GEOCHEMICAL ENGINEERING PROGRAM
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GEOCHEMICAL ENGINEERING PROGRAM

INTRODUCTION

This report is the first of a series of quarterly interim progress reports to be issued by Battelle, Pacific Northwest Laboratory (PNL) to document preliminary results of three closely related geothermal programs sponsored by the U.S. Department of Energy, Division of Geothermal Energy:

1. Corrosion of Iron-base Alloys versus Alternate Materials
2. Development of Probes for Down Hole and In-line Chemical Analysis at High Pressure, High Temperature Geothermal Fluids
3. Manual for Geothermal Fluid-Gas Analyses.

1. CORROSION OF IRON-BASE ALLOYS VERSUS ALTERNATE MATERIALS

D. W. Shannon, E. M. Woodruff

This geothermal corrosion program is to determine why geothermal brines are corrosive to economical iron-base alloys. Geothermal resources that can be developed with iron-base alloys will have a significant economic advantage over geothermal sites that would require extensive use of expensive alloys. Data developed in this program will be used to guide selection and design of near-term plants.

The program objectives are:

- To clarify corrosion factors important to materials selection for geothermal power plants
- To establish a set of brine composition and temperature limits for carbon steels in geothermal brines and report final results by the end of FY 1978.

The program involves tests of many materials in high pressure equipment where a wide variety of brine chemistries can be studied. The validity of these lab tests was checked by one field test in actual geothermal brine during 1977 which confirmed lab corrosion rates measured at 150C, but not at 50C.

TECHNICAL APPROACH

The laboratory tests to date have demonstrated that brine chemistry and temperature are very important in determining corrosion rates of carbon steels. Variables found to be important include pH, temperature, salinity, and dissolved oxygen. The specific grade of carbon steel was found to be unimportant to corrosion rates, although alloying with chromium and molybdenum was beneficial. The corrosion rate of some grades of carbon steel was found to vary by a factor of 100 in various synthetic brines. These variations are believed to be due to changes in composition and structure of the films that formed on the carbon steel; Fe_3O_4 , FeCO_3 , FeS , and FeCl_2 scales were all identified in different brines. Low corrosion rates were observed when Fe_3O_4 formed on carbon steel. Factors that cause film breakdown will accelerate corrosion.

As the sulfide to sulfate ratio varies from well to well, so does the redox potential (EH) of the brine change. Also if dissolved oxygen leaks into a geothermal system it is possible to raise the redox potential to levels where Fe^{+3} and Fe_2O_3 would form. Such an oxidizing brine system would be highly corrosive to steels. Electrochemical studies are planned (both lab and field) to relate redox potential to corrosion.

The program is divided into two tasks:

Task 1. Laboratory Tests

High-pressure autoclaves are used to expose various alloys to synthetic brines with variations in temperature and brine chemistry. Corrosion rates are measured as functions of temperature, EH, pH, salinity and specific brine components. Films that form on steels are examined for composition and structure.

Task 2. Field Tests

The field corrosion tests, which are compared to the laboratory tests, will determine corrosion rates of different alloys subjected to brine at the Department of Energy Geothermal Energy Component Test Site in the Imperial Valley, California. Alloys were tested varying exposure times at different temperature regimes, brine flow rates, and brine pH. A field test was conducted at East Mesa Well 6-1 during 1977. The initial results are presented in this report.

TASK 1. LABORATORY TESTS - D. W. Shannon

Results of the previous laboratory test work were written up and published separately.^(1,2) During the past quarter, the equipment was being revised for a restart of tests in January 1978.

TASK 2. FIELD TESTS - E. M. Woodruff and D. W. Shannon

Field corrosion tests were conducted during 1977 for comparison with laboratory tests. A corrosion test facility was fabricated late in 1976 and delivered to the Department of Energy (then the Energy Research and Development Administration) Geothermal Component Test Site in the Imperial

Valley, California, where brine from the Bureau of Reclamation East Mesa Well 6-1 was made available for tests of this type. Testing was conducted in two stages starting with wellhead brine at a pH of 5.8 on March 5, 1977. Samples were discharged after nominally 2-, 4- and 6-week exposures. Then acid injection equipment was installed, new samples were charged, and the experiment repeated with the pH lowered to 4.6 to 4.8. This second test ended on June 28, 1977, three days earlier than planned, when flow from Well 6-1 became erratic, and it was no longer possible to control pressure and flow in test sections. The test involved five alloys, each exposed at three temperatures and three flow velocities. The composition of each alloy is shown in Table 1-1. Each test section contained 20 cylindrical specimens (4 of each alloy) confined by Teflon insulating spacers to direct flow down the bore, exposing only the inside surface of the specimens. Pre-and post-test weight determinations were made, film deposits were removed chemically, and final stripped weights taken as indicated in the procedure outlined in Table 1-2. It was necessary to also strip external deposits formed by inadvertent leakage past the sample ends.

Field Test Equipment

The self-contained corrosion test unit is shown in Figure 1-1. An expanded diagram of the unit is shown in Figure 1-2. In practice, the inlet brine temperature was about 160°C, and sufficient air cooling occurred before reaching the second bank of samples so that water cooling in the first heat exchanger was not required. However, it was necessary to install a flow delay tank with baffles and a gas bleed system upstream of the brine pump to eliminate pump cavitation caused by entrained CO₂. The well was operated with single-phase artesian flow of about 50 gal/min. About 15 gal/min of this was pressurized by the pump on the test inlet. By maintaining a positive overpressure, flashing was suppressed, gases remained in solution through the test unit and very little scaling resulted.

As samples were removed at 2-week intervals, they were replaced by pipe lengths to maintain internal flow characteristics. A typical test section is shown in Figure 1-3.

