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Corrosivity of Geothermal Brines Progress Report for Period Ending December 1976

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MASTER

OAK RIDGE NATIONAL LABORATORY

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CORROSIVITY OF GEOTHERMAL BRINES
PROGRESS REPORT FOR PERIOD ENDING DECEMBER 1976

F. A. Posey, A. A. Palko, and A. L. Bacarella

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ABSTRACT

Studies carried out during the FY1976 transition quarter and during the first quarter of FY1977 on the corrosivity of ferrous materials in synthetic geothermal brines are described. Several modifications were made to the original designs of the reference and test electrode assemblies of the refreshed, stirred titanium autoclave system for making electrochemical measurements up to at least 200°C. These changes greatly improved the reliability of the experimental system. Anodic and cathodic polarization curves were measured for type A212B carbon steel in 4 M NaCl at pH = 5 up to 200°C. On the basis of extrapolation of Tafel lines from these measurements and on the basis of measurements of polarization resistance it was possible to estimate the spontaneous corrosion rate of A212B carbon steel in deaerated 4 M NaCl, pH = 5, from room temperature up to 200°C. The influence of sweep rate and direction on estimation of corrosion rates from potentiodynamic polarization curves is discussed. The influence of chloride ion concentration on the anodic polarization behavior and the spontaneous corrosion rate of iron at 25°C, pH = 5, is described. Plans for continuation of the research during the remainder of FY1977 are presented.

INTRODUCTION

This report describes the results of continuing studies on the corrosion of ferrous materials in synthetic geothermal brines. A previous report¹ was concerned principally with studies carried out during FY1976. As stated earlier, the purpose of these studies, which are sponsored by the Division of Geothermal Energy of the U. S. Energy Research and Development Administration, is to develop a basic understanding of corrosion processes of ferrous materials such as iron and carbon steel in geothermal brines. A quantitative knowledge of the kinetics of corrosion processes in synthetic geothermal brines and the influence of such

variables as solution composition and temperature on them can be expected to provide a scientific basis for interpretation of field corrosion tests, on-line corrosion measurements, and plant corrosion experience, and perhaps suggest rational means for control or mitigation of corrosion during various stages of geothermal plant operation.

During the previous report period some electrochemical measurements were carried out on the spontaneous corrosion potentials and corrosion rates, and on the kinetics of the anodic and cathodic corrosion reactions of iron and carbon steel in 4 M NaCl solution over the pH range from 1 to 11 at temperatures up to 85°C in a conventional Pyrex electrochemical cell. In addition, a refreshed, stirred titanium autoclave system was designed, constructed, and tested; this assembly was designed to permit electrochemical measurements to be made up to at least 200°C in corrosive aqueous saline media. The effect of pH on hydrolysis, precipitation, and electrochemical reactivity of ferrous and ferric ions in 4 M NaCl at 25°C was studied, and implications for plant operation were discussed. In addition, the pitting potential of type 304 stainless steel in deaerated synthetic brine was measured as a function of temperature from 25° to 85°C.

The observations reported here represent further progress towards the establishment of a baseline of data on the electrochemical kinetics of corrosion of iron and carbon steel in concentrated sodium chloride solutions. Data on electrochemical aspects of the corrosion of ferrous materials under geothermal conditions are virtually nonexistent, and nearly all reported electrochemical work on ferrous materials in concentrated chloride solutions has so far been restricted to room temperature. During this period we have successfully investigated the polarization behavior and corrosion rate of carbon steel in 4 M NaCl, pH = 5 (at room temperature), all the way from room temperature up to 200°C. Several modifications to the reference and test electrode assemblies of the refreshed, stirred titanium autoclave system were required as the experiments progressed, and these are discussed below. Precautions which must be observed with respect to the choice of sweep rate and other aspects of the use of the potentiodynamic method for measurement of polarization curves and for estimation of corrosion rates by measurement of polarization resistance are discussed in some detail. In addition, the effect of

chloride ion concentration on corrosion of iron at room temperature, pH = 5, is described. Finally, plans for continuation of the research during the forthcoming period are presented.

As noted in the previous report,¹ these studies are a cooperative effort among personnel of the Chemistry Division and the Metals and Ceramics Division at ORNL. Once again the authors are indebted to J. C. Griess and J. H. DeVan of the Metals and Ceramics Division for their many contributions to both the technical and the administrative aspects of this work.

