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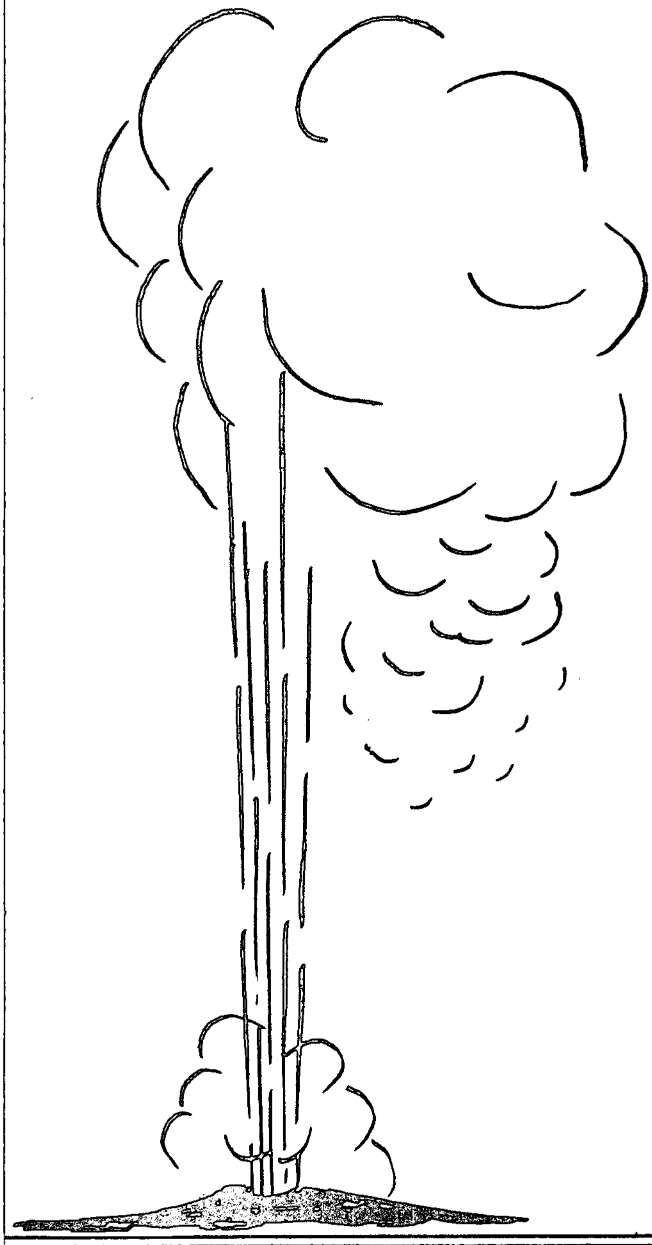

GEOPRESSURED-GEOTHERMAL TEST OF THE EDNA DELCAMBRE NO. 1 WELL, TIGRE LAGOON FIELD, VERMILION PARISH, LOUISIANA: ANALYSIS OF WATER AND DISSOLVED NATURAL GAS

Final Report

MASTER

By
B. E. Hankins
O. C. Karkalits

September 1978

Work Performed Under Contract No. EY-76-S-05-4937

McNeese State University
Lake Charles, Louisiana

U. S. DEPARTMENT OF ENERGY

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FINAL REPORT

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DEPARTMENT OF ENERGY

DIVISION OF GEOTHERMAL ENERGY

by

McNeese State University

Lake Charles, Louisiana 70609

entitled

GEOPRESSURED-GEOTHERMAL TEST OF THE EDNA DELCAMBRE NO. 1 WELL, TIGRE LAGOON FIELD, VERMILION PARISH, LOUISIANA:

ANALYSIS OF WATER AND DISSOLVED NATURAL GAS

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U.S. DOE CONTRACT NO. EY-76-S-05-4937

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ACKNOWLEDGMENT

Our appreciation is given to Cities Service Company, Lake Charles Operations, Lake Charles, Louisiana, for gratuitously performing all of the mass spectrometric determinations and for making the data available for this report.

The assistance of the U.S. Geological Survey, Baton Rouge, Louisiana; Menlo Park, California; and Denver, Colorado is recognized for providing some of the analytical procedures, test data for comparison between laboratories, and test data for other determinations.

Battelle Pacific Northwest Laboratories in Richland, Washington, made data available for some of the heavy metals and we are grateful for their permission to include the values in this report.

ABSTRACT

The presence of large volumes of hot water (250-425°F) containing dissolved natural gas in the Gulf of Mexico coastal areas at depths of 5,000 to 25,000 feet (the geopressured zone) has been known for several years. Because natural gas and oil from conventional production methods were relatively inexpensive prior to 1973, and because foreign oil was readily available, no economic incentive existed for developing this resource.

With the oil embargo and the resulting rapid escalation in prices of oil and gas since 1973, a new urgency exists for examining the economic potential of the geopressured-geothermal resource. The main objective of the research reported here was to determine the volume of gas dissolved in the geopressured water, as well as the qualitative and quantitative composition of the water and the dissolved gas. A further objective was to use an existing shut-in gas well so that drilling time and the attendant costs could be avoided.

The Edna Delcambre et al. No. 1 gas well, shut-in since June 1975, was made available for the project. The well is located about eight miles south of Delcambre, Louisiana in Tigre Lagoon Field, Vermilion Parish, Louisiana. Operations at the well-site were begun by Osborn-Hodges-Roberts-Wieland Engineering on January 29, 1977. Two geopressured sand-bed aquifers were tested: sand No. 3 at a depth of 12,900 feet and sand No. 1 at a depth of 12,600 feet. Each aquifer was subjected to flow tests which lasted approximately three weeks in

each case. The temperature in sand No. 3 was about 238°F. and the pressure was about 10,990 psig. The temperature in sand No. 1 was about 234°F. with a pressure of 10,600 psig. Water flow rates from sand No. 3 varied from 2,500 to 9,000 barrels per day. The net sand thickness of sand No. 3 was 52 feet and the permeability was 40.6 millidarcies. Water flow rates on sand No. 1 varied from 1,200 to 11,800 barrels per day. The net sand thickness of sand No. 1 was 30 feet and the permeability was 364 millidarcies.

Water samples were obtained during flow testing of the two geopressured aquifers. The water contained 11.3-13.3% dissolved solids. The water was acidic, but in-line measurements of pH were 1-2 pH units lower than comparable samples measured in the on-site laboratory. Several radioactive species were measured. Radium-226 was found to be approximately 10 times more concentrated than the average amount observed in surface waters. No appreciable amount of heavy metals was detected.

Recombination studies at bottom-hole conditions indicate the solubility of natural gas per barrel of water to be about 24 SCF. The methane content was 93-95%, and the gas had a heating value in the range of 1,020-1,070 B.T.U./cu.ft. During the flow tests, the gas/water ratio at the well-head was observed to be 45-88 SCF/Bbl water produced. Collections of bottom-hole samples from each of the sand-bed aquifers were attempted with a wire-line sampler. Several attempts were made to obtain representative samples but none of the attempts proved to be satisfactory. Although the bottom-hole test results are reported, the data are considered to be unreliable.

The project was a collaborative effort by Osborn-Hodges-Roberts-Wieland Engineering and McNeese State University. OHRW Engineering did the following: (1) located a suitable well, (2) obtained leases, (3) recompleted the well and obtained bottom-hole water samples, (4) supervised all operations at the well-site, (5) made dynamic flow tests and other engineering studies on the reservoirs (two sand-bed aquifers), (6) negotiated the disposition of the well when field operations were completed, and (7) analyzed the data to describe the reservoir characteristics.

McNeese State University did the following: (1) prepared geological maps of the area near the well, (2) obtained samples and performed most of the analytical work (some chemical analyses were sub-contracted to outside laboratories), and (3) interpreted the gas and water analytical data.

The final reports on project activities are being issued in three parts under the general title Geopressured-Geothermal Test of the Edna Delcambre No. 1 Well, Tigre Lagoon Field, Vermilion Parish, Louisiana.

The separate sections are as follows:

1. Well Completion, Testing, and Production Data Analysis by OHRW Engineering.
2. Analysis of Water and Dissolved Natural Gas by McNeese State University.
3. Geology of the Tigre Lagoon Field, Planulina Basin by McNeese State University.

I. INTRODUCTION

Subsequent to the oil embargo of 1973, the U.S. Department of Energy was established and charged with the responsibility for developing alternate sources of energy, particularly those that do not depend on combustible fossil minerals. One of the most promising alternate sources of energy is geothermal water or steam. Geopressured-geothermal energy is one of the varieties of geothermal energy that looks promising, and is the variety with which this report is concerned.

The term "geopressure" was coined by C.A. Stuart (13). It refers to sedimentary deposits in which the pressure is greater than would be expected from static pressure of the overburden at the depth of sediment under study. The geopressured zones along the northern Gulf of Mexico coast typically have pressures from 1.2 to 2 times as great as the hydropressured zone at the same depth, and have been recognized as different in nature from hydropressured zones.

The geopressured-geothermal resource is different from a hydropressured-geothermal resource in that the water of the resource possesses higher pressures and contains dissolved natural gas. Both of the geothermal resources, however, have hot water as a source of thermal energy. The geopressured-geothermal resource in the northern Gulf of Mexico basin underlies a surface area of approximately 150,000 square miles, extending from the Mexican border to the Mississippi border along the coast lines of Texas and Louisiana. Recent estimates of the magnitude of dissolved natural gas alone are enormous. In a 1975 report, Papadopulos (12) and colleagues at the U.S. Geological Survey estimated the dissolved natural gas underlying the on-shore section of the Gulf Coast at 24,000 quads. Jones (5) estimated the dissolved natural gas in the Gulf Coast, both on-shore and off-shore, at 49,000 quads. It is apparent that recovery of only a small percentage of the dissolved natural gas could supply a large proportion of the nation's energy demand.

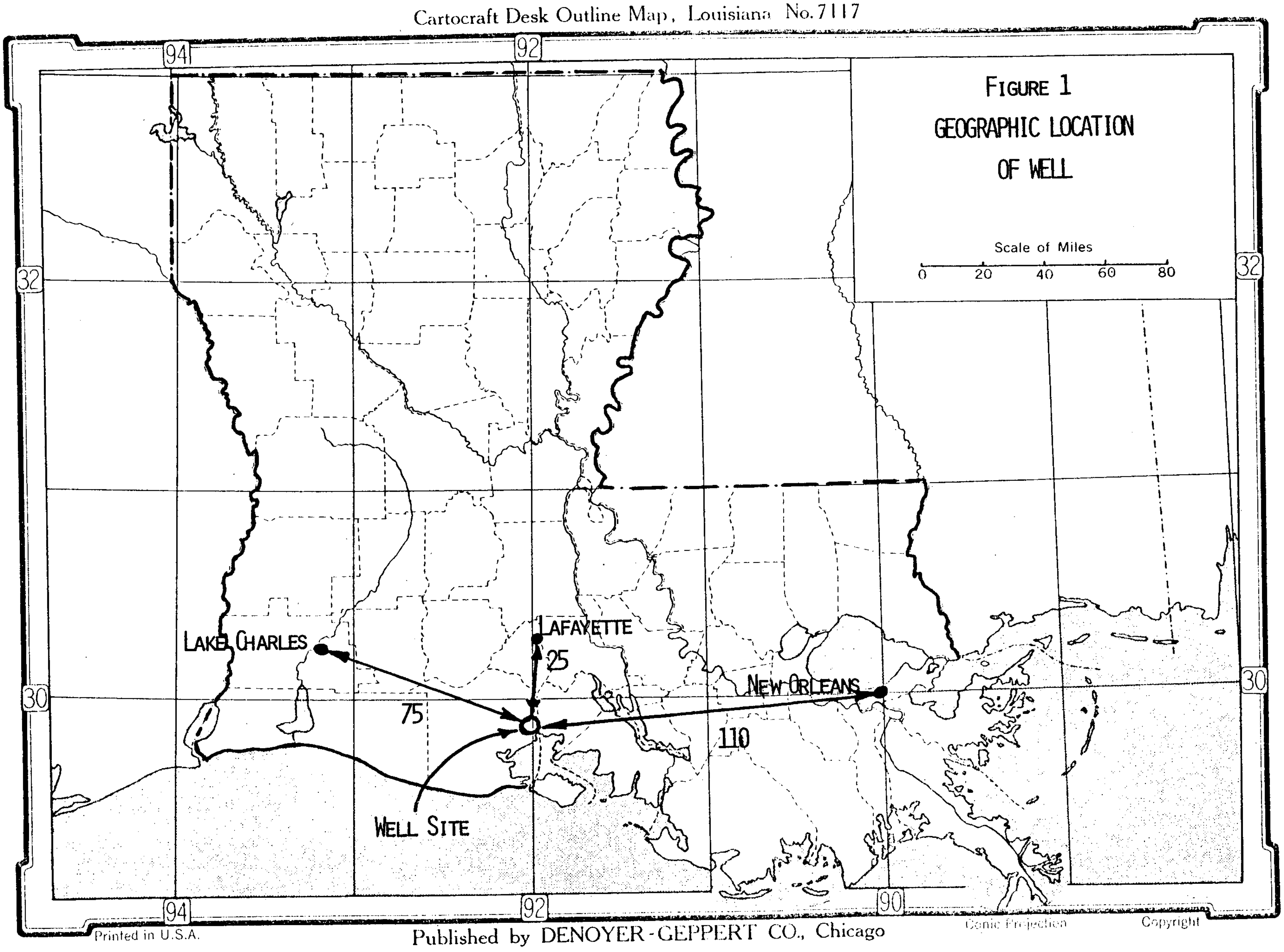
About 1974 the suggestion was made that since the geopressured zone of the Louisiana coastal areas had been tapped by hundreds of oil and gas wells, geopressured water could be obtained for study from an existing shut-in well. An attractive feature of this suggestion was that the expense of drilling could be avoided by this approach, and the logical first step toward developing this source would be to analyze the water obtained for dissolved gas content and chemical components. This concept formed the basis for the research which is the subject matter for this report.

