DEVELOPMENT OF THE HIGH-TEMPERATURE
REDOX ELECTRODE

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ANALYSIS OF HIGH-PRESSURE, HIGH-TEMPERATURE
GEOTHERMAL FLUIDS

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SUMMARY AND CONCLUSIONS

The oxidation-reduction (known as redox) electrode was studied in a pH range corresponding to that found in a CO_2 -silicate buffered system at temperatures ranging from 100 to 250°C. Oxidizing conditions were created by injecting oxygen; the greatest reducing conditions, by using hydrogen. The sulfur system (H_2S , HS^- , S^2) was not examined at this time, but future work will include this system since it is an important component of the geothermal brine.

Both a platinized platinum (Pt-Pt) and a bare platinum (Pt-foil) electrode respond to the redox environment. The response does not appear to indicate thermodynamic equilibrium with the chemical environment; instead a "mixed potential" response is indicated. The difference in potential between a strong oxidizing environment (0.4-ppm O_2) and a strong reducing environment (0.5-atm H_2) is typically >1 volt at all temperatures. The magnitude of this response makes the platinum electrode a suitable sensor for continuous monitoring of the geothermal environment for oxygen intrusions. The platinized platinum redox electrode is superior to the bare platinum electrode.

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INTRODUCTION

Any system used to control scaling or corrosion in a geothermal power plant must include provisions for monitoring and verifying the fluid chemistry. Current methods, which are not entirely satisfactory, include grab sampling for later analysis. A better method would involve inserting in-line or down-hole chemical sensor probes. Using such sensors, continuous on-line data could be produced without the problems associated with sampling, such as infrequency, contamination, or chemistry changes caused by cooling. In-line probes for high-temperature geothermal environments are beyond the current commercial state of the art; however, technological advances have occurred in recent years, largely because of the need for such probes in high-pressure nuclear power plants.

This program, Development of the High-Temperature Redox Electrode, attempts the difficult task of adapting electrochemical devices for geothermal applications. The program is being performed by the Pacific Northwest Laboratory (PNL)^(a) for the Department of Energy (DOE).

The redox electrode (generally gold or platinum) has been used for years to measure the general "oxidativeness" of the geochemical and biological environment at close-to-ambient temperatures.^(1,2) The technique has been used to determine the amount of dissolved oxygen and to imply what chemical species are in thermodynamic equilibrium. Unfortunately, measurement at ambient conditions has been difficult to apply because:

- Electrochemical reactions may reach equilibrium very slowly.
- Electrode surfaces are easily contaminated.
- Reaction rates at equilibrium (exchange currents) may be low.

In addition, poor reproducibility of results has plagued experimenters.^(3,4)

Ideally, all species in a solution should be in equilibrium. When a bare metal electrode is placed into this solution, it should act as an electron source/sink for the various oxidized/reduced species so that the equilibrium electron energies of the ions determine the energy level of the electrons in

(a) Operated for DOE by Battelle Memorial Institute.

the electrode. Thermodynamically, the potential of this electrode would indicate the type and concentrations of redox species that could be in solution. In reality, however, all species are not in equilibrium and the bare metal electrode may not be inert (as a result of corrosion); therefore, it may react with some of the species in solution or may even assist in achieving equilibrium between species. Consequently, a bare electrode may not respond in a Nernstian (reversible or thermodynamic) manner to a changing redox environment.

One particularly well-studied system⁽⁵⁾ is the oxygen electrode on platinum (at 25°C) in acid solution. The theoretical potential (ϵ) for this system is 1.23 V; however, 1.06 V is generally observed. The potential dependence upon oxygen partial pressure is also not correct at low oxygen partial pressures for this equilibrium:

This indicates that oxygen is not in equilibrium with water on the platinum electrode. Exchange current densities (reaction rate at equilibrium) are in the range of 10^{-7} A/cm², which is very low for a single redox couple to be able to define the potential.⁽⁴⁾ There is good evidence that a mixed potential controls the potential in the $\text{O}_2/\text{H}_2\text{O}$ redox couple that consists of the reaction defined in Equations (1) and (2).

where Pt - O represents an adsorbed oxygen atom on the platinum surface. A mixed potential controlling the cell potential indicates that the process is no longer at equilibrium but is kinetically controlled by two dissimilar reactions so that the total anodic current equals the total cathodic current (absolute value) at the steady-state potential.

In general, the steady-state mixed potential⁽⁶⁾ is always between the equilibrium potentials for the anodic and cathodic reactions and lies closest to the equilibrium potential of the faster reaction. There is a strong indication that in the best case the platinum electrode can respond to the redox

environment in a Nernstian manner and that in the worst case the electrode will only approximately respond to the redox environment because a mixed potential is controlling the potential or the exchange currents are extremely low compared to other adsorptive phenomena.