MODIFICATIONS TO REFERENCE AND TEST ELECTRODE ASSEMBLIES

The reference electrode assembly which was originally used with the refreshed, stirred titanium autoclave system was a slight modification of the design published by Wilde,² which allows pressure drop to be absorbed in a compressible fiberglass plug which allows a small, controlled leak rate of electrolyte into an external reference electrode compartment maintained at room temperature. As experiments progressed, it became apparent that some leakage was present between the liquid inside the reference electrode bridge and the metal components of the autoclave system, thus causing instabilities in the potentiostat control circuit. Therefore, a modified reference electrode assembly was designed which avoids the leakage problem which was encountered with the original design. A schematic cross section of this assembly is shown in Fig. 1. The primary conical seal is located several centimeters above the autoclave lid; this arrangement allows the entire seal assembly to be operated at a temperature considerably below that of the autoclave itself. The Teflon tube terminates below the surface of the liquid in the autoclave and is fitted with a Teflon bubble deflector which helps prevent bubbles from entering the bridge assembly and causing resistance problems. The primary conical seal is actuated by a thrust screw which forces a thrust ring down upon the long Teflon conical seal and tube piece. A second set of thrust screws and thrust rings forces a Teflon plunger piece down upon the compressible fiberglass plug which absorbs the pressure drop and allows a controlled leak rate of electrolyte to the external reference electrode

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Fig. 1. Schematic diagram of reference electrode bridge assembly.

compartment. The O-ring seal shown in Fig. 1 is needed to prevent leakage of electrolyte to the metal components of the bridge assembly. This assembly has proven to be reliable in continued use up to 200°C.

During the course of development of the improved reference electrode bridge assembly, some materials other than Teflon were used which, it was hoped, would provide more high-temperature rigidity and improved compressibility characteristics compared with pure Teflon. One reference electrode assembly was constructed from glass-filled Teflon. This assembly worked satisfactorily for a while but it was found in studies at the higher temperatures and pressures that glass-filled Teflon has a certain small, but finite, porosity which eventually allows excessive leakage of highly conducting electrolyte, thus once again causing potentiostat control problems. Still another reference electrode assembly was constructed from Rulon, a proprietary filled Teflon which has many uses as a material for bearings and seals. However, this material also possessed enough porosity so that continued operation at high temperatures and pressures led to leakage of salt solution through the Rulon components to the metal components of the reference electrode bridge assembly. We conclude from this experience that construction of the present bridge assembly should be based upon use of pure Teflon, and this limits practical use of the system to temperatures which are not greatly in excess of 200°C for very long periods of time. Optionally, it may be possible to provide enough cooling of the seal assembly to permit extended operation at temperatures in the autoclave which are somewhat in excess of 200°C.

The test electrode assembly used in the refreshed, stirred titanium autoclave system is essentially the same as that described by Agrawal, Damin, McCright, and Staehle.³ However, the shape of the Teflon-covered titanium contact rod was modified to include a shoulder which, acting in conjunction with the conventional Teflon packing gland assembly, prevented the test electrode from gradually creeping out of the packing gland during the cool-down period following operation at high temperature and pressure. Other components of the titanium autoclave test system are essentially the same as those described previously.¹

POLARIZATION OF CARBON STEEL AS A FUNCTION OF
TEMPERATURE IN 4 M NaCl, pH = 5

A set of anodic and cathodic polarization curves for type A212B carbon steel (0.358% C, 0.62% Mn, 0.18% Si, 0.033% S, 0.012% P) in deaerated 4 M NaCl at pH = 5 (room temperature) is shown in Fig. 2. This figure shows how the polarization curves change as the temperature is increased from 25° to 200°C, and the data exhibit a number of interesting features. All curves were obtained starting from the open-circuit or corrosion potential and scanning either cathodically or anodically at a constant rate of 0.1 mV/sec. As discussed below, use of this slow scan rate was found to be necessary to ensure that results observed during positive or anodic scans were essentially the same as those observed during negative or cathodic scans during the measurement of polarization resistance, particularly at the lower temperatures.

