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Linear Polarization Measurements at High Temperatures in Hypersaline Geothermal Brines

UNITED STATES DEPARTMENT OF THE INTERIOR

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Linear Polarization Measurements at High Temperatures in Hypersaline Geothermal Brines

By Stephen D. Cramer and Paul B. Needham, Jr.

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BUREAU OF MINES

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LINEAR POLARIZATION MEASUREMENTS AT HIGH TEMPERATURES IN HYPERSALINE GEOTHERMAL BRINES

by

Stephen D. Cramer[1] and Paul B. Needham, Jr.[2]

ABSTRACT

The Bureau of Mines conducted a series of in situ linear polarization measurements in high-temperature, high-pressure hypersaline geothermal brines at the Bureau of Mines Geothermal Test Facility in the Imperial Valley of California. The measurements represented an evaluation of the linear polarization technique for obtaining instantaneous corrosion rates of materials of construction in flowing hypersaline hydrothermal fluids that rapidly form scales on exposed surfaces. A special method was devised for use with the linear polarization technique that resulted in obtaining corrosion rates for 1020 carbon steel, 316 and 430 stainless steel, titanium, various nickel-based alloys, and aluminum 6061 under strong scale-forming conditions. The measurements also provided information on scale-deposition rates in various geothermal environments. Exploratory in situ potentiostatic polarization measurements were made in the flowing brines to qualitatively determine scale-deposition effects on the electrochemical measurements.

INTRODUCTION

Corrosion is one of the major problems that must be solved in order to fully develop the Nation's geothermal resources. The determination of materials needed for constructing geothermal resource recovery plants, including those for minerals recovery, power generation, and secondary process facilities, requires the recognition of the special needs of the industry. Recent development of geothermal resources, found mainly in the Western United States, is focusing on liquid-dominated geothermal reservoirs in which the working fluids are highly corrosive, high-temperature brines. Located in the Imperial Valley of southern California are six large and distinct liquid-dominated known geothermal resource areas (KGRA). Of particular interest to the Bureau

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of Mines is the Salton Sea KGRA containing hypersaline brines, which offer a high potential for the recovery of valuable mineral and metal products (3).[3]

The brines from the Salton Sea KGRA are, typically, discharged from the wellhead at temperatures in excess of 200° C; downhole brine temperatures of 350° C have been reported (13). Total dissolved solids, largely as chlorides of the alkali and alkaline earth metals, are in the range of 20 to 30 wt-pct. In addition, the brines contain heavy-metal ions, dissolved gases including carbon dioxide with lesser amounts of hydrogen sulfide, ammonia, methane, and hydrogen, and may be saturated with silica. These constituents result in the formation of complex scales on metal surfaces exposed to the brine.

In the present work, brine was used from geothermal well Magmamax 1, located on the Salton Sea KGRA, which flowed into the Bureau of Mines Geothermal Test Facility (fig. 1). The facility was designed for testing materials to provide several of the important process steps that will be found in