A prototypical example⁽⁷⁾ of a redox system in thermodynamic equilibrium is the ferric/ferrous couple in 1-molar (M) H_2SO_4 on a platinum electrode. It has been verified that the redox reaction has the following stoichiometry:

Exchange currents (which have a concentration dependence) are in the range of 10^{-3} to 10^{-2} A/cm². The equilibrium potential has a Nernstian response based on the ionic activities:

$$\varepsilon = \varepsilon^\circ - \frac{RT}{F} \ln \frac{a_{\text{Fe}^{+2}}}{a_{\text{Fe}^{+3}}} \quad (4)$$

This equilibrium behavior is caused by the large exchange current density, which "swamps out" the contribution of other electrochemical reactions at the platinum surface. There are a number of other "true equilibrium" processes that take place on a platinum electrode; and, in general, they are all characterized by a large exchange current.

There is great interest in using the redox electrode for chemical monitoring in high-temperature geothermal environments. It is expected that at elevated temperatures the electrochemical reactions at the electrode would reach equilibrium faster; therefore, the measurement would more likely indicate the general oxidativeness of the chemical environment. The response to the entry of oxygen is especially important since a number of studies have revealed that this can result in catastrophic corrosion rates.^(8,9)

EXPERIMENTAL PROCEDURES

The experimental setup that was used is shown in Figure 1. Since oxygen was present in the synthetic brines, all parts from the pump outlet to the autoclave outlet were made of titanium because it is generally inert to this environment. A platinized platinum (Pt-Pt) electrode (2.6 cm^2) and a bare platinum foil (Pt-foil) electrode (2.8 cm^2) were used.

Before each experiment, the Pt-Pt electrode was replatinized for 2 minutes in a 2% solution of platinum chloride in 2 normal (N) hydrochloric acid;⁽¹⁰⁾ and the Pt-foil electrode was treated with boiling, concentrated nitric acid for 2 minutes. The electrodes were then mounted in titanium Conax[®] fittings. An external reference electrode was used for convenience and is discussed in other publications.^(11,12)

During each experiment, potentials were measured on the standard hydrogen electrode (SHE) scale. The autoclave was continuously refreshed at rates of 3 to 20 ml/min, and all experiments were carried out at one solution composition (see Table 1) at temperatures ranging from 100 to 250°C. Due to the difficulty of the experiments, there was time to test only one brine composition. The pH of this system was in the range of many geothermal resources whose pH is controlled by the CO_2 -silicate system.

TABLE 1. Solution Composition

NaCl	0.43 molal ($\sim 2.5\%$)
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	7.5×10^{-3} molal (450 ppm SiO_2)
Na_2SO_4	7.3×10^{-3} molal (400 ppm SO_4^{2-})
$\text{CO}_2 \approx 1 \text{ atm}$	
pH (25°C) = 5.7	

[®] Conax Corporation, Buffalo, New York.

FIGURE 1. Experimental Setup

Dissolved oxygen content was controlled (0 to 1 ppm) by blending CO₂ and air and sparging this mixture through the solution at ambient conditions. It could be monitored at the autoclave inlet and outlet by the Winkler method; however, content was usually determined with Chemetrics Dissolved Oxygen Test Kits®. Above 100 ppb oxygen could be measured to within 50 ppb using these kits, and below 100 ppb it could be measured to within 5 ppb.

Two general types of experiments were carried out.

- The dissolved oxygen content was held constant and the temperature of the autoclave was varied.
- The autoclave temperature was held constant while the dissolved oxygen content was varied.

The experiments usually ran for 3 to 5 days and often required 18-24 hours to obtain each data point to be assured of a steady-state potential. The continual problem of oxygen consumption caused by corrosion processes in the autoclave made it difficult to keep a constant dissolved oxygen content inside the autoclave while the temperature was varied.

Electrode exchange currents were measured at various temperatures and dissolved oxygen contents by perturbing the steady-state potential using a battery-rheostat combination. Potentials and currents were measured using a high-input impedance digital voltmeter. A potentiostat could not be used because of the poor resolution in measuring currents in the low microampere range. At the end of each experiment, cyclic voltammetry (CV) experiments were carried out at 10 mV/sec at approximately ± 1 -V extremes from the steady-state potential and at 250°C. CV quickly "road maps" the type and number of electrochemical reactions that take place on the electrode surface.

Figure 2 shows some selected experimental and theoretical potential data based upon Biernat and Robins' ⁽¹³⁾ high-temperature thermodynamic calculation. Using the procedure outlined in Appendix A, pH was calculated as a function of temperature for the brine composition shown in Table 1. The theoretical data in Figure 2 were calculated using the calculated pH of the experimental

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FIGURE 2. Selected Theoretical and Experimental Redox Potentials on a Pt-Pt Electrode

conditions. Oxygen concentrations in the range of 0 to 450 ppb were controlled by mixing air with CO_2 . The CO_2 partial pressure varied from 1.0 to 0.8 atm, but CO_2 is one of the species controlling pH. However, calculations (Appendix A) indicated that since this effect would amount to only 0.1-pH unit, it could be ignored.

Another problem arose concerning the partial pressure of the gas at various temperatures, which must be known to make calculations of the potential. The H_2 or O_2 partial pressure is controlled at ambient conditions; and by knowing Henry's Law⁽¹⁴⁾ constants at higher temperatures, the partial pressures can be calculated at higher temperatures.

