**Development of Electrical and
Electrochemical Probes for Down
Hole and In-Line Chemical Analysis
of High Pressure, High Temperature
Geothermal Fluids**

**Interim Report -
Period Ending October 1977**

by
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November 1977

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INTRODUCTION

Any system to control scaling or corrosion in a geothermal power plant needs ways to monitor and verify the fluid chemistry. Currently this is done by sampling and analysis. A much better method would be to insert chemical sensor probes in-line or down hole. Such sensors could give continuous data without the problems of sampling, and sample contamination or change due to cooling. In-line probes for high temperature geothermal environments are beyond the current commercial state-of-the-art. However, advances in such technology has occurred in recent years, largely because of need for such probes in high pressure nuclear power plants. This program attempts the very difficult task of adapting electrochemical devices to geothermal applications.

The objectives of this program are to develop probes that can determine the water chemistry of high temperature geothermal fluids. The probes are intended to be used in both the geothermal reservoir and power generating equipment, measuring the water chemistry at the bottom of the well, through the turbine, and finally at the condensers and reinjection equipment. The data from these probes are needed to predict and control corrosion, scaling, and pollution. The entire probe system includes a high temperature reference electrode, oxidation potention (redox potential), conductivity probe, pH, corrosivity, and specific ion probe (sulfide). Work started on the reference electrode and conductivity probe during FY 1976.

SUMMARY AND CONCLUSIONS

The objective of this study for FY 1977 was to develop a reference electrode and conductivity probe that would operate in the geothermal environment and provide data. The conditions of the geothermal environment to which the probes must operate were defined as 250°C, widely varying salinity, large amounts of dissolved CO₂, and H₂S, and the potential for deposition of mineral scale. This work also involved a study of sealing materials. Midway through the work, a field test was carried out at East Mesa, 6-1 well which involved the reference electrode, electrodeless conductivity probe, redox electrode, and instantaneous corrosion rate measurement (by linear polarization).

A high temperature-pressure, thermodynamic reference electrode was developed which was demonstrated to be operative in a simulated geothermal environment up to 250°C containing the contaminants that would affect its operation. This probe is an essential part of all electrochemical measurements of pH, oxidation potential, or sulfide ions.

An electrodeless conductivity probe was developed for use in the geothermal environment. This design is particularly resistant to the effects of scale deposition. Development of this probe required the solution of a seal problem which will be useful to solving other seal problems in the geothermal industry. This probe should be useful for measuring salinity, steam/brine ratios in two-phase flow, flashing point, and as a liquid-level control.

A large number of sealing materials were investigated for use in the 250°C geothermal environment. From this study, PNL has developed a spring-loaded seal that may have other applications in the geothermal industry.

The field test of the conductivity probe and reference electrode at East Mesa was a success. The conductivity probe successfully predicted the total dissolved solids content of the brine, and the redox probe data coupled with Pourbaix diagrams indicated FeS and FeS₂ as surface film present on the electrodes and test loop. Instantaneous corrosion rate methods were demonstrated to be easily set up and convenient to operate.

The conductivity probe and reference electrode are now ready for further field tests which must be conducted in the future in order to demonstrate the usefulness of these devices and to test reliability under the rigorous conditions in real geothermal systems.

STUDY OF SEALING MATERIALS

One of the major problems in high temperature and pressure aqueous studies is the creation and maintenance of flexible, electrically insulating seals. Insulating sealants are necessary to prevent high pressure liquids from contaminating environments at lower pressures, to permit construction materials of widely differing thermal expansion coefficients to be used together, and to provide electrical insulation between an electrochemical

probe and the probe body. At the start of this work, it was discovered that the seal problems had not been solved for long term reliability at temperatures over 200°C. Our initial goal for probe operating conditions was 250°C and a pressure difference of 1000 psi.

Most of the sealant materials used at lower temperatures are not reliable at 250°C. Manufacturers' literature show that such common seal materials as Kel-F, viton, neoprene, silicone rubber, and epoxies are not suitable for aqueous temperatures over 200°C. Most organic polymers will hydrolyze. At first glance, ceramic-to-metal seals could be candidates, but they usually contain appreciable amounts of silica and alumina which are quite soluble at the higher temperatures, and would be expected to eventually leak.