At pH = 5 two simultaneous cathodic processes are closely superimposed, as may be seen by inspection of the cathodic polarization curves in Fig. 2. At potentials near the open-circuit or corrosion potential the cathodic process consists mainly of the reduction of hydrogen ions to form molecular hydrogen, while at more negative electrode potentials the cathodic process is principally the reduction of the solvent water to form molecular hydrogen as product. Under the stirring conditions which pertain to these measurements (vigorous stirring with a magnetic stirrer inside the titanium autoclave) there is little evidence of a limiting current for convective diffusion of hydrogen ions to the electrode surface, as would have been observed easily in experiments conducted at lower pH. However, the rate of the cathodic process was observed to be under partial mass-transport control in the vicinity of -0.9 V at 25°C and in the vicinity of -1.05 V at 150° and 200°C, as evidenced by the typical appearance of the voltammetric scans in these potential regions. The dashed lines shown on the cathodic polarization curves of Fig. 2 are lines of slope $2.303(2RT/F)$, which corresponds to the classical value of the slope (rate of change of electrode potential per decade of current density) of cathodic polarization curves for the hydrogen-evolution reaction from hydrogen ions onto iron.

Fig. 2. Polarization of A212B carbon steel in deaerated 4 M NaCl, pH = 5.

The slope of the anodic polarization curve at 25°C (cf. curve A in Fig. 2) is $2.303(RT/F)$, for the rate of change of electrode potential per decade of current density, which corresponds to non-steady-state conditions observed by others⁴ in the vicinity of room temperature. However, the slopes of the anodic polarization curves at the higher temperatures (cf. curves B, C, and D in Fig. 2) are all equal to $2.303(2RT/3F)$, which corresponds to the dissolution mechanism advanced by Bockris⁵⁻⁷ and by Kelly.⁸ Perhaps the most singular feature of the data in Fig. 2 is the observation that the specific rate of the anodic iron-dissolution reaction actually decreases as the temperature increases from 150° to 200°C. One possible interpretation of this finding may be based upon the fact that hydrogen ion activity (and concentration) in concentrated chloride solutions is known to increase substantially with increasing temperature.⁹ For example, the apparent ionization quotient of water in 4 M NaCl at 200°C is approximately 2.8×10^{-11} , compared with approximately 8×10^{-15} in the same solution at 25°C. Adsorbed "hydroxy" species have been postulated as reaction intermediates or catalysts by a number of workers⁴ to explain the values of slopes of polarization curves, pH-dependencies of corrosion potentials and corrosion rates, and other observable quantities in the iron corrosion system. Although no absolute means exists for comparing the hydrogen ion activity in 4 M NaCl at 200°C with that at 150°C (or at lower temperatures), it is entirely likely that the increased acidity at 200°C could reduce the surface concentration of adsorbed "hydroxy" reaction intermediates so that the rate of the overall corrosion reaction decreases with increasing temperature in spite of the "normal" tendency of all "simple" activation-controlled reactions to increase in rate with increasing temperature. It should be noted that the anodic iron-dissolution reaction itself is under pure "activation" rate control and is not affected by stirring in the region of electrode potentials examined in this work. Alternatively, it is possible that enhanced adsorption of chloride ions at elevated temperatures may also displace adsorbed reaction intermediates in the iron-dissolution reaction. We have no way of evaluating the separate contributions of increase in the thermal energy of the environment, increase in the hydrogen ion activity, and possible alteration in adsorption of chloride ions on the overall kinetics of the partial

processes in the iron corrosion system. This kind of ambiguity about the origin of thermal effects on reaction rates, of course, is present to a greater or lesser extent in all electrochemical systems.