TABLE 1-1. Materials Compositions of Field Test Samples

Carbon Steels	Carbon	Mn	P	S	Si	Ni	Cr	Mo	N	Cu	Fe	Al
SAE 1010 Tube ^(a)	0.03	0.27	0.017	0.006	0.005	0.03	0.009	0.006	--	0.06	Rem.	--
A53B Tube ^(a)	0.23	0.71	0.010	0.019	0.15	0.26	0.010	0.007	--	0.008	Rem.	--
Chromium Steels												
4130 Tube ^(a)	0.28	0.48	0.009	0.011	0.25	0.05	0.82	0.16	--	0.007	Rem.	--
E-Brite 26-1 Tube ^(a)	0.01	<0.10	0.015	0.011	0.18	0.09	26.2	1.06	--	0.005	Rem.	0.05
410 Tube ^(a)	0.10	0.39	0.010	0.009	0.51	0.33	11.89	0.03	--	0.03	Rem.	0.17

(a) Heats used in field test

TABLE 1-2. Preparation and Cleaning Procedures Used on Field Test Samples

1. Specimen cylinders were stamped to identify with 1/8-in.-high letters and numbers.
2. Cylinders were cleaned in acetone to remove any surface oil.
3. Cylinders were cleaned in 200 ml H_2O , 200 ml conc. HCl , and 5 ml formaldehyde with light brushing for 3 minutes to remove mill scale. Cylinders were rinsed in H_2O and dried with acetone.
4. Inner and outer surfaces were polished with 320-grit emery cloth.
5. Cylinders were rinsed thoroughly and dried with acetone.
6. Cylinders were stored in a dessicator.
7. Cylinders were measured (OD, ID and length) for surface area.
8. After at least one hour in the dessicator the cylinders were weighed to 0.1 mg.
9. Cylinders were placed in polyethylene sleeving with dessicant and sealed for transfer to the exposure site.
10. Cylinders were exposed to brine in test loop at East Mesa.
11. Test loop shut down and flushed with dioxygenated water.
12. Cylinders were removed from the test loop and rinsed with dioxygenated water and dried with a hot air blower at the test site.
13. Cylinders were shipped to the laboratory in sealed polyethylene tubing with dessicant.
14. Upon arrival at the laboratory, cylinders were placed in a dessicator.
15. Cylinders were weighed.
16. Inner holes of cylinders were plugged, and then cylinders were cleaned in a mixture of 200 ml H_2O , 200 ml conc. HCl , and 5 ml formaldehyde, which was contained in an ultrasonic cleaner. (Exposure to the stripping solution varied; the average time was 45 sec.) Cylinders were rinsed in H_2O and acetone, then dried with a hand dryer and dessicated.
17. After at least one hour in the dessicator the cylinders were weighed. The corrosion film weight was calculated.
18. The total surface area of the cylinders was stripped with a mixture of 200 ml H_2O , 200 ml conc. HCl , and 5 ml formaldehyde for 3 minutes in an ultrasonic cleaner, rinsed in H_2O , brushed lightly, stripped again for 1 minute, rinsed in water, brushed if needed, dried with acetone and a hand dryer, and placed in the dessicator.
19. After at least one hour of time in the dessicator, the cylinders were weighed. MPY corrosion rates were calculated.
20. Cylinders were placed in alkaline permanganate for 5 minutes in an ultrasonic cleaner, rinsed with water, dried with acetone and dryer, and put in the dessicator.
21. After at least one hour, cylinders were reweighed and MPY corrosion rates were recalculated. In most instances MPY corrosion rates did not change from that calculated after the 50% HCl strip.

FIGURE 1-1. Field Test Unit for Containing Corrosion Samples and Controlling Flow and Temperature

GEOHERMAL CORROSION FIELD TESTS (EXPANDED VIEW)

FIGURE 1-2. Expanded Diagram of the Corrosion Field Test Unit

FIGURE 1-3. Typical Test Section (30 in. long overall)

Brine Analysis

A sampling and analysis scheme illustrated in Figure 1-4 was devised to monitor brine characteristics during the test. Brine samples were taken when corrosion specimens were discharged, and returned to PNL for analysis. The analysis of a sample of inlet brine taken at the gas separator during the first stage of corrosion tests is given in Table 1-3. As noted, some determinations were made in the field.

Corrosion and Film Weight Data

Preliminary weight change data are summarized in Table 1-4 for samples exposed for 6 weeks in both wellhead and acidified brines.

There was very little mineral scale deposit on the samples. Since the test was run with pump overpressure, the CO_2 remained in solution and scaling was suppressed. The 6-1 well is noted for heavy scaling under flashing conditions and we observed such scaling when we depressurized the fluid in the bypass. Some corrosion product scale was present, especially on the acidified run.

The acidification increased the corrosion rates of A 53 B, 1010, and 4130 by 3 to 5 times. There was no increased corrosion for the 410 and E-Brite 26-1 upon acidification. The acidification reduced scale on the corrosion resistant 410 and E-Brite 26-1 slightly, but slightly increased the film thicknesses on the carbon steels, probably because of increased corrosion rates increasing the corrosion films.

Characterization of Geothermal Field Test Samples - R. Wang

Geothermal field test samples were characterized by x-ray diffraction (XRD), x-ray energy spectroscopy (XES), optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The objective of this study is to correlate the scale deposit and corrosion behavior with the formation conditions. Experimental procedures were developed to obtain crystal structures and overall composition of the thin scale deposit, as well as variation of the microstructure and composition throughout the sample thickness. The microstructure of the thin scale deposit was investigated

FIGURE 1-4. Brine Sampling, Treatment, and Analysis Scheme for Corrosion Test, DOE Geothermal Component Test Facility, East Mesa Well 6-1

TABLE 1-3. Analysis of East Mesa 6-1 Brine, 3-17-77

Parameter	Value
HCO_3^-	87 mg/l
$\text{CO}_3^{=}$	0 mg/l
Conductivity	28,200 μmhos
SiO_2	260 lab, 300 field (mg/l)
Fluoride	1.9 mg/l
Calcium	720 mg/l
Sodium	7,000 mg/l
pH	5.57 field at 25°C
Potassium	750 mg/l
Strontium	110 mg/l
Magnesium	23 mg/l
TDS	21,131 mg/l
Lithium	34 mg/l
Iron	2.8 mg/l
Chloride	11,875 mg/l
Zinc	0.07 mg/l
Copper	<0.04 mg/l
Manganese	0.8 mg/l
$\text{SO}_4^{=}$	28 mg/l
Al	<0.7 mg/l
Barium	14 mg/l
Antimony	1.7 mg/l
$\text{S}^{=}$	4.6 mg/l
Boron	20 mg/l
Si-AA	148 (317 SiO_2) mg/l
NH_3	42 nessler, 36 electrode
O_2 (field)	0 mg/l
H_2S (field)	2.9 mg/l
CO_2 (field)	7,450 mg/l
CO_2 (from NaOH stabilizing solution)	2,350 mg/l

TABLE 1-4. Corrosion and Film Weight Data for Alloys Exposed Six Weeks in Wellhead Brine (pH 5.8) and Acidified Brine (pH 4.6 to 4.8)

