APPLICATION OF LINEAR POLARIZATION
TECHNIQUES TO THE MEASUREMENT OF CORROSION
RATES IN SIMULATED GEOTHERMAL BRINES

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SUMMARY

The linear polarization or polarization resistance (PR) technique was investigated in high- and low-salinity geothermal brines at 150 and 250°C on a low carbon steel (A53B) and a ferritic stainless steel (E-brite 26-1) with and without the presence of oxygen in the brine. There was good agreement between weight loss data and the results from linear polarization data. Oxygen generally accelerated the corrosion rate, and in the presence of oxygen the usual form of the PR equation must be replaced by the mass transfer equation to predict corrosion rates correctly. Results of the study were compared with the corrosion rate output of commercial PR instrumentation, and it was concluded that this instrumentation is adequate for field investigations in which oxygen is absent. However, when oxygen is present, commercial instruments may underestimate actual corrosion rates considerably.

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INTRODUCTION

Geothermal brines contain significant quantities of dissolved solids in a reduced state that can be very corrosive to operating equipment. Significant amounts of dissolved chlorides, sulfides, silicates, carbon dioxide-carbonates, etc., as well as high liquid velocities and the presence of particulates can result in shortened equipment lives. Conditions controlled by the operator--such as oxygen entry, pH control by acid injection or CO₂ control, or addition of scale inhibitors--can also result in conditions leading to enhanced corrosion rates. A corrosion rate monitoring system is needed that responds to rapidly changing corrosion conditions and that can be easily installed by the plant operator.

In response to this need Pacific Northwest Laboratory (PNL)^(a) has conducted a study to determine whether commercial corrosion measuring equipment using the polarization resistance (PR) method can be easily adapted for use in geothermal environments.

Two notable reviews on the general subject of the PR technique have been published by Fontana and Staehle (1970) and Callow, Richardson, and Dawson (1976). The Callow paper includes a useful summary of PR data for many alloys (iron, aluminum, copper-nickel, etc.). In general, the PR technique is considered capable of predicting corrosion rates in the laboratory within a factor of two. In the field where the interplay of corrosion rate determining variables is more complex, the ability to predict actual corrosion rates may be poorer. The theoretical relationships for the PR technique are shown below:

$$I_{\text{corr}} = B \left(\frac{1}{R_p} \right) \quad (1)$$

(a) Operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute.

where

$$B = \frac{\beta_a \beta_c}{2.30(\beta_a + \beta_c)} \quad (2)$$

$$\frac{1}{R_p} = \frac{\Delta I}{\Delta E} \quad (3)$$

The corrosion current density (I_{corr}) is linearly related to the reciprocal of the polarization resistance (R_p). When the system is polarized a few millivolts (mV) from the corrosion potential ($\Delta E < 20$ mV), the measured current (ΔI) permits the calculation of R_p . The proportionality constant (B) is related to the anodic and cathodic Tafel slopes (β_a and β_c , respectively). Although the Tafel slopes vary widely, the B value is relatively constant and falls within the range of 10–45 and 18–41 mV for carbon steels and stainless steels, respectively (Callow, Richardson, and Dawson 1976). Commercial PR instrumentation is designed to make use of Equation (1) by polarizing the corroding specimen ± 10 or ± 20 mV, measuring the current, and directly displaying the corrosion rate in mils per year (mpy). Equation (1) applies only if:

- Mixed potential theory applies and the corrosion potential of the system is > 50 mV from the reversible potential of either the anodic or cathodic reaction.
- Both the anodic and cathodic reactions are activation controlled. These conditions are often found in the corroding environment; however, when the cathodic reaction is under mass transport control (such as when oxygen enters the system), Equation (1) no longer applies. The PR relationship under this condition is

$$I_{\text{corr}} = \left(\frac{\beta_a}{2.3} \right) \left(\frac{1}{R_p} \right) \quad (4)$$

One of the unresolved problems in using PR methods is to recognize when Equation (1) or (4) applies since there can be a large difference between B and B_a especially if the metal is partially passivated.