McNeese State University made a proposal to open a geopressured shut-in oil or gas well, obtain the desired data, and report the results. The proposal was accepted and funded as of June 1, 1975. Technical assistance was offered from two non-university sources: namely; Osborn-Hodges-Roberts-Wieland Engineering of Bryan, Texas and Dr. Paul H. Jones, Professor of Geology at Louisiana State University. The OHRW group was given responsibility for searching for a shut-in well, opening the well, recompleting the well as a water well, obtaining samples of the water, and making engineering studies of reservoir characteristics. Dr. Jones served as Geological Consultant to the project. McNeese State University was responsible for the chemical analysis of the gas and the water samples, the geological interpretation of data, preparation of geological maps of the reservoir, and collaborating closely with OHRW in the operations at the well-site.

The early weeks of the project were spent in the search for a suitable well--a difficult and engrossing undertaking. The most promising well offered to the project was the Edna Delcambre No. 1, Tigre Lagoon Field, in Vermilion Parish, Louisiana. The well, offered by Coastal States Gas Producing Company, was therefore used as a source of geopressured water. The location of the well is shown in Figure 1. Additional information about the well and the legal procedures involved with leasing and related matters are given in the Interim Report presented to the Department of Energy and issued in 1977 (6).

Because the Delcambre well was located in a marsh, all operations were conducted by means of boats and barges. McNeese State University and OHRW Engineering each had separate prime contracts with DOE to conduct the work. OHRW Engineering entered into numerous sub-contracts for such services as well-logging, mud supply, pipe and tubing, and similar services.

After suitable contracts for the work had been drafted and agreed to by all parties, field operations began at the well-site on



January 29, 1977 and were completed July 21, 1977. Two aquifers were tested: sand #3 at 12,900 feet and sand #1 at 12,600 feet. The top of the geopressured zone at the well-site occurred at approximately 12,300 feet. Flow tests on each sand-bed aquifer continued for approximately three weeks. Sand #3 achieved flow rates of about 2,500 to 9,000 barrels per day during the test period. The bottom-hole pressure was 10,990 psig and the bottom-hole temperature was 238°F. Flow rates on sand #1 ranged from 1,200 to 11,800 barrels per day. Although there was some sand produced from sand #3, virtually no sand was produced from sand #1, primarily because the flow rate was increased in smaller increments for sand #1. The bottom-hole pressure on sand #1 was about 10,600 psig and the bottom-hole temperature was 234°F.

The engineering aspects of producing geopressured water and determining reservoir characteristics is emphasized in a separate report by OHRW entitled Well Completion, Testing, and Production Data Analysis. The geology of the Tigre Lagoon Field and the area of the Delcambre well is presented in a report under separate binding by McNeese State University entitled Geology of the Tigre Lagoon Field, Planulina Basin. The present report focuses on the analysis of the water and the dissolved gases and contains the qualitative and quantitative data for the separator water/separator gas samples and the bottom-hole gas/bottom-hole water samples. Knowledge of the chemical composition of the water and gas is important from the following viewpoints:

1. If dissolved solids are present in significant amounts, what should be the ultimate disposition of the water? Can valuable minerals be recovered? Are noxious and/or poisonous species present? Will heat exchangers be plugged? Will equipment be corroded? What environmental problems are presented?

2. How much gas is present? Is the water saturated with gas? What is the composition of the gas? Are noxious and/or poisonous species present? What is the heating value of the gas?

Figure 2 shows the approach to the well-site with the drilling rig on the extreme right. The test barge, located in the central section, contained the high pressure separator, chokes, gauges, pumps, and other equipment necessary for the engineers to obtain the flow data and to dispose of the salt water effluent in a disposal well drilled earlier (see Figures 3 and 4). Most of the flow samples were taken from stations located on the test barge. In-line probes monitored certain physico-chemical properties of the water continuously as it flowed through the test barge equipment. A quarters barge is seen on the left in Figure 2. It housed a small laboratory, monitoring equipment, and the recorders for the in-line probes, as well as sleeping quarters for the technical crews.

The following kinds of samples were collected from sand #3 (perforated from 12,870 feet to 12,919 feet) and sand #1 (perforated from 12,571 feet to 12,605 feet):