The only polymeric material currently used at temperatures of 250°C is Teflon, but it softens and extrudes so that the seal eventually leaks unless periodically tightened. A number of materials of unknown high temperature aqueous properties were tested in 1% NaCl brines for 24 hours at 250°C (See Table 1) in the hope of finding some material that performs better than Teflon. Adhesives were especially interesting since they could be poured into place to form gaskets. In testing adhesives, a 1/8-inch diameter alumina disk (0.040-inch thick) was bonded to a 316 stainless steel plate and to an etched Rulon ($\text{SiO}_2\text{-Al}_2\text{O}_3$ filled Teflon) plate following the adhesive manufacturer's instructions. Polyimides were thought to be promising since some of them have good service lives in air at over 400°C. A perfluorinated elastomer was also included in the test. The perfluorinated elastomer was purchased as an O-ring and placed in a compression fixture similar to the way it would be used in service.

The polyimide, PTFE (polytetrafluoroethylene), and silicone adhesives all failed. The PTFE and polyimide adhesives dissolved while traces of the silicone remained as a soft solid. Only the nitrile phenolic maintained its bond.

The only rigid polymer that survived the test was the $\text{SiO}_2\text{-Al}_2\text{O}_3$ filled PTFE and since it has twice the strength of PTFE, should be superior to PTFE for 250°C applications. The rigid polyimide decomposed to become a sponge-like mass. This was particularly disappointing since its high temperature properties in air were excellent.

TABLE 1. Polymers Tested for High Temperature Performance
(250°C) in 0.1 Molal KCl

Adhesives

Silicones:

- a) Silicone 1
- b) Silicone 2
- c) Silicone 3

PTFE:

- a) PTFE 1

Polyimide:

- a) Polyimide 1
- b) Polyimide 2

Nitrile Phenolic:

- a) Nitrile Phenolic 1

Rigid Polymers

PTFE filled with $\text{SiO}_2\text{-Al}_2\text{O}_3$:

- a) PTFE 2

Polyimide:

- a) Polyimide 3

Elastomers

Perfluorinated Elastomer:

- a) PTFE 3

The O-ring perfluorinated elastomer did not decompose but it was extruded through the 0.005-inch gap in the seal holder. The elastomer inside the seal holder had reshaped itself to fit the fixture and is a strong indication that it became a viscous liquid and flowed at 250°C. This material does not act as a true elastomer at 250°C and would not make a reliable seal.

From this material of construction study, it was concluded that the $\text{SiO}_2\text{-Al}_2\text{O}_3$ filled PTFE was superior to PTFE and that this family of polymers was the only high-temperature polymers useful for the seal problems at 250°C. Only the nitrile-phenolic adhesive had any promise at 250°C.

In carrying out the development of the reference electrode and conductivity probe, other observations on the seal problem were made. Initially, Rulon was used for the reference electrode bodies (see Figure 1), but it was quickly discovered that the electrical properties of Rulon broke down after being subjected to 250°C water. The impedance across the Rulon was the order of a few thousand ohms and since the reference electrode circuits were of a much higher impedance to ground this constituted a short-to-ground. In circuits which are low impedances, this impedance of Rulon would not interfere with its use. It is hypothesized that the silica and alumina in Rulon hydrolyzed and became an ionic conductor. Fortunately, Rulon-type materials exist with zirconium oxide substituted for the silica and alumina. Zirconia does not seem to hydrolyze and electrical breakdown should not occur. Unfortunately, a domestic source for Zirconia-filled Teflon has not been found. Consequently, Teflon had to be used for the reference electrode bodies with its attendant inferior strength. It was also discovered that two types of Teflon exist: reprocessed and virgin. The reprocessed is not suitable for seals or electrode bodies since it is porous and results in a low impedance short-to-ground by becoming wetted with ion-conducting solutions. Only the virgin Teflon should be used.

A major problem with the development of an electrodeless conductivity probe centered around the high pressure end seal (Figure 2). This probe used a Rulon seal. It would hold the autoclave pressure up to 250°C (550 psi) but then leak on the cool-down. An autopsy of the probe indicated that the gasket

FIGURE 1. Drawing of High Temperature, High Pressure Silver-Silver Chloride Electrode Used at PNL. Design based on work of A. Agrawal, Ohio State University.