The problem of linearity of $(\partial I / \partial E)$ near E_{corr} has been extensively examined in the PR literature (Fontana and Staehle 1970) because I_{corr} is proportional to $(\partial I / \partial E)_{E_{\text{corr}}}$ only at the corrosion potential, and any nonlinearity of $I = f(E)$ could lead to an error in $(\partial I / \partial E)_{E_{\text{corr}}}$ obtained by extrapolation from ± 10 or ± 20 mV. Laboratory studies (Fontana and Staehle 1970) have revealed that $I = f(E)$ is often nonlinear; but the error is not significant when E_{corr} is greater than RT/F (R = gas constant; T = Kelvin temperature scale; and F = Faraday's constant) from both the equilibrium potential of the corrosion reaction and the reduction reaction. Conditions for a small error are usually encountered.

The only paper on the use of commercial PR instrumentation in geothermal brines was published by Harrar, McCright, and Goldberg (1977). Their experiment was conducted in Niland, California, with a brine of 20% solids content using Petrolite® three-electrode equipment. The brine was cooled to 100°C for all corrosion measurements, and acid injection was used to lower the pH. In one experiment the PR electrodes were used as weight loss coupons but were exposed for only 16–25 hours. Weight loss data for carbon steels and Cr–Mo steel did not correlate well with PR data (PR data for carbon steel was 100 and 250 mpy for pH 3.4 and 2.3, respectively) although the correlation was good for 400 series alloys.

This paper evaluates the use of the PR technique at 150 and 250°C in 3% and 20% brines with and without oxygen. The experimental procedure is explained, and the results of the evaluation are presented.

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CONCLUSIONS AND RECOMMENDATIONS

The agreement between weight loss corrosion rates and those calculated from the PR technique is quite good. Examination of the operation of commercial PR instruments indicates that they should perform well in geothermal brines at elevated temperature. However, when oxygen or some other depolarizer enters the system, commercial instrumentation may give erroneously low readings. When oxygen is known to be present, the commercial readings should be multiplied by at least a factor of five for steels.

EXPERIMENTAL PROCEDURE

All experiments were carried out in a refreshed 1-liter titanium autoclave—a similar setup was used by Posey and Palko (1979). Solutions were stored in a 55-gal polyethylene drum and injected into the autoclave at about 1 liter/h. Deoxygenated conditions were maintained by a CO₂ purge and a small amount of hydrazine. The oxygen partial pressure (typically 1 ppm in solution) was controlled by mixing air and CO₂ and sparging through the solution. Oxygen in solution was measured by the Winkler Method. Solution compositions are shown in Table 1.

The reference electrode shown in Figure 1 permits the potential to be placed on the high-temperature hydrogen scale. Further details are discussed elsewhere (Danielson 1979), but the electrode operates at autoclave pressure and ambient temperature. Consequently, the potential contains a contribution from a thermal liquid junction potential. The Soret effect is slow to develop; therefore, the potential is relatively constant with time, which permits the design to be referenced to the high-temperature hydrogen electrode (see Table 2). No attempt was made to correct the potential for the liquid junction potential.

Figure 2 shows the specimen electrode configuration. Cylinder electrode specimens were used so that the results would be compatible with those attained from the cylindrical weight loss specimens used in earlier experiments (Shannon 1977). Belleville spring washers were used to keep a constant pressure on the polytetrafluoroethylene (PTFE) seals to minimize crevice corrosion problems. The specimen electrode holder that is shown in Figure 3 is an improved design of Agrawal et al. (1975). It is constructed of corrosion-resistant zirconium and is covered with a heat-shrinkable PTFE to minimize stray corrosion currents. It was tested without the electrodes; a PTFE threaded bolt was inserted in the end, and it was heated to 150°C in the autoclave containing brine. The ac impedance between it and the autoclave was greater than 10⁶ ohms. An electrode specimen of ASTM-type A53B carbon steel (0.27% C, 0.71% P, and remainder Fe) and E-brite 26-1 stainless steel (26.2% Cr, 1.0% Mo, <0.001% C, and remainder Fe) of 6.7 cm² was included in each experiment. For deoxygenated experiments, there were five weight loss specimens of both A53B and