1. Separator water samples
2. Separator gas samples
3. Bottom-hole water samples

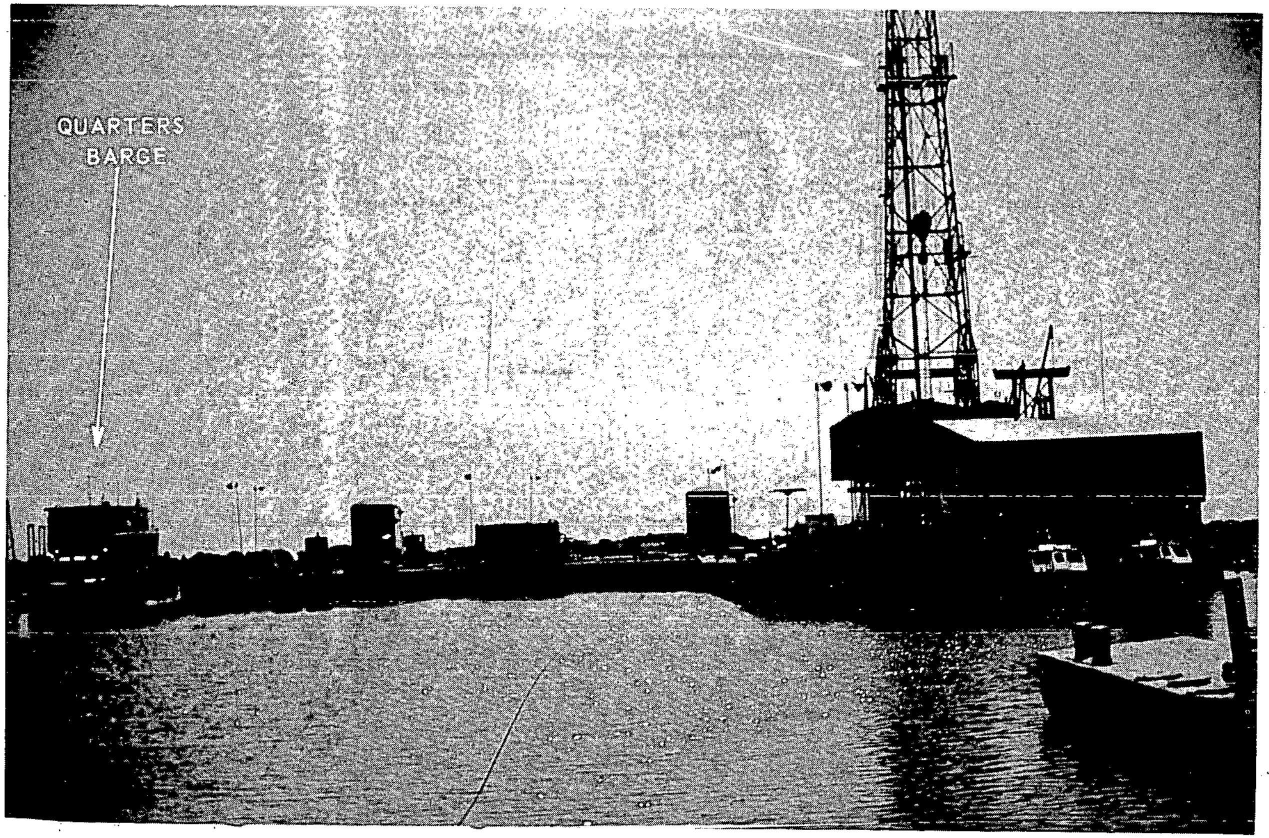


FIGURE 2

PHOTOGRAPH OF EQUIPMENT AT WELL SITE

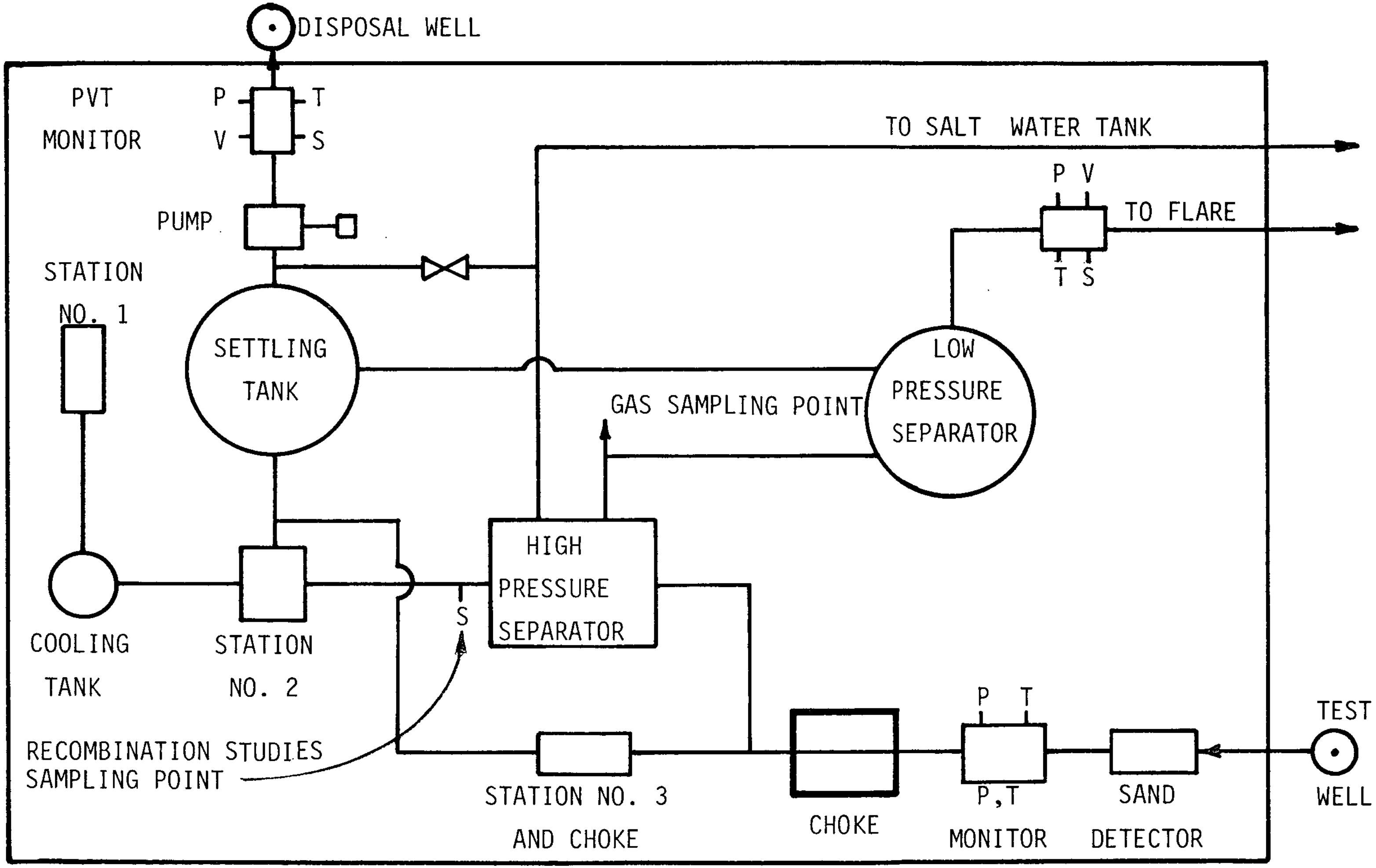


FIGURE 3

MAJOR EQUIPMENT LAYOUT ON TEST BARGE AT WELL-SITE

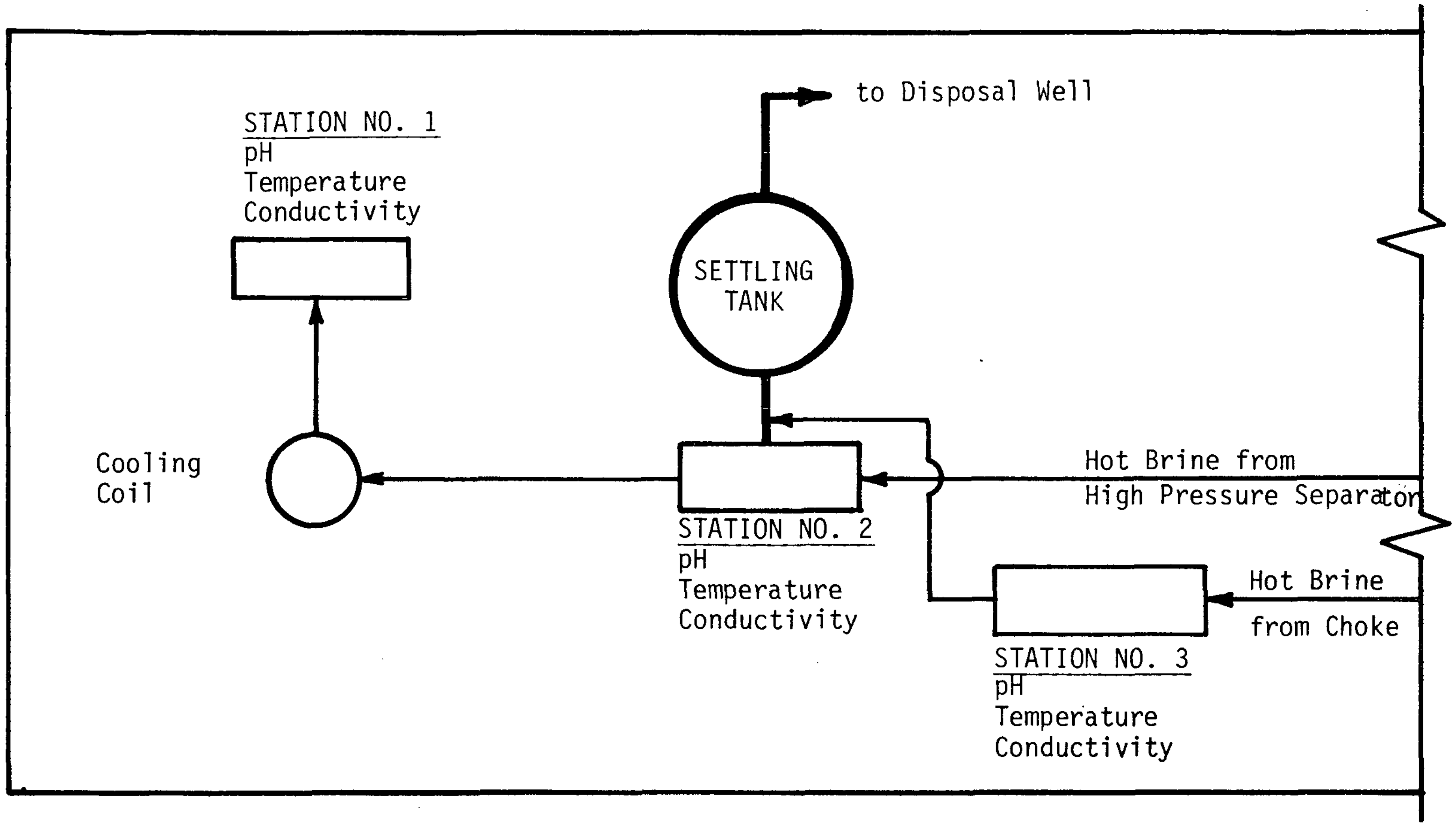


FIGURE 4

LAYOUT OF EQUIPMENT FOR PHYSICO-CHEMICAL MEASUREMENTS ON TEST BARGE

The separator water samples and the bottom-hole water samples were analyzed in the on-site laboratory as well as in the McNeese laboratory in Lake Charles. The composition of the separator gas samples was determined after the samples were returned to McNeese. Recombination and differential liberation studies were performed on selected gas and water samples taken from the separator as well as on pure methane and separator "stock tank" water. A summary of the analyses performed follows:

A. At Well-Site

Conductance, temperature, pH, turbidity, bicarbonate, carbonate, chloride, dissolved silicate, total hardness, calcium hardness, dissolved solids (estimated), and density (estimated) determinations were performed in the well-site laboratory on almost all of the samples collected. Viscosity was estimated for a few of the samples.

B. At McNeese Campus

Density, viscosity, dissolved solids, iron, sulfate, barium, dissolved silicate, suspended solids, bicarbonate, pH, total hardness, conductance, chloride, copper, manganese, zinc, boron, arsenic, chromium, mercury, lead, cadmium, strontium, sodium, potassium, calcium, and magnesium determinations were performed in the McNeese laboratories in Lake Charles.

C. Other Laboratories

Four separator gas and water samples from Sand #3 and six separator gas and water samples from Sand #1 were sent to the U.S.G.S. laboratories in Denver, Colorado, for measurements of radioactive species. Radon was determined in both separator gas and separator water while gross α, gross β, radium-226, and uranium were determined in the separator water samples only.

One separator water sample from each sand was submitted to the Center for Bio-Organics at the University of New Orleans to determine the trace organics present.

The following sections of the report will emphasize the extreme difficulty in obtaining bottom-hole samples. Some of the data collected and reported here are probably unreliable and no firm conclusions can be drawn from the bottom-hole samples. The pH of the geopressured waters in the formation cannot be determined using equipment currently available. This study indicates that the *in situ* pH value is probably lower than measured values using in-line surface equipment. Many chemical determinations change rapidly with time, (pH, carbonate, bicarbonate, suspended solids, etc.) indicating the need for on-site analysis. The dissolved silicate values were found to be a function of aquifer temperature. The values obtained agreed closely with published solubility data for quartz in acidic waters.

The general title for all the reports issued on this project is *Geopressured-Geothermal Test of the Edna Delcambre No. 1 Well, Tigre Lagoon Field, Vermilion Parish, Louisiana*. The subtitles are as follows:

1. *Well Completion, Testing, and Production Data Analysis* by OHRW.

2. Analysis of Water and Dissolved Natural Gas by McNeese State University.

3. Geology of the Tigre Lagoon Field, Planulina Basin by McNeese State University.

II. OBJECTIVES OF STUDY

The project objectives were agreed upon by all parties concerned before the testing program began.

A. PREPARE GEOLOGIC MAPS OF RESERVOIR

Prepare detailed geological maps of each of the two sands to be tested with each map encompassing an area defined by an approximate ten-mile radius of the test well and askewed areally to the north.

1. Structure-contour on top and bottom of each sand.
2. Cumulative net sand thickness for each of the above sections.
3. Map of top of the geopressured zone.
4. An isothermal map at 200^{0} (and one at 250^{0}F if possible).

B. SECURE AND ANALYZE RESERVOIR FLUID

Secure fluid samples from each of the two sands tested under conditions of temperature and pressure approaching _in situ_ values. Perform tests on the samples to determine:

1. Viscosity, density, compressibility.
2. Total dissolved solids (including silica).
3. Salinity (including chemical analysis of dissolved solids).
4. Dissolved gas content.
5. Spectroscopic analysis.
6. Total undissolved solids.

C. DETERMINATION OF RESERVOIR FLOW RATES

D. DETERMINATION OF SAND PROBLEMS

E. DETERMINATION OF THE Kh VALUES OF THE SANDS

F. DETERMINATION OF HOW ADDITIONAL DYNAMIC TESTS ON GEOPRESSURED RESERVOIRS CAN BE ACCOMPLISHED

III. EQUIPMENT LAYOUT ON TEST BARGE AT WELL-SITE

The layout of equipment on the test barge was prepared by Otis Engineering in collaboration with OHRW Engineering and is shown schematically in Figure 3. Further details on the equipment are provided in the report by OHRW. This report will concentrate on the use of the equipment for obtaining water and gas samples for analytical purposes.

A. MAJOR EQUIPMENT FOR ENGINEERING FLOW TESTS

The flow of geopressured-geothermal water is shown by the arrows in Figure 3. Water from the well flows through the sand detector, a flow monitoring station, then through a choke where the pressure is reduced from well-head pressure to 1440 psig. The main stream flows from the choke into the high pressure separator in which the natural gas evolved from the water is separated from the salt water. The gas flows through a low pressure separator and to a flare located on the bank of the barge slip while the hot salt water, now at approximately 300 psig pressure, flows into a settling tank, which serves as a reservoir from which the injection pump takes suction. The salt water is reinjected into a disposal well at a depth of about 2,500 feet below the land surface. Some additional natural gas is evolved in the settling tank, and this gas flows to the flare via the low pressure separator.

B. ANALYTICAL EQUIPMENT LAYOUT

The test barge was equipped with sampling stations for gas and water as well as with three monitoring stations (Figure 4). Each monitoring station contained an in-line conductivity cell, an in-line temperature sensing device (thermocouple), an in-line pH measuring device (glass electrode), and a valve for regulating the flow of brine through the assembly. Provisions were made for obtaining a sample of the fluid that passed through the monitoring station.

Station #3 was located in a small slip-stream of geothermal brine taken from the discharge of the main choke (at 1,440 psig), which then passed into the inlet of the settling tank. A second choke (variable) was placed directly ahead of the monitoring station in an attempt to protect the in-line components. Some success was attained at this station in making the three measurements from the Sand #3 test but scaling, excessive gas evolution, and pressure fluctuations due to plugging of the variable choke, caused many problems. In fact, wide pressure variations along with high temperatures, caused several pieces of the in-line equipment to fail.

Stations #2 and #1 were located in the effluent water stream from the high pressure separator with a cooling coil placed between them. The cooling coil consisted of several turns of stainless steel tubing kept cool by immersion in a 55 gallon drum of ice-chilled water. Because of the scaling problems associated with Station #3 during tests on Sand #3, the equipment for making in-line measurements was moved to Station #2 for the tests on Sand #1. This alternative proved better and more in-line measurements were obtained, but plugging of the choke still prevented a continuous readout. In fact, all of the in-line equipment malfunctioned, due to the high pressure and high temperature of the brine encountered on the test barge, before completion of the test.

All of the gas samples were taken at the sample point on the gas effluent from the high pressure separator (Figure 3). Most of the water samples were taken at Station #1 (Figures 3 and 5), where provisions were made for passing the water, under pressure, through the in-line filters. Filtered or unfiltered water samples could be obtained, as desired, and the porosity of the membrane filter could be changed with ease.

The in-line measurements are discussed, in detail, in Section IV.A.5. The collection and composition of the gas samples are given in Section IV.B., and the water analyses are described in Section IV.A. (1-4).

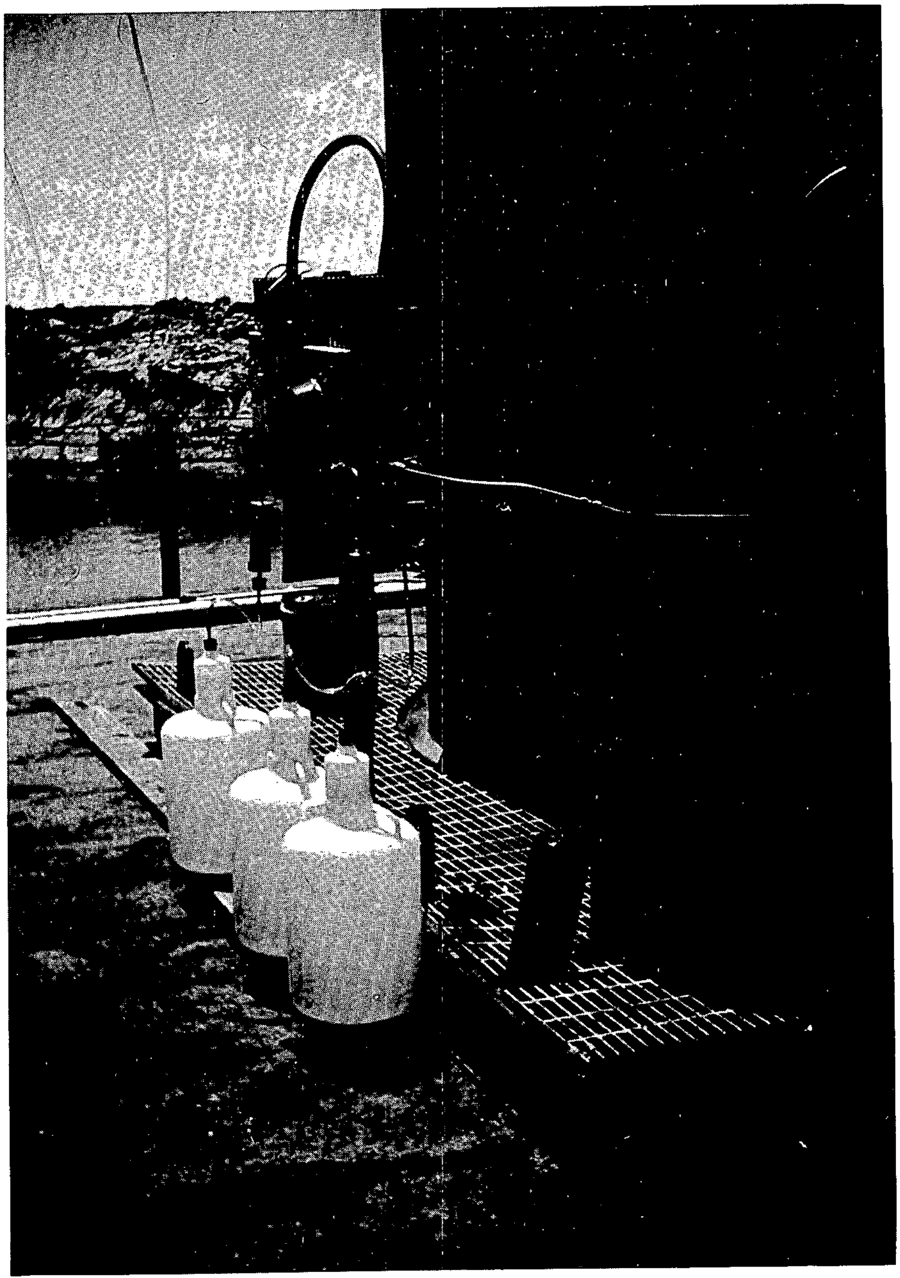


FIGURE 5

PHOTOGRAPH SHOWING SAMPLING AT STATION NO. 1

IV. CHEMICAL ANALYSES

A. WATER SAMPLES FROM HIGH PRESSURE SEPARATOR

1. Collection Procedures

Figure 3 shows the physical placement of the equipment on the test barge. Sample collection stations for flowing water samples were located at Stations #1, #2, and #3. Almost all of the water samples were collected at Station #1 after the geothermal brine had gone through a cooling coil. Table I shows how the samples were treated after collection and defines abbreviations used below.