Examination of Figure 2 reveals two important points.

- There is a large difference in potential between an oxidizing and a reducing environment. Consequently, even a partial, nonthermodynamic response may be large enough to be useful in describing the redox behavior of the solution.
- The potential of a thermodynamic oxygen electrode is not very sensitive to changes in oxygen concentration.

Experimental potentials of 0.4- and 0.1-ppm oxygen are less than thermodynamic values and are strongly related to changes in oxygen concentration. This behavior indicates a nonthermodynamic response of the Pt-Pt electrode; the steady-state potential is probably caused by a mixed potential response, which will result in a superior sensitivity to oxygen that will benefit the response of the electrodes when used in a process control manner.

The Pt-Pt electrode responds to the increasing reducing environment of the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system, but agreement with thermodynamic calculations is not good. Agreement with the greatest reducing environment-- $\text{H}_2/\text{H}_2\text{O}$ --is quite good and may be indicative of a true thermodynamic response since the exchange current density of the $\text{H}_2/\text{H}_2\text{O}$ system is very large at ambient temperatures.⁽⁷⁾

Ideally, for an electrode to have a thermodynamic response, all redox couples in solution must be in equilibrium. If they are not all in equilibrium or if the electrode is corroding, a mixed potential response may control the

steady-state potential. If the exchange currents for the redox equilibria are much larger than for the redox or corrosion reactions not in equilibrium, the electrode could still have a thermodynamic response.

Figures 3 and 4 show the potential of the Pt-Pt and Pt-foil electrodes, respectively, as a function of oxygen concentration. Generally, 18 to 24 hours were required to obtain each data point. During the first part of the experiment either oxygen concentration or temperature would be changed, and then hours of observation were required to verify that the potential was steady.

The absolute speed at which the electrodes responded to sudden chemistry or temperature changes was impossible to determine because of the low flow rate of solution in the autoclave or the slow temperature response of the autoclave.

FIGURE 3. Experimental Redox Potentials of a Pt-Pt Electrode

FIGURE 4. Experimental Redox Potentials of a Pt-Foil Electrode

At a flow rate of 10 ml/min, it takes 100 minutes to change the solution in the autoclave once, and several changes are needed before the autoclave solution reaches the steady concentration level.

At all temperatures, the Pt-Pt electrode reached a steady potential faster than the Pt-foil electrode and would be the recommended electrode for use as a process control instrument. The higher the temperature, the faster a steady potential was reached. For example, at 100°C it could easily require

15 hours for the Pt-Pt electrode to reach steady state; while at 250°C, it could require less than 4 hours after an oxygen concentration change. It is probable that at temperatures above 100°C the electrode will respond within minutes to a radical change in solution oxidation state and, consequently, could serve as a process control device.

As indicated in Figure 3, the Pt-Pt electrode is the more sensitive to a changing oxygen concentration. The scatter in the data, however, would indicate that the potential response is probably not a good indicator of the absolute oxygen concentration. Widely differing chemistries were not investigated in this study, but the potential response will probably also be determined by other water chemistry variables. The conclusion from this study is that the Pt-Pt electrode will be of value by its *relative* response to oxygen and that it will serve as a rapid diagnostic instrument for disastrous oxygen intrusions.

To gain further insight into the potential response, an attempt was made to determine the exchange current (I°) at each temperature as a function of oxygen concentration (see Tables 2 and 3). A battery and a large value resistance box were used to polarize the electrodes at a constant current. At least three data points were needed to calculate the anodic and cathodic Tafel slopes and the exchange current. The procedure is outlined in more detail in Appendix B.

In general, the exchange currents are very low (a few microamps) for both platinum electrodes. According to Jones and Greene,⁽¹⁵⁾ the lower the exchange currents, the longer it takes a perturbing process (electrode polarization) to reach a steady state. Because of experimental constraints only 30 to 45 minutes could be allotted to acquire each data point; in most cases it was clear that this data point was not taken under steady-state conditions (that is, the potential was still changing with time). However, the theoretical expressions given in Appendix B require a steady-state value to calculate the values given in Tables 2 and 3. This explains why the computer program was unable to converge to a solution for the exchange current and Tafel slopes for most of the experiments. It also implies that the calculated Tafel slopes and exchange

TABLE 2. Pt-Pt Kinetic Data

	O ₂ , ppb	Anodic Tafel, mV	α	Cathodic Tafel, mV	β	I°, μA	$\Delta I/\Delta E$, μA/mV
250°C	400	(a)		(a)			0.14
	200	(a)		(a)			0.14
	0	(a)		(a)			0.66
200°C	400	173	0.54	92	1.02	6.0	0.23
	150	(a)		(a)			0.19
	10	(a)		(a)			0.17
150°C	400	(a)		(a)			0.21
	200	(a)		(a)			0.15
	15	---		---			---
100°C	450	(a)		(a)			0.077
	60	(a)		(a)			0.048

(a) Indicates that the current-potential data did not permit convergence to a solution.