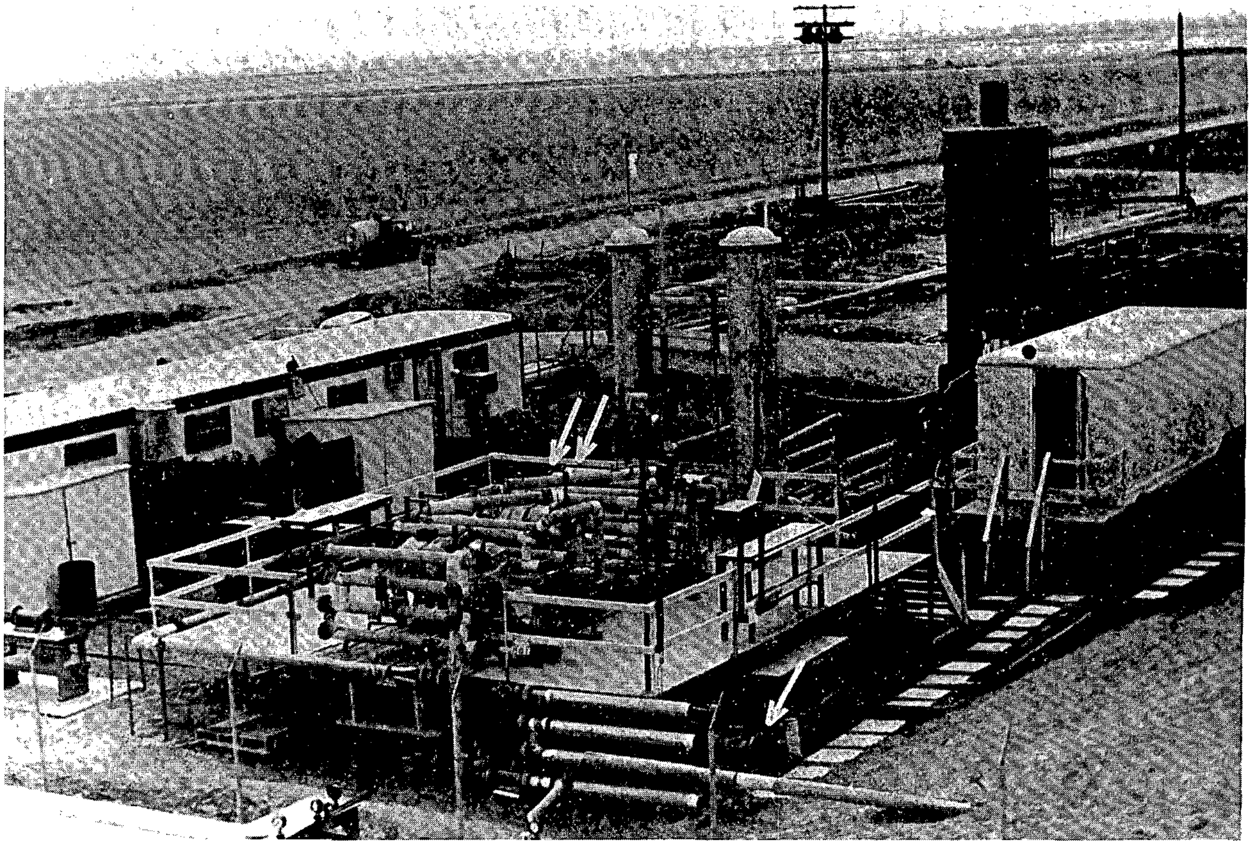

FIGURE 1. - Bureau of Mines Geothermal Test Facility located on the Salton Sea Known Geothermal Resource Area (KGRA) near Calipatria, Calif. (Arrows show the approximate locations of the electrochemical test packages.)

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

a geothermal resource recovery plant. It incorporates two stages of steam separation that allow the brines to flash-evaporate at successively lower pressures and temperatures. A representative analysis for the major constituents of the unflashed input brine from Magmamax 1, together with wellhead temperature, pressure, and pH, is shown in table 1. Typical values of the chloride content, temperature, pressure, and pH are also given in table 1 for the concentrated brine following two stages of steam separation and for the steam condensate. Dissolved gases, particularly carbon dioxide, are stripped from the brine at each stage of steam separation. This results in the higher values of pH observed for the concentrated brine compared with those of the unflashed input brine.

TABLE 1. - Chemical analysis of brines in three process streams of the Bureau of Mines Geothermal Test Facility

Constituent concentration	Input brine	Concentrated brine (second stage)[1]	Steam condensate[1]
Na....................ppm..	46,900	-	-
Ca....................ppm..	22,700	-	-
K.....................ppm..	7,870	-	-
Mn....................ppm..	603	-	-
Sr....................ppm..	558	-	-
Fe....................ppm..	477	-	-
Li....................ppm..	148	-	-
Pb....................ppm..	36	-	-
Cl....................ppm..	118,200	128,000	8,620
Temperature..........° C..	229	178	~100
Pressure............psig..	302	140	0
pH........................	5.1	5.7	6.7

[1] Dashes indicate no measurement taken.

The present work describes our initial experience in applying the linear polarization technique to in situ corrosion measurements in high-temperature, high-pressure geothermal environments. Originally developed by Stern and Geary (15), the technique is widely used to study corroding systems (4-9, 11, 14). Commercial instrumentation based on the technique relies on the fact that, for many corroding systems, the corrosion kinetics in a narrow region around the corrosion potential are nearly linear. It is assumed that the reversible potentials of competing oxidation-reduction reactions are sufficiently far removed from the corrosion potential that the corrosion reaction is dominant and that ohmic and concentration effects are minimal. Since electrochemical measurements in complex, high-temperature geothermal brines have not been made before, the present application may raise questions that can only be answered by further study in the laboratory and the field. However, at the time the polarization measurements were made, a 30-day weight-loss corrosion test involving 6,400 corrosion test coupons was in progress at the Geothermal Test Facility (2), and there was a unique opportunity to compare and evaluate measurements using the two techniques.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Roger J. Dexter, Western Region Marketing Coordinator, Petrolite Corp., Stafford, Tex., for use of the M-103 corrosion rate instrument, M511-E industrial probes, and electrode materials at the Geothermal Test Facility, Imperial Valley, Calif.

EXPERIMENTAL PROCEDURES

Linear polarization measurements were made with the Petrolite M-103E portable corrosion rate instrument.[4] The three-electrode technique (4-9, 11, 14) was employed using cylindrical electrodes of identical material for the working, counter, and reference electrodes. All measurements were made with respect to the potential of the freely corroding electrode by superimposing a signal of ±10 mv dc. Given the assumptions inherent in the instrumentation, the measured current was converted directly into a corrosion rate for the test material, expressed as mils per year (mils/yr) of surface thickness lost.

Because of the high temperature and pressure of the brine, the electrodes were mounted on Petrolite M-511E industrial probes designed for pressures up to 600 lb/sq in and temperatures up to 260° C. The electrode assemblies were exposed to the brine and condensate environments through a specially designed electrochemical test package (fig. 2) that was, in turn, mounted on one of seven in situ corrosion test packages. Mounted in this way, the electrode assembly could be inserted directly into the corrosion test package for optimum exposure of the electrodes to the flowing brine.