Figure 5 is a close-up photograph of Station #1 showing samples being collected. The RU sample was collected by allowing the water to flow into a plastic receiving bottle. The FU sample was collected by allowing the water to flow through one of the in-line stainless steel cylinders shown in Figure 5 that had been fitted with a 0.4 μm nucleopore membrane filter. An exploded view of the in-line filter is shown in Figure 6. Portions of the RU and FU samples were acidified with nitric acid (∿3 ml. of 1:1 HNO_3/1) to prepare the RA and FA samples. The acid treatment prevented the precipitation of certain ions and is a standard procedure used by water analysis laboratories. An RU sample, under operating pressure and temperature, was collected at Station #2 in a 500 ml. stainless steel Whitey cylinder fitted with valves, each time an RU sample was collected

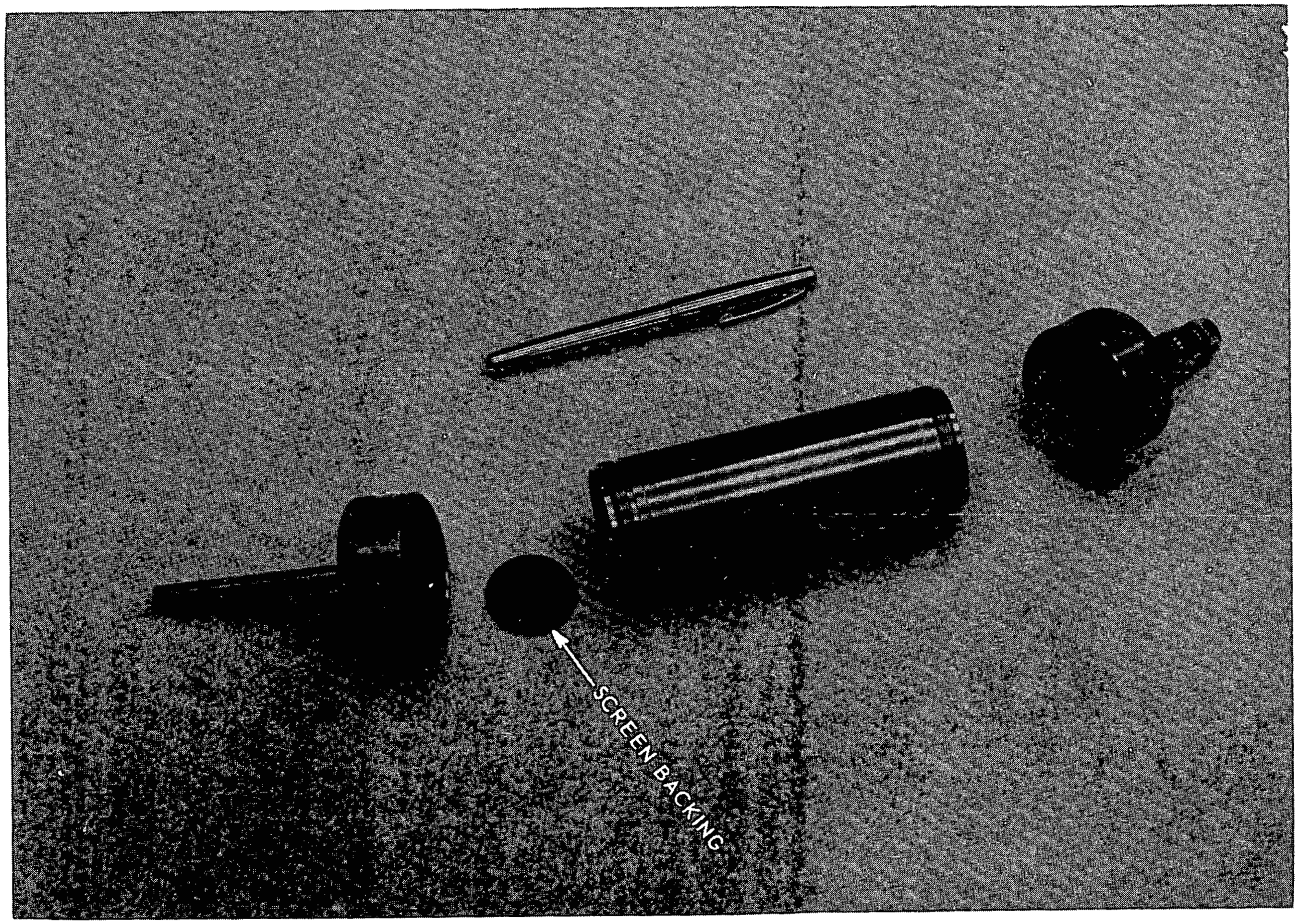


FIGURE 6

EXPLODED VIEW OF IN-LINE FILTERS

at Station #1. It was felt that a sample collected under these conditions would not precipitate after standing. The RUSS sample container (raw unfiltered, stainless steel) is shown in Figure 7.

2. Analyses Performed

Tables II, III, IV, and V list those determinations performed on RU, FU, FA, and RUSS samples respectively.

TABLE I

Treatment of Water Samples After Collection

1. Raw Untreated (RU)
2. Filtered Untreated (FU)
3. Raw Acidified (RA)
4. Filtered Acidified (FA)

TABLE II

Determinations Performed on RU Samples

pH

Temperature - °C

Conductance - μmhos/cm

Bicarbonate - as mg $CaCO_3/l$

Carbonate - as mg $CaCO_3/l$

Turbidity - j.t.u.

Suspended solids - mg/gallon

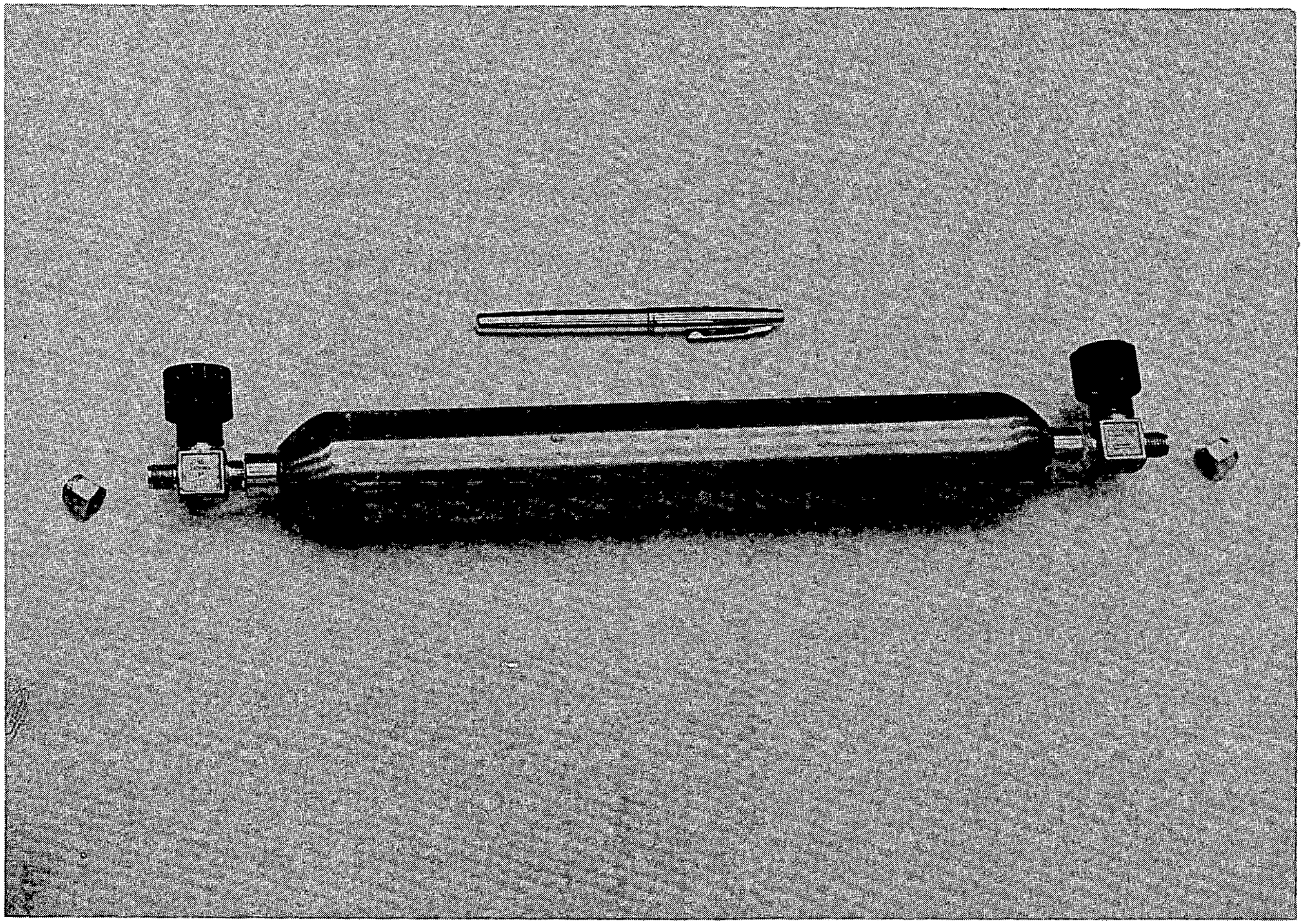


FIGURE 7

CYLINDER USED TO COLLECT RU SAMPLE UNDER PRESSURE

TABLE III

Determinations Performed on FU Samples

Chloride - as mg Cl^-/l

Dissolved silicate - as mg SiO_2/l

Dissolved solids - mg/l

Total hardness - as mg $CaCO_3/l$

Calcium hardness - as mg $CaCO_3/l$

Boron - as mg B/l

TABLE IV

Determinations Performed on FA Samples

(mg/l)

- Iron
- Barium
- Sulfate
- Copper
- Zinc
- Arsenic
- Chromium
- Mercury
- Strontium
- Sodium
- Potassium
- Calcium
- Magnesium
- Lead
- Cadmium
- Viscosity (centipoise @ 20°C)

TABLE V

Determinations Performed on RUSS Samples

Temperature - ^{o}C

pH

Density (corr'd to $20^{o}C$) - g/ml.

Dissolved solids - mg/l

Total hardness - as mg $CaCO_3/l$

Calcium hardness - as mg $CaCO_3/l$

Chloride - as mg Cl^{-}/l

Carbonate - as mg $CaCO_3/l$

Bicarbonate - as mg $CaCO_3/l$

Table VI shows those determinations that were conducted on-site, and Table VII lists those that were conducted in the McNeese labs in Lake Charles. The on-site density, dissolved solids and viscosity determinations were approximated and were repeated in the McNeese labs because a constant temperature water bath was impractical to install at the lab on the barge; also, vibrations were too severe on the barge to use an analytical balance. Viscosity measurements were performed only on FA samples because FU samples contained a precipitate and RUSS samples precipitated after standing a short time. The 0.4 μm membrane filters used to collect the filtered samples on the test barge were weighed to determine the amount of suspended solids. The volume has been normalized to one gallon in all

TABLE VI

Analyses Conducted On-Site

pH
Temperature
Conductance
Turbidity
Bicarbonate
Carbonate
Chloride
Dissolved silicate
Density (estd.)
Dissolved solids (estd.)
Total hardness
Calcium hardness
Viscosity (estd.)

TABLE VII

Analyses Conducted in McNeese Labs

Density
Viscosity
Dissolved solids
Iron
Barium
Sulfate
Dissolved silicate
Suspended solids
Copper
Manganese
Zinc
Boron
Arsenic
Chromium
Mercury
Lead
Cadmium
Strontium
Sodium
Potassium
Calcium
Magnesium

cases. Boron and dissolved silicate were determined spectrophotometrically; sulfate was determined gravimetrically after purification by column chromatrography; barium, copper, chromium, manganese, arsenic, mercury and lead were determined by neutron activation analysis; the other metals were determined by atomic absorption or flame spectrometry. Chloride, calcium hardness, total hardness, carbonate, and bicarbonate were determined with titration procedures. Many, but not all of the procedures, were those adopted by the U.S. Geological Survey (1). The methods used are listed in Appendix A.

3. Analytical Data and Discussion

A total of 18 flowing samples were collected from Sand #3 between 5-22-77 and 6-07-77, and 29 flowing samples were collected from Sand #1 between 6-23-77 and 7-13-77. Table VIII lists the number assigned to each sample from Sand #3 and the date it was collected; Table IX is similar except it covers samples collected from Sand #1. Tables X through XXXV list the values obtained for the determinations on the samples from each sand. A summary of these tables and additional data are included in Appendix B. Although all samples were not subjected to every determination, some trends are apparent for many of them. To help in comparing the different samples, the tables also show typical values for the flowing samples and typical values for the bottom-hole samples from both sands. The range of values is enclosed in

TABLE VIII

SAMPLE COLLECTION SCHEDULE

FLOWING WATER - SAND #3

Date Collected	Sample No.	Date Collected	Sample No.
05-22-p.m.	1F*	05-30-p.m.	10
05-23-p.m.	2	05-31-a.m.	11
05-24-p.m.	3	06-02-p.m.	12
05-26-a.m.	4F*	06-03-a.m.	13
05-27-a.m.	5F*	06-03-p.m.	14
05-27-p.m.	6	06-04-a.m.	15
05-28-a.m.	7	06-04-p.m.	16
05-28-p.m.	8	06-05-a.m.	17
05-29-a.m.	9	06-07-p.m.	18

*Denotes sample from flare line. All others from separator.