Alloy	Temperature °C	Flow Rate ft/sec	Corrosion Rate (mils/year)		Film Weight (mg/cm ²)	
			Wellhead	Acidified	Wellhead	Acidified
1010	160	10	2.0 ± 0.5	8.3 ± 0.4	5.7 ± 0.8	4.6 ± 0.7
1010	160	5	1.8 ± 0.1	11.3 ± 5.0	8.2 ± 0.8	5.2 ± 0.1
1010	160	1	2.2 ± 0.7	9.5 ± 0.4	4.0 ± 0.7	6.0 ± 1.1
1010	150	10	1.8 ± 0.1	--	1.9 ± 0.4	3.7 ± 0.1
1010	150	5	2.6 ± 1.6	9.0 ± 0.6	1.9 ± 0.2	4.8 ± 0.1
1010	150	1	1.5 ± 0.1	10.5 ± 1.5	1.5 ± 0.1	4.0 ± 0
1010	50	10	2.1 ± 0.6	2.2 ± 0.2	0.4 ± 0	0.7 ± 0
1010	50	5	3.4 ± 3.7	1.8 ± 0.4	0.5 ± 0.1	0.4 ± 0.1
1010	50	1	1.4 ± 0	1.6 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
A53B	160	10	2.0 ± 0.6	9.4 ± 1.6	5.1 ± 0.8	4.5 ± 0.5
A53B	160	5	1.8 ± 0.1	9.3 ± 0.6	9.4 ± 0.3	4.9 ± 0.6
A53B	160	1	3.7 ± 1.7	11.4 ± 1.6	5.7 ± 1.9	4.9 ± 0.1
A53B	150	10	2.6 ± 0.1	18.3 ± 0.6	3.4 ± 0.1	4.4 ± 0.3
A53B	150	5	1.3 ± 0.2	9.8 ± 1.0	2.1 ± 0.2	5.6 ± 0.9
A53B	150	1	1.8 ± 0.4	9.4 ± 1.3	2.3 ± 0.2	4.7 ± 0.4
A53B	50	10	0.5 ± 0	5.6 ± 0.2	0.9 ± 0.1	2.3 ± 0.1
A53B	50	5	1.0 ± 0.4	4.8 ± 0.2	0.8 ± 0.2	1.4 ± 0.1
A53B	50	1	1.8 ± 0	2.8 ± 0.4	0.4 ± 0	1.3 ± 0.4
4130	160	10	2.1 ± 0.6	17.0 ± 3.7	4.4 ± 0.4	7.4 ± 1.2
4130	160	5	2.3 ± 0.2	19.3 ± 1.8	9.5 ± 0.4	8.1 ± 0.4
4130	160	1	3.3 ± 1.3	--	5.7 ± 1.9	5.5 ± 0.1
4130	150	10	2.5 ± 0.8	18.3 ± 0.6	2.6 ± 0.8	5.1 ± 1.8
4130	150	5	2.4 ± 0.3	15.5 ± 1.4	3.1 ± 0.4	5.6 ± 0.9
4130	150	1	2.3 ± 0.4	11.0 ± 2.8	2.2 ± 0.5	4.0 ± 0.4
4130	50	10	1.3 ± 0.2	5.4 ± 2.5	0.4 ± 0.1	1.1 ± 0.6
4130	50	5	2.4 ± 0.3	5.0 ± 0.6	0.3 ± 0.1	0.8 ± 0.3
4130	50	1	2.9 ± 0.3	3.5 ± 0.2	0.1 ± 0.1	0.1 ± 0.1

TABLE 1-4 (contd)

Alloy	Temperature °C	Flow Rate ft/sec	Corrosion Rate (mils/year)		Film Weight (mg/cm ²)	
			Wellhead	Acidified	Wellhead	Acidified
E-Brite 26-1	160	10	<0.1	6.3 + 8.8	3.2 + 0.2	0.3
E-Brite 26-1	160	5	0.5 + 0.6	0.1	5.3 + 0.5	0.5 + 0.3
E-Brite 26-1	160	1	0.2	0.1	1.1 + 0.2	0.1 + 0.1
E-Brite 26-1	150	10	0.1	0.1	0.7 + 0.2	0
E-Brite 26-1	150	5	0.1	0.1	1.0 + 0.1	0
E-Brite 26-1	150	1	0.3 + 0.3	0.1	0.4 + 0	0
E-Brite 26-1	50	10	0.5 + 0.7	0	0.3 + 0.1	0.6 + 0.1
E-Brite 26-1	50	5	0.1 + 0.1	0	0.5 + 0.1	0.4 + 0.0
E-Brite 26-1	50	1	0.4 + 0.6	0	0.2 + 0.1	0.2 + 0.0
410 SS	160	10	0.5 + 0.1	0.6 + 0.9	3.0 + 0.2	0.2 + 0.1
410 SS	160	5	0.5	2.0 + 1.0	5.9 + 0.5	0.7 + 0.2
410 SS	160	1	1.0 + 0.3	--	3.4 + 0.9	0.1
410 SS	150	10	0.6 + 0.1	1.3 + 0.3	1.5 + 0.0	0
410 SS	150	5	0.5 + 0.1	1.8 + 0.6	1.3 + 0.1	0.7 + 0.3
410 SS	150	1	0.6	0.1	0.8 + 0.1	0.6 + 0
410 SS	50	10	0.2	0	0.4 + 0.1	0.9 + 0
410 SS	50	5	0.3 + 0	0	0.5 + 0.1	0.5 + 0.0
410 SS	50	1	0.2 + 0	0	0.2 + 0	0.2 + 0.1

for the first time by TEM. With combined characterization techniques of this kind, we have obtained important information regarding the scale formation and corrosion behavior for materials under different temperature, time, pH, and relative position with respect to the brine inlet. This quarter's work was concentrated primarily on the samples tested at a flow rate of 5 ft/sec.

Phase Identification

Crystalline phases of the scale deposit and corrosion product were investigated by XRD analysis. Samples for XRD were prepared by cutting the sample rings open and then flattening them with a vise. Diffraction patterns were recorded by diffractometer scans of 2θ between 10° and 70° at a rate of $1^\circ/\text{min}$ with $\text{CuK}\alpha$ radiation. Phase identification was made by comparison of the intensity and the 2θ angle of the diffraction peaks with those of possible phases assumed from the elemental composition of the sample determined from XES.

The current status of phase identification is summarized in Table 1-5. The results should be considered as tentative because further analysis is needed for the complex diffraction patterns containing several major and minor phases. Traces of crystalline phases shown in some samples are due either to thin scale deposit or small amounts of corrosion. It is expected that the cross-section studies described in the next section will help to determine those unidentified phases.