FIGURE 2. High Pressure-High Temperature Electrodeless Conductivity Cell

had extruded out of the air gaps at the stationary seal surfaces during the operation at high temperatures and then shrunk upon the cool-down. We think we have solved this problem with the conductivity probes and by doing so have discovered a general approach to the seal problem. Calculations indicate that Rulon and Teflon have a volume increase of 7% and 15%, respectively, on going from 25 to 250°C. This volume increase is much greater than the volume increase of the stainless steel electrode body, and consequently, the internal pressure of the captive seal material on the probe body increases tremendously. The seal material must extrude through the gaps and relieve the internal pressure or this device would probably split open. On cool-down, the seal shrinks, the internal pressure drops below the external pressure, and the external environment enters. Our design is two-fold: to reduce the gaps through which the seal can extrude to 0.002 to 0.004 inch, and to spring-load the seal so the volume increases on heating can be compensated by compression of the spring without the attendant huge increase in internal seal pressure. This is shown in Figure 2. This design can probably be applied to all the difficult seal problems. It may also mean that by using this design with currently available high-temperature seal materials (Teflon, Rulon), the temperature limits for reliable sealing may be extended to 350°C water, an increase of 100°C from what can be done now.

In summary, the only suitable insulating seals for use to 250°C are Teflon and Rulon. Rulon breaks down electrically and can only be used in low impedance applications. A nitrile-phenolic adhesive was found to survive up to 250°C and may be worthy of further study. A new seal concept has been discovered which has improved the reliability of the conductivity probes and may be applicable to other seal problems. It consists of reducing the air gaps through which a seal can extrude, and to spring load the seal so that the large seal volume increase (on increased temperature) is taken up by compression of the spring, rather than by extrusion. This may permit Rulon and Teflon to be used up to 350°C, conditions not thought to be possible before. More work needs to be carried out on this new sealing concept.

REFERENCE ELECTRODE DEVELOPMENT

The first electrochemical device that must be developed is a stable, reproducible reference electrode. Its function is to maintain a constant potential at each temperature so that the potential of other electrochemical devices can be referenced to it. Any change in potential is then due to the other electrochemical device, and would indicate some change in the chemical environment. The pH electrode, redox probe, and specific ion electrode (these are devices PNL will develop in FY 78) are all dependent upon a reference electrode. PNL set out to develop a reversible, reference electrode.

We surveyed the literature on high temperature reference electrodes, but we could not find any satisfactory design which could be adopted for use in the contaminated, geothermal environment. Of the many reference electrodes used at room temperature, only the silver-silver chloride system (Ag-AgCl) has been adequately researched for high temperature operation. The work of Greeley, et al,⁽¹⁾ was devoted to measuring the standard potential of Ag-AgCl on the hydrogen scale at temperatures up to 275°C, and this electrode was assumed to be reversible. We chose to study this system in greater detail. The geothermal environment contains many species that would disturb the potential of the Ag-AgCl electrode; consequently, it must be protected by use of a salt bridge. Such an electrode system has recently been developed by Agrawal.⁽²⁾ It is shown in Figure 1. The unique feature of this design is the internal Zirconia (ZrO_2) sand saturated with the electrolyte (0.01M KCl). The sand prevents convection and consequently, linear diffusion conditions prevail so that outside contaminants must slowly diffuse through the sand before reaching the vicinity of the Ag-AgCl. Electrode life at 250°C should be measured in weeks.

There are a number of high temperature reference electrodes mentioned in the literature. All those based on Ag-AgCl used Greeley's data to place the potentials on the hydrogen scale. Not one of these experimenters has ever tested the performance of their electrode to see if it is Nernstian (reversible) in behavior. Their criteria of correct operation is that the potential of their reference versus a freely corroding electrode (inside an autoclave) is constant; this has no relationship to reversibility. Reversible electrodes

are the best type not only because thermodynamic data can be gathered from them but it is likely that experimenters all over the world can assemble the reversible electrode and get the same reference potential. We felt it was important to determine if our electrode design was reversible. If it was reversible, this would encourage other experimenters to use this design so that their scientific data would be on the same thermodynamic scale and would permit comparison of the data.

There are two major ways to experimentally determine if a reference electrode is reversible. One way is to directly measure its potential on the hydrogen scale and compare its potential to conditions under which its performance is known to be reversible. This could be carried out by measuring the potential of the PNL reference electrode on the hydrogen scale and then comparing its response to the work of Greeley, et al. Another technique is to make use of concentration cells with transference to determine if the change in potential with activity fits the Nernstian expression.

$$\Delta E = -(2t_+) \frac{RT}{F} \ln \frac{a_{\bar{+}}(1)}{a_{\bar{+}}(2)} \quad (1)$$

where t_+ = transference number of cation
 R = gas constant
 T = temperature, °K
 F = Faraday constant
 $a_{\bar{+}}$ = mean chloride ion activity

Both procedures were used at PNL.