TABLE 1. Synthetic Brine Compositions

Low Salinity

No Oxygen	Oxygen
3% NaCl	3% NaCl
450-ppm SiO_2 (as SiO_3^{2-})	450-ppm SiO_2 (as SiO_3^{2-})
0.5-ppm S^{2-}	700-ppm SO_4^{2-}
Hydrazine (5 drops of 64%/200 liters)	CO_2 -Air Sparge
1-atm CO_2	pH = 5.7 at 25°C
pH = 5.7 at 25°C	

High Salinity

No Oxygen	Oxygen
20% NaCl	20% NaCl
450-ppm SiO_2 (as SiO_3^{2-})	450-ppm SiO_2 (as SiO_3^{2-})
0.5-ppm S^{2-}	700-ppm SO_4^{2-}
Hydrazine (5 drops of 64%/200 liters)	CO_2 -Air Sparge
1-atm CO_2	pH = 5.5 at 25°C
pH = 5.5 at 25°C	

E-brite. In oxygenated experiments two weight loss specimens of each were used to reduce the rate of oxygen consumption. Each experiment lasted 7-8 days in order for the corrosion rates to approach a steady state.

Electrochemical measurements were made with a potentiostat. Slow potential scan-current measurements (0.02 mV/s) up to +20 mV from E_{corr} were made each day and $(\partial I / \partial E)_{E_{\text{corr}}}$ was determined. After slow scan methods indicated a steady corrosion rate, voltage step-function measurements at ± 10 mV were made to simulate the operation of some commercial PR instruments. On the final day of the experiment, Tafel slopes were measured at the same slow scan rate (up to ± 100 mV from E_{corr}) followed by cyclic voltammetry (CV) scans at 10 mV/s at ± 1 V extremes from E_{corr} . The CV experiments always started in a cathodic direction.

FIGURE 1. Reference Electrode

TABLE 2. Quasi-Reference Electrode Potentials (0.100 m KCl) on the Standard Hydrogen Scale (SHE)

Temperature, °C	$E_{\text{Ag,AgCl}}_{25^\circ\text{C}}$	$-E_{\text{SHE}_T}^\circ, \text{V}$
25		0.287
90		0.227
125		0.188
150		0.159
200		0.097
250		0.026

FIGURE 2. Electrode Specimen

FIGURE 3. Electrode Holder Using Standard Pressure Connector

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EXPERIMENTAL RESULTS

Experiments were carried out at 150 and 250°C with and without oxygen. Only low-salinity brines were used at 150°C, but both high- and low-salinity brines were used at 250°C. The results of these tests are summarized in Table 3; the average $1/R$ value at $(\partial I/\partial E)_{E_{\text{corr}}}$ for each experiment is also shown. Typical corrosion rate data as a function of time, see Figure 4, start high and quickly approach a lower steady rate. Average values of $1/R$ are needed for comparison with weight loss data.

Tafel slopes were determined at the end of each experiment since the measurement would significantly perturb the system from the corrosion potential. The slopes were usually very large, in line with electrochemical processes taking place on passive or heavily filmed surfaces. The Tafel slopes were used to calculate a B value (shown in Table 4); an average corrosion rate could be calculated as shown in Table 3 by combining this B value with the average $1/R$. In general, corrosion rates determined by both methods were in good agreement.

To determine if commercial PR instrumentation will correctly measure corrosion rates, it is necessary to determine if $\Delta I/\Delta E$ values obtained by polarizing the electrode ± 10 mV will result in the same $1/R$ determined from $(\partial I/\partial E)_{E_{\text{corr}}}$. This comparison is shown in Table 5 where $1/R$ values are compared with $\Delta I/\Delta E$ values obtained at anodic and cathodic polarizations; agreement between the two is quite good. The $\Delta I/\Delta E$ values at $+10$ and -10 mV agree fairly well, indicating that the anodic and cathodic Tafel parameters must be similar. In general, the average value of $\Delta I/\Delta E$ at ± 10 mV underestimates the $1/R$ value, but the difference is usually less than 30%.