INFLUENCE OF SWEEP RATE AND DIRECTION ON POTENTIODYNAMIC POLARIZATION CURVES: APPLICATION TO ESTIMATION OF CORROSION RATES

The polarization curves shown in Fig. 2 were measured by the potentiodynamic method, using a constant sweep rate for electrode potential of 0.1 mV/sec. We have found that use of such a slow sweep rate is essential in the iron system, especially at lower temperatures, to ensure that kinetic effects due to such factors as slow attainment of steady-state concentrations of adsorbed reaction intermediates or excessive current due to charging of the double layer or readjustment in interfacial pseudocapacity do not distort the measured polarization curves. As noted above, our most self-consistent polarization curves were obtained by first allowing the steel electrode to stabilize at its spontaneous corrosion potential in the complete absence of applied current, and then polarizing either anodically or cathodically at the rate of 0.1 mV/sec. This procedure ensures that the measured polarization curves correspond to conditions which exist at the spontaneous corrosion potential. In general, considerable "hysteresis" is observed in the iron (or carbon steel) system after polarization of the electrode to potentials which are very far removed (more than a few tens of millivolts) from the open-circuit potential. Thus, reversal of the potential sweep at potentials far removed from the spontaneous corrosion potential, even at a low sweep rate, may not produce a polarization curve which satisfactorily retraces the original back to the open-circuit potential. As indicated above, this is particularly true at temperatures below approximately 100°C.

In addition to measuring anodic and cathodic polarization curves, it was desirable to measure the "polarization resistance," or the tangent to the (electrode potential)-(applied current) characteristic, evaluated at zero applied current. In simple electrochemical systems under steady-state

conditions, this slope or polarization resistance is inversely related to the spontaneous corrosion rate, and its measurement is therefore a convenient means for monitoring the corrosion rate with minimal disturbance of the system. It is especially convenient if a potentiodynamic method, perhaps involving alternate anodic and cathodic potential sweeps (i.e., a triangular potential sweep) can be used. However, the applicability of this method must be demonstrated in each corrosion system to which it is applied.

We have carried out a large number of measurements of this type on carbon steel in 4 M NaCl at pH = 5 and at various temperatures as a function of sweep rate and amplitude of the potential excursion with respect to the open-circuit or spontaneous corrosion potential. Again we found that it is necessary, for best results, to use a very low sweep rate (on the order of 0.1 mV/sec) and to limit the amplitude of the potential sweep to no more than 10 or 20 mV on each side of the spontaneous corrosion potential of the system. Under these conditions it is possible to obtain essentially the same (electrode potential)-(applied current) characteristic, and thus the same polarization resistance, regardless of the sweep direction, in the present system.

The claim has been made, especially in literature provided or cited by purveyors of equipment for application of triangular potential sweeps to corrosion or other electrochemical systems and recording of the resulting (electrode potential)-(applied current) characteristics, that it is possible to average the applied current observed during anodic and cathodic sweeps and thus obtain the "true" polarization curve of the system, from which the polarization resistance and thus the corrosion rate may presumably be computed. The method is supposed to be independent of the sweep rate used in the measurement. In our experience, this can only be approximately true for the simplest electrochemical systems; it is certainly not generally true for the iron system.

The assumptions which underlie the proposed method are easy to see from the following considerations. If $i_T(+)$ and $i_T(-)$ are the total applied current densities observed during anodic and cathodic sweeps, respectively, we may assume that these current densities are composed of

Faradaic and non-Faradaic components. Thus, we have

$$i_T(\uparrow) = i_F(\uparrow) + i_N(\uparrow) \quad (1)$$

and
$$i_T(\downarrow) = i_F(\downarrow) + i_N(\downarrow), \quad (2)$$

where $i_F(\uparrow)$ and $i_F(\downarrow)$ are the Faradaic current densities for anodic and cathodic sweeps and $i_N(\uparrow)$ and $i_N(\downarrow)$ are the corresponding non-Faradaic current densities. It is desired to subtract the non-Faradaic contribution to the total observed applied current density to yield the Faradaic current density, which is simply the net current density of the interfacial reactions with no contributions from double layer charging or other capacity-like currents (e.g., pseudocapacity current due to alteration in the surface concentrations of adsorbed ions and/or reaction intermediates). For the method of average currents to be valid, it is necessary first of all that

$$i_F(\uparrow) = i_F(\downarrow) = i_F, \quad (3)$$

so that the net Faradaic current density depends only upon the electrode potential, $E(t)$, where t is time, and not upon the rate or direction of the sweep or upon the prior history of the electrode. In other words, the net Faradaic current density must adjust very rapidly to the value of the electrode potential. Furthermore, it is assumed that the non-Faradaic current density may be expressed by

$$i_N(\uparrow) = C \cdot E'(\uparrow) = C \left| \frac{dE(t)}{dt} \right| \quad (4)$$