TABLE IX

SAMPLE COLLECTION SCHEDULE

FLOWING WATER - SAND #1

Date Collected	Sample No.	Date Collected	Sample No.
06-23-p.m.	1F*	06-30-a.m.	15
06-23-p.m.	2	06-30-p.m.	16
06-24-a.m.	3	07-01-a.m.	17
06-24-p.m.	4	07-01-p.m.	18
06-25-a.m.	5	07-02-a.m.	19
06-25-p.m.	6	07-02-p.m.	20
06-26-a.m.	7	07-03-a.m.	21
06-26-p.m.	8	07-07-p.m.	22
06-27-a.m.	9	07-08-a.m.	23
06-27-p.m.	10	07-10-a.m.	24
06-28-a.m.	11	07-10-p.m.	25
06-28-p.m.	12	07-11-p.m.	26
06-29-a.m.	13	07-12-a.m.	27
06-29-p.m.	14	07-13-a.m.	28
		07-13-p.m.	29

*Denotes sample from flare line. All others from separator.

parentheses. The typical values listed are the average values obtained (and rounded to the appropriate number of significant figures) for those determinations not showing a trend. This assumes, of course, that all of the values should be the same, an assumption that is not necessarily valid. In order to clarify this problem partially, the standard deviation has been calculated for the values listed, and this has been compared with the standard deviation for the method as determined by U.S.G.S. In this manner it was ascertained that certain determinations were essentially constant; i.e., the error inherent in the method could account for the deviation between samples. Discussion of these cases is given in the text. Selected values are marked with an asterisk in Tables X through XXXV and these are also discussed in the text. A few typical values are listed for some determinations that show a trend. In these cases the stabilized value has been used as the typical value. Replicate determinations are shown for some samples; e.g., iron, chromium, etc., to indicate the precision of the method.

In comparing the values in Tables X through XXXV, one should note that samples #1 through #5 in Sand #3 were collected while different sections of the zone were being perforated. In view of the fact that certain determinations; e.g., chloride and sodium, show marked changes in concentration in this region, it is not surprising to find variations throughout the flow period.

Similarly, samples #24-#29 in Sand #1 should be disregarded in attempting to detect trends because the well was flowing at high rates and some of the surface equipment either malfunctioned or failed completely during the late stage of the test. This caused frequent interruptions in flow while the faulty equipment was repaired.

Table X is a listing of pH values obtained on samples from both sands. In general, the pH decreases in both flowing tests, with time, although the effect is much more pronounced in Sand #3. Fluctuations in flow rate, gas volume and composition, temperature, and separator efficiency seem to affect the measured pH values. No simple correlations are apparent with this many variables; however, the time interval between collection of the sample and the pH measurement is quite significant due to evolution of the gas dissolved in the water. The absolute values for pH from both sands are open to question, and the ramifications of this will be discussed in detail later when the in-line pH measurements are tabulated (See section IV.A.5).

Table XI lists the values for turbidity. The time trend is to a lower value, generally, as the well water tends to flush out fine sand particles as flow proceeds. This is quite evident in data from Sand #3. The high value shown for Sample #18 may be the result of increased sand production near the end of the test run. That sample was the last one taken before the well

Sand #1 Flowing Water

Sample	
1F	6.26
2	5.95
3	6.16
4	6.32
5	6.20
6	6.19
7	6.17
8	6.16
9	6.14
10	6.09
11	6.01
12	6.14
13	6.13
14	5.96
15	6.19
16	6.29
17	5.92
18	6.15
19	6.13
20	6.28
21	6.18
22	6.02
23	6.04
24	6.10
25	6.06
26	-
27	6.28
28	6.12
29	6.17

Sand #3 Flowing Water

Sample	
1F	6.83
2	6.98
3	-
4F	6.87
5F	6.45
6	6.60
7	6.56
8	6.28
9	6.50
10	6.24
11	6.19
12	6.42
13	6.17
14	6.27
15	6.12
16	6.33
17	6.24
18	6.19

TYPICAL VALUES (RANGE)

Sand #1

Flowing: 6.1

Bottom-hole: 6.3

Sand #3

Flowing: 6.2

Bottom-hole: 6.4

TABLE X

pH TEST RESULTS

Sand #1 Flowing Water

Sample	
1F	70
2	55
3	55
4	42
5	28
6	42
7	13
8	7
9	18
10	12
11	28
12	17
13	8
14	21
15	11
16	20
17	42
18	44
19	11
20	8
21	25
22	10
23	30
24	22
25	71
26	-
27	54
28	31
29	-

Sand #3 Flowing Water

Sample	
1F	-
2	63
3	-
4F	-
5F	-
6	45
7	35
8	14
9	22
10	26
11	28
12	35
13	27
14	28
15	34
16	33
17	28
18	65

TYPICAL VALUES (RANGE)

Sand #1

Flowing: - (7-71)

Bottom-hole: 30

Sand #3

Flowing: - (14-65)

Bottom-hole: 41

TABLE XI

TURBIDITY (J.T.U.)

was shut-in to obtain bottom-hole samples and considerable sand had accumulated in the separator. For the #1 Sand flowing test, the choke was changed between samples #6-7, 10-11, 14-15, 18-19, 21-22, 23-24, 25-26. and 27-28. Note that the turbidity was often higher just before the choke was changed, which was contrary to expectations. No explanation can be offered for this observation. Increased sand production before a choke change does not appear to be logical. In comparing these values, remember that differences in turbidity values below ∿30 are not especially significant.

The suspended solids values are shown in Table XII and also show a decrease, generally, as the well is flushed, but the value reaches a small number after stabilization. The conductance values are shown in Table XIII and the values for Sand #3 are essentially the same for all samples. The bottom-hole value for Sand #3 agrees well with the flowing samples. The conductance values for Sand #1 vary more than those for Sand #3, and the values for Samples #11, #15, and #25 have been rejected because the other determinations, principally chloride, sodium, and dissolved solids, do not show these samples to be significantly different. The conductance was not determined on a Sand #1 bottom-hole sample partly because of the small volume of sample available and partly because the sample started precipitating quickly, making it essentially impossible to get an accurate value.

Sand #1 Flowing Water

Sample	
1F	-
2	-
3	-
4	-
5	-
6	-
7	2.6
8	1.1
9	0.4
10	2.5
11	1.0
12	0.8
13	1.2
14	1.0
15	0.8
16	2.1
17	0.7
18	1.0
19	0.1
20	0.1
21	-
22	-
23	-
24	-
25	-
26	-
27	-
28	-
29	-

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	-
5F	-
6	55
7	24
8	30
9	20
10	-
11	1.0
12	0.65
13	-
14	0.15
15	0.30
16	0.35
17	0.55
18	0.30

TYPICAL VALUES (RANGE)

Sand #1

Flowing: -

Bottom-hole: -

Sand #3

Flowing: -

Bottom-hole: -

TABLE XII

SUSPENDED SOLIDS (Mg/GALLON)

Sand #1 Flowing Water

Sample		
1F	166,000	
2	155,000	
3	164,000	
4	161,000	164,000
5	162,000	
6	163,000	
7	162,000	
8	159,000	
9	159,000	
10	164,000	
11	153,000*	
12	163,000	
13	157,000	
14	164,000	
15	173,000*	
16	161,000	
17	158,000	
18	165,000	166,000
19	161,000	
20	162,000	
21	158,000	
22	163,000	
23	161,000	
24	161,000	
25	152,000*	
26	-	
27	166,000	
28	162,000	
29	162,000	

Sand #3 Flowing Water

Sample		
1F	142,000	
2	-	
3	145,000	
4F	-	
5F	145,000	
6	143,000	149,000
7	146,000	
8	144,000	
9	144,000	146,000
10	-	
11	146,000	
12	148,000	
13	147,000	
14	143,000	
15	145,000	
16	141,000	
17	143,000	
18	-	

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	162,000 (155,000-166,000)
Bottom-hole:	-
	Sand #3
Flowing:	145,000 (141,000-149,000)
Bottom-hole:	142,000

TABLE XIII

SPECIFIC CONDUCTANCE (μmhos/cm)

Dissolved solids data are shown in Table XIV. Values were obtained in the barge laboratory during flow testing, but these values have considerable error. Vibrations were too severe to allow use of an analytical balance at the barge lab. Values in Table XIV were obtained on RUSS samples for the flowing water and an FA sample (Sand #1) and an RA sample (Sand #3) for the bottom-hole water. Precision, as expected, was excellent because these determinations were made with analytical balances. Note that both bottom-hole values are higher than the respective flowing water samples. The difference is significant and will be discussed later.

Density values are shown in Table XV. Estimated values were obtained in the laboratory on the barge, for the same reasons given above for the dissolved solids determination, and better values were obtained at McNeese on RUSS samples. The density was determined at room temperature and corrected, with standard tables, to 20°C. Density values for bottom-hole samples from both sands are higher than the respective flowing sands. A higher density for bottom-hole samples is consistent with the dissolved solids data in Table XIV.

A possible explanation for differences in the dissolved solids and density values between bottom-hole and flowing samples is precipitation of solids (from the flowing samples) in the separator. An alternative explanation exists because measurements

Sand #1 Flowing Water

Sample	
1F	-
2	133,450
3	-
4	133,790
5	-
6	133,840
7	-
8	133,390
9	-
10	133,360
11	-
12	133,480
13	-
14	133,360
15	-
16	-
17	-
18	133,030
19	-
20	133,300
21	-
22	133,850
23	-
24	-
25	132,980
26	-
27	-
28	-
29	-

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	-
5F	-
6	113,180
7	113,320
8	-
9	-
10	113,400
11	113,410
12	-
13	113,280
14	113,480
15	113,330
16	-
17	-
18	113,230

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	133,440 (132,980-133,850)
Bottom-hole:	134,170
	Sand #3
Flowing:	113,330 (113,180-113,480)
Bottom-hole:	113,700

TABLE XIV

DISSOLVED SOLIDS (mg/l)

Sand #1 Flowing Water

Sample	
1F	-
2	1.0852
3	-
4	1.0861
5	-
6	1.0858
7	-
8	1.0854
9	-
10	1.0853
11	-
12	1.0853
13	-
14	1.0857
15	-
16	-
17	-
18	1.0847
19	-
20	1.0850
21	-
22	1.0843
23	-
24	-
25	1.0842
26	-
27	-
28	-
29	-

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	-
5F	-
6	1.0700
7	1.0709
8	-
9	-
10	1.0708
11	1.0719
12	-
13	1.0710
14	1.0721
15	1.0715
16	-
17	-
18	1.0711

TYPICAL VALUES (RANGE)

Sand #1

Flowing: 1.0852 (1.0842-1.0861)

Bottom-hole: 1.0879

Sand #3

Flowing: 1.0712 (1.0700-1.0721)

Bottom-hole: 1.0784

TABLE XV

DENSITY (g/ml @ 20°C)

were not made on samples treated in the same manner. Density and dissolved solids determinations were made on RUSS samples for flowing water but RUSS fluids were not suitable for these determinations on bottom-hole water because some precipitation had occurred; therefore, FA or RA samples were used for these determinations on bottom-hole fluids. Perhaps some of the differences noted are related to the acidification with nitric acid which, upon heating to 180°C, would convert many anions, particularly chloride, to nitrates with an attendant increase in weight. The latter explanation makes the bottom-hole values too high; the former explanation makes the flowing values too low. Both explanations are consistent with the data.

Viscosity values are shown in Table XVI. The difference between flowing and bottom-hole values is caused almost completely by the difference in density which is used in the calculation of viscosity.

Table XVII lists the bicarbonate values. Note that the values for Sand #1 generally decrease with time until Sample #22. This is probably caused by precipitation of carbonate at higher temperatures as a result of increased flow rates as the test progressed. This is indicated by scaling of the equipment and partial plugging of the disposal well during the latter part of the test. The well was shut-in between Samples #21 and #22 to obtain bottom-hole samples and the value of 1,200 mg. $CaCO_3/l$

Sand #1 Flowing Water

Sample	
1F	-
2	1.245
3	-
4	1.247
5	-
6	1.249
7	-
8	1.253
9	-
10	1.248
11	-
12	1.250
13	-
14	1.249
15	-
16	-
17	-
18	1.247
19	-
20	1.246
21	-
22	1.249
23	-
24	-
25	1.244
26	-
27	-
28	-
29	-

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	-
5F	-
6	1.197
7	1.190
8	-
9	1.188
10	1.197
11	1.196
12	-
13	1.197
14	1.197
15	1.197
16	-
17	-
18	1.190

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	1.248 (1.244-1.253)
Bottom-hole:	1.247
	Sand #3
Flowing:	1.194 (1.188-1.197)
Bottom-hole:	1.212

TABLE XVI

VISCOSITY (CENTIPOISE @ 20°C)

Sand #1 Flowing Water

Sample	
1F	1170
2	1130
3	1130
4	-
5	1070
6	1060
7	1030
8	1030
9	1010
10	1020
11	1040
12	1000
13	1010
14	1020
15	1080
16	980
17	990
18	970
19	970
20	960
21	970
22	1200*
23	990
24	1010
25	-
26	-
27	970
28	1020
29	1020

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	-
5F	-
6	1110
7	1110
8	1050
9	1070
10	1030
11	1030
12	1030
13	1030
14	1080
15	1060
16	1100
17	1050
18	1070

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	-
Bottom-hole:	1120
	Sand #3
Flowing:	1060 (1030-1110)
Bottom-hole:	1300

TABLE XVII

BICARBONATE (as mg $CaCO_3/l$)

was obtained on the first sample after flow was restarted. Note that the value on Sample #22 of 1,200 agrees well with the bottom-hole value (1,120) and the values obtained at slow flow rates at the beginning of the test (1,170 and 1,130). Values obtained after Sample #22 are difficult to correlate due to frequent choke changes, separator pressure changes, and certain equipment and/or connection failures during the latter stages of the test. The difference between the flowing and bottom-hole values for Sand #3 may be the result of starting the flow at higher rates than in Sand #1 (2,500 bbls/day vs. 1,200 bbls/day) and increasing the rates faster (100% vs. 75% of the previous flow rate or less). The differences between flowing water samples in Sand #3 probably are not significant; i.e., the standard deviation for the method is ±3.4% as reported by U.S.G.S. and the standard deviation of samples #6-#18 inclusive is only ±2.8%.