The experimental setup is shown in Figure 3. The first series of experiments were to directly measure the PNL Ag-AgCl reference electrode potential versus a H_2 electrode at the same temperature and then compare the work to that of Greeley. Good agreement would indicate that our reference was reversible. Unfortunately, the Teflon bodied Ag-AgCl electrode is incompatible with H_2 since hydrogen gas rapidly diffuses through Teflon and reduces the AgCl:

FIGURE 3. Drawing of Autoclave Assembly for Hydrogen Electrode and Room Temperature Ag-AgCl Reference Electrode (operates at autoclave pressure). $\text{H}_2\text{-CO}_2$ in gas phase (25°C) in 1:1 ratio. Other electrodes can be substitutes for those shown.

A way around this problem is to measure the potential of the hydrogen electrode versus some other quasi-reference electrode not affected by hydrogen, run other experiments with the Ag-AgCl reference versus this same quasi-reference electrode, and then subtract the data to put the Ag-AgCl reference on the hydrogen scale:

$$\begin{array}{rcl}
 E_{\text{Ag,AgCl}} - E_{\text{quasi-reference}} & = & X \\
 E_{\text{H}_2} - E_{\text{quasi-reference}} & = & Y \\
 \hline
 E_{\text{Ag,AgCl}} - E_{\text{H}_2} & = & X - Y
 \end{array} \tag{2}$$

The first quasi-reference electrode used a salt bridge (0.1M KCl saturated asbestos wick) leading from the autoclave, through a pressure reducer, and outside to a room temperature calomel electrode. A simple and unique design for the pressure reducer based on a Conax fitting is shown in Figure 4.

There are two potential errors in using a pressure reducing salt bridge, the thermal liquid junction potential (TLJP) and the streaming potential. The TLJP error is estimated to be about ± 0.03 mv/deg⁽³⁾ for KCl solutions (about 7 mv at 250°C) and can probably be ignored. The streaming potential is an electro-kinetic phenomena which in its simplest form can be expressed as:

$$E_{\text{sp}} \propto \frac{P}{C}$$

where P = pressure

C = concentration of ions

and can have a very large value (several hundred mv). It was soon recognized that the streaming potential was not reproducible and this technique could not be used. The streaming potential⁽⁴⁾ is also a function of pore size of the salt bridge inside the pressure reducing fitting. Experimentally, the potential could be varied by ± 20 mv at 250°C by a loosening or tightening of the Conax fitting. By pressuring the autoclave at 25°C with a gas (up to 160 psi) with the electrodes and salt bridge (0.1M KCl) in place, a linear streaming potential-pressure effect of 0.084 mv/psi was measured. The potential at 160 psi could be varied by 4 mv by tightening or loosening the Conax fitting. Higher pressures would probably have a much greater effect on the potential shift due to the pore size. Based on the streaming potential-pressure effect measured at 25°C, a pressure of 550 psi (equivalent to water vapor pressure at 250°C) for 0.1M KCl would give a streaming potential of 46 mv. It is recommended that salt bridge devices with a streaming potential be avoided in high temperature reference electrodes.

FIGURE 4. Drawing of a Pressure Reducing Salt Bridge

To avoid the streaming potential, another type of reference electrode was developed as shown in Figure 5. This Ag-AgCl quasi-reference electrode operates at room temperature, but at autoclave pressure. Hydrogen gas does not interfere with the room temperature Ag-AgCl, and any H_2 diffusing of the electrode would not be a problem. The TLJP still exists but it is estimated to be a small value, and provided it is reproducible, it will add to zero as shown by Equation 2. The Soret effect⁽⁵⁾ should also be considered since it can affect the potential and create unreproducible results. The Soret potential results whenever an electrolyte passes through a temperature gradient. The ions concentrate at the cooler junction and change the activity of the ions to which the electrode is reversible. This effect is probably small with the quasi-reference electrode since the inner Teflon tube containing the electrolyte has a large diameter and passes through a temperature gradient. This will result in convection and prevent any concentration gradients from existing. Experimentally, the potential of Ag-AgCl electrode in the autoclave at 250°C versus the quasi-reference was measured for 10 days with 0.1M KCl and remained constant within ± 2 mv. This should indicate that the Soret effect is not important for this experimental setup. This data is shown in Figure 6.

