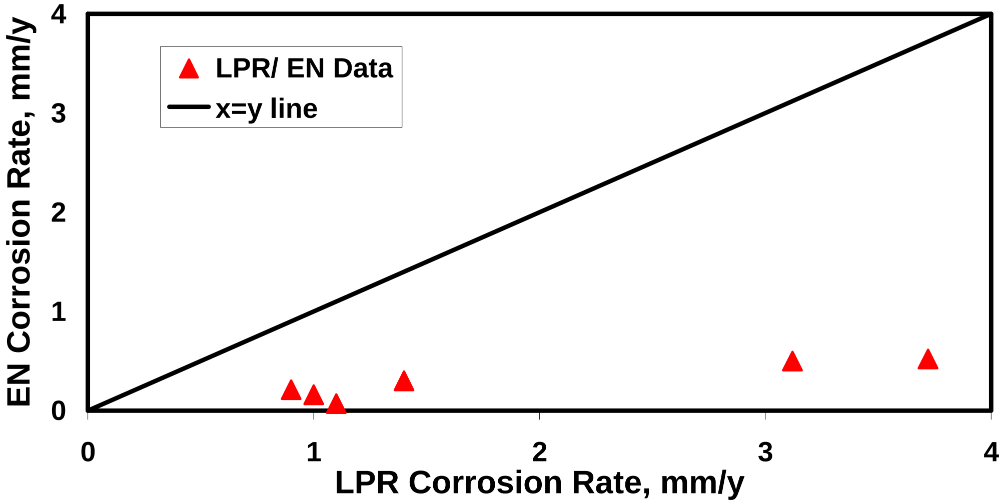

Figure 7 – Comparison of electrochemical noise to linear polarization corrosion rates.

ECR PROBES -- STERN GEARY CONSTANT

The choice of the Stern-Geary (B) constant may be the most important factor affecting reported electrochemical corrosion rates. As can be seen in equation 1, corrosion rate (i_{corr}) is directly proportional to B. Within reason, a B value could be chosen to make the ECR probe corrosion rates coincide with

Table 2 – Stern-Geary constants measured by the HDA technique.

Alloy	Stern Geary Constant (B), V/decade		
	450ºC	500ºC	600ºC
4130 CS	0.0117	0.0130	–
304L SS	–	0.0156	0.0182
316L SS	–	0.0130	0.0130

– = not measured

mass loss corrosion rates. For the data reported here, 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

Table 2 shows that the Stern-Geary constants measured for all of the experiments ranged from 0.0117 to 0.0182 V/decade. The average value of B was 0.0141V/decade. This average is approximately 50% of 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 6 and 7. 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. B averaged 0.0141 V/decade in the high temperature corrosion environments reported 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 CS coupons and probes.
- A stable zero baseline (near 0 mm/y) was achieved for ECR probes fabricated using a zirconia/magnesia potting compound and an additional curing step at 500ºC for 20 hours.
- Based on using the hardware/software combination reported here, LPR corrosion rates appeared to measure more accurate (compared to mass loss corrosion rates) corrosion rates than the EN technique.

REFERENCES

1. T.M. Linjeville, K.A. Davis, G.C. Green, W.M. Cox, R.N. Carr, N.S. Harding, and D. Overacker, “On-Line Technique for Corrosion Characterization in Utility Boilers, Proceedings of Power Production in the 21st Century: Impacts of Fuel Quality and Operations,” United Engineering Foundation, Snowbird, UT, October 28-November 2, 2001.
2. T.M. Linjeville, J. Valentine, K.A. Davis, N.S. Harding, and W.M. Cox, “Prediction and Real-time Monitoring techniques for Corrosion Characterization in Furnaces,” Materials at High Temperatures, Vol. 20, No. 2, pp. 175-184, 2003.
3. D.M. Farrell, W.Y. Mok, and L.W. Pinder, “On-line Monitoring of Furnace-Wall Corrosion in a 125 MW Power Generation Boiler,” Materials Science and Engineering, Vol. A121, pp. 651-659, 1989.
4. D. M. Farrell, “On-line Monitoring of Fireside Corrosion in Power Plant,” 12th International Corrosion Congress, Vol. 12, pp. 4131-4140, 1993.

5. G. Gao, F.H. Stott, J.L. Dawson, and D.M. Farrell, “Electrochemical Monitoring of High-Temperature Molten Salt Corrosion,” Oxidation of Metals, Vol. 33, Nos. 1/2, pp. 79-94, 1990.
6. G.J. Bignold and G.P. Quirk, “Electrochemical Noise Measurements in a 500 MW Steam Turbine to Maximize Lifetime Under Changing Operational Demands,” Paper no, 02333, CORROSION/2002, NACE International, Houston, TX, 20 pp, 2002.
7. B. S. Covino, Jr., J. H. Russell, S. D. Cramer, G. R. Holcomb, S. J. Bullard, M. Ziomek-Moroz, S. A. Matthes, and M. L. White, “The Role of Ash Deposits in the High Temperature Corrosion of Boiler Tubes,” Paper no.03718, CORROSION/2003, NACE International, Houston TX, 12 pp., 2003.
8. D. A. Eden and B. Breene, “On-Line Electrochemical Corrosion Monitoring in Fireside Applications,” Paper No. 03361, CORROSION/2003, NACE International, Houston, TX, 10 pp., 2003.