Table 6 shows the corrosion potentials of A53B and E-brite 26-1 on the standard hydrogen electrode (SHE) scale after the corrosion rate has reached a steady state. When oxygen is present, the slowly corroding E-brite is considerably anodic to the A53B. Corrosion film compositions are also predicted from high-temperature Pourbaix diagrams. Table 7 outlines the salient features from CV experiments.

TABLE 3. Corrosion Data

Experiment	A538			E-Brite 26-1			Notes
	Weight Loss, mg/dm ² -d (mpy)	Linear Polarization, mg/dm ² (mpy)	Average 1/R, μA/mV	Weight Loss, mg/dm ² (mpy)	Linear Polarization, mg/dm ² (mpy)	Average 1/R μA/mV	
1.0	26.3 ±1.1 (4.8 ± 0.2)	19.2 (3.5)	2.4	2.52 ± 0.11 (0.46 ± 0.02)	---	0.37	Low Salinity No O ₂ 150°C
1.1	138.6 (25.3)	---	2.1	15.3 (2.8)	---	0.90	Low Salinity 1-ppm O ₂ 150°C
1.2	12.11 ±0.11 (2.21 ± 0.02)	20.3 (3.7)	1.5	3.95 ± 0.27 (0.72 ± 0.05)	7.12 (1.3)	0.47	Low Salinity No O ₂ 250°C
1.3	221.9 ±18.1 (40.5 ± 3.3)	197 (36)(a)	4.6	3.23 ± 0.22 (0.59 ± 0.04)	5.48 (1.0)	0.41	Low Salinity 1-ppm O ₂ 250°C
1.4	40.8 ±2.6 (7.45 ± 0.47)	35.6 (6.5)	4.7	3.67 ± 0.27 (0.67 ± 0.05)	7.12 (1.3)	0.46	High Salinity No O ₂ 250°C
1.5	41.6 ±3.3 (7.6 ± 0.6)	15.9 (2.9)	4.7	1.92 ± 0.05 (0.35 ± 0.01)	2.69 (0.49)	0.14	High Salinity 1-ppm O ₂ 250°C

(a) Mass transport equation used for calculation.

FIGURE 4. Typical Polarization Resistance Data as a Function of Time for Experiment 1.0

TABLE 4. Tafel Data

Experiment	Anodic Tafel, mV		Cathodic Tafel, mV		B from Tafel Data, mV		B from Corrosion Data, mV		Notes
	A53B	E-Brite	A53B	E-Brite	A53B	E-Brite	A53B	E-Brite	
1.0	158	---	72	---	21.5	---	29	18	Low Salinity No O_2 150°C
1.1	---	---	---	---	---	---	177	46	Low Salinity 1-ppm O_2 150°C
1.2	378	234	108	152	36	40	22	22	Low Salinity No O_2 250°C
1.3	265	349	182	114	65	30	129	21	Low Salinity 1-ppm O_2 250°C
1.4	191	534	61	115	20	41	23	21	High Salinity No O_2 250°C
1.5	26	196	120	299	9	51	24	37	High Salinity 1-ppm O_2 250°C

TABLE 5. Polarization Resistance Data

Experiment	A53B			E-Brite 26-1		
	$(\partial I/\partial E)_{E_{\text{corr}}}$ $\mu\text{A/mV}$	$\Delta I/\Delta E, \mu\text{A/mV}$		$(\partial I/\partial E)_{E_{\text{corr}}}$ $\mu\text{A/mV}$	$\Delta I/\Delta E, \mu\text{A/mV}$	
		+10 mV	-10 mV		+10 mV	-10 mV
1.0	1.9	1.8	1.8	0.08	0.15	0.15
1.1	2.4	1.5	1.0	1.0	0.80	0.70
1.2	1.5	1.0	1.0	0.30	0.38	0.30
1.3	4.2	3.0	---	0.42	0.45	---
1.4	4.9	3.7	5.0	0.50	0.30	0.44
1.5	4.2	3.0	4.0	0.12	0.15	0.10