Characterization of Sample Cross-Section

A large effort was devoted to the characterization of the microstructure and composition of the sample cross-section for understanding of the scale formation and corrosion behavior. The cross-section samples were prepared by a vacuum impregnation technique using a liquid resin curable at room temperature. This technique preserves the thin scale deposits during the polishing process. The sample was then diamond polished from the coarsest to the finest stage. The diamond polishing eliminates the possible contaminants such as Al and Si contained in alumina and corundum polishing compounds, respectively.

TABLE 1-5. Phases Identified in Films on Geothermal Field Test Samples by X-ray Diffraction (Tentative)

Sample ^(a) Location	Temperature °C	Flow ft/sec	Material ^(b)				
			1010	A53B	4130	410	E-Brite 26-1
IA4	160	10	$\text{Fe}_{0.955}\text{S}$ (Troilite) $(\text{Zn}, \text{Fe})\text{S}$ (Marmatite) FeAs Unidentified phases				
IB4	160	5	[Same as IA4]				
IC4	160	1	$\left[\begin{array}{l} \text{Fe}_{0.955}\text{S} \text{ (Troilite)} \\ \text{FeAs} \end{array} \right]$				
IIB4	150	5	[Same as IC4]				
AIB4	160 (Acidified)	5	$\left[\begin{array}{l} \text{Fe}_{0.955}\text{S} \\ \text{FeAs} \\ \text{Unidenti-} \\ \text{fied phases} \end{array} \right]$				
AIIB4	150 (Acidified)	5	$\left[\begin{array}{l} \text{Fe}_{0.955}\text{S} \\ \text{FeAs} \\ \text{Unidenti-} \\ \text{fied phases} \end{array} \right]$				
IIIB4	50	5	[No Crystalline Phases shown]				
AIIB4	50 (Acidified)	5	[No Crystalline Phases shown - Containing amorphous Sb_2S_3]				

(a) All samples exposed 4 weeks. See Figure for location.

(b) In general, composition of films is not affected by alloy composition.

Typical scale deposits are shown in Figure 1-5 to illustrate the two types of scale formation, thin and thick scales. Micro-chemical analysis from electron-beam excited x-ray energy spectroscopy shows that Fe and Si were homogeneously distributed throughout the thickness as the major elements. Occasionally, As and Sb-rich layers were found near the outer layer surface of the scale deposit.

The corrosion products are illustrated in Figure 1-6 to show the layered microstructures. Figure 1-7 illustrates the composition variations with respect to the microstructure along the thickness of the sample CZ-136 (1010 carbon steel). The outermost layer on the surface contains As and Sb. The main body of the corrosion product consists of Fe and Si. Elemental S was observed near the outer part of the deposit. A high concentration of Si was found in the inner part of the scale and at the interface between the corrosion product and the base-material. Because Si and Fe are present in much higher concentration than other elements and the amount of S was not sufficient to tie down the Fe in the forms of Fe-S, it is possible that a large part of the Fe is in the form of amorphous FeSiO_3 mixed with amorphous SiO_2 .

Transmission Electron Microscopy

Thin scale deposit about 3 μm thick consisting only of the oxides of silicon and iron from sample FY-168 (E-Brite 264) was investigated with a 200 kV transmission electron microscope. The sample was prepared by coating the scale with carbon and then stripping it from the base-material. TEM was done at the edges of the sample. Figure 1-8 is probably the first TEM micrograph ever taken of a scale deposit from geothermal field test samples. The electron micrograph shows that the deposit was rather dense, containing no void or holes. The micrograph consisted of dark vein-like strips and light areas; the latter were due to the thinness of the film. We have not been able to determine what causes the dark vein-like pattern.

Next Quarter

For the next quarter, characterization of field test samples will be carried out to identify crystalline phases of severely corroded samples and

A. Thin Scale on FY-132; E-Brite 26-1 Exposed at 165°C,
5 ft/sec, 4 weeks, pH 4.6 to 4.8

B. Thick Scale on CX-24; 4130 Steel Exposed at 165°C,
5 ft/sec, 4 weeks, pH 5.6 to 5.8

FIGURE 1-5. Scanning Electron Micrographs Showing
Two Types of Scale Formation

A. Pitting on CZ-139; 1010 Carbon Steel exposed at 165°C, 5 ft/sec, 4 weeks, pH 4.6 to 4.8

B. Severe Corrosion of CZ-136; 1010 Carbon Steel exposed at 165°C, 5 ft/sec, 4 weeks, pH 4.6 to 4.8

FIGURE 1-6. Scanning Electron Micrographs Showing Pitting and Corrosion

FIGURE 1-7. Scanning Electron Microanalysis Showing Composition Variations in the Cross-Section of the Field Test Sample CZ-136 (1010 Carbon Steel exposed at 165°C, 5 ft/sec, 4 weeks, pH 4.6 to 4.8)

FIGURE 1-8. Transmission Electron Micrograph of Thin Scale Deposit from Geothermal Field Test Sample FY-168 (E-Brite 26-1 exposed at 150°C, 5 ft/sec, 4 weeks, pH 4.6 to 4.8)

to determine the structure of the thin scale. A series of autoclave laboratory samples will be characterized to compare with the field test samples at similar conditions.

2. DEVELOPMENT OF PROBES FOR DOWN HOLE AND IN-LINE CHEMICAL ANALYSIS OF HIGH PRESSURE, HIGH TEMPERATURE GEOTHERMAL FLUID

M. J. Danielson and O. H. Koski

The purpose of this program is to develop electrical and electrochemical devices to measure the water chemistry at the high temperatures and pressures encountered in the geothermal environment, both down hole and above the ground. Knowledge of the water chemistry can be invaluable in predicting and controlling scaling, corrosion, and pollutant release. Being able to recognize and control these three problems will be necessary if geothermal power generation is to become economically feasible.

In FY-77 a thermodynamic high temperature Ag, AgCl reference electrode was developed in the laboratory that was operative in conditions encountered in geothermal brines (dissolved H_2S and varying salinities). A reference electrode was the first electrochemical device to be developed since other electrochemical devices are dependent upon it. An electrodeless conductivity probe was also developed in the laboratory⁽³⁾ in FY-77. This design was chosen because its operation is very resistant to scale deposition effects.

In FY-78, work is proceeding in three tasks to develop electrochemical probes and test them in the field.