TABLE 3. Pt-Foil Kinetic Data

	O ₂ , ppb	Anodic Tafel, mV	α	Cathodic Tafel, mV	β	I°, μA	$\Delta I/\Delta E$, μA/mV
250°C	400	554	0.19	136	0.76	0.98	0.022
	200	(a)		(a)			0.023
	0	(a)		(a)			0.035
200°C	400	597	0.16	125	0.75	0.68	0.015
	150	339	0.28	103	0.91	0.50	0.011
	10	(a)		(a)			0.015
150°C	400	56	1.50	247	0.34	0.44	0.022
	200	(a)		(a)			0.005
	15	(a)		(a)			0.005
100°C	450	(a)		(a)			0.0040
	60	(a)		(a)			0.0024

(a) Indicates that the current-potential data did not permit convergence to a solution.

currents are not reliable for those occasions when the data did permit convergence to a solution. However, the program does calculate an average $\Delta I/\Delta E$, which is proportional to the exchange current.

Based on the data in Tables 2 and 3, these general observations can be made:

- The exchange current decreases as the oxygen concentration decreases.
- The exchange current decreases with temperature (assuming the proportional constant between I° and $\Delta I/\Delta E$ is independent of temperature).
- The exchange current is approximately a factor of 10 greater on the Pt-Pt electrode than on the Pt-foil electrode.

These observations are compatible with both a mixed potential and an equilibrium process controlling the potential. Moreover, in the few cases where an exchange current could actually be calculated, the value was generally too small to assume safely that it was the only major reaction controlling the potential. The general kinetic equation for both equilibrium and mixed potential systems is:

$$\Delta I = I^\circ \left[\exp \left(\frac{RT}{F} (\alpha) \Delta E \right) - \exp \left(- \frac{(\beta)RT}{F} \Delta E \right) \right] \quad (5)$$

where

- ΔI = measured current
- ΔE = polarization from steady state
- R = ideal gas constant
- T = temperature, absolute
- F = Faraday constant
- α, β = transfer coefficients
- I° = exchange current

When $\alpha + \beta = 1$, the process is likely to be at equilibrium; but when $\alpha + \beta \neq 1$, the process is under mixed potential control. Calculated values for α and β are shown in Table 3. At 250 and 200°C the sum is close enough to 1 to possibly indicate an equilibrium process, but at 150°C a mixed potential process is indicated. The only data for Pt-Pt is at 200°C, and it indicates a mixed potential process. There is, however, an inconsistency: The exchange current

of the Pt-Pt electrode is higher than the Pt-foil electrode and *should* be closer to a true equilibrium (which the Pt-foil data indicates). Unfortunately, the quality of data in Tables 2 and 3 will probably not support accurate calculation of exchange currents and Tafel slopes and can be used only in a relative manner. This type of study would be very important in determining the mechanism by which platinum electrodes respond to the redox environment; however, considerably more experiment time will be required because these electrodes approach steady state so slowly.

The electrochemically active area of the Pt-Pt and Pt-foil electrodes was determined in one of the last experiments (outlined in Appendix C). The geometric areas of the Pt-Pt and Pt-foil electrodes are 2.6 and 2.8 cm², respectively; but the true electrochemical area is respectively 280 and 10.4 times the geometric area. Thus, the Pt-Pt electrode has an electrochemical area 25 times greater than the Pt-foil electrode (due to the platinum black that is deposited on the surface during electrode preparation). Data provided in the previous section of this document indicated that the Pt-Pt exchange current was approximately 10 times greater than the Pt-foil exchange current due to the greater surface area on the Pt-Pt electrode.

The purpose of the CV experiments (carried out at 250°C) was to quickly determine the number of electrochemical reactions that are taking place on the electrode surface relative to the steady-state potential. Two typical examples are shown in Figures 5 and 6; the experiments were carried out at 300- and 50-ppb O₂, respectively. Data for the Pt-foil electrode is not shown because the currents are much lower than for the Pt-Pt and noise obscured the data. Beginning at steady-state potential the CV experiments scanned in the anodic direction to 1.0 V (versus the steady-state potential), reversed to cathodic -1.0 V, and returned to the steady-state potential. Examination of Figure 5 (300-ppb O₂, E steady_{state} = 0.18-V SHE) indicates oxygen evolution on the forward anodic scan with a reduction peak on the reverse scan at +240 mV (0.42-V SHE) that may be caused by reduction of oxygen. Another reduction peak at -160 mV (0.02-V SHE) may be the reduction of a platinum oxide. Hydrogen evolution is approached as scanning continues in a cathodic direction.