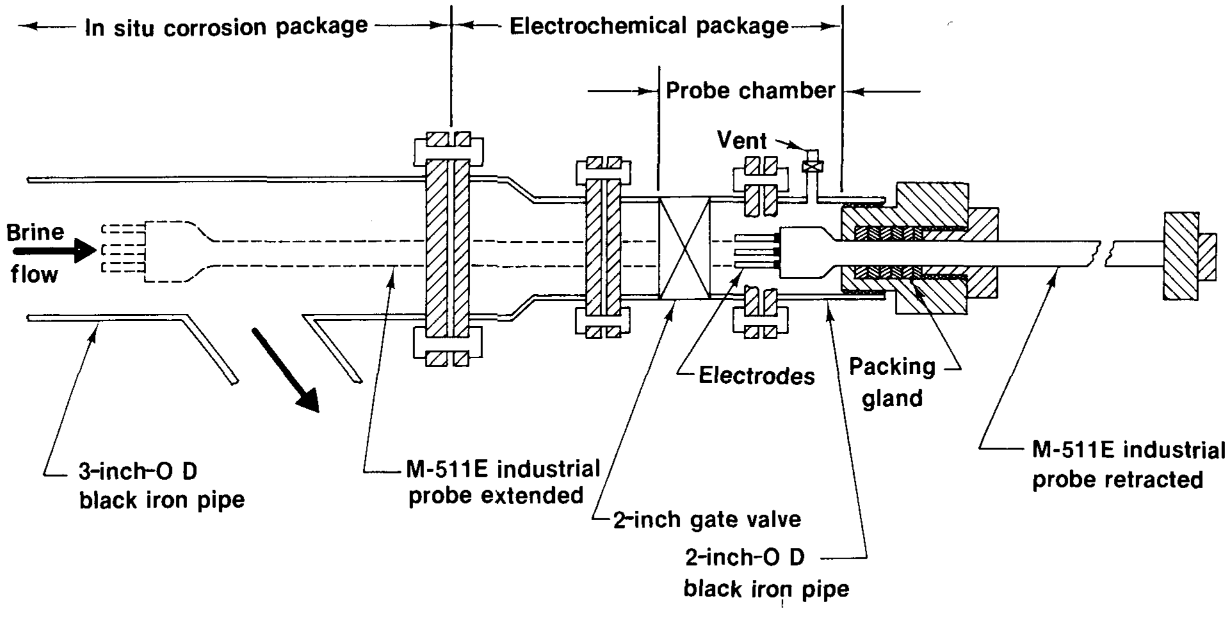

FIGURE 2. - Schematic diagram of electrochemical test package mounted on in situ corrosion test package.

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[4] Use of specific trade names does not imply endorsement by the Bureau of Mines.

The electrochemical package served three functions: (1) to isolate the probe during installation, (2) to provide access to the highly turbulent brine flowing through the corrosion test package, and (3) as a containment vessel that allowed hot brine to slowly circulate through the probe chamber and around the electrodes. Before making the polarization measurements, the gate valve was opened, filling the probe chamber with brine, and the vent (fig. 2) was opened for 1 to 2 min, purging the probe chamber of trapped air. The probe was then extended through the gate valve into the flowing brine or retained in the retracted position exposed to the brine inside the probe chamber. Purging of the probe chamber and the circulation of the brine removed air from the electrode surroundings.

Polarization Measurements

Linear polarization measurements were made in each of the three process streams listed in table 1: (1) the unflashed input brine, (2) the concentrated brine following two stages of steam separation, and (3) the steam condensate. Measurements were begun immediately following the insertion of the electrodes into the brine and were repeated periodically for times up to 40 hours after the initial exposure. The measurements were made in pairs by polarizing the working electrode first cathodically and then anodically. The reported corrosion rates were the average of the consecutive cathodic and anodic values. The electrodes were at their "open-circuit" or corrosion potential between measurements.

Electrode Preparation

Sets of electrodes were made from eight metals and alloys chosen for their widely differing compositions and resistances to corrosion. These were 1020 carbon steel, 316 and 430 stainless steel, Monel 400, aluminum 6061, Inconel 625, Hastelloy C-276, and titanium. The dimensions of the electrodes were selected to compensate for chemical and physical differences between the metals and alloys so that the measurements could be made without further calibration. Measurements were made with each set of electrodes in the input brine, and further measurements were made with the 1020 carbon steel electrodes in the concentrated brine and steam condensate.

The electrodes were mechanically polished to a 240-grit finish using silicon carbide abrasive, washed with water, rinsed with methanol, and air dried. They were weighed before each test to within ±0.5 mg, and threaded onto glass-insulated mounting pins on the M-511E probes. These mounting pins were isolated from the brine using flat sealing gaskets of Viton A rubber or Teflon.

At the end of each test, the probe-electrode assembly was washed with water, rinsed with methanol, and dried with forced air. On removal of the electrodes, the mounting pins were immediately examined for any fluid leakage around the gasket. (Tests were repeated if leakage was observed at either the working or reference electrodes.) The electrodes were rinsed with methanol, dried a second time, and reweighed to determine the weight change of the electrode resulting from either corrosion or scaling. The electrodes were then examined with a microscope for localized corrosion.

Used electrodes were reconditioned by repeating the surface-grinding technique to remove corrosion products and scale accumulation. Dimensional changes in the electrodes were checked with a micrometer. In all other respects, the reconditioned and new electrodes were treated identically.

Potentiostatic polarization measurements, to qualitatively determine the effect of scale deposition on the corrosion kinetics, were made using a Wenking 66TA potentiostat.