Task 1. Field Test of Conductivity Probes

The electrodeless conductivity probes developed in FY-77 are scheduled to be field tested.

Task 2. Laboratory Study of Probes

This task is proceeding with the investigation of a redox probe.

Task 3. Linear Polarization Method

This method of measuring instantaneous corrosion rates will be investigated although work was not started this reporting period.

TASK 1. FIELD TEST OF CONDUCTIVITY PROBES

A field test has been arranged with Republic Geothermal in California at the East Mesa test site for February 1978. PNL is building five units of the type shown in Figure 2-1. This design is a heavy duty model of the laboratory version. PNL's geothermal consultant, Dr. Otto Vetter, has reported that steam velocities can approach sonic velocities; consequently, the probes are built very strong to resist the high forces that could be encountered in the test loop. Electrical connections at the junction box are made weatherproof. The internal design of the electrodeless probe is the same as the laboratory models. Both the spool piece and the packing nut contain a stepped-down portion which prevents the ceramic tube from being pushed out of the probe by the liquid forces. Each probe has been autoclave tested. A conax fitting is to be used to make the pressure seal between the probe and the test loop. The conductivity probe can be slid in and out of the test loop pipe through the Conax seal. This may make it possible to detect different types of two-phase flow, such as steam passing through the center of the pipe with liquid flowing at the sides versus slug-flow or well dispersed bubbles. Two-phase flow would be recognized with an electrodeless conductivity probe by a variable output as the liquid column inside the ceramic tube is replaced with steam.

Five individual electronics packages and associated cabling have been built. Each contains a pulse generator and receives for one probe. The data from these will be fed to a data-logger which will print out the conductivity values from each probe.

Initially, two probes were potted with a potting compound to fill the spaces around the toroids inside the probe body. This was to act as a back up real in case the Rulon gasket leaked since the probe is very sensitive to internal moisture. Unfortunately, the potting compound decomposed at elevated temperatures and shorted out the toroid coils so that this approach had to be abandoned. The spring-loaded seal has been very successful in the laboratory; the field experiments will serve as additional testing. The absolute number of temperature cycles to 250°C before the seal leaks (without adjustment of the packing nut) has not been determined.

FIGURE 2-1. Field Model of the Electrodeless Conductivity Probe

TASK 2. LABORATORY STUDY OF PROBES

The redox probe (also known as E_h probe) is currently being investigated. Ideally in a simple equilibrium case as shown:

the E_h of this system would be the electrochemical potential (E) on the standard hydrogen scale. If the system was in equilibrium, a platinum (or some other inert metal) electrode could be inserted into the solution and the potential, E , measured versus a standard hydrogen electrode. In reality, these systems are complicated by containing more than two components, but it can often be assumed that all the components are in equilibrium with each other; thus, the E_h measurement can still be correct. Ideally, E_h would indicate the general "oxidativeness" of the geothermal environment, and this could imply the general type of brine chemistry. Further, geothermal brines are usually in a highly reduced state. Any intrusion of oxygen (which greatly accelerates corrosion rates) would raise the "oxidativeness" of the brine environment and could be recognized by an E_h measurement.

E_h measurements have not been carefully examined at elevated temperatures, but a major problem at ambient conditions is that the inert metal electrode (usually platinum) is slowly poisoned and becomes unresponsive to the environment. Secondly, the measured E_h values do not often respond to those calculated from thermodynamics. Elevated temperatures generally increase reaction rates, and this assists reactions into reaching equilibrium. It is hoped that the elevated temperatures encountered in brine systems will prevent electrode poisoning and improve the thermodynamic reversibility on the electrode surface.

A number of experiments were run using both a platinized platinum (Pt-Pt) and a bare platinum foil (Pt-foil) electrode subjected to environments of differing oxidation potential (or oxidativeness). Their electrochemical potential was measured versus the PNL thermodynamic reference electrode⁽³⁾ inside a refreshed autoclave (Inconel 600) at temperatures of 25 to 250°C. The autoclave always contained 0.1 M KCl. On two occasions, oxygenated brine was injected to determine the platinum electrode response. The oxygenated

experiments were of a short duration because of rapid corrosion attack on the autoclave. Extended experiments in oxygenated brines and brines containing hydrogen sulfide must wait until the titanium autoclave is received.

Figures 2-2 through 2-6 are the high-temperature Pourbaix diagrams for the Fe-H₂O system calculated by Biernot and Robins⁽⁴⁾ for the temperature range of 25-300°C. To determine if the redox electrodes are operating correctly, their response is compared to the theoretical response shown on the diagram.

Before discussing the experimental data, a few words must be said about Pourbaix diagrams. Line A in each figure (diagonal lines) corresponds to oxygen reduction:

and line B corresponds to hydrogen evolution:

The dark solid lines refer to the domains of equilibrium of the principal species, and the short dashed lines are the domains of equilibrium between ionic species. It is important to note that in order to calculate these diagrams, an entropy must be assigned to the hydrogen ion, consequently, the potential of reaction B is not zero at a pH of zero. This does not fit the definition of the standard hydrogen electrode (SHE) which is zero at all temperatures (the experimental data of this study is on the SHE scale). The potential axis of Figures 2-2 through 2-6 should be shifted (by the reader) so that zero volts correspond to the intercept of line B at a pH of zero.

The experimental systems were all buffered with CO₂. The pH values of both 0.5 and 1.0 atm CO₂ systems were very constant with temperatures⁽¹⁾ at about 4.3. The system containing 0.5 atm H₂ will give almost the same theoretical potential as a 1.0 atm H₂ system within a few mV.

Table 2-1 shows the data extracted from the Pourbaix diagrams. Only two significant figures are shown because the diagrams are redrawn from those in the original article, and the potentials were read directly.

FIGURE 2-3. Potential/pH Diagram for Fe-H₂O System at 100°C⁽⁴⁾

FIGURE 2-4. Potential/pH Diagram for Fe-H₂O System at 150°C⁽⁴⁾

FIGURE 2-5. Potential/pH Diagram for Fe-H₂O System at 200°C⁽⁴⁾

FIGURE 2-6. Potential/pH Diagram for Fe-H₂O System at 300°C⁽⁴⁾

Tables 2-2 through 2-5 show the experimental data of this study. From the experimental data, it is observed that the Pt-Pt electrode and Pt-foil electrode data do not agree with each other until the temperature is about 200°C. Other scientists have made the observation at 25°C with the hydrogen electrode that a bare Pt-foil is slow to reach equilibrium. Elevated temperatures increase the reactive rates so that equilibrium can be reached on the sluggish responding Pt-foil. A Pt-Pt electrode should be the electrode of choice for temperatures below 200°C.