The hydrogen electrode consisted of a platinized-platinum wire inserted in 0.100 Molal KCl electrolyte. A 1:1 mixture of H_2 - CO_2 gas was bubbled through the autoclave for 20 to 30 minutes until the potential was stable versus the quasi-reference electrodes, and then the autoclave was closed (static operation) and the temperature increased in steps until reaching 250°C. The criteria of an acceptable experiment was that the room temperature rest potential after the experiment be within 10 mv of the starting rest potential. The experimental data (average of several experiments) corrected to 1 Atm H_2 and CO_2 partial pressure is shown in Figure 7. To make the pressure correction, the noncondensable gases are assumed to be ideal, and the liquid and gas volumes in the autoclave must be known at each temperature in order to calculate the pressures at each temperature. Also shown in Figure 7 are the calculated potentials based on standard potential data of Greeley, et al. To correct the standard potentials to these experimental

OVERALL VIEW

DETAILED VIEW OF ELECTRODE

FIGURE 5. External Reference Electrode

FIGURE 6. Potential Difference Between a Silver-Silver Chloride Electrode at 25°C (at autoclave pressure) and Another at the Autoclave Temperature and Pressure

conditions, a high temperature pH must be calculated, and this requires the Henry Law⁽⁶⁾ constants for CO₂ and the dissociation constant⁽⁷⁾ for carbonic acid (H₂CO₃) at each temperature. There is good agreement between the experimental and calculated data up to 120°C, and then the divergence becomes large. To illustrate the sensitivity of the H₂ electrode, the potential difference between the experimental and calculated values in the range of 160 to 250°C could be due to an error of 0.25 pH units in calculating the high temperature pH value. We cannot find an explanation for the difference in

FIGURE 7. Plot of $E_{\text{Ag, AgCl}} - E_{\text{H}_2}$ in 0.10 Molal KCl as a Function of Temperature. Data corrected to 1 atm H_2 and CO_2 partial pressure.

the experimental and calculated data; it could be due to errors in Greeley's data, errors in Henry's Law and dissociation constant data, or some malfunction in the experimental H_2 electrode. However, it can be concluded that the PNL Ag-AgCl reference electrode is reversible in the range of 25 to 120°C by analogy to Greeley's data.

To demonstrate the reversibility at temperatures to 250°C, concentration cells with transference were used. High temperature Ag-AgCl electrodes with electrolytes of 1.00, 0.100, 0.0100, and 0.00100 M KCl were inserted into the autoclave containing 0.100 M KCl and their performance referenced to the silver, silver chloride (0.1 M KCl) electrode operating at room temperature and autoclave pressure. This experimental setup is illustrated in Figure 3. The Pt electrode shown in the figure is replaced with the PNL Ag-AgCl reference electrode. The method of calculation is illustrated below:

$$\begin{array}{rcl}
E_{\text{Ag}(0.01 \text{ M})_T} - E_{\text{Ag}(0.1 \text{ M})_{25}} & = & X \\
E_{\text{Ag}(0.1 \text{ M})_T} - E_{\text{Ag}(0.1 \text{ M})_{25}} & = & Y \\
\hline
E_{\text{Ag}(0.01 \text{ M})_T} - E_{\text{Ag}(0.1 \text{ M})_T} & = & X - Y
\end{array} \quad (4)$$

Since the TLJP always involves 0.1 M KCl, its affect on equation (4) should subtract out to zero, and the data will have a thermodynamic basis so that it can be compared to values calculated from the Nernst expression for concentration cells with transference. The Nernst expression is shown below:

$$E_{\text{Ag}(0.01 \text{ M})_T} - E_{\text{Ag}(0.1 \text{ M})_T} = -2(t_+) \frac{RT}{F} \ln \frac{a_{\bar{+}}(0.01)}{a_{\bar{+}}(0.1)} \quad (5)$$

where t_+ = transference of cation, 0.5
 R = gas constant
 T = absolute temperature
 F = Faraday constant
 $a_{\bar{+}}$ = mean ionic activity of KCl

The transference number of the potassium ion is about 0.5 at 25°C and is estimated⁽⁸⁾ to remain relatively constant to over 250°C. The mean ionic activities of KCl must be known in order to calculate the cell potential. There is a lack of literature data on $a_{\bar{+}}$ of KCl, but Greeley, et al,⁽⁹⁾ have measured the mean ionic activity of HCl in the range of 1 to 10^{-3} molal. For 0.1 M KCl and below, the values are very similar to the mean ionic activities of HCl. The 1.0 M KCl system has not been studied, and the data for HCl will not approximate the values for this system. Two methods were used to calculate the mean ionic activity for 1.0 M KCl: an approximate calculation technique by Cobble, et al,⁽¹⁰⁾ and the experimentally determined values of Gardner⁽¹¹⁾ for the 1.0 M NaCl system. Cobble's equation is shown below. The constants will be found in the original paper.