RESULTS AND DISCUSSION

Chemical, fluid dynamic, and thermodynamic properties of the geothermal brine delivered to the Bureau's Geothermal Test Facility varied because of fluctuations in the operation of Magmamax 1. Consequently, the initial experiments were directed toward identifying the properties of the brine and/or the test facility that would affect the polarization measurements.

Brines from the Salton Sea KGRA readily form scales on exposed metal surfaces. These scales range in composition from amorphous silica and silicates to heavy-metal sulfides and calcite (1-2, 10), depending upon the processing of the brine. Two sets of electrodes, exposed for 3 hours to the input brine, are shown in figure 3 with the resulting layers of scale, consisting predominantly of galena. (A third set of clean, unexposed electrodes is shown for comparison.) The typical structure of the predominant galena scale is illustrated by the scanning electron micrograph in figure 4 using scale formed on 15-day weight-loss coupons exposed to input brine.

Exploratory potentiostatic polarization measurements were made in unflashed input brine to qualitatively determine the effect of scale on the observed electrode kinetics. Type 430 stainless steel electrodes in the retracted position were used for the measurements. Beginning at a potential 100-mv cathodic to the open-circuit potential, the potential was swept at a rate of 20 mv/min in the anodic direction (fig. 5). Curve A corresponds to electrodes that were initially free of scale when the potential sweep began. Curve B corresponds to electrodes that were extended into the flowing input brine for 3 hours to allow the scale to form, but it was retracted prior to the potential sweep measurements. The currents observed for the initially scale-free electrodes were suppressed by several orders of magnitude when the galena-based scale was present. The initially scale-free electrodes exhibited a region of current instability in the potential range of +200 to +500 mv, which essentially disappeared when the electrodes were covered with scale. The small negative potentials at the crossover between cathodic and anodic kinetics were probably due to slight differences in the surface condition of the working and reference electrodes.

Preliminary linear polarization measurements were made using carbon steel electrodes in the concentrated brine. The measured currents became increasingly unstable as the electrodes were positioned further into the flowing brine. With the electrodes fully inserted into the brine, the currents were extremely difficult to measure. Reynolds number calculations indicate the brine is highly turbulent in the vicinity of the electrodes when they are in the extended position. Turbulence produces erosive conditions that can delay

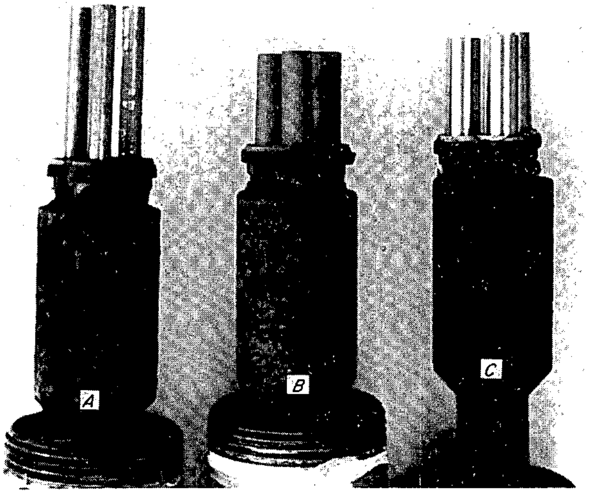

FIGURE 3. - Electrodes exposed to unflashed input brine. *A*, 430 stainless steel, before exposure; *B*, titanium, 3.2-hour exposure; *C*, 316 stainless steel, 3.4-hour exposure.