The most reducing environment for these experiments was the H^+-H_2 system, and the electrode response agreed with the theoretical response fairly well. A step up in oxidativeness was the $Fe_2O_3-Fe_3O_4$, $Fe^{+2}-Fe_3O_4$ systems. The response of these temperatures was similar. An examination of the Pourbaix diagrams indicates that Fe^{+2} may be unstable in this pH range and could convert to Fe_3O_4 ; hence, the similarity of response. The agreement between experiment and theory for the $Fe_2O_3-Fe_3O_4$ systems was also fairly good. When oxygen was injected in these two systems at 200°C, the potential shifted over 150 mV in a direction indicating increasing oxidativeness of the environment. The response was rapid and was noticed within a few minutes after starting the injection of oxygenated brine. This is important evidence that the redox probe will be able to report oxygen intrusions into geothermal systems. The potential response is far removed from the theoretical O_2-H_2O values. This behavior⁽⁵⁾ is also observed at ambient conditions, and the theoretical response of the O_2-H_2O equilibrium is almost never observed. Rather, the potential is nearer the range of the $O_2-H_2O_2$ equilibrium ($E_{SHE} \approx 0.4$ V at pH of 4 at 25°C).⁽⁶⁾ Oxygen injected into the reduced system in the autoclave is most likely oxidizing the Fe_3O_4 to Fe_2O_3 keeping the free oxygen concentration low and producing some H_2O_2 as an intermediate product. The electrode may be responding to a steady state condition (mixed potential) rather than a true equilibrium. Longer term experiments with oxygen will be carried out in a titanium autoclave when it is received from the manufacturer.

TABLE 2-1. Potentials^(a) Picked from Pourbaix Diagram in Various Equilibria

Temperature, °C	Fe-Fe(OH) ₂	Fe ⁺² -Fe(OH) ₃	Fe ⁰ -Fe ₃ O ₄	Fe ₃ O ₄ -Fe ₂ O ₃	O ₂ -H ₂ O	H ⁺ -H ₂
25	-.40	+.19	--	--	+.95	-.25
100	-.48	-.48	--	--	+.75	-.35
150	--	--	-.55	-.20	+.70	-.38
200	--	--	-.60	-.28	+.65	-.40
300	--	--	-.73	-.35	+.50	-.50

(a) Potentials shown are on the SHE scale

TABLE 2-2. Redox Electrode Experimental Data for 0.5 atm H₂-0.5 atm CO₂

Temperature, °C	$E_{\text{Pt-Pt}} - E_{\text{SHE}}$	$E_{\text{Pt-foil}} - E_{\text{SHE}}$
20	-.239, -.259	+.018, -.097
120	-.355, -.344	-.195, -.345
160	-.405, -.384	-.389, -.371
200	-.454, -.438	-.441, -.430
250	-.524, -.506	-.508, -.491

TABLE 2-3. Redox Electrode Experimental Data for 1 atm CO₂

Temperature, °C	$E_{\text{Pt-Pt}} - E_{\text{SHE}}$	$E_{\text{Pt-foil}} - E_{\text{SHE}}$
20	-.013, -.052	+.409, +.359
120	-.182, -.191	+.192, +.255
160	-.265, -.227	-.050, +.088
200	-.320, -.289	-.219, -.202
250	-.402, -.376	-.385, -.375

TABLE 2-4. Redox Electrode Experimental Data for Fe₂O₃-Fe₃O₄-1 atm CO₂

Temperature, °C	$E_{\text{Pt-Pt}} - E_{\text{SHE}}$	$E_{\text{Pt-foil}} - E_{\text{SHE}}$
20	+.119, -.054	+.346, +.315
120	-.211, --	+.179, --
160	-.212, -.276	-.080, +.046
200	-.285, -.296	-.229, -.286
250	-.381, --	-.393, --

(Injected 0.5 atm air - 0.5 atm CO₂ at 1 liter/hr)

200	-.070	+.022 after 60 min
	-.152	+.008 after 4 hr

TABLE 2-5. Redox Electrode Experimental Data for
100 ppm Fe^{+2} - Fe_3O_4 -1 atm CO_2

<u>Temperature, °C</u>	<u>$E_{\text{Pt-Pt}} - E_{\text{SHE}}$</u>	<u>$E_{\text{Pt-foil}} - E_{\text{SHE}}$</u>
20	-.026	-.072
120	-.186	+.016
160	-.267	-.162
200	-.350	-.367
250	-.416	-.437
(Injected 0.5 atm air - 0.5 atm CO_2 at 1 liter/hr)		
200	-.095	-.053 after 75 minutes

3. MANUAL FOR GEOTHERMAL FLUID-GAS ANALYSES

J. C. Watson, E. M. Woodruff, J. G. Douglas, and O. Vetter, Consultant

Details of the chemical composition of geothermal brines and gases are needed to assess the impact of these materials on corrosion and scaling, plant design, and environmental issues. The sampling and analysis procedures under consideration for performing the determinations are those regarded as state-of-the-art. The involvement of organizations presently concerned with geothermal activity is necessary to identify these procedures.

Task 1. Survey Existing Sampling and Analysis Methods

The objective of this task is to collect the existing sampling and analysis methods presently used in the geothermal industry into a manual of recommended procedures. It is not intended that the manual contain other than existing methods with the exception that modifications of these methods as deemed appropriate to the uniqueness of sampling and analysis of geothermal samples are mentioned.

Task 2. Conduct Methods Evaluation at PNL

The objectives of this task are to a) fabricate the appropriate sampling equipment to be used in the evaluation of geothermal sampling methods; and b) to further evaluate methods of analysis reported by participants in the survey of existing methods (Task 1). The most important techniques to be evaluated for b) above are the use of plasma emission spectroscopy and ion exchange chromatography.

Task 3. Conduct Cooperative Methods Evaluation with Participating Laboratories

The objective of this task is to conduct a field evaluation of existing sampling procedures to determine their effectiveness under field conditions and to compare the procedures relatively. The comparative results will be incorporated in the final manual of recommended sampling and analysis procedures.

TASK 1. SURVEY EXISTING SAMPLING AND ANALYSIS METHODS - E. M. Woodruff,
J. C. Watson, J. G. Douglas and O. Vetter, Consultant

Input for the survey of existing analysis methods for geothermal fluids and gases was provided by a group of 20 participating laboratories under sub-contracts. Two sets of geothermal liquid samples collected during the summer of 1977 were distributed to participants of the program and the participants were asked to analyze the samples using their own existing procedures. The participants were asked to provide information on methods used and in addition were asked to provide input for the survey in the form of comments on existing procedures and statistical information relative to the methods used.