FIGURE 5. Cyclic Voltammetry Scan (10 mV/sec) at Pt-Pt Electrode, 250°C, 300-ppb O₂

During the reverse scan in the anodic direction, two small peaks caused by hydrogen oxidation are observed at -700 mV and -300 mV. Double reduction peaks for hydrogen are observed at ambient conditions as well.⁽⁵⁾

Although Figure 6 (50-ppb O₂, $E_{\text{steady state}} = -0.50\text{-V SHE}$) at first seems to indicate a different behavior, it becomes obvious that the steady-state potential is displaced almost 700 mV in the cathodic direction from that in Figure 5. While scanning in the anodic direction, two peaks are seen before

FIGURE 6. Cyclic Voltammetry Scan (10 mV/sec) at Pt-Pt Electrode, 250°C, 50-ppb O₂

entering a region of slow oxygen evolution. These two peaks are not seen on repeated scans; therefore, they may represent some surface contamination. On the return scan, an oxygen reduction peak is seen at 600 mV (0.1-V SHE), but nothing further is observed until hydrogen evolution is encountered. Hydrogen oxidation is observed at 0 mV (-0.5-V SHE) on the first return scan.

In general, the CV scans reflect the usual oxidation-reduction reactions of hydrogen and oxygen; the exceptions are the small anodic (175-mV) and cathodic (-160-mV) peaks in Figure 5. If a mixed potential reaction is due to platinum corrosion, this additional reaction would be indicated in a CV scan. Unfortunately, thermodynamic data for the platinum system does not exist at ambient temperatures to permit calculation of high-temperature Pourbaix diagrams. Consequently, it is not possible to predict at what potential platinum oxidation would be observed.

The evidence is strongest for a mixed potential mechanism with the platinum electrodes reacting with the redox environment rather than a thermodynamic (equilibrium) response to the oxygen concentration. This is most clearly seen from the potential response data of Figure 2. The experiments to determine the exchange current and Tafel slopes do not point clearly to either mechanism, with the exception that the exchange currents are too small for one equilibrium redox reaction to be the major kinetic control of the potential. CV experiments are also unclear as to whether the platinum is corroding and whether by this mechanism it is giving rise to a mixed potential response. Since the solution environment was very free of contaminants, it seems likely that the potential response to oxygen is due to a corrosion reaction driven by the reduction of oxygen. Estimated exchange currents for the Pt-Pt electrodes are about 1 microamp/cm² (geometric area), which would correspond to a very low corrosion rate of less than 1 mil per year (mpy).^(a) A mixed potential response usually would not permit the estimation of the general nature of the redox environment by simply comparing the measured potential to that predicted from a Pourbaix diagram (which considers reactions at thermodynamic equilibrium). However, the exception to this response occurs when the exchange currents for the redox couples are much larger than those caused by the corrosion of platinum. An electrode with mixed potential response could be a very sensitive indicator of the entry of oxygen, particularly if the corrosion rate is very low. Therefore, the Pt-Pt electrode probably will act as a sensitive indicator of oxygen intrusion into geothermal brines.

(a) 1 mpy would correspond to approximately 50 mg/cm²/year.

FUTURE WORK

Current work has outlined the behavior of the redox electrode (at a specific pH) as a function of oxygen partial pressure and in several different reducing environments without oxygen. However, since geothermal brines are more complex than represented in this study, further work could make the response of the redox electrode more quantitative.

Due to time and funding constraints, the S-H₂O system was not covered in this study. Future work is also necessary to verify the behavior of the redox electrode in solutions containing hydrogen sulfide (H₂S). The redox couple H₂S-SO₄²⁻ should be investigated as should the nonequilibrium case of H₂S-O₂ in which sulfur is undergoing oxidation (this condition has been observed in the field). Another case for study is the redox electrode response to the redox couple Fe⁺²-Fe⁺³, which must exist whenever oxygen reacts with the brine.

These proposed studies will essentially complete the examination of all major redox reactions expected in the brine, and the knowledge gained from the work will assist in interpreting the response of the redox electrode.

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APPENDIX A

HIGH-TEMPERATURE pH CALCULATIONS

HIGH-TEMPERATURE pH CALCULATIONS

Calculation of a high-temperature pH requires the solution of a large number of simultaneous equations and the knowledge of activity coefficients and equilibrium constants at these elevated temperatures. Fortunately, NaCl is the major species that will control the activity coefficient for all other species in this case; and it has been studied in some detail at temperatures up to 300°C.⁽¹⁾ Although high-temperature equilibrium constants are available,⁽²⁾ their accuracy may be doubtful.

In these experiments, the solution was equilibrated at ambient conditions with a controlled partial pressure of CO₂ and air. Generally, CO₂ did not fall below 0.8 atm. This solution was injected into the autoclave at high pressure. The two major species controlling pH in these synthetic brines are CO₂ and silicate. Silicate was added as the meta-silicate (Na₂SiO₃·9H₂O), but unfortunately no high-temperature data exists for this species. Instead, the ortho-silicate species (SiO₄⁴⁻) is considered at elevated temperatures.