TABLE 6. Steady-State Corrosion Potentials On SHE

Experiment	A53B	E-Brite 26-1	Predicted Phases from Pourbaix Diagrams(a)		Notes
			A53B	E-Brite 26-1	
1.0	-0.522	-0.264	FeS	FeS, Cr ₂ O ₃	Low Salinity No O ₂ 150°C
1.1	-0.409	-0.106	Fe ₃ O ₄	Fe ₃ O ₄ , Fe ₂ O ₃ , Cr ₂ O ₃	Low Salinity 1-ppm O ₂ 150°C
1.2	-0.684	-0.646	FeS	FeS, Cr ₂ O ₃	Low Salinity No O ₂ 250°C
1.3	-0.486	-0.229	Fe ₃ O ₄	Fe ₂ O ₃ , Cr ₂ O ₃	Low Salinity 1-ppm O ₂ 250°C
1.4	-0.599	-0.592	FeS, Fe ₃ O ₄	Fe ₃ O ₄ , Cr ₂ O ₃	High Salinity No O ₂ 250°C
1.5	-0.571	-0.227	Fe ₃ O ₄	Fe ₂ O ₃ , Cr ₂ O ₃	High Salinity 1-ppm O ₂ 250°C

(a) Syrett et al. 1977; Biernat and Robins 1972.

TABLE 7. Cyclic Voltammetry Data

<u>Experiment</u>	<u>Observations, Cathodic Direction</u>	<u>Observations, Anodic Direction</u>	<u>Notes</u>
1.0: A53B E-Brite	H ₂ Evolution H ₂ Evolution	General Corrosion Passivity $E_{\text{prot}} - E_{\text{corr}} = 20 \text{ mV}$	Low Salinity No O ₂ 150°C
1.1: A53B E-Brite	H ₂ Evolution H ₂ Evolution	General Corrosion Passivity $E_{\text{prot}} - E_{\text{corr}} = -150 \text{ mV}$	Low Salinity 1-ppm O ₂ 150°C
1.2: A53B E-Brite	H ₂ Evolution H ₂ Evolution	Passive Region Passivity $E_{\text{prot}} - E_{\text{corr}} = 240 \text{ mV}$	Low Salinity No O ₂ 250°C
1.3: A53B E-Brite	H ₂ Evolution H ₂ Evolution	Passive Region Passivity $E_{\text{prot}} - E_{\text{corr}} = 160 \text{ mV}$	Low Salinity 1-ppm O ₂ 250°C
1.4: A53B E-Brite	H ₂ Evolution H ₂ Evolution	General Corrosion Passivity $E_{\text{prot}} - E_{\text{corr}} = 160 \text{ mV}$	High Salinity No O ₂ 250°C
1.5: A53B E-Brite	Film Reduction Peak and H ₂ Evolution H ₂ Evolution	General Corrosion Passivity $E_{\text{prot}} - E_{\text{corr}} = 170 \text{ mV}$	High Salinity 1-ppm O ₂ 250°C

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DISCUSSION

The primary purpose of this work was to determine if commercial PR instrumentation could correctly measure corrosion rates. Data in Table 3 indicate good agreement between weight loss measurements and the $1/R$ value determined from linear polarization experiments. Other experiments involving a ± 10 -mV step function (to determine $\Delta I/\Delta E$), which replicate the operation of some commercial instruments, were in good agreement with linear polarization data. In general, the agreement between weight loss and linear polarization data was considerably better than the factor of two agreement mentioned by others (Fontana and Staehle 1970; Callow, Richardson, and Dawson 1976).

By using the weight loss data and the average $1/R$, a B value was calculated as shown in Table 4 that would seem to be more accurate than the value calculated from Tafel slopes since it was based on actual corrosion data. For A53B in the absence of oxygen, B was 24 ± 3 mV; while for all cases of E-brite, B was 28 ± 11 mV. Commercial instruments have this B value hard-wired in place, and it is important to know this value if it becomes necessary to correct the output of the commercial instrument. The B value for the Petrolite PR instrument is calculated to be 36 mV based on the electrode area for their standard 1018 mild steel electrode. The internal B value for the Corrater® is not known. Based on the variability of B values measured in the laboratory (especially for E-brite) and the fact that corrosion conditions in the field are more variable and different from laboratory conditions, the hard-wired B value of 36 mV in the Petrolite is acceptable as a direct measure of the corrosion rates since the error is less than a factor of two when compared to average B values.