Interim Manual of Sampling and Analysis Procedures for Geothermal Fluids and Gases - J. C. Watson

The round robin field programs involving the participating laboratories were conducted in July and August 1977. The first set of geothermal samples was collected at the East Mesa Geothermal Field, Imperial Valley, California, using Mesa 6-2 wellhead brine. The intent was to begin the test program using a relatively simple brine (Mesa 6-2 being ~0.5% dissolved solids) in order to evaluate the analytical methods. An example of the data generated by the participants is the data for sulfate analysis as depicted in Figure 3-1. The data indicate a spread of $\pm 30\%$ from the mean value of 151 mg/l. In all, forty parameters were investigated to characterize the brine from the East Mesa 6-2 well.

The second round robin was conducted using brine from the Geothermal Loop Experimental Facility, Niland, California. The sample was taken from the first stage flash unit and contained ~22% dissolved solids. An examination of the data for sulfate from the Woolsey #1 first stage flashed brine as shown in Figure 3-2 indicates a spread of $\pm 300\%$ from the mean value of 63 mg/l. This degree of spread might be due to the higher concentrations of matrix components in this brine.

The methods of analysis used by the participants have been written on standardized formats similar to the one shown in Figure 3-3. For the two round robins conducted, 219 different methods were used to evaluate the forty parameters of interest.

- GRAVIMETRIC WITH IGNITION
- TURBIDIMETRIC
- AA (BaSO_4 ppt, AA ON Ba)
- ◇ GRAVIMETRIC WITH DRYING
- △ FLAME EMISSION (BaSO_4 ppt, EMISSION ON Ba)
- ▲ ION EXCHANGE CHROMATOGRAPHY

FIGURE 3-1. East Mesa 6-2 Wellhead Brine - Sulfate Analysis

FIGURE 3-2. Woolsey #1 First Stage Flashed Brine - Sulfate Analysis

Ca

Calcium

Analysis: Flame Emission

No.

Method: Calcium is determined by aspirating the sample into a nitrous oxide-acetylene flame and the emission intensity at 422.7 nm from calcium is measured by a spectrophotometer.

Sample Handling: Use raw acidified or filtered acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and adding 5 ml HNO_3 per liter of sample.

Range: >0.05 mg/l

Precision: <0.5 mg/l $\pm 25\%$
>0.5 mg/l $\pm 5\%$

Accuracy: <0.5 mg/l $\pm 25\%$
>0.5 mg/l $\pm 5\%$

Cross Reference:

Literature Reference:

Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 33-65.
W. Snelleman, Spectrochim. Acta, **23B**, 403 (1968).

Reagents:

Calcium atomic absorption standard solution or calcium carbonate
Hydrochloric acid (to dissolve calcium carbonate)
Nitrous oxide gas cylinders
Potassium chloride or potassium nitrate

Equipment:

Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.
Nitrous oxide burner head.

- Remarks:**
1. Addition of potassium chloride or potassium nitrate to give a final concentration of 2000 mg/l K is necessary to suppress ionization.
 2. Slightly higher height of observation in flame reduces potential chemical interferences.
 3. Use of standard additions and matrix matching of alkali and alkaline earth metal ions recommended.

FIGURE 3-3. Format of Methods Manual

Sampling methods are described on a format similar to the one shown in Figure 3-4. These sampling methods will be evaluated during the current fiscal year program.

The interim manual is in the final stages of compilation and will be released in February for comments by participants in the round robin. Final printing is scheduled for July 1978.

TASK 2. CONDUCT METHODS EVALUATION AT PNL - J. C. Watson and J. G. Douglas

Methods of analysis identified by the participating laboratories in the round robin program which are innovative and show particular promise for analyzing geothermal samples are currently being evaluated at PNL. Also under study are improvements and modifications of existing procedures as reported by the participating laboratories.

Evaluation of New Instrumental Procedures for Analyzing Geothermal Samples - J. C. Watson

As demonstrated during the geothermal round robin test program, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ion exchange chromatography have shown promise for analyzing geothermal samples. ICP-AES procedures allow for the rapid determination of metal ion concentrations in solution samples containing up to 3% dissolved solids without dilution. The simultaneous determination of a large number of metal components in geothermal brines is possible with this procedure. An evaluation of the capability of plasma emission spectroscopy for handling geothermal samples was made. Geothermal brine samples containing from 0.5 to 15% total dissolved solids were analyzed by a Jarrell-Ash Plasma Atomcomp system. The data obtained for two of the brines, East Mesa 6-1 well (2.5% dissolved solids) and Woolsey #1 well (15% dissolved solids) are presented in Table 3-1. The first brine was run undiluted while the Woolsey brine was diluted 10:1. Values obtained by conventional analyses (atomic absorption, spectrophotometric, etc.) are presented for comparison. Following initial calibration of the instrument average analysis time is about 1 minute for the 18 brine components. PNL has received a Jarrell-Ash plasma spectrometer capable of simultaneously analyzing 31 different metal ion brine components. Installation of this instrument is

APPLICATION:

Downhole sampling.

SAMPLE TYPE:

Liquid and gas.

SAMPLE POINT:

Wellbore

REFERENCE: Fournier, R.O. and J.C. Morgenstern, "A Device for Collecting Down-Hole Water and Gas Samples in Geothermal Wells," U.S.G.S. Prof. Paper 750-C, p. C151-155, 1971.

DESCRIPTION:

1. Sampler in open position is lowered using a long flexible stainless steel tube into the wellbore and fluid flows through it during descent. Closure is accomplished by nitrogen gas pressure applied from the surface through the flexible tube to a piston and plunger within the sample chamber. Continued application of nitrogen gas pressure during withdrawal of the device prevents leakage caused by changing conditions of temperature and pressure.
2. All materials are stainless steel except for one teflon o-ring, two viton o-rings, and several other teflon parts.
3. A modification of the lower end of the sampler using a special gas extraction fitting allows the sampler to be used for gas sampling.
4. Additional references: a) Fournier, R. O. and A. H. Truesdell, "A Device for Measuring Down-Hole Pressures and for Sampling Fluids in Geothermal Wells," U.S.G.S. Prof. Paper 750-3, p. C146-C150, 1971.
b) Fournier, R. O. and J. M. Thompson, "Geothermal Down-Hole Sampling Instrumentation," Proceedings, 2nd Workshop on Sampling and Analysis of Geothermal Effluents, Las Vegas, NV, February, 1977.