Table XVIII shows the chloride values. The average value for Sand #3 (Sample #6-#18 inclusive) is 67,100 ±300 at the 95% confidence level. The values obtained in the early part of the test are clearly higher and probably represent a vertical chloride gradient in the perforated zone. The zone was initially perforated with 68 shots; it was perforated a short time later with 96 additional shots. A lower chloride value was obtained after the second perforation and this lower value persisted throughout the remainder of the test on Sand #3. The chloride

Sand #1 Flowing Water

Sample	
1F	80,800
2	80,400
3	80,400
4	80,500
5	80,600
6	80,400
7	80,400
8	80,400
9	80,500
10	80,500
11	80,700
12	80,600
13	80,700
14	80,600
15	80,400
16	80,400
17	80,000
18	81,100 81,200
19	80,000 80,400
20	80,700
21	80,700
22	80,500
23	80,400
24	80,400
25	80,700
26	-
27	79,300*
28	81,100
29	78,900*

Sand #3 Flowing Water

Sample	
1F	79,400
2	78,800
3	77,200
4F	79,200
5F	67,000
6	67,200
7	67,000
8	67,300
9	67,000
10	67,000
11	67,000
12	-
13	67,000
14	67,100
15	67,400
16	67,100
17	66,900
18	66,800

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	80,500 (80,000-81,200)
Bottom-hole:	79,800
	Sand #3
Flowing:	67,100 (66,800-67,400)
Bottom-hole:	67,100

TABLE XVIII

CHLORIDE (mg/l)

values for Sand #1 are essentially constant. Values for Samples #27 and #29 may be somewhat low since they are outside 2σ limits (80,457±915). Dilution caused by fresh water from shale is possible for these samples, but it is not considered likely because of the "normal" value found for Sample #28. A more likely explanation is that these samples were taken during the last days of the test when many equipment failures were experienced, and these are probably reliable values measured on non-representative samples.

Dissolved silicate values are shown in Table XIX. All silica values for Sand #3 are thought to be somewhat low. The electrical power generator on the quarters barge, where the on-site laboratory was housed, did not have an adequate frequency or voltage control; therefore, it was impossible to make adequate spectrophotometric measurements for the determination of dissolved silicate. A constant voltage transformer was available but did not furnish a constant voltage because of the frequency fluctuations. The SiO_2 values for Sand #3 were obtained later at McNeese on FU samples. A portable electrical generator, used for laboratory instrumentation only, was purchased and installed between tests on Sand #3 and Sand #1. All of the SiO_2 data for Sand #1 were obtained on-site. In order to evaluate the possible effect of obtaining Sand #3 SiO_2 data at McNeese at a later date, the SiO_2 determinations were repeated for Sand #1 samples at McNeese. An average of 5

Sand #1 Flowing Water

Sample	
1F	-
2	60
3	60
4	60
5	58
6	57
7	58
8	56
9	57
10	-
11	-
12	56
13	56
14	58
15	57
16	56
17	55
18	55
19	55
20	55
21	-
22	-
23	-
24	-
25	-
26	-
27	-
28	-
29	-

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	56
5F	-
6	54
7	-
8	56 56
9	56
10	57
11	56
12	58 56
13	-
14	60
15	-
16	61 59
17	61
18	59 57

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	57 (55-60)
Bottom-hole:	59
	Sand #3
Flowing:	57 (54-61)
Bottom-hole:	-

TABLE XIX

DISSOLVED SILICATE (as mg SiO_2/l)

determinations gave 51, which is 6 mg. SiO_2/l lower than originally determined in the laboratory on the test barge. This would indicate that the SiO_2 value for Sand #3 should be about 63, which is in line with expectations since the temperature, and thus the solubility of SiO_2, is higher in Sand #3 than in Sand #1 (7).

Calcium values are listed in Table XX. The values with an asterisk seem to be out of line with the others within a group. The U.S.G.S. reports a precision of 5% for this method and all of these values fall within that range at 3.5%; however, the starred values are outside 2σ limits in this study (2046±143 and 1670±120). Magnesium values are shown in Table XXI, and the value of 143 for sample #8 (Sand #1) is low. Magnesium, calcium, and strontium determinations are made on the same sample dilution. Sample #8 for all of these measurements is low (Tables XX through XXII) and a dilution error was probably made. Strontium values are listed in Table XXII. The value of 500 mg. Sr/l for #23 in Sand #1 probably cannot be justified. The boron values listed in Table XXIII are somewhat high, but this is apparently not uncommon along the Gulf Coast. The sodium values shown in Table XXIV vary somewhat more for Sand #1 than Sand #3. Some variation is no doubt caused by the large dilution factor (10,000:1) used in the determination. In order to evaluate this possibility, a sample was diluted 1:100 and then again 1:100

Sand #1 Flowing Water

Sample	
1F	-
2	2030
3	2100
4	2000
5	2030
6	2070
7	2070
8	1770*
9	2030
10	2100
11	2070
12	1970
13	2030
14	1970
15	1930
16	2070
17	2070
18	2030
19	2100
20	2070
21	2070
22	2070
23	2030
24	2100
25	2100
26	2100
27	2130
28	2070
29	2100

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	1830* 1770
5F	-
6	1630
7	1670
8	1630
9	1630 1630 1630
10	1720 1670
11	1630
12	1600
13	1650
14	1770 1560* 1670
15	1710 1670
16	1630
17	1650 1670
18	1680 1700 1680 1700

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	2060 (1930-2130)
Bottom-hole:	2060
	Sand #3
Flowing:	1660 (1600-1770)
Bottom-hole:	1620

TABLE XX

CALCIUM (mg/l)

Sand #1 Flowing Water

Sample	
1F	-
2	183
3	183
4	183
5	183
6	183
7	180
8	143*
9	177
10	183
11	183
12	177
13	180
14	177
15	177
16	183
17	187
18	187
19	183
20	187
21	187
22	183
23	187
24	187
25	187
26	183
27	183
28	180
29	183

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	-
5F	-
6	163
7	163
8	160
9	160 161
10	-
11	163
12	160 161 163 161
13	157
14	161 158
15	159
16	167 165
17	163 160 158
18	159

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	183 (177-187)
Bottom-hole:	178
	Sand #3
Flowing:	161 (158-167)
Bottom-hole:	161

TABLE XXI

MAGNESIUM (mg/l)

Sand #1 Flowing Water

Sample	
1F	-
2	370
3	400
4	370
5	400
6	400
7	430
8	330
9	400
10	430
11	370
12	370
13	400
14	330
15	330
16	400
17	400
18	430
19	400
20	400
21	430
22	430
23	500*
24	430
25	430
26	430
27	370
28	400
29	400

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	300
5F	-
6	290
7	280
8	290
9	300
10	310
11	290
12	300 290
13	280
14	310
15	310
16	280
17	290
18	300

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	400 (330-430)
Bottom-hole:	330
	Sand #3
Flowing:	290 (280-310)
Bottom-hole:	310

TABLE XXII

STRONTIUM (mg/l)

Sand #1 Flowing Water

Sample	
1F	-
2	64
3	-
4	-
5	-
6	64
7	-
8	-
9	-
10	66
11	-
12	-
13	-
14	60
15	-
16	-
17	-
18	60
19	-
20	-
21	-
22	-
23	60
24	-
25	-
26	-
27	65
28	-
29	65

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	58
5F	-
6	61 60 60
7	59
8	62 62
9	61 61
10	57
11	61
12	61
13	62
14	57 61
15	56
16	57 61
17	57
18	61 62

TYPICAL VALUES (RANGE)

Sand #1

Flowing: 63 (60-66)

Bottom-hole: 58

Sand #3

Flowing: 60 (56-62)

Bottom-hole: 58

TABLE XXIII

BORON (mg/l)

Sand #1 Flowing Water

Sample		
1F	-	
2	46,000	46,000
3	47,000	
4	45,000	
5	45,000	
6	46,000	45,000
7	47,000	
8	45,000	47,000
9	47,000	
10	45,000	49,000
11	50,000	50,000
12	42,000	
13	45,000	
14	46,000	45,000
15	47,000	
16	50,000	
17	45,000	
18	45,000	45,000
19	43,000	
20	43,000	
21	45,000	
22	48,000	
23	44,000	46,000
24	46,000	
25	46,000	
26	47,000	
27	45,000	47,000
28	47,000	
29	43,000	

Sand #3 Flowing Water

Sample		
1F	-	
2	-	
3	-	
4F	47,000	
5F	-	
6	42,000	
7	43,000	
8	43,000	
9	40,000	
10	44,000	
11	40,000	
12	43,000	43,000
13	41,000	
14	45,000	
15	44,000	
16	45,000	
17	44,000	
18	43,000	

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	46,000 (42,000-50,000)
Bottom-hole:	47,000
	Sand #3
Flowing:	43,000 (40,000-45,000)
Bottom-hole:	43,000 (42,000-44,000)

TABLE XXIV

SODIUM (mg/l)

and the sodium was determined instrumentally. The dilution and determination steps were repeated ten times. A 2σ variation of 2,100 was obtained, which indicates that much of the variation seen in Table XXIV is introduced in this manner. The apparently high value for Sample #4F in Sand #3 must certainly be caused by the chloride gradient mentioned earlier in the chloride discussion (See Table XVIII).

The potassium values in Table XXV show essentially no difference between sands. Sample #26 from Sand #1 seems low when compared to all of the other data. The trend for zinc in Sand #3 (Table XXVI) is unmistakable and is surely the result of cleaning out the system at start-up. The pipe dope used during installation of various units on the test barge contained about 25% zinc. The zinc values for Sand #1 are much more constant from sample to sample, but note that the values are about 10 times higher than the stabilized values obtained in Sand #3. The variability in the bottom-hole values may be caused by using impure mercury in the process of transferring the sample from the bottom-hole sampling device to the high pressure container.

The iron values are shown in Table XXVII. Values from Sand #3 vary somewhat, but the major differences are probably real. Values from samples taken during the early part of the flow from Sand #1 show higher values and decrease during the

Sand #1 Flowing Water

Sample		
1F	-	
2	290	310
3	280	
4	280	
5	270	
6	290	310
7	290	
8	280	
9	280	
10	290	310
11	270	
12	290	
13	290	
14	280	320
15	300	
16	290	
17	290	
18	290	310
19	290	
20	290	
21	290	
22	290	
23	280	310
24	290	
25	290	
26	260*	
27	290	320
28	300	
29	280	320

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	290
5F	-
6	300
7	300
8	290
9	290
10	290
11	300
12	290
13	280
14	290
15	290
16	280
17	290
18	290

TYPICAL VALUES (RANGE)

Sand #1

Flowing: 290 (270-320)

Bottom-hole: 310

Sand #3

Flowing: 290 (280-300)

Bottom-hole: 270

TABLE XXV

POTASSIUM (mg/l)

Sand #1 Flowing Water

Sample	
1F	-
2	1.0
3	1.2
4	1.1
5	1.3
6	1.3 1.3 1.3 1.3
7	1.1
8	1.1
9	1.1
10	1.0 1.1 1.2 1.1
11	1.0
12	1.0
13	1.0
14	1.0 0.94 1.0 0.98
15	0.90
16	1.0
17	1.1
18	1.1
19	1.1
20	1.0
21	1.1
22	1.0
23	1.1
24	1.1
25	1.1
26	1.0
27	1.0
28	1.0
29	1.0

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	15.
5F	-
6	5.2
7	3.0
8	1.7
9	1.2
10	0.79
11	0.40
12	0.10
13	0.20
14	0.16
15	0.14
16	0.10
17	0.20
18	0.13

TYPICAL VALUES (RANGE)

Sand #1

Flowing: 1.1 (0.90-1.33)

Bottom-hole: (1.1-1.7)

Sand #3

Flowing: -

Bottom-hole: (1.3-8.4)

TABLE XXVI

ZINC (mg/l)

Sand #1 Flowing Water

Sample			
1F	-		
2	21.4		22.5
3	25.2		24.6
4	27.0		28.7
5	24.1		25.4
6	23.5		24.3
7	16.3		17.9
8	14.8	16.8	17.4
9	16.3		18.0
10	17.2		19.0
11	14.9		15.8
12	14.0		15.2
13	14.9		16.0
14	12.2		13.6
15	11.1		12.1
16	11.4		
17	9.5		
18	8.7		
19	9.8		
20	10.3		
21	11.3		
22	11.8		
23	11.0		
24	10.8		
25	10.8		
26	10.0		
27	10.1		
28	11.1		
29	10.0		

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	5.8
5F	-
6	4.9
7	9.0
8	8.7
9	9.2
10	8.3
11	7.9
12	7.1
13	7.6
14	7.8
15	8.0
16	7.8
17	8.2
18	7.5

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	-
Bottom-hole:	(18-35)
	Sand #3
Flowing:	-
Bottom-hole:	(60-117)

TABLE XXVII

IRON (mg/l)

test to values about the same as seen in Sand #3. The higher initial values from Sand #1 are probably caused by the much lower flow rate and, therefore, longer contact time between water and separator. As a result, the acidic water dissolved more iron from the separator. The higher values from the bottom-hole samples are probably the result of the well being shut-in during the sampling process and the acidic nature of the water results in dissolution of the tubing. Iron was determined at McNeese on flowing samples taken from the low pressure side of the separator. U.S.G.S. personnel took samples at this same point and the values obtained for iron agreed with the McNeese values; however, additional samples were collected by U.S.G.S. personnel on the high pressure side of the separator. Values for iron on the latter samples were considerably lower (0.4-1.0 mg. Fe/1), which suggests that much of the iron found in the former samples was introduced as a result of the fluid passing through the separator and picking up iron as it erodes the separator (7).