$$(\log \gamma_{\pm})_T = (\log \gamma_{\pm})_{25} - \frac{\sqrt{I}}{1 + \sqrt{I}} (A_T - A_{25}) \quad (6)$$

where $\gamma_{\pm}$ = mean ionic activity coefficient
 I = ionic strength
 A = constants, see original paper

The activity coefficients for KCl were estimated from the 1.0 M NaCl data by determining

$$\frac{\partial a_{\pm} \text{ NaCl}}{\partial T} \quad (7)$$

and then applying this value to the activity coefficient data of KCl (1.0 M) at 25°C to correct it to other temperatures. This correction is necessary because the mean ionic activities of 1.0 M KCl and NaCl are significantly different at 25°C, but we assumed the temperature effects on $a_{\pm}$ were similar. This expression for 1.0 M KCl is shown:

$$\ln \gamma_{\pm} = 2.113 - 0.0213T + (0.5897 \times 10^{-4})T^2 - (0.458 \times 10^{-7})T^3 \quad (8)$$

where T = absolute temperature

These data are shown in Table 2.

TABLE 2. Mean Ionic Activity of 1.0 Molal KCl

<u>Temp.</u>	<u>$a_{\pm}$, Cobble</u>	<u>$a_{\pm}$, from 1.0 M NaCl Data</u>
25°C	0.61	0.61
60°C	0.58	0.58
120°C	0.53	0.55
160°C	0.48	0.51
200°C	0.43	0.46
250°C	0.35	0.36

The concentration cell data is shown in Table 3. The response of the PNL Ag-AgCl reference electrode is Nernstian within a few mv in the concentration range of 1 to 10^{-2} molal at temperatures to 250°C. This Nernstian response is strong evidence that the reference electrode is acting in a thermodynamic manner. Consequently, the electrode potential is likely to be reproducible in other laboratories.

TABLE 3. Concentration Cell Data

Temp. °C	Measured $E_{\text{Ag}(1\text{ M})_T} - E_{\text{Ag}(0.1\text{ M})_T}$ (Volt)	Calculated Value (Volt)	Absolute Difference (mv)
25	-0.054	-0.052	2
60	-0.055	-0.058	3
120	-0.062	-0.067	5
160	-0.060	-0.071	11
200	-0.071	-0.074	3
250	-0.078	-0.081	3

Temp. °C	Measured $E_{\text{Ag}(0.01\text{ M})_T} - E_{\text{Ag}(0.1\text{ M})_T}$ (Volt)	Calculated Value (Volt)	Absolute Difference (mv)
25	+0.055	+0.056	1
60	0.063	0.062	1
120	0.078	0.072	6
160	0.077	0.079	2
200	0.079	0.085	6
250	0.085	0.088	3

Temp. °C	Measured $E_{\text{Ag}(0.001\text{ M})_T} - E_{\text{Ag}(0.1)_T}$ (Volt)	Calculated Value (Volt)	Absolute Difference (mv)
25	0.105	0.113	8
60	0.102	0.126	24
120	0.112	0.150	38
160	0.088	0.162	74
200	0.056	0.176	120
250	Electrode Failed	--	--

The next step in the development of the PNL high temperature-pressure reference electrode was to determine if any gaseous species in the geothermal environment could diffuse directly through the side of the Teflon electrode body into the electrode compartment and interfere with the electrode response. Hydrogen gas is known to rapidly diffuse through Teflon, but it is present in very low concentrations in geothermal brines and is not expected to interfere. Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are present in higher quantities. CO_2 is not known to interfere with Ag-AgCl electrode (this electrode has no pH response), but H_2S can react with AgCl to form the very insoluble silver sulfide (Ag_2S).