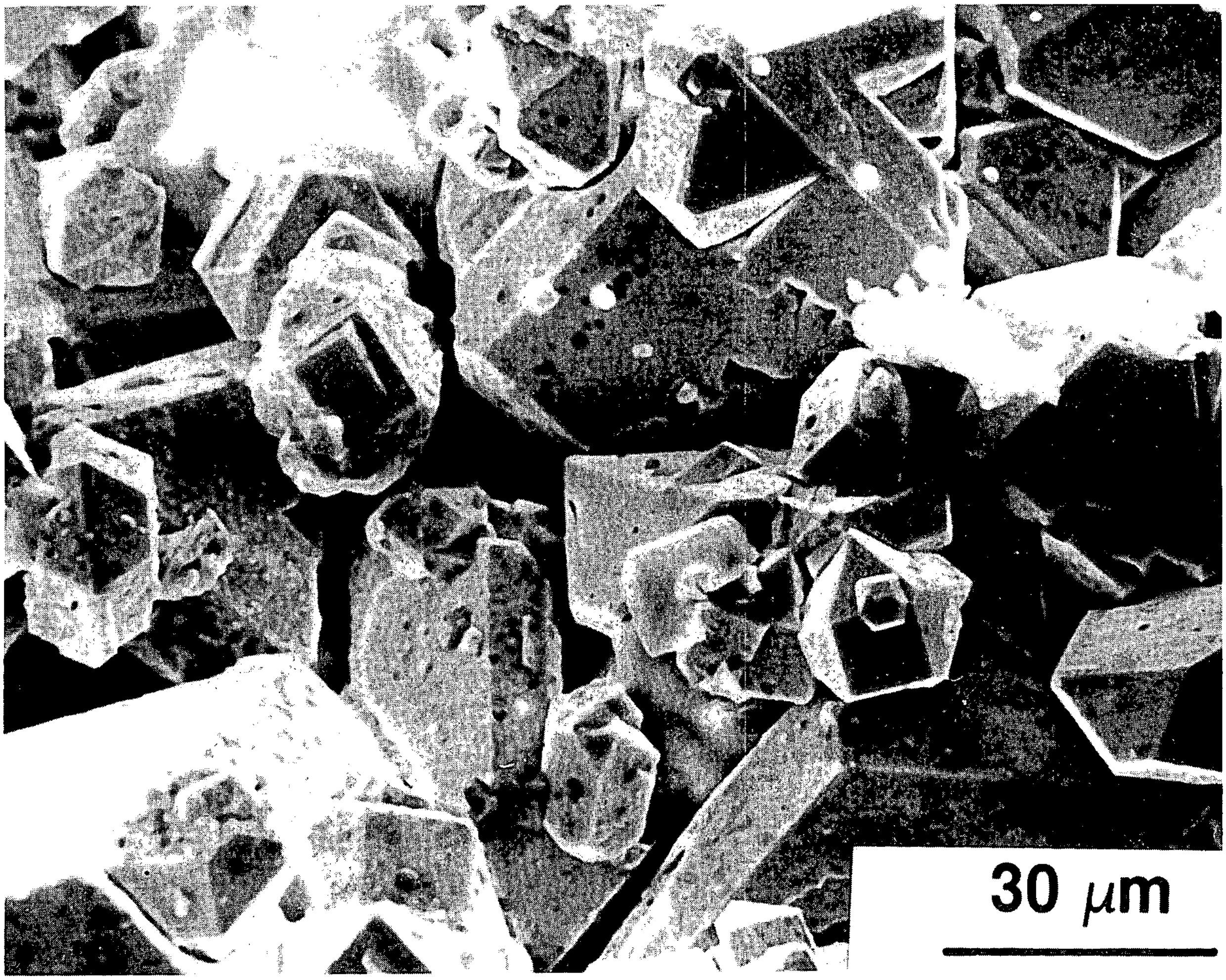

FIGURE 4. - Galena-based scale formed on weight-loss coupons exposed to unflashed input brine for 15 days.