Assuming that all meta-silicate is converted to ortho-silicate:

Interestingly, the first and second ionization constants⁽²⁾ for the two silicate species are about the same at ambient temperatures, which indicates that the above assumption is realistic. All the equilibria are shown below:

$$(\text{H}_2\text{CO}_3) = K_0 P \quad (2)$$

$$(\text{H}_2\text{CO}_3)(\text{Soln}) = (\text{H}^+) + (\text{HCO}_3^-) \quad K_1 \quad (3)$$

$$(\text{HCO}_3^-) = (\text{CO}_3^{2-}) + (\text{H}^+) \quad K_2 \quad (4)$$

$$(\text{H}_4\text{SiO}_4) = (\text{H}^+) + (\text{H}_3\text{SiO}_4^-) \quad K_3 \quad (5)$$

$$(H_3SiO_4^-) = (H^+) + (H_2SiO_4^{2-}) \quad K_4 \quad (6)$$

$$(HSO_4^-) = (H^+) + (SO_4^{2-}) \quad K_5 \quad (7)$$

$$\text{Molality} \quad Na_2SO_4 = X = M_{HSO_4^-} + M_{SO_4^{2-}} \quad (8)$$

$$\text{Molality} \quad Na_2H_2SiO_4 = Y = M_{H_2SiO_4^{2-}} + M_{H_3SiO_4^-} + M_{H_4SiO_4} \quad (9)$$

$$M_{Na^+} + M_{H^+} = M_{HCO_3^-} + 2M_{CO_3^{2-}} + M_{H_3SiO_4^-} + 2M_{H_2SiO_4^{2-}} + M_{HSO_4^-} + 2M_{SO_4^{2-}} \quad (10)$$

It is important to note that Equations (3) through (7) require that activities be substituted; while Equations (8) through (10) are in molalities. Appropriate substitutions result in the following equation:

$$2Y = (H^+) = \frac{K_o PK_1}{\gamma_1^2 (H^+)} + \frac{2K_o PK_1 K_2}{\gamma_2 \gamma_1^2 (H^+)^2} + Y \left[\frac{K_3 K_4}{(H^+)^2 \gamma_1^2 \gamma_2 + (H^+) H_3 \gamma_2 + K_3 K_4} \right] \cdot$$

$$\left[\frac{(H^+)^{\gamma_2}}{K_4} + 2 \right] - \frac{X(H^+)^{\gamma_2}}{K_5 + (H^+)^{\gamma_2}} \quad (11)$$

where

(H^+) = hydrogen ion activity

X, Y = sulfate, silicate molalities

γ_1, γ_2 = activity coefficients for monovalent and divalent ions

Equation (11) can be solved as a polynomial using numerical techniques or by using the iterative method used in this report--inserting various values of (H^+) and keeping X constant until the correct Y value is calculated. Table A.1 indicates the activity coefficients for NaCl.⁽¹⁾ The experimental constants and calculated pH values using Equation (11) are shown in Table A.2.

TABLE A.1. Activity Coefficients

T, °C	NaCl $\gamma_{\pm 1}$	NaCl $\gamma_{\pm 2}$
25	0.69	0.23
100	0.66	0.19
150	0.60	0.13
200	0.54	0.085
250	0.45	0.041

TABLE A.2. Equilibrium Constants and Calculated pH Values^(a)
for Experimental Solutions Used in These Tests

	Temperature, °C				
	25 ^(b)	100	150	200	250
K_0	3.47×10^{-2}	3.47×10^{-2}	3.47×10^{-2}	3.47×10^{-2}	3.47×10^{-2}
K_1	4.2×10^{-7}	3.9×10^{-7}	1.95×10^{-7}	7.41×10^{-8}	2.19×10^{-8}
K_2	4.67×10^{-11}	7.24×10^{-11}	4.57×10^{-11}	1.95×10^{-11}	6.31×10^{-12}
K_3	1.58×10^{-10}	1.26×10^{-9}	1.59×10^{-9}	10^{-9}	5.0×10^{-10}
K_4	1.99×10^{-12}	10^{-11}	10^{-11}	10^{-11}	3.2×10^{-12}
K_5	1.12×10^{-2}	10^{-3}	1.82×10^{-4}	3.1×10^{-5}	5.1×10^{-6}
pH at 1-atm CO ₂	5.67	5.69	5.9	6.2	6.6
pH at 0.8-atm CO ₂	5.77	5.78	6.0	6.3	6.7
pH at 0.5-atm CO ₂	5.98	5.98	6.1	6.5	6.9

(a) $X = 7.5 \times 10^{-3}$ Molal
 $X = 7.3 \times 10^{-3}$ Molal.

(b) The success of the calculation can be judged at 25°C since the measured pH at 1-atm CO₂ is 5.68 and the calculated pH is 5.67.

REFERENCES

1. Liu, C., and W. Lindsay. 1972. "Thermodynamics of Sodium Chloride Solutions at High Temperatures." J. Soln. Chem. 1:1.
2. Naumov, G., B. Ryzhenko, and I. Khodakovsky. 1974. "Handbook of Thermodynamic Data." PB-226-722, U.S. Geological Survey (translated edition), Menlo Park, California.