When oxygen enters the system, the cathodic reaction approaches mass transport control; and Equation (4) must be used to calculate the corrosion rate. Unfortunately, the $\Delta I/\Delta E$ behavior from commercial instruments does not give any warning that corrosion conditions have changed. Examination of the $1/R$ data of experiments 1.1 and 1.3 in Table 3 does not show any large change;

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consequently, by assuming Equations (1) and (2) always hold, the actual corrosion rate could be underestimated by a factor of five or more. The only clue is the potential data of Table 6. By mixed potential theory, the corrosion potential will always be closest to the reaction with the largest exchange current density. The A53B electrode is corroding relatively freely; and when the rapidly reacting oxygen enters the system, the corrosion potential does not greatly change in the anodic direction. However, the E-brite is passivated (small exchange current density) and the corrosion potential is shifted in a more anodic direction. This is particularly true at 250°C when the rate of oxygen consumption should be faster.

A thermodynamic reference electrode is required for this observation; but since the commercial instruments use freely corroding specimens of the same material, this observation could not be made. Either a thermodynamic reference electrode should be used or the instruments should include a very slowly corroding specimen along with the iron electrode, and the potential between the slow and the more rapidly corroding electrodes should be monitored to warn when oxygen has entered.

When oxygen is known to be present, the reading of the commercial PR instrumentation for steels should be multiplied by at least a factor of five for a more realistic corrosion rate. Although only one oxygen level was studied in these experiments, mass transport control implies that the corrosion rates for a carbon steel will be proportional to the oxygen level.

Since the Tafel slopes are rarely the same for anodic and cathodic reactions, the current measured at +10 mV will not be the same as at -10 mV; and the commercial instrument will give differing corrosion rates. A simple average of these two corrosion rates is more likely to approximate the $(\partial I / \partial E)_{E_{\text{corr}}}$ than either value separately and is a useful rule of thumb for field personnel. This interpretation is shown graphically in Figure 5.

The corrosion rates for A53B in high-saline brine were much lower than those observed by others (Harrar, McCright, and Goldberg 1977; Shannon 1977) and may be due to the higher brine pH used in our experiments. (Corrosion rates typically increase as pH is decreased.) As a first approximation, a

FIGURE 5. Illustration of a Method to Approximate $(\partial I / \partial E)_{E_{\text{corr}}}$ from $\Delta I / \Delta E$, Potential Step Data

first-order dependence of corrosion rate on hydrogen ion activity is possible. Harrar, McCright, and Goldberg (1977) studied corrosion rates in the pH range of 2.3–3.4 at 100°C and measured rates greater than 100 mpy for carbon steel. Shannon (1977) studied corrosion rates in 20% brine at 250°C (pH = 4.7) and measured rates on mild steel of about 100 mpy. Cramer et al. (1979) measured corrosion rates in 20% brine with a pH of 6.1 (simulated Salton Sea brine) at 232°C and found the general corrosion rate on mild steel to be 5 mpy while in 100-ppm O_2 brine the corrosion rate was over 1000 mpy. The pH value has a profound effect on corrosion rates, and the corrosion rates measured in this study are consistent with those measured by others at higher pHs.

In the CV data shown in Table 7, the scan rates are too rapid to approach a steady state; but the method can point out some general features of the