As a first approximation to the electrode response to H_2S , the reference electrode potential would change, responding to the increased concentration of chloride ion released as the sulfide reacts with the AgCl. When the PNL reference electrode was placed in an electrolyte of 0.1 M NaCl with 100 ppm H_2S (pH = 5.5) at 200°C and monitored versus the room temperature quasi-reference, the potential changed 1.5 mv/hr. When this performance is contrasted with the behavior without H_2S (potential changed ± 2 mv in 10 days), it can be seen that H_2S is a serious interference. The direction of this potential shift indicates an increasing concentration of Cl^- with time and fits the hypothesis of the mechanism of interference. In the next series of experiments, a stainless steel sheath was loosely fitted around the Teflon body to act as a physical barrier to the H_2S . The potential changed by 0.3 mv/hr. This improved performance indicated that the shield was assisting. Further experiments were carried out with tighter shields, but the drift in potential could not be eliminated. Finally, a high temperature reference electrode was designed using a zirconium oxide tube as the insulating electrode body. This model is shown in Figure 8. The electrode body acts as a physical barrier to the diffusion of hydrogen gas and hydrogen sulfide. It has been tested in 100 ppm hydrogen sulfide at 200°C for 36 hours, and the potential was constant within 2 mv (versus the quasi-reference electrode). It has also been autoclave tested in 0.5 atm hydrogen gas at 200°C for 24 hours with no observed change in potential (versus quasi-reference electrode).

FIGURE 8. High Temperature Reference Electrode Resistant to Hydrogen and Hydrogen Sulfide External Environment (not shown in drawing, but silver wire covered with heat shrunk PTFE)

This reference electrode is ready for use in the geothermal environment. The stainless steel outer shell serves to not only hold the ZrO_2 tube in place to make a captive seal, but also serves to ruggedize it for use in the field.

In summary, reference electrodes involving a streaming potential (especially in dilute solutions and high pressures) should be avoided. PNL has shown that their high temperature Ag-AgCl reference electrode has a thermodynamic response, and consequently is likely to be reproducible. A high temperature model has been designed and tested which operates in the contaminated geothermal environment.

CONDUCTIVITY CELL

Solution conductivity is a useful measurement because it can indicate the amount of dissolved solids in solution or salinity differences from different aquifers (when used in well logging). Continuous monitoring of the conductivity can be a useful operational parameter to indicate when changes in the water chemistry of a geothermal plant occur. Conductivities can change due to changing flow conditions in the well (two-phase flow in the bore-hole, earthquakes) and also in the associated piping above ground (pipe breakage, scale deposition reducing internal pipe and valve diameters, oxygen enters the system).

A review of the literature revealed that there are three basic designs: the four-electrode, two-electrode, and the electrodeless. Surface fouling from scale deposition is expected to be a problem in the geothermal environment. The first two designs depend on bare metal electrodes which must make electrical (and ionic) contact with the solution. Deposited scales are likely to be insulating and would quickly make the first two designs inactive. Only the electrodeless model does not need to make electrical contact with the solution; consequently, it would still operate with scale deposits. The electrodeless model was chosen for further study. At this stage, manufacturers (Foxboro, Bechman, Honeywell, Nus, and Balsbaugh) of commercial electrodeless conductivity devices were contacted to determine if they could provide PNL with high temperature models (operate to 250°C). They were not able to do this, and PNL set out to develop its own model based on an earlier design⁽¹²⁾ developed for the nuclear industry. It is the intention of PNL that after the probe is developed, commercial vendors will be sought to manufacture it.

The newest design of the electrodeless conductivity probe is shown in Figure 2. Basically, the probe consists of two torroidally wound coils, one driven by a pulsing DC voltage and the other acting as a receiver. The electromagnetic field from the driven coil is coupled through the solution and induces a current in the receiver coil. The induced current is proportional to the conductivity. It is not clear from the drawing, but there is an air gap between the spool and the support ring of about 0.004 inch. This break in the circuit prevents the electromagnetic field created by the driven coil from coupling through the case of the probe to the receiver coil and acting as a short-circuit to the solution conduction path. The electronics associated with the probe have already been developed from earlier work,⁽¹²⁾ but the probe design will be flexible enough to use the electronics from commercial manufacturers.

Most of the PNL efforts have been devoted to solving the seal problems, temperature properties of the coils, and determining the accuracy and reliability of measuring high temperature conductivities. The latest seal design shown in Figure 2 was discussed in detail in the first section on Sealing Materials. Early designs could not be temperature cycled without leaking, but current designs can now be cycled. It is believed that this seal design can be applied to other difficult seal problems, and it may be possible to extend the temperature limits of this seal to over 300°C.

The output from this probe looks like a damped harmonic oscillator with the peak voltage height proportional to the conductivity. PNL has observed that the peak voltage response of the torroidal coils is independent of temperature, and consequently, any change in output will be due to changes in solution conductivity. Initially, ferrite torroids were tried, but their Curie point (temperature at which the magnetic properties rapidly change) was about 240°C, below the temperature limit set for this project. Tap-core torroids were tested and found to have a Curie point above 250°C and are now used in all the probes. The torroids are wound with a high temperature, polyimide insulated wire--other insulation types (varnish, polyester) would

break down at 250°C. A ceramic tube (ZrO_2) is inserted in the probe to fix the cell constant. By changing the length and inside diameter of the tube, the cell constant can be adjusted so that the response of the probe can be optimized to match the solution conductivity.