APPENDIX B

CORROSION CALCULATIONS

CORROSION CALCULATIONS

The general equation describing electrochemical kinetics is:

$$I = I_{\text{corr}} \left[\exp\left(\frac{2.3 \Delta\phi}{b_a}\right) - \exp\left(\frac{-2.3 \Delta\phi}{b_c}\right) \right] \quad (1)$$

where

I_{corr} = corrosion current at steady-state potential

$\Delta\phi = \phi - \phi_{\text{corr}}$ = perturbation away from corrosion potential

b_a = anodic Tafel parameter

b_c = cathodic Tafel parameter

There are three unknowns in Equation (1), and a minimum of three data points would be needed to calculate I_{corr} , b_a , and b_c . Equation (1) is in a transcendental form, which prevents a straightforward solution; however, Mansfeld has published a form of the equation that permits the use of linear least squares for numerical solving. Unfortunately, Mansfeld did not publish his computer program; his final equation is shown below:^(a)

$$\ln \left[\frac{W^\circ I_i}{\sinh W^\circ P_i} \right] = \ln A_o + X P_i + \left[\frac{W^\circ P_i}{\tanh W^\circ P_i} - 1 \right] \frac{Z}{W^\circ} \quad (2)$$

where

$$A_o = \frac{1}{2.303 R_p}$$

$$\frac{1}{b_c} = W + X$$

$$\frac{1}{b_c} = W - X$$

(a) Those interested in more detail should consult Reference 1 of this Appendix.

$$P = 2.30 \Delta\phi$$

$$I_{\text{corr}} = \frac{b_a b_c}{2.30(b_a + b_c)R_p}$$

Equation (2) is in a form in which the linear least squares technique can be applied. Various sets of current and potential data are used, along with an initial guess for W° ; and by linear least squares, a value for Z can be calculated. An improved estimate of W is calculated by $W = W^\circ + Z$, and the calculation is repeated until changes in W are very small. I_{corr} , b_a , and b_c can then be calculated easily. The linear least squares computer program (written in FORTRAN) is provided on the following pages.

REFERENCES

1. Mansfeld, F. 1973. "Tafel Slopes and Corrosion Rates from Polarization Resistance Measurements." Corrosion. 29:397.

```

      C   LEAST SQUARES METHOD TO DETERMINE CORROSION RATES
0001     DIMENSION A(20,2),B(3,4),C(3)
0002     WRITE(7,1)
0003 1    FORMAT('0','INSERT NUMBER OF DATA SETS USING FORMAT I3')
0004     READ(5,*)N
0005     WRITE(7,5)
0006 5    FORMAT('0','INSERT DATA IN MICROAMPS AND MILLIVOLTS USING FORMAT
/ 2F8.0/')
0007     READ(5,7) ((A(I,J),J=1,2),I=1,N)
0008 7    FORMAT(2F8.0)
      C   INITIAL VALUES
0009     W=.01
      C   CALCULATE P FROM POTENTIAL DATA
0010     DO 8 I=1,N
0011       A(I,2)=A(I,2)*2.303
0012 8    CONTINUE
      C   CALCULATE SUM PI
0013 9    CONTINUE
0014       B(1,1)=1.*N
0015       SUM=0.0
0016       DO 12 I=1,N
0017 12   SUM=SUM+A(I,2)
0018       B(1,2)=SUM
      C   CALCULATE SUM FI
0019       SUM=0.0
0020       DO 15 I=1,N
0021         WPI=W*A(I,2)
0022         FIW=((WPI/TANH(WPI))-1.)/W
0023         SUM=SUM+FIW
0024 15   CONTINUE
0025       B(1,3)=SUM
      C   CALCULATE SUM YI
0026       SUM=0.0
0027       DO 18 I=1,N
0028         WPI=W*A(I,2)
0029         YIW=ALOG(W*A(I,1)/((EXP(WPI)-EXP(-WPI))/2.))
0030         SUM=SUM+YIW
0031 18   CONTINUE
0032       B(1,4)=SUM
      C   CALCULATE COEFFICIENT B(2,1)
0033       B(2,1)=B(1,2)
      C   CALCULATE SUM PI**2
0034       SUM=0.0
0035       DO 21 I=1,N