current-potential relationship. For A53B, the anodic scan almost always indicated general corrosion while for E-brite passivation was usually present. CV can indicate in a general way the onset of pitting (Baboian 1977). A material susceptible to pitting shows a larger current on the return half of the anodic scan, and the point at which the two currents are equal is defined as E_{prot} (that is, the current on the return half of the cycle was always below that of the first half of the cycle). The E-brite always showed an E_{prot} that was less than 200 mV from the corrosion potential. In experiment 1.1, it was below E_{corr} , indicating that pitting was rapidly taking place. Visual observation of the weight loss coupons never revealed pitting on the A53B, but E-brite was usually pitted even without the presence of oxygen. E_{prot} was close to E_{corr} so that occasional potential perturbations resulted in the initiation of pits. Pit density was rarely above 5 pits/cm² (except on the electrodes that were made extremely anodic on CV scans) with a depth less than 0.013 cm (0.005 in.). The passive condition of E-brite explains the resistance to uniform corrosion of this alloy, but pitting makes it unsuitable for engineering application in brines. The general anodic corrosion behavior of the A53B based on CV observations indicates that the addition of depolarizing species (such as O₂) and improved mass transport conditions will result in increased corrosion rates. Cathodic behavior for both materials did not reveal any current peaks, and the return cycle (second half of the cathodic scan) generally superimposed on the first cycle.

Experiment 1.5 was an exception in the case of A53B. A reduction peak was observed on the first half of the cathodic cycle but was not seen on later CV scans. Experiment 1.5 is interesting because the A53B did not show an enhanced corrosion rate in the presence of oxygen although all previous experiments in low-salinity brines with oxygen resulted in enhanced corrosion rates. It appears that a protective film could have been present even though the anodic CV scan did not show any passivation. Experiment 1.5 will be investigated further.

There were no apparent surface films on E-brite in any of these experiments. A53B typically had a black, porous, and poorly adherent film under both oxygenated and reducing conditions (except in experiment 1.5 where the film was

black, quite thin, and adherent). X-ray diffraction studies were carried out on A53B surfaces exposed to reducing conditions at 150°C: FeCO_3 , FeS , and FeS_2 were found. From Table 6 only FeS was predicted. No other surface determination studies were carried out at higher temperatures. No Pourbaix diagram for elevated temperatures calculated to date considers the FeCO_3 species; this species should be included for completeness. Work by Shannon (1977) indicates that the corrosion rate (at constant brine composition without sulfide) is much higher from 50–150°C than above 150°C. Preliminary calculations of the stability field for FeCO_3 indicates that it is a dominant iron film at lower temperatures but is displaced by a more protective Fe_3O_4 film at temperatures above 150°C.

REFERENCES

- Agrawal, A., et al. 1975. "A Trouble-Free Electrode Holder for Use in Autoclave Electromechanical Tests." Corrosion 31:262.
- Baboian, R., ed. 1977. Electrochemical Techniques for Corrosion. National Association of Corrosion Engineers, Houston, Texas.
- Biernat, R., and R. Robins. 1972. "High-Temperature Potential/pH Diagrams for the Iron-Water and Iron-Water-Sulfur Systems." Electrochimica Acta 17:1261-1283.
- Callow, L., J. Richardson, and J. Dawson. 1976. "Corrosion Monitoring Using Polarization Resistance Measurements." British Corrosion J. 11(3):123-139.
- Cramer, S., et al. 1979. "Corrosion Studies in High Temperature, Hypersaline Geothermal Brines." Paper #59, NACE, Corrosion/79, Atlanta, Georgia.
- Danielson, M. 1979. "The Construction and Thermodynamic Performance of an Ag-AgCl Reference Electrode for Use in High Temperature Aqueous Environments Containing H₂ and H₂S." Corrosion 35(5):200-204.
- Fontana, M., and R. Staehle, eds. 1970. Advances in Corrosion Science and Technology. Vol. 6, pp. 163-262. Plenum Press, New York.
- Harrar, J., R. McCright, and A. Goldberg. 1977. Field Electrochemical Measurements of Corrosion Characteristics of Materials in Hypersaline Geothermal Brines. UCRL-52376, Lawrence Livermore Laboratory, Livermore, California.
- Posey, F., and A. Palko. 1979. "Corrosivity of Carbon Steel in Concentrated Chloride Solution." Corrosion 35(1):38-42.
- Shannon, D. 1977. Corrosion of Iron-Base Alloys Versus Alternative Materials in Geothermal Brines. PNL-2456, Pacific Northwest Laboratory, Richland, Washington.
- Syrett, B., et al. 1977. Corrosion Chemistry of Geothermal Brines, Part 2. AER76-00713, Stanford Research Institute, Menlo Park, California.

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