FIGURE 3-4. Format of Sampling Methods

TABLE 3-1. ICP-AES Analysis of Geothermal Brines

	East Mesa 6-1 Separator (2.5% Dissolved Solids)		Woolsey #1 (15% Dissolved Solids)	
	Atomic Absorption PNL (ppm)	Plasma-Arc Jarrell-Ash (ppm)	San Diego Gas and Electric (AA) (ppm)	Plasma-Arc Jarrell-Ash (ppm)
Na	7,200	6,012, 6,417	40,000	40,430
K	680	691, 767	10,000	8,847
Ca	786	755, 826	20,000	22,180
Fe	2	4, 4	150	127
Mn	0.6	0.66, 0.67	475	413
Zn	0.1	0.24, 0.25	125	110
Cu	<0.04	0.0	1	1
Pb	<0.5 (old data)	0.0233, 0.0240	30	37
Al	<0.7	0.0	1	0
Sr	100	125, 127	340	386
Ba	15	15, 15	150	85
Si	120	128, 132	170	150
Mg	18	14, 14	160	139
B	12	14, 15	250	278
Ag	0.013 (old data)	0.013	0.2	0.35
As	0.26 (old data)	0.55, 0.58	--	10
Ni	<0.01 (old data)	0.0007, 0.0006	--	2
Cr	<0.01 (old data)	0.0007, 0.0006	--	0.25

currently underway. Procurement is underway for an ion exchange chromatograph. This instrument is capable of sequentially analyzing a brine sample for halide ions (fluoride, chloride, bromide, etc.), sulfate, phosphate, nitrate and nitrite. The lower detection limits for these components are in the parts per billion (ppb) range. In addition, a slight modification of this instrument allows for analysis of lithium, sodium, potassium, ammonia, rubidium and cesium in the ppb range. The analysis of these components and the anionic species mentioned above have traditionally been difficult using conventional procedures.

Geothermal Analytical Laboratory Organization - J. G. Douglas

Improvements have been made in laboratory conditions for conducting the work associated with the various geothermal programs at PNL. Existing instrumentation consists of:

- gas chromatograph for analysis of H_2 , CO_2 , N_2 , O_2 and light hydrocarbons in geothermal gases
- two single-beam spectrophotometers for colorimetric analyses
- various pH and millivolt meters for pH and ion selective electrodes.

The following instrumentation is to be added and operational by mid-February 1978:

- atomic absorption unit (in use during the past year in a temporary location) with a new graphite furnace accessory
- automatic titration system which arrived December 5, 1977 (This system will provide rapid, routine determination of brine alkalinity, chloride, carbonate, and other titratable parameters.)
- Hewlett-Packard 21MX microcomputer. This system, as of January 13, 1978, is awaiting final transfer approval from the Richland DOE office. The computer is expected to automate certain data-taking, data-reduction, tabulation, and graphing tasks that are presently done laboriously by hand.

In the near future, the addition of an electronic balance (to be interfaced with the computer) will simplify corrosion sample weighing and cataloging.

Geothermal Analytical Methods Evaluation - J. G. Douglas

Because of the complex nature of geothermal brines, it is apparent that any selected sampling and analysis scheme must be carefully evaluated for accuracy, precision and interferences. Other criteria for evaluation that cannot be overlooked are:

- Approximate performance time for the technique: how quickly can results be obtained?
- Simplicity of the technique: what technical background is required of the analyst to perform the task?
- Multi-element capability: can more than one component be determined simultaneously?

Other factors may enter into the evaluation of an analytical technique, especially when sampling constraints are applied.

The geothermal round robin tests uncovered several techniques that fit the above criteria:

- spark source mass spectroscopy
- inductively coupled plasma-atomic emission spectroscopy
- ion chromatograph.

At present, none of these capabilities exist in the laboratory, although the latter two will be available soon.

To date, we have evaluated the suitability of a number of instrumental and wet techniques to analyze geothermal brines. Examples in particular have been sodium and calcium by atomic absorption (AA) and fluoride by ion-selective electrode.

- 1) Sodium is successfully analyzed by diluting the sample until the sodium concentration is about 10 to 50 mg/l with a 200 mg/l potassium ion background. AA analysis is then conducted with an air-acetylene flame at 330.3 nm using a sodium lamp. The sample absorbance is compared to an absorbance versus concentration curve derived from standard solutions of sodium with a 2000 mg/l potassium background.

- 2) Calcium is analyzed by diluting the sample until the calcium concentration is between 0.02 and 3 mg/l with a background of 2000 mg/l potassium; a nitrous oxide-acetylene flame is used, and absorbance is measured at 422.7 nm using a calcium lamp. The concentration curve derived from calcium standards (2000 mg/l K, 0.12 N HCl matrix) is used to obtain the sample concentration. We have noticed that aluminum will depress the calcium absorption signal in the nitrous oxide flame if the burner height is not carefully selected; we use a sample (rather than a standard) to optimize burner height (i.e., get the highest stable signal), and thus minimize the effect of chemical interference which varies with burner height.
- 3) Fluoride is analyzed with a fluoride-selective combination electrode; the potential in mV's for a series of fluoride standards is plotted against the log of the standard concentrations, and the sample potential is measured against this line to yield the log of the concentration of fluoride in the sample. Background matrices and pH's of samples and standards are matched as nearly as possible, but problems still arise. Whereas the standard curve gives close to a theoretical slope of about 59 mV/decade, standard additions to actual geothermal brines show usually only 85% recovery of the known spikes. It has been found that a fluoride distillation often helps diminish some sample interferences, but that only 87% of the fluoride is usually recovered in a distillation. Unless careful consideration of these interferences is made, seriously low fluoride results will be reported.

TASK 3. CONDUCT COOPERATIVE METHODS EVALUATION WITH PARTICIPATING LABORATORIES -

E. M. Woodruff, J. C. Watson, S. J. Thompson, D. E. Robertson, R. J. Serne, R. G. Sullivan and O. Vetter, Consultant

Survey of Existing Methods and Field Test Program - J. C. Watson

A compilation of 28 sampling methods reported in the literature has been included in the interim manual "Sampling and Analysis Methods for Geothermal Fluids and Gases," January 1978, preliminary edition. The field test program to be conducted during March 1978 will evaluate the sampling procedures contained in the interim manual.

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