```

```

0036 21 SUM=SUM+A(I,2)**2
0037 B(2,2)=SUM
C CALCULATE SUM FI*PI
0038 SUM=0.0
0039 DO 24 I=1,N
0040 WPI=W*A(I,2)
0041 FIW=((WPI/TANH(WPI))-1.)/W
0042 24 SUM=SUM+FIW*A(I,2)
0043 B(2,3)=SUM
C CALCULATE SUM YI*PI
0044 SUM=0.0
0045 DO 27 I=1,N
0046 WPI=W*A(I,2)
0047 YIW=ALOG(W*A(I,1)/((EXP(WPI)-EXP(-WPI))/2.))
0048 27 SUM=SUM+YIW*A(I,2)
0049 B(2,4)=SUM
C CALCULATE COEFFICIENT B(3,1)
0050 B(3,1)=B(1,3)
C CALCULATE COEFFICIENT B(3,2)
0051 B(3,2)=B(2,3)
C CALCULATE SUM FI**2
0052 SUM=0.0
0053 DO 30 I=1,N
0054 WPI=W*A(I,2)
0055 FIW=((WPI/TANH(WPI))-1.)/W
0056 30 SUM=SUM+FIW**2
0057 B(3,3)=SUM
C CALCULATE SUM YI*FI
0058 SUM=0.0
0059 DO 33 I=1,N
0060 WPI=W*A(I,2)
0061 FIW=((WPI/TANH(WPI))-1.)/W
0062 YIW=ALOG(W*A(I,1)/((EXP(WPI)-EXP(-WPI))/2.))
0063 33 SUM=SUM+FIW*YIW
0064 B(3,4)=SUM
C CALL SUBROUTINE TO PERFORM GAUSSIAN ELIMINATION METHOD
0065 35 CALL GAUS1(B,C,N)
C TEST C3
0066 IF(ABS((C(3)/W)).LE.0.0001)GO TO 70
0068 W=W+C(3)
0069 GO TO 9
C CALCULATE TAFEL SLOPES AND CORROSION RATE-
0070 70 BA=1./(W+C(2))
0071 BC=1./(W-C(2))
0072 CORCUR=EXP(C(1))*1./((1./BA+1./BC)
C WRITE OUTPUT DATA
0073 WRITE(7,38)BA,BC,CORCUR
0074 38 FORMAT('1','ANODIC TAFEL= ',E10.3/'1','CATHODIC TAFEL= ',E10.3/
/ '1','CORROSION CURRENT(MICROAMP)= ',E10.3)
0075 STOP

```

APPENDIX C

SURFACE AREA DETERMINATION

SURFACE AREA DETERMINATION

The method used by Biegler et al.⁽¹⁾ was used to determine the surface area of the Pt-Pt and Pt-foil electrodes. Basically, the technique involves the electrodeposition of hydrogen onto the surface of the metal. By knowing the charge necessary to form a monolayer of adsorbed hydrogen and the area covered by each hydrogen atom, the real area (electrochemical) can be calculated. The charge associated with a monolayer of hydrogen is commonly taken as 210 microcoulombs/real cm².⁽¹⁾

Figures C.1 and C.2 are cyclic voltammograms of Pt-Pt and Pt-foil electrodes in 1N H₂SO₄. Potentials are on the saturated calomel scale. Each electrode was held at 1.18 V for 90 seconds before being scanned cathodically at 20 mV/sec. The first major cathodic peak is the reduction of oxygen, which is quickly followed by twin peaks associated with the formation of hydrogen. The scan direction is quickly reversed before hydrogen is evolved from the electrode.

It is difficult to integrate the charge from an experimental voltammogram directly. A better procedure according to Biegler is to measure the charge to a potential corresponding to a fractional hydrogen coverage that is less than unity. Biegler recommends -0.22 V (on the saturated calomel scale) on smooth platinum for a coverage of 0.8. This experimenter made the assumption that the coverage was the same for Pt-Pt and Pt-foil at the same limiting potential. Areas from Figures C.1 and C.2 were integrated and a charge was calculated by cutting out the areas and weighing them.

REFERENCES

1. Biegler, T., D. Rand, and R. Woods. 1971. "Limiting Oxygen Coverage on Platinized Platinum; Relevance to Determination of Real Platinum Area by Hydrogen Adsorption." J. Electroanal. Chem. 29:269.

FIGURE C.1. Cyclic Voltammetry Scan (20 mV/sec) of Pt-Pt Electrode in 1-M H₂SO₄, 25°C

FIGURE C.2. Cyclic Voltammetry Scan (20 mV/sec) of Pt-Foil Electrode in 1-M H_2SO_4 , 25°C

APPENDIX D

CONVERTING POTENTIALS ON THE Ag, AgCl SCALE TO TO THE STANDARD HYDROGEN ELECTRODE (SHE) SCALE

CONVERTING POTENTIALS ON THE Ag, AgCl SCALE TO
THE STANDARD HYDROGEN ELECTRODE (SHE) SCALE

An external reference electrode was used in these studies and in the field. The construction and potential response of this electrode are covered in the original paper;⁽¹⁾ but for completeness, the information needed to place the potentials on the SHE has been provided.

The advantages of using the SHE scale are that high-temperature Pourbaix diagrams are calculated on this scale and the scale permits a comparison of experimental data with these diagrams so that water chemistry conclusions can be made. In making a measurement, the positive lead of the voltmeter must be connected to the redox electrode and the negative lead to the reference electrode. The measured potential must be assigned the polarity that the meter indicates. When this potential is added to data below (at the correct temperature of the redox electrode), the potential is placed on the SHE scale. If the temperature is between the data points shown, a linear interpolation of the potential data can be made.

TABLE D.1. Potential Data

<u>T, °C</u>	<u>$E_{\text{Ag, AgCl, 0.1M KCl 25°C}} - E_{\text{SHE}_T}$</u>
	<u>V</u>
25	0.287
90	0.227
125	0.188
150	0.159
200	0.097
250	0.026

REFERENCE

1. Danielson, M. J. 1979. "The Construction and Thermodynamic Performance of an Ag-AgCl Reference Electrode for Use in High-Temperature Aqueous Environments Centering H₂ and H₂S." Corrosion. 35(5):200.

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