$$i_N(\downarrow) = C \cdot E'(\downarrow) = -C \left| \frac{dE(t)}{dt} \right|, \quad (5)$$

so that the total differential capacity, C , also depends only upon the potential, $E(t)$, and is independent of the direction of the sweep or of the prior history of the electrode. In Eqs. (4) and (5), $E'(\uparrow)$ and $E'(\downarrow)$ refer to the time rate of change of electrode potential during anodic and cathodic sweeps, respectively, and $|dE(t)/dt|$ is the absolute value of the potential sweep rate. Under these assumptions, insertion of Eqs. (3), (4), and (5) into Eqs. (1) and (2) and addition lead to the simple expression

$$i_F = \frac{i_T(\uparrow) + i_T(\downarrow)}{2}. \quad (6)$$

In our experience with the iron system Eq. (6) is limited to use with triangular potential sweeps of both small amplitude and very low sweep rate because the assumptions which underlie its use are not even approximately valid otherwise.

Similar considerations apply to the measurement of polarization resistance by the triangular potential sweep method. For example, the net Faradaic current density of a "simple" corrosion system might be expressed by

$$i_F = i_F(t) = i_0 \left\{ \exp \left[+ \frac{\beta_a F}{RT} [E(t) - E_0] \right] - \exp \left[- \frac{\beta_c F}{RT} [E(t) - E_0] \right] \right\}, \quad (7)$$

where i_0 and E_0 are the spontaneous corrosion current density and corrosion potential, respectively; $E(t)$ is the electrode potential at time t , β_a and β_c are the transfer coefficients of the anodic and cathodic partial processes, and RT/F is the thermal volt equivalent. An expression like Eq. (7) could be used, for example, to describe the portions of the polarization curves in Fig. 2 which are near the corrosion potentials. The total current density of the system is given by

$$i_T(t) = i_F(t) + C \frac{dE(t)}{dt}, \quad (8)$$

which is analogous to Eqs. (1) and (2), where $i_F(t)$ is given by Eq. (7). Differentiation of Eq. (8) with respect to time and rearrangement, with the added assumption that C does not change very rapidly with E , lead to Eq. (9)

$$\frac{dE(t)}{di(t)} = \frac{dE(t)/dt}{di(t)/dt} = \frac{RT}{i_0 F} \left/ \left\{ \beta_a \exp \left[+ \frac{\beta_a F}{RT} [E(t) - E_0] \right] + \beta_c \exp \left[- \frac{\beta_c F}{RT} [E(t) - E_0] \right] \right\} \right. \quad (9)$$

for the polarization resistance. In those situations where the sweep rate is so low that the observed data are essentially the same as those pertaining to the steady state, the polarization resistance evaluated at $i_T(t_0) = 0$ corresponds closely to the condition $E(t_0) \approx E_0$, where t_0 is the time during the potential sweep at which the total current crosses zero. In this case, we have also, $i_T(t_0) \approx i_F(t_0) = 0$. Consequently, the corrosion current density may be estimated from

$$i_o = \frac{RT}{F} \frac{(1)}{(\beta_a + \beta_c)} \left/ \frac{dE}{dt} \right|_{i_T = i_F = 0}, \quad (10)$$

which is the now-classical expression relating corrosion rate and polarization resistance when the net Faradaic current density is described by the simple form of Eq. (7).

However, when non-Faradaic currents cannot be neglected it is necessary to determine $E(t_o)$ from the condition (cf. Eq. (8))

$$i_T(t_o) = i_o \left\{ \exp \left[+ \frac{\beta_a F}{RT} [E(t_o) - E_o] \right] - \exp \left[- \frac{\beta_c F}{RT} [E(t_o) - E_o] \right] \right\} + C \cdot E' = 0, \quad (11)$$

where $E' = E'(+)$ or $+|dE(t)/dt|$ during anodic sweeps and $E' = E'(+)$ or $-|dE(t)/dt|$ during cathodic sweeps. Inspection of Eq. (11) shows that when $E' > 0$, during anodic sweeps, $E(t_o) < E_o$, and the "apparent" open-circuit potential is less noble than the "real" corrosion potential which would be observed in the absence of polarization. Correspondingly, when $E' < 0$, as during cathodic sweeps, $E(t_o) > E_o$, and the "apparent" open-circuit potential is more noble than the spontaneous corrosion potential. In principle, solutions for $E(t_o)$ from Eq. (11) for various sweep rates, when inserted into Eq. (9) (evaluated at t_o), lead to values of the "apparent" polarization resistance, which may be greater than or less than the "real" polarization resistance, depending upon the magnitude and sign of E' , etc.