The response of our electrodeless conductivity probe is shown in Figure 9. There is good agreement between the literature values⁽¹³⁾ and those experimentally measured. This is strong evidence that the probe is operating predictably and accurately.

Future work on the probe will center on matching the spring constant of the flexure ring to the deformation forces of the Rulon seal, as well as more tests to determine the reliability, accuracy, and life at 250°C. More field studies will also be carried out.

FIELD TEST

PNL built and operated a corrosion test loop at the East Mesa site, 6-1 well. To gain some field experience, we took a small package of probes and placed them in the 150°C loop for a six-day study. The probes included a redox electrode, electrodeless conductivity probe, PNL high temperature reference electrode, and a Petrolite corrosion measuring device. Water chemistry of the well at 25°C was 5.9 pH, total sulphur of about 10^{-4} molal, and CO_2 of about 10^{-2} molal.

The redox electrode was a bare platinum foil (area $\approx 2 \text{ cm}^2$), and its potential was measured against the PNL reference electrode. The potential was relatively constant at -0.400 volt on the 150°C hydrogen scale. The corrosion test loop (iron) was -0.500 volts on the same scale. The platinum electrode developed a thin, black coating. Biernot, et al.,⁽¹⁴⁾ have calculated the Pourbaix Diagram for the Fe-S- H_2O system at 150°C. Adjusting their data for sulphur concentration of 10^{-4} M and assuming the pH at 150°C is 5.9, the potential on the platinum electrode falls in the range of Fe, FeS_2 equilibrium and the iron pipe in the Fe, FeS equilibrium. We do not have any confirming identification of the surface films, but iron sulfides are the likely species. Thermodynamically, platinum redox probes are thought to react only to the H_2 gas - H^+ equilibrium; consequently, the potential should

FIGURE 9. Ratio of the Conductivity at Temperature, T , to the Conductivity at 18°C Plotted as a Function of Temperature for 0.100 Molal KCl

reflect only the pH and hydrogen gas fugacity. In reality, the platinum electrode becomes coated with other metallic sulfide and oxide films, and its potential response probably shifts to reflect the dominant species equilibrium (with higher exchange current) on its surface. Consequently, this field test indicates that the redox probe does give information on the surface species when coupled with a thermodynamic reference electrode.

The electrodeless conductivity probe functioned well. Since conductivity is proportional to the dissolved solids content, the probe response permitted an estimation of the dissolved solids. By assuming the brine was 100% NaCl, the probe estimated the dissolved solids to be 21,000 ppm. An actual chemical analysis measured 22,000 ppm. This is good agreement and indicates the usefulness of this tool.

Two sets of Petrolite mild steel probes were installed (in 50°C and 150°C loop) to determine instantaneous corrosion rates by linear polarization. The rates in both loops were fairly constant throughout the experiment. Corrosion rates of about 0.10 and 0.70 mils per year were measured in the 50° and 150°C loops, respectively. Corrosion data (by weight loss) from the mild steel coupon samples in other portions of the loop have not been analyzed to see if these data are realistic. This field study demonstrated the simplicity of using linear polarization techniques to get instantaneous corrosion rates. The power of this technique is the measuring of corrosion rates at any moment. Operationally, it can quickly determine when highly corrosive conditions (leakage of air) occur and alert the operator to take corrective actions.

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APPENDIX 1

TRADE NAMES FOR MATERIALS TESTED IN TABLE 1

Adhesives

Silicones:

- a) Dow Corning. 1204 Primer followed by 3145RTV
- b) General Electric. #154
- c) General Electric. #156

Teflon:

- a) DuPont. 851-204 Teflon dispersion (self-priming)

Polyimide:

- a) Monsanto. Skybond 705 liquid
- b) Upjohn. 2080-D liquid

Nitrile Phenolic:

- a) B.F. Goodrich Industrial Products. PL605-4

Rigid Polymers

Teflon:

- a) Dixon Corp. (Bristol, RI), Rulon (Alumina-silica filled Teflon)

Polyimide:

- a) Dixon Corp. Meldin 6000

Elastomers

Kel-rez;

- a) DuPont. Perfluroelastomer with chemical properties similar to Teflon

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