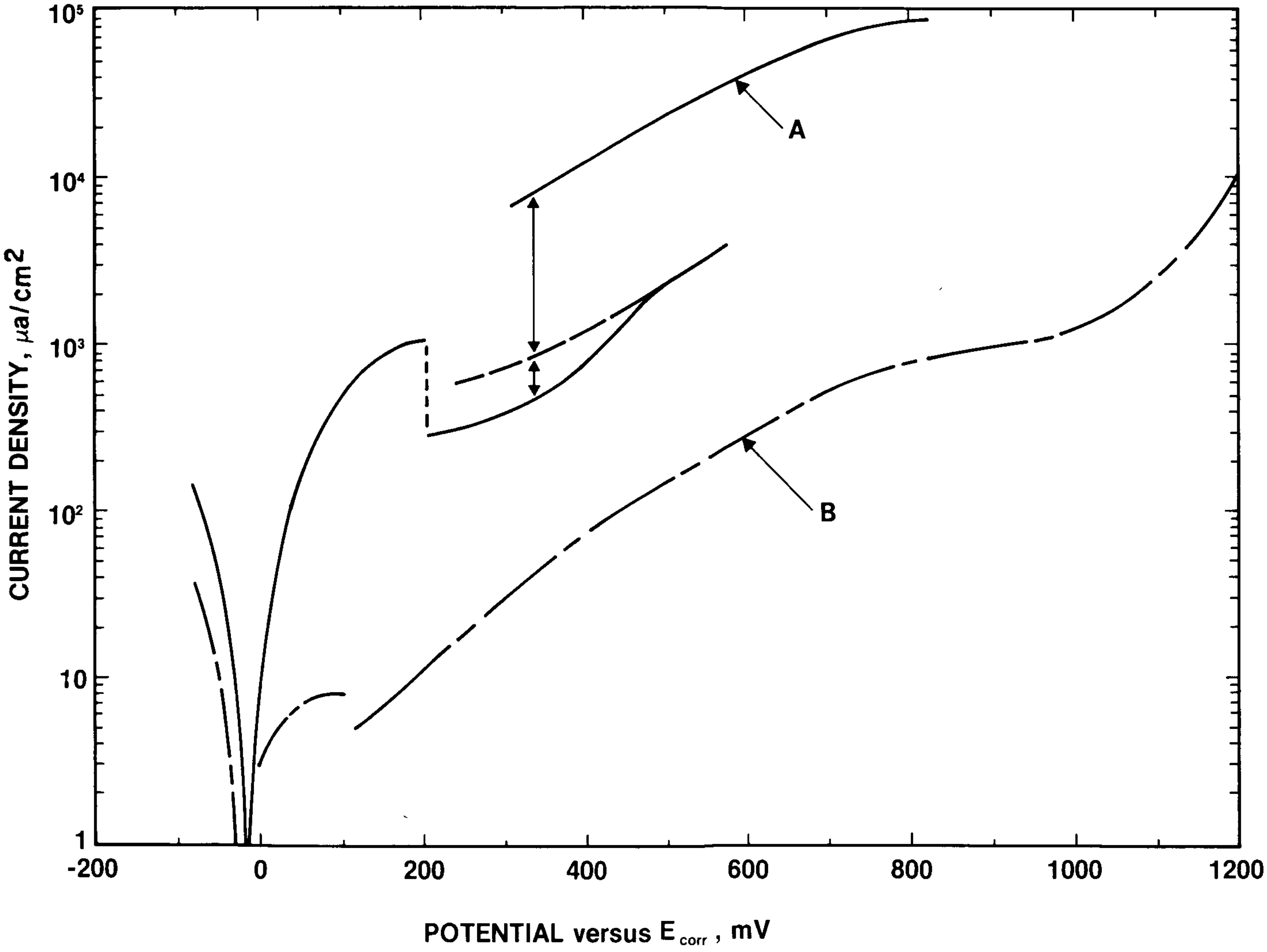

FIGURE 5. - Potentiostatic polarization curves for 430 stainless steel exposed to unflashed input brine. A, initially scale-free electrodes; B, electrodes exposed 3 hours to flowing brine. Potentials measured with respect to the corrosion potential, E_{corr}, of 430 stainless steel.

or disrupt the deposition of scale on the corroding surface. These changes in the condition of the scale on the corroding surface can lead to current fluctuation of one order of magnitude or more, as the potentiostatic polarization measurements indicated. Consequently, all subsequent linear polarization measurements were made with the probe in the retracted position and the electrodes exposed to brine slowly circulating within the probe chamber, which resulted in experimentally more reproducible conditions.

Even with the probe in the retracted position, however, current instabilities were observed at periodic intervals during linear polarization measurements. These instabilities correlated precisely with the operation of certain automatic pressure and flow-rate control valves in the Geothermal Test Facility. The functioning of these valves produced local changes in pressure within the corrosion test packages. Analysis of the pressure variations showed that at certain times the pressure in the vicinity of the electrode assembly dropped below the saturation pressure of the brine, and boiling occurred in the fluid surrounding the electrodes. Consequently, for all subsequent linear polarization measurements, the procedure was to close the 2-inch gate valve on the electrochemical package before each measurement, temporarily isolating the probe chamber from the flowing brine and possible transient pressure effects. Immediately following the measurement, the gate valve was reopened. This procedure yielded a consistent set of measurements that was relatively free of distortions produced by the control functions of the Geothermal Test Facility.

The scaling rates for the three process streams were determined by weight-gain measurements of electrodes exposed for times ranging from several hours up to 40 hours. These measurements were made with the probes in the retracted position so that the results could be used to interpret the subsequent linear polarization measurements. The weight-gain results are shown in figure 6, expressed in mg/cm^2 based on the nominal exposed electrode surface areas. Carbon steel electrodes were used in the concentrated brine and steam condensate, and all of the electrode materials except aluminum 6061 were used for measurements in the input brine. The scale deposition rates, obtained as the slope of the curves, were 0.31 mg/cm^2/hr for the input brine, 0.094 mg/cm^2/hr for the concentrated brine, and 0.032 mg/cm^2/hr for the steam condensate. The scale from the input brine was hard and adherent, scale from the concentrated brine was hard and moderately adherent, and scale from the steam condensate was soft and poorly adherent.

Instantaneous corrosion rates for 1020 carbon steel were determined periodically by the linear polarization technique in the input brine, concentrated brine, and steam condensate for exposures up to 14 hours. During this time, as shown by figure 6, scale steadily accumulated on the surface of the electrodes. The corrosion results (fig. 7) were strongly dependent upon the type of scale formed and the scale deposition rate. In the steam condensate, where the scaling rate was low and the scale was relatively nonadherent, the corrosion rate was independent of the exposure time. In the concentrated brine, where the scale depositon rate was more rapid and the scale was moderately adherent, the corrosion rate declined gradually owing to the increasing thickness of the scale. In the input brine, where the scaling rate was triple that