Cadmium values are shown in Table XXVIII and it can be seen that Sand #1 values are more consistent than those from Sand #3. Chromium values are shown in Table XXIX and show higher values for both sands at the end of each test period. Starred values on Sand #3 were determined by atomic absorption spectrometry, after concentration by extraction into an organic

Sand #1 Flowing Water

Sample		
1F	-	
2	0.29	
3	0.31	
4	0.29	
5	0.28	
6	0.26	
7	0.28	
8	0.27	
9	0.31	
10	0.28	
11	0.29	
12	0.30	
13	0.31	
14	0.31	
15	0.31	
16	0.28	
17	0.27	
18	0.31	
19	0.29	
20	0.27	
21	0.30	
22	0.32	
23	0.33	
24	0.32	
25	0.32	
26	0.32	
27	0.30	0.32
28	0.31	
29	0.32	0.30

Sand #3 Flowing Water

Sample	
1F	-
2	-
3	-
4F	0.39
5F	-
6	0.57
7	0.43
8	0.56
9	0.42
10	0.60
11	0.38
12	0.31
13	0.44
14	0.48
15	0.45
16	0.50
17	0.30
18	0.41

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	0.30 (0.26-0.33)
Bottom-hole:	0.31
	Sand #3
Flowing:	0.45 (0.30-0.60)
Bottom-hole:	(0.29-0.72)

TABLE XXVIII

CADMIUM (mg/l)

Sand #1 Flowing Water

Sample		
1F		
2	0.006	0.007
3		
4		
5		
6		
7		
8		
9		
10	<0.002	0.002
11		
12		
13		
14		
15		
16		
17		
18	0.008	0.007
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29	0.013	0.014

Sand #3 Flowing Water

Sample		
1F		
2		
3		
4F	0.007*	0.007*
5F		
6	0.008 0.007	0.003* 0.004*
7	0.009*	0.005*
8	0.008*	0.005*
9	0.002*	
10	0.008	0.007* 0.005*
11	0.008*	0.005*
12	0.002*	0.002*
13	0.005*	0.006*
14	0.008	0.008 0.002*
15	0.007*	0.004*
16	0.002*	
17	0.002*	
18	0.025 0.024	0.006* 0.004*

TYPICAL VALUES (RANGE)

Sand #1

Flowing: -

Bottom-hole: -

Sand #3

Flowing: -

Bottom-hole: -

TABLE XXIX

CHROMIUM (mg/l)

solvent, but the values obtained were at the lower limit of detection. In order to verify these values and to improve the precision, selected samples were re-analyzed for chromium using neutron activation analysis after the preconcentration technique. The precision for the latter values is better than for the former ones but a significant difference between methods is evident for Sample #18. More samples should have been analyzed in order to resolve the differences noted and to verify a trend toward higher chromium values, if one existed, but this was not done because of an administrative decision concerning the expected date for the final report. In fact, only selected samples were analyzed for most of the trace metals (and sulfate) for this same reason.

The copper values in Table XXX trend downward for Sand #1 but appear to be constant for Sand #3. The 0.034 value for Sample #14 on Sand #3 must be an incorrect measurement for which there is no apparent explanation. Tables XXXI-XXXIV give the values for arsenic, mercury, lead and barium. Note that bottom-hole samples contain about 2-2.5 times more barium than the flowing samples. Sulfate (Table XXXV) shows lower values for Sand #1 than for Sand #3, and there appears to be a slight decrease with time in both sands, but this may not be significant in view of the fact that sulfate was determined gravimetrically.

a. Comparison of Data Between On-Site Lab and McNeese Labs

As mentioned previously, RUSS samples were collected at

Sand #1 Flowing Water

Sample		
1F		
2	0.038	0.034
3		
4		
5		
6		
7		
8		
9		
10	0.022	0.022
11		
12		
13		
14		
15		
16		
17		
18	0.016	0.015
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29	0.010	0.011

Sand #3 Flowing Water

Sample		
1F		
2		
3		
4F		
5F		
6	0.016	0.014
7		
8		
9		
10	0.017	0.017
11		
12		
13		
14	0.017	0.034*
15		
16		
17		
18	0.018	0.018

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	- (0.010-0.038)
Bottom-hole:	-
	Sand #3
Flowing:	0.017 (0.014-0.018)
Bottom-hole:	-

TABLE XXX

COPPER (mg/1)

Sand #1 Flowing Water

Sample	
1F	
2	< 0.05
3	
4	
5	
6	
7	
8	
9	
10	< 0.05
11	
12	
13	
14	
15	
16	
17	
18	< 0.05
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	< 0.05

Sand #3 Flowing Water

Sample	
1F	
2	
3	
4F	
5F	
6	< 0.05
7	
8	
9	
10	< 0.05
11	
12	
13	
14	< 0.05
15	
16	
17	
18	< 0.05

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	< 0.05
Bottom-hole:	-
	Sand #3
Flowing:	< 0.05
Bottom-hole:	-

TABLE XXXI

ARSENIC (mg/l)

Sand #1 Flowing Water

Sample	
1F	
2	< 0.02
3	
4	
5	
6	
7	
8	
9	
10	< 0.02
11	
12	
13	
14	< 0.02
15	
16	
17	
18	< 0.02
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	< 0.02

Sand #3 Flowing Water

Sample	
1F	
2	
3	
4F	
5F	
6	< 0.02
7	
8	
9	
10	< 0.02
11	
12	
13	
14	< 0.02
15	
16	
17	
18	< 0.02

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	< 0.02
Bottom-hole:	-
	Sand #3
Flowing:	< 0.02
Bottom-hole:	-

TABLE XXXII

MERCURY (mg/l)

Sand #1 Flowing Water

Sample	
1F	
2	< 0.2
3	
4	
5	
6	
7	
8	
9	
10	< 0.2
11	
12	
13	
14	
15	
16	
17	
18	< 0.2
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	< 0.2

Sand #3 Flowing Water

Sample	
1F	
2	
3	
4F	
5F	
6	< 0.2
7	
8	
9	
10	< 0.2
11	
12	
13	
14	< 0.2
15	
16	
17	
18	< 0.2

TYPICAL VALUES (RANGE)

Sand #1

Flowing: < 0.2

Bottom-hole: -

Sand #3

Flowing: < 0.2

Bottom-hole: -

TABLE XXXIII

LEAD (mg/l)

Sand #1 Flowing Water

Sample		
1F		
2	2.2	2.3
3		
4		
5		
6		
7		
8		
9		
10	3.8	4.1
11		
12		
13		
14		
15		
16		
17		
18	3.0	2.8
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29	2.8	2.9

Sand #3 Flowing Water

Sample		
1F		
2		
3		
4F		
5F		
6	2.7	2.4
7		
8		
9		
10	3.0	2.9
11		
12		
13		
14		
15		
16		
17		
18	2.5	2.7

TYPICAL VALUES (RANGE)

Sand #1

Flowing: 3.0 (2.2-4.1)

Bottom-hole: 6.3

Sand #3

Flowing: 2.7 (2.4-3.0)

Bottom-hole: 6.2

TABLE XXXIV

BARIUM (mg/l)

Sand #1 Flowing Water

Sample				
1F				
2	152	155	148	
3				
4				
5				
6				
7				
8				
9				
10	146	142	141	
11				
12				
13				
14				
15				
16				
17				
18	139	138	142	145
19				
20				
21				
22				
23				
24				
25	142	142	146	
26				
27				
28				
29	134	134	135	

Sand #3 Flowing Water

Sample			
1F			
2			
3			
4F			
5F			
6	210	214	208
7			
8			
9			
10	203	208	196
11			
12			
13			
14	200	204	206
15			
16			
17			
18	182	179	188

TYPICAL VALUES (RANGE)

	Sand #1
Flowing:	-
Bottom-hole:	150
	Sand #3
Flowing:	-
Bottom-hole:	211

TABLE XXXV

SULFATE (mg/l)

Station #2, under pressure. The sample cylinders were opened at McNeese and pH, bicarbonate, and total hardness were redetermined and compared with the values obtained at the well-site. This was done in order to evaluate the possibility of collecting samples at the well-site and performing all analyses in a conventional laboratory; i.e., no on-site analyses would be performed. Table XXXVI lists representative samples and shows that some of the RUSS containers holding Sand #3 samples had lost pressure. The pH determined at McNeese was considerably higher than the pH determined at the well-site; e.g. Samples #6 and #7. The total hardness and bicarbonate values were consistently higher when determined at the McNeese labs. Sample numbers refer to Table VIII.

The Sand #1 RUSS samples were collected in a slightly different manner. The container was filled with gas from the separator at separator pressure, then connected in-line at Station #2. The container was allowed to fill with fluid from the separator, at constant pressure, by cracking the exit valve on the container and opening the entrance valve to the container and the valve supplying effluent from the separator.

Table XXXVII lists the values obtained for pH, bicarbonate, total hardness, and chloride in both laboratories on representative samples from Sand #1. It can be seen that the pH values are higher for those containers that lost pressure, which

Sample No.		6	7	10	14	15
pH	On-Site	6.60	6.56	6.24 @ 53°C	6.27 @ 48°C	6.12 @ 43°C
	McNeese	7.08	6.97	6.20 @ 29°C	6.17 @ 29°C	6.67 @ 29°C
Total Hardness	On-Site	6120	6040	6080	5960	6000
	McNeese	6420	6440	6270	6420	6270
Bicarbonate	On-Site	1110	1110	1030	1080	1060
	McNeese	1720	1360	1300	1400	1460
Pressure on RUSS Cylinder		None	Some	High	High	Medium

TABLE XXXVI

COMPARISON OF VALUES OBTAINED AT WELL-SITE VS. MCNEESE LABS

SAND #3

Sample No.		2	4	6	8	25
pH	On-Site McNeese	5.95 @ 32°C 5.97 @ 22.5°C	6.32 @ 40°C 6.30 @ 22.5°C	6.19 @ 36°C 6.38 @ 22.5°C	6.16 @ 37°C 6.67 @ 22.5°C	6.06 @ 32°C 6.45 @ 21.5°C
Total Hardness	On-Site McNeese	6750 6870	6820 6910	6760 6880	6750 6810	-- --
Bicarbonate	On-Site McNeese	1130 1230	-- --	1060 1240	1030 1180	-- --
Chloride	On-Site McNeese	80,300 80,500	80,500 80,700	80,400 80,900	80,400 80,700	-- --
Pressure on RUSS Cylinder		High	High	None	None	None

TABLE XXXVII

COMPARISON OF VALUES OBTAINED AT WELL-SITE VS. MCNEESE LABS

SAND #1

agrees with the results from Sand #3. The total hardness and bicarbonate values obtained in both laboratories agree more closely than those in the previous table. Chloride was redetermined for the Sand #1 samples and these values are also included in Table XXXVII. Agreement between on-site values and McNeese values is good. Sample numbers refer to Table IX.

One sample that had lost pressure (#25, Table XXXVII) was repressurized with separator gas, placed in an oven at $234^{o}F$ for several days, and shaken sporadically. The container was opened and the pH was found to be 6.16, indicating the correlation, as expected, between pH and pressure in the container.

This study indicates that an on-site laboratory is needed in order to obtain reliable data for certain determinations. It is possible that in future field work, techniques can be developed that would make on-site analyses unnecessary. A more thorough study should be undertaken on future geopressured-geothermal projects in order to evaluate this prospect completely.

b. Emission Spectrographic Analysis

An emission spectrographic qualitative procedure was used to identify metals from the dissolved solids determinations. The high sodium content of the evaporated samples suppressed the line intensities for various elements which resulted in poor sensitivities. The primary purpose of the spectrographic examination was to identify elements that had been omitted in the analysis scheme. Manganese was identified in this manner, and four samples were analyzed by neutron activation analysis. Values of 1.56, 1.55, and 1.47 mg Mn/l were obtained for Samples #6, #10, and #14, respectively, of Sand #3. A value of 1.62 mg Mn/l was obtained for Sample #10 of Sand #1.

The dissolved solids from the RUSS samples were evaluated spectrographically also. As expected, the solids from the RUSS samples contained more iron, nickel, and chromium than the solids obtained at the well-site.

As a matter of interest, the solids obtained from the precipitation of RU samples were examined. They were found to be much higher in iron, barium, strontium, silicon, manganese, magnesium, calcium, and others when compared to the dissolved solids samples. This is probably the result of precipitation and co-precipitation, which effectively increases the concentration of an element, and a lower sodium content which decreases the suppression effect.