In general the analytical solution of Eq. (11) for $[E(t_o) - E_o]$ in terms of conventionally defined functions may only be carried out for certain values of β_a and β_c (e.g., $\beta_a = \beta_c = 1/2$). However, an approximate solution is possible when sweep rate and amplitude are small enough so that $E(t_o)$ is near to E_o . In that case expansion of exponentials in Eq. (11) to first-order terms leads to the relation

$$\lim_{E(t_o) \rightarrow E_o} [E(t_o) - E_o] = - \frac{RT}{(\beta_a + \beta_c)F} \cdot \frac{C E'}{i_o}. \quad (12)$$

Equation (12) shows that, as expected, $E(t_o)$ will be close to E_o when capacity and sweep rate are low and when the corrosion current density is large. Correspondingly, under the same condition, expansion of

exponentials in Eq. (9) and use of Eq. (12) lead to Eq. (13) for the apparent polarization resistance.

$$\lim_{E(t_0) \rightarrow E_0} \left. \frac{dE(t)}{di(t)} \right|_{t=t_0} = \frac{RT}{i_0(\beta_a + \beta_c)F} \left/ \left\{ 1 - \frac{(\beta_a - \beta_c) C E'}{(\beta_a + \beta_c) i_0} \right\} \right. \quad (13)$$

Since the "true" polarization resistance is related to the corrosion rate by Eq. (10), it follows that the "apparent" corrosion rate is given by

$$i_{o,app} = \frac{RT}{F} \frac{1}{(\beta_a + \beta_c)} \left/ \left. \frac{dE(t)}{di(t)} \right|_{i_T(t_0) = 0} \right. = i_0 \left\{ 1 - \frac{(\beta_a - \beta_c) C E'}{(\beta_a + \beta_c) i_0} \right\} \quad (14)$$

Consequently, under these rather restrictive conditions it should be possible to evaluate the "true" corrosion rate by averaging the "apparent" corrosion rates estimated from anodic and cathodic portions of the triangular potential sweep according to

$$i_0 = \frac{i_{o,app}(+) + i_{o,app}(-)}{2}, \quad (15)$$

where $i_{o,app}(+)$ and $i_{o,app}(-)$ are the apparent corrosion current densities estimated from anodic and cathodic sweeps, respectively.

As noted above, however, the method of averaging currents from triangular potential sweeps is not generally valid because of kinetic complications encountered in real corrosion systems, for which use of a simple, "steady-state" type of rate expression like Eq. (7) may not be a sufficiently good approximation to the (time-dependent) behavior of the real system. Our results show that application of the method to the iron system, while useful and convenient, should be carried out with caution, and the limitations of the potential sweep method should be recognized in the interpretation of the data.

VARIATION OF CORROSION RATE OF CARBON STEEL
IN 4 M NaCl, pH = 5, WITH TEMPERATURE

Extrapolation of polarization curves such as those shown in Fig. 2 to the spontaneous corrosion potential allows an estimate to be made of the spontaneous corrosion current density in the absence of externally applied current. In addition, one may estimate the corrosion current density by measurement of the polarization resistance under suitable conditions, as discussed above (e.g., by judicious use of Eq. (10)). We have made measurements of both types on type A212B carbon steel in 4 M NaCl solution at temperatures between 25° and 200°C, and the results are shown in Fig. 3. Within the limitations of our estimates, which were based upon both measurements of polarization resistance and extrapolation of polarization curves (Tafel lines), the corrosion rate varies in the expected manner, according to the Arrhenius-type plot of Fig. 3. The spontaneous corrosion rate under these conditions exhibits an apparent activation energy of $\Delta H^{0\ddagger} \sim 7.7$ kcal/mole. The apparent activation energy depends upon the activation energies of the individual anodic and cathodic partial processes in the iron corrosion system in a complex manner, which probably also involves changes in the surface concentrations of reaction intermediates with temperature as well as the usual thermal effects on reaction rates. Nevertheless, the magnitude of the corrosion rates at the higher temperatures is of some interest, since these rates represent what can be expected for corrosion of carbon steel in strong brines under deaerated conditions in the absence of significant amounts of oxidizable or reducible substances. As noted below, we also plan to obtain complementary sets of data at pH = 7, 4, and 3 over the same temperature range.