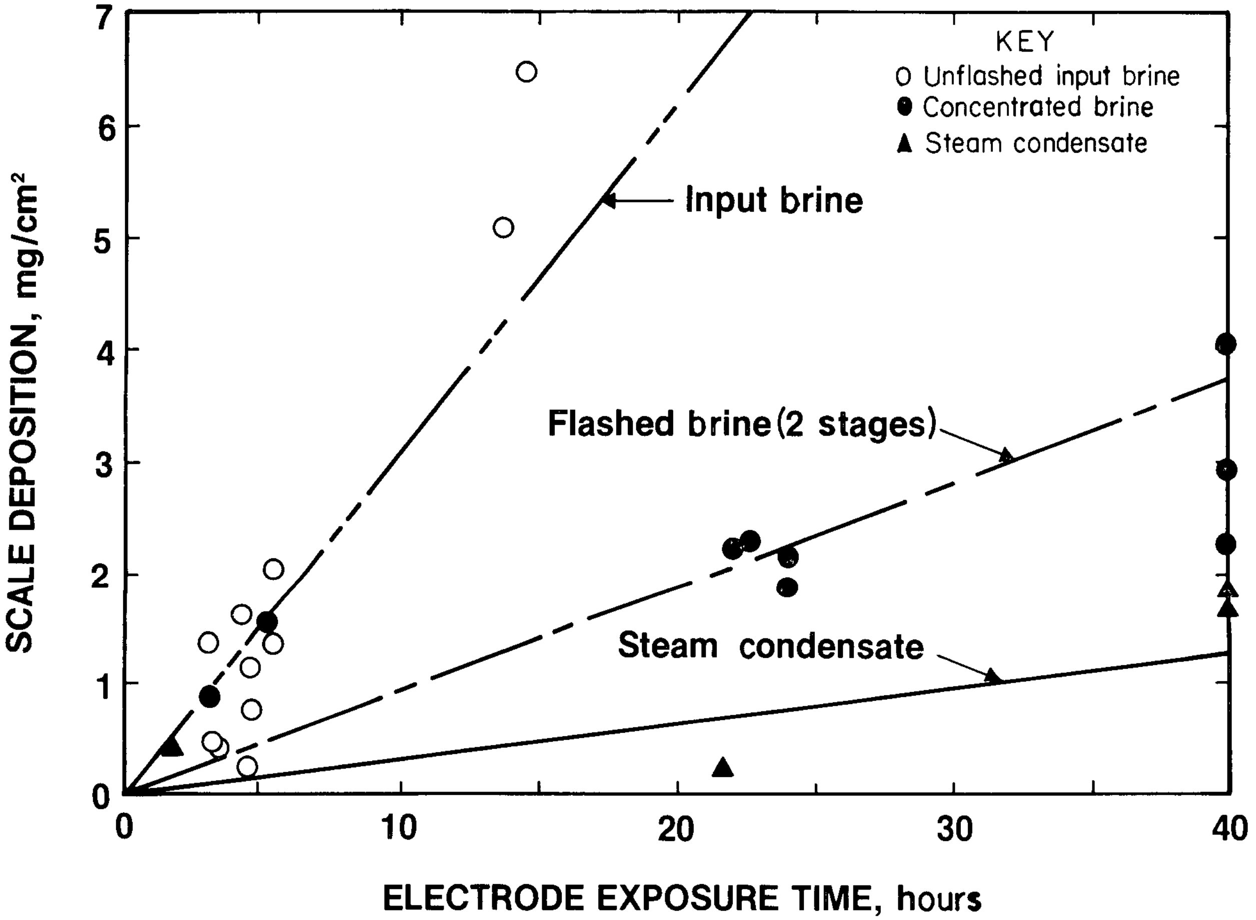

FIGURE 6. - Scaling characteristics of three process streams.

in the concentrated brine, the corrosion rate dropped even more sharply because of the rapid growth of the scale layer. The area of the metal exposed to the brine is known only for times that are short relative to the scale deposition rate, that is, at the beginning of the exposure when scale formation is slight. The strong correlation between scale deposition rate, scale adhesion, and declining corrosion rate suggests the results observed for the input and concentrated brines occurred primarily because scale growth reduced the area of metal exposed to the brine, not because the actual corrosion rate was changing.

Actual corrosion rates based on the known surface area were obtained from the linear polarization measurements by extrapolating time-dependent data, illustrated by figure 7, to zero exposure time, corresponding to the condition where the electrode surface was free of scale. Under these conditions, the corroding surface (assuming uniform general corrosion) and the nominal surface area of the electrode were equivalent. As a practical matter, the data in figure 7 suggest that the corrosion measurements obtained in the first 15 min for the input brine and in the first 30 to 40 min for the concentrated brine provide a reasonable estimate of the actual corrosion rate. In any case, the

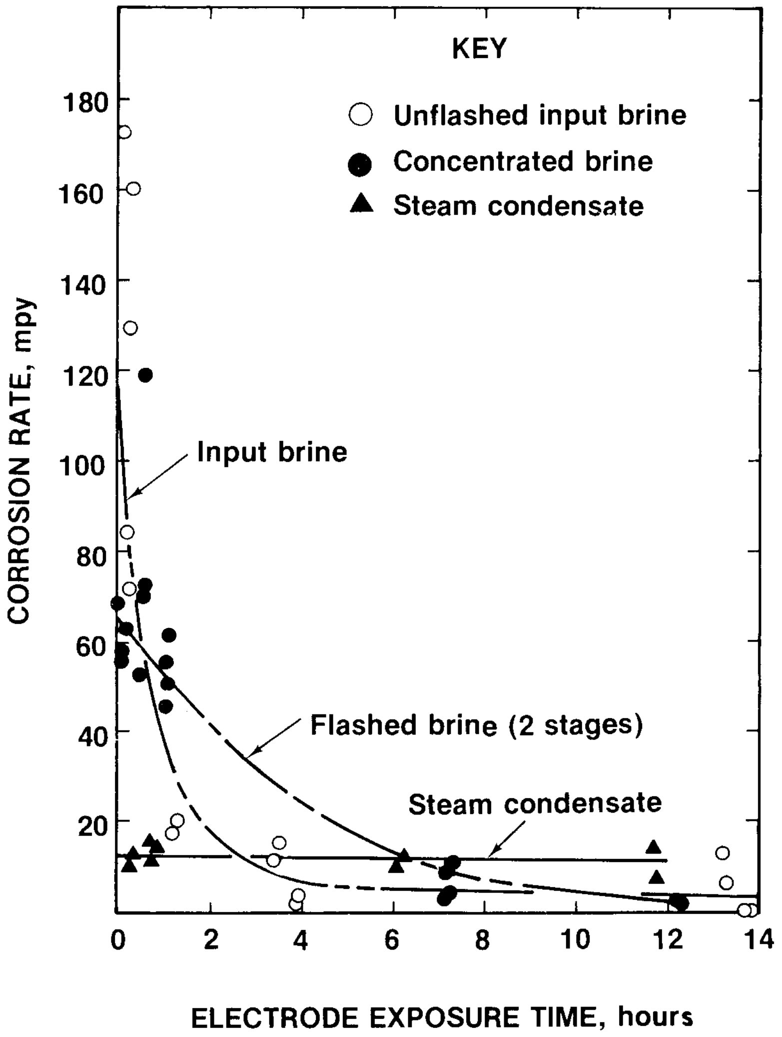

FIGURE 7. - Corrosion of 1020 carbon steel measured by linear polarization during a period when scale was depositing on the electrode surfaces.

actual corrosion rate will be referred to here as the scale-free corrosion rate, emphasizing that the observed decline in the corrosion rate was the result of scale deposition, which reduced the area of metal exposed to the brine. Subsequent corrosion measurements were made by plotting time-dependent linear polarization data obtained over a 3-hour period and then extrapolating to zero-exposure time. The results of the measurements for the eight alloys are given in table 2. Carbon steel corroded at rates ranging from 12 mils/yr in the steam condensate to 145 mils/yr in the input brine. Corrosion rates in the input brine ranged from 0.2 mil/yr for titanium to 610 mils/yr for aluminum 6061. The aluminum 6061 electrodes were the only ones to experience observable localized corrosion during the 3-hour test exposures. Microscopic examination showed that they had pitted severely.

Included in table 2 are the results of the 15-day in situ weight-loss measurements (2) that were run concurrently with the linear polarization measurements in the same three process steps at the Geothermal Test Facility. At the end of the 15-day weight-loss tests, examination of the test coupons showed that they were thickly coated with scale. Although these coupons had been exposed for much longer times, the scales had compositions and properties similar to those observed on the linear polarization electrodes. In view of the persistant growth of scales in the input and concentrated brines, the corrosion of the weight-loss samples was probably retarded by the scales in a manner similar to that shown by the linear polarization measurements (fig. 7). Consequently, the measured corrosion rate for the weight-loss coupons could be interpreted as the time-averaged value of the instantaneous corrosion rate or, equivalently, as the area-averaged value, where scale coverage is considered a function of time. In this model, the upper limit of the corrosion rate for the weight-loss samples would be, by definition, the scale-free value obtained by linear polarization. For extended exposures, the observed corrosion rate for the weight-loss samples should be equal to or less than that obtained by linear polarization. (See table 2.)

TABLE 2. - Corrosion rates in Magmamax 1 brine obtained by linear polarization and weight-loss techniques

Alloy	Test environment	Linear polarization results, mils/yr	Weight-loss results,[1] mils/yr
Aluminum 6061.......	Input brine........	610	([2])
1020 carbon steel...	.....do............	145	67
Monel 400...........	.....do............	62	([2])
316 stainless steel.	.....do............	5.6	.7
430 stainless steel.	.....do............	3.1	.6-2.2
Inconel 625.........	.....do............	.8	0
Hastelloy C-276.....	.....do............	.4	.1
Titanium............	.....do............	.2	([2])
1020 carbon steel...	Concentrated brine.	62	48
Do...............	Steam condensate...	12	([2])

[1] Fifteen-day exposure (2).

[2] Corrosion rate not measured.

The placement and method of using the polarization electrodes described represents a departure from typical field polarization applications in which the electrodes are continuously exposed to the working system for long, unattended periods. However, such a departure may be necessary in high-temperature, hypersaline geothermal brines because of unstable conditions linked with variations in the chemistry, fluid dynamics, and thermodynamics of the brine, and because of the massive scaling associated with the brine (1, 10). Until techniques for scale control have been developed (1, 13), the best approach for making corrosion measurements by the linear polarization technique would appear to involve measurements on initially scale-free electrodes in exposures of short duration. This, however, need not detract from either the potential usefulness of the technique for measuring corrosion rates in such environments, or its importance for monitoring changes in the corrosiveness of specific process steps.

CONCLUSIONS

These studies have shown that the linear polarization technique is applicable to corrosion measurements in high-temperature, hypersaline geothermal brines as long as the following essential modifications of the method are made: (1) The electrodes must be isolated from highly turbulent brine flows to give experimentally reproducible conditions, (2) the electrodes must be isolated from nonsteady conditions related to the control functions of facility equipment, particularly those that may reduce the pressure below the saturation pressure of the brine and cause boiling and two-phase flow around the electrodes, and (3) the corrosion rate must be obtained for electrodes free of scale, which can be obtained by extrapolating the time-dependent corrosion data to zero-exposure time.

The corrosion rates for scale-free electrodes were shown to represent the upper limit for the corrosion of extended exposure weight-loss coupons. In this model, the deposition of scale reduced the area of the corroding surface. Consequently, the observed corrosion rates for weight-loss coupons in exposures of 15 days were substantially less than values obtained for scale-free electrodes by the linear polarization technique.

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