INFLUENCE OF CHLORIDE ION CONCENTRATION ON
POLARIZATION OF IRON AT 25°C, pH = 5

In addition to the work carried out in the refreshed, stirred titanium autoclave system, measurements are continuing in a conventional Pyrex electrochemical cell on the effect of pH and chloride ion concentration on the corrosion of iron and carbon steel in NaCl solutions.

Fig. 3. Corrosion rate of A212B carbon steel in 4 M NaCl, pH = 5, as a function of temperature.

Some anodic polarization curves obtained on iron electrodes at 25°C , $\text{pH} = 5$, as a function of chloride ion concentration are shown in Fig. 4. These have been corrected for the IR drop between the tip of the reference electrode capillary and the electrode surface; this IR drop, of course, is more significant in the solutions of lower salt content. The results of Fig. 4 show that very little effect occurs as the NaCl concentration changes from 0.1 to 0.5 M , but as the concentration increases to 2 M , and then to 4 M , the rate of the iron-dissolution reaction decreases, and the chloride ion acts as an inhibitor. The inhibiting effect of halide ions on the corrosion of iron has been recognized for many years,¹⁰⁻¹² although most studies have been carried out in strongly acidic solutions. The inhibiting effect increases with halide ion concentration and, as might have been expected, is most pronounced for iodide, intermediate for bromide, and least for chloride. It is very likely that adsorption of chloride ions onto the electrode surface displaces hydroxy surface intermediates which are involved in the mechanism of the iron-dissolution reaction, but these data are not extensive enough to allow determination of reaction mechanisms.

The anodic polarization curves (Tafel lines) in Fig. 4 may be extrapolated to the spontaneous corrosion potentials in the respective solutions to give estimates of the spontaneous corrosion rates as a function of NaCl concentration. The extrapolations are indicated by the dashed lines in Fig. 4. We note from these results that increasing chloride ion concentration also decreases the rate of the hydrogen-evolution reaction. The corrosion rates are plotted as a function of the NaCl concentration in Fig. 5. The dashed line drawn through the data points at 2 M and 4 M NaCl has a slope of -2. This is consistent with the hypothesis that the rates of both the iron-dissolution and the hydrogen-evolution reactions vary approximately inversely with the square of the chloride ion concentration in this region. However, other data will be required as a function of pH and temperature before this conclusion could be adequately substantiated.

Fig. 4. Effect of chloride ion concentration on polarization of iron, $T = 25^\circ\text{C}$, $\text{pH} = 5.0$.

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Fig. 5. Effect of chloride ion concentration on corrosion rate of iron, $T = 25^{\circ}\text{C}$, $\text{pH} = 5.0$.

RESEARCH PLANS FOR THE FORTHCOMING PERIOD

As indicated above, we plan to extend our studies in the refreshed, stirred titanium autoclave system to different values of (room-temperature) pH, probably to include pH = 3, 4, and 7 with the NaCl concentration maintained at 4 M over the temperature range from 25° to 200°C. Later, we expect to carry out a few runs at different NaCl concentrations to verify and extend the results of the studies below 100°C in the conventional Pyrex electrochemical cell.

Some earlier measurements¹ considered the variation with temperature of the pitting potential of type 304 stainless steel in a deaerated simple synthetic brine from room temperature up to approximately 85°C. We plan to extend these measurements to 200°C since the relationship of the pitting potentials of austenitic stainless steels to their spontaneous corrosion potentials has not been investigated in deaerated strong brines such as those encountered under geothermal conditions.

In addition to the experimental work, as time permits, we plan to carry out a survey of prior work on electrochemical aspects of the corrosion of iron and carbon steel in chloride solutions. This material should be useful to ourselves and to others as a basis for comparison and interpretation.

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