4. Data from other Laboratories

Many laboratories requested samples from the well and some sent personnel to the site to collect samples. Some of the laboratories wished to perform special analyses while others were interested in a complete analysis. McNeese subcontracted two analyses to outside laboratories; i.e., U.S.G.S. Labs in Denver performed the determinations for radioactive products, and the University of New Orleans's Center for Bio-Organic Studies performed the work on trace organics.

a. Radioactivity

Separator gas and separator water samples were collected and sent to the U.S.G.S. Labs in Denver for the determination of radioactive elements. Four samples from Sand #3 and six samples from Sand #1 were analyzed. Gas samples were collected at the separator gas collection point(s) shown in Figure 3 in 75 ml. stainless steel Whitey cylinders fitted with valves. These cylinders were identical to those used to collect RUSS samples (Figure 7) except for the difference in size. Only radon was determined on these gas samples. Flowing water samples were collected, at a point as near the exit on the downstream side of the separator as possible, in containers furnished by the U.S. Geological Survey (Figure 8). In practice, the glass vial was filled with water from the separator and the plastic tubes placed on either end of the sample tube were wired closed. Only dissolved radon was determined on these water samples. A one liter plastic bottle was used to collect samples at Station #1 (Figures 3 and 5) for all of the other radionuclides. Tables XXXVIII and XXXIX list the results of these tests. The ^{226}Ra values obtained from both sands are about a factor of 10 higher than the average found in surface waters; consequently, the radioactivity of the water certainly should be investigated

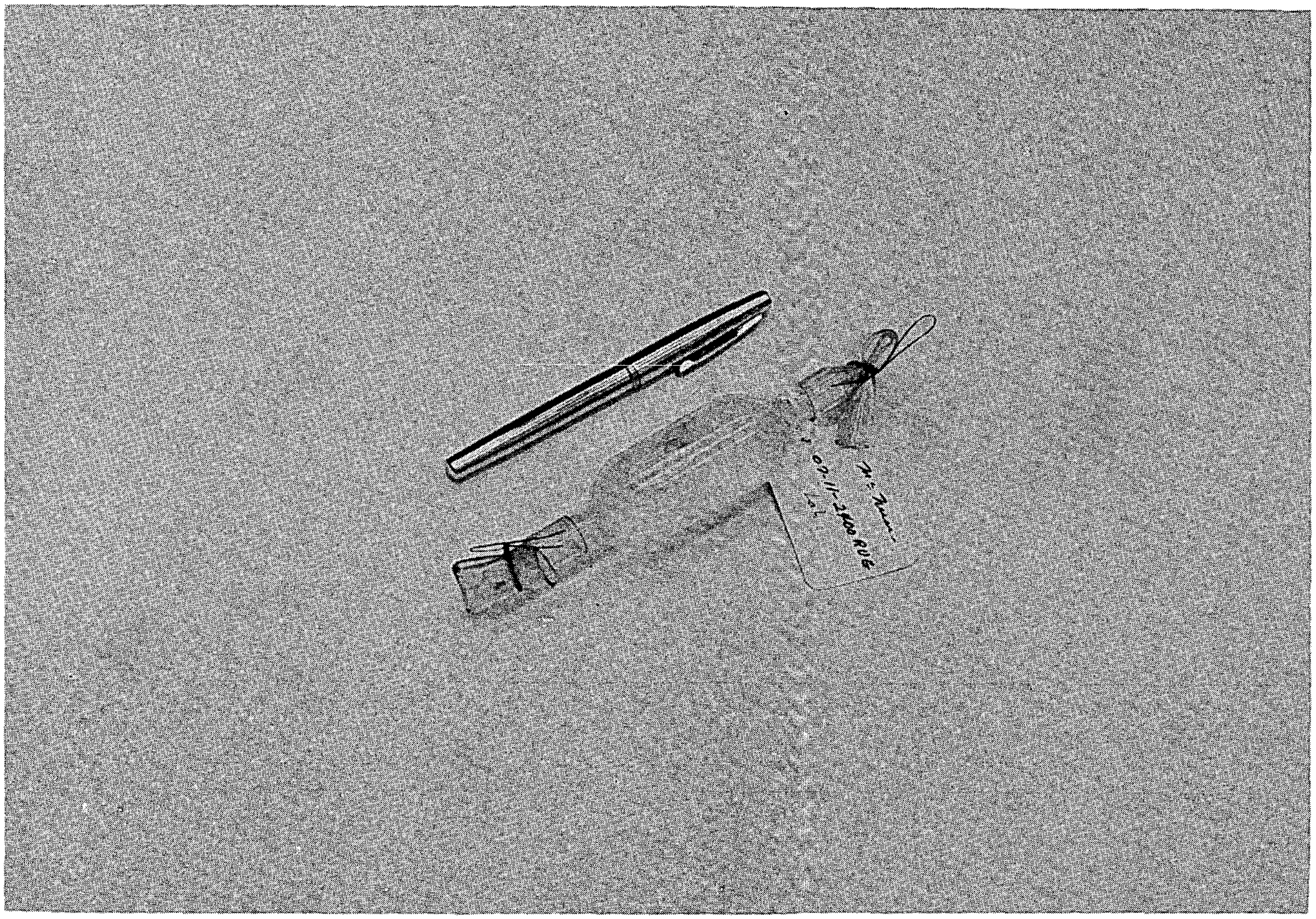


FIGURE 8

COLLECTION CONTAINER FOR DISSOLVED RADON

Collection Date	05-24-pm	05-31-am	06-03-pm	06-07-pm
^{222}Rn in gas, pCi/l	15	100	61	64
^{222}Rn in solution pCi/l	-	-	540	300
Gross β as pCi ^{137}Cs/l	1400	1100	1900	1800
Gross α as μ g U/l	14000	6900	13000	6300
Gross β as pCi^{90}Sr/l	1300	920	1600	1500
^{226}Ra, pCi/l	280	310	480	500
U, μ g/l	0.10	0.11	0.2	0.06

TABLE XXXVIII

RADIOACTIVE ELEMENTS IN SEPARATOR WATER

SAND #3

Collection Date	6-24-pm	6-27-pm	6-28-pm	6-30-pm	7-03-pm	7-11-pm
^{222}Rn in gas, pCi/l	41	50	59	55	31	24
^{222}Rn in solution pCi/l	-	-	150	330	140	190
Gross β as pCi ^{137}Cs/l	440	1200	1200	800	1100	1300
Gross α as μ g U/l	1700	11000	6400	4100	6400	10000
Gross β as pCi^{90}Sr/l	400	1100	1100	700	960	1200
^{226}Ra, pCi/l	86	140	230	240	360	370
U, μ g/l	0.10	0.09	0.07	0.01	0.01	0.05
K, dissolved, mg/l				290	300	320
^{40}K, pCi/l				220	220	240

TABLE XXXIX

RADIOACTIVE ELEMENTS IN SEPARATOR WATER

SAND #1

further. Note also that the ^{226}Ra values increase with time from each sand, i.e., about a factor of two in Sand #3 and a factor of four in Sand #1. This is considered quite significant and underscores the need for additional study, especially with regard to fractionation of the uranium chain. The uranium values from Sand #1 show some decrease with time, which is also consistent with fractionation of the chain. The total potassium values determined in Denver agreed with those determined at McNeese (compare Table XXXIX with Table XXV).

b. Trace Organics

One-gallon samples, in glass containers, were collected at Station #1 (Figures 3 and 5), to be sent to the University of New Orleans' Center for Bio-Organics. One sample from each sand was sent. Each sample was extracted with hexane, 40% benzene-60% hexane, and methanol, and a gas chromatographic-mass spectrometric procedure was applied to the extracts (8) (10) (11) (15). Only compounds above a molecular weight of 150 were sought as these would appear to be the ones of most interest from environmental and health aspects. Tables XL, XLI, and XLII list the compounds and amount, when determined, present in the samples. Both samples appear to be saturated, as might be expected, with hydrocarbons. The column used to obtain the data shown in Table XLII did not have sufficient resolution to permit the identification of individual components.

Compound	Sand #3	Sand #1
n-undecane	4.8	22.6
C_5 cyclohexane	trace	2.9
n-dodecane	13.3	44.3
C_{13} branched alkane	3.4	10.9
C_6 cyclohexane	trace	4.9
unknown	2.7	7.3
C_7 cyclohexane	4.9	12.2
n-tridecane	32.4	78.5
C_{14} branched alkane	2.4	3.1
C_7 cyclohexane	3.6	8.9
C_{14} isoalkane	6.2	12.9
unknown	10.2	18.1
n-tetradecane	62.5	120.
C_5 decaline	trace	trace
C_8 cyclohexane	5.8	13.0
C_{16} isoprenoid (tent.)	28.1	49.4
n-pentadecane	78.3	138.
C_9 cyclohexane	7.4	9.5
unknown	11.8	20.1
n-hexadecane	85.8	141.
C_{10} cyclohexane and branched alkane	37.5	66.3

TABLE XL

HYDROCARBONS IN HEXANE EXTRACT (μg/l)

Compound	Sand #3	Sand #1
n-heptadecane	87.1	161.
pristane	49.2	88.8
C_{10} cyclohexane	9.6	19.0
n-octadecane	71.3	133.
phytane	78.8	35.5
C_n-cyclohexane (tent.)	3.9	7.8
n-nonadecane	56.1	115.
n-eicosane	47.2	102.
n-heneicosane	40.5	90.5
n-docosane	33.3	76.5
n-tricosane	28.3	69.8
n-tetracosane	23.8	62.2
n-pentacosane	20.5	57.1
n-hexacosane	16.5	46.4
n-heptacosane	13.3	38.8
n-octacosane	9.9	28.0
n-nonacosane	8.9	25.8
n-triacontane	6.5	18.8
n-hentriacontane	trace	16.6

TABLE XL (CONT'D)

HYDROCARBONS IN HEXANE EXTRACT (µg/l)

Compound	Sand #3	Sand #1
naphthalene	58.8	48.8
C_1 naphthalene	25.8	34.0
C_1 naphthalene	25.5	31.4
C_7 benzene	trace	1.32
biphenyl	3.94	8.53
C_2 naphthalene (isomer)	3.82	6.08
C_2 naphthalene (isomer)	trace	trace
C_2 naphthalene (isomer)	65.8	14.8
C_2 naphthalene (isomer)	9.32	19.0
C_2 naphthalene (isomer)	7.41	16.2
C_2 naphthalene (isomer)	8.95	17.9
C_2 naphthalene (isomer)	4.02	7.30
C_8 benzene	trace	1.53
C_1 biphenyl	5.58	11.8
C_1 biphenyl	1.52	4.88
C_3 naphthalene	1.54	6.57
dibenzofuran (tent.)	1.77	4.92
C_3 naphthalene	1.96	5.31
C_3 naphthalene	3.54	8.63
C_3 naphthalene	5.14	6.70

TABLE XLI

HYDROCARBONS PRESENT IN 40% BENZENE-60% HEXANE EXTRACT (μ g/l)

Compound	Sand #3	Sand #1
C_3 naphthalene	7.14	1.38
fluorene or methyl acenaphthalene	trace	3.25
C_3 naphthalene	7.75	12.8
C_2 biphenyl	1.78	4.68
C_2 biphenyl	3.44	1.68
C_2 biphenyl	7.86	1.42
xanthene (tent.)	trace	trace
C_2 biphenyl	4.74	1.78
C_{10} benzene	4.64	trace
C_4 naphthalene	trace	trace
C_5 naphthalene	5.14	trace
C_4 naphthalene	trace	trace
C_4 naphthalene and C naphthalene	3.82	1.13
C_1 fluorene or C acenaphthalene	1.36	trace
C_3 biphenyl	5.46	1.60
C_4 naphthalene	7.20	4.00
C_4 biphenyl	1.58	trace
C_4 naphthalene and C biphenyl	1.37	trace
phenanthrene	6.76	2.42
C_2 fluorene isomer	1.18	trace

TABLE XLI (CONT'D)

HYDROCARBONS PRESENT IN 40% BENZENE-60% HEXANE EXTRACT (μ g/l)

Compound	Sand #3	Sand #1
C_2 fluorene isomer	1.46	trace
C_2 fluorene isomer	2.10	trace
C_1 phenanthrene (or anthracene)	3.43	trace
C_1 phenanthrene (or anthracene)	2.71	trace
C_1 phenanthrene (or anthracene)	4.94	trace
C_1 phenanthrene (or anthracene)	2.68	trace
C_1 phenanthrene (or anthracene)	1.09	trace

TABLE XLI (CONT'D)

HYDROCARBONS PRESENT IN 40% BENZENE-60% HEXANE EXTRACT (μ g/l)

1. Alcohols
2. Aldehydes
3. Ketones
4. Acids
5. Aromatic Phenols
6. Oxygenated Alkyl Benzenes

TABLE XLII

CLASSES OF HYDROCARBONS PRESENT IN METHANOL EXTRACT (μg/l)

c. Analyses Performed by Other Laboratories

Battelle Northwest (Richland, Washington) and U.S.G.S. (Menlo Park, California) determined a number of ions not sought by McNeese and not in the original objectives of the project (4) (7). In the interest of completeness of this report, these values are listed in Table XLIII.

5. In-line Physico-Chemical Measurements

The in-line equipment was meant to measure the pH, conductance, and temperature continuously. Initially, one set of probes was placed at each of the sampling stations; i.e., Stations #1, #2, and #3 in Figure 3. Figure 9 shows the in-line pH cell (assembled) and Figure 10 shows an exploded view of the cell. The pH cell also housed a thermocouple for temperature measurements. Figure 11 shows a disassembled view of the conductance cell. The in-line probes on the test barge were connected by cables to appropriate amplifiers and monitors located in the on-site laboratory on the quarters barge. A multi-point recorder with six inputs monitored any two of the three sets continuously; i.e., the recorder could accept any of the nine possible signals but only six at one time. Figure 12 shows the conductance monitor, pH monitor, and recorder.

The restrictions placed on the in-line equipment were severe with respect to pressure and temperature. A manufacturer that could supply equipment capable of withstanding both high

Ion	Amount
Al	0.005 mg/l
Br	65 mg/l
I	25 mg/l
NH_4^+	90 mg NH_3/l
F	0.95 mg/l
Li	5.8 mg/l
Be	0.065 mg/l
Sn	0.065 mg/l
Ni	< 0.05 mg/l
Se	0.00072 mg/l
Ag	0.00039 mg/l
Cs	0.100 mg/l
Sc	0.0000074 mg/l
Rb	0.459 mg/l
Co	0.00017 mg/l
Sb	0.00079 mg/l
$S^=$	0.5 mg H_2S/l
Hg	7 nanograms/l
H_2S	1 ppm

TABLE XLIII

ANALYSES PERFORMED BY OTHER LABORATORIES - SAND #3 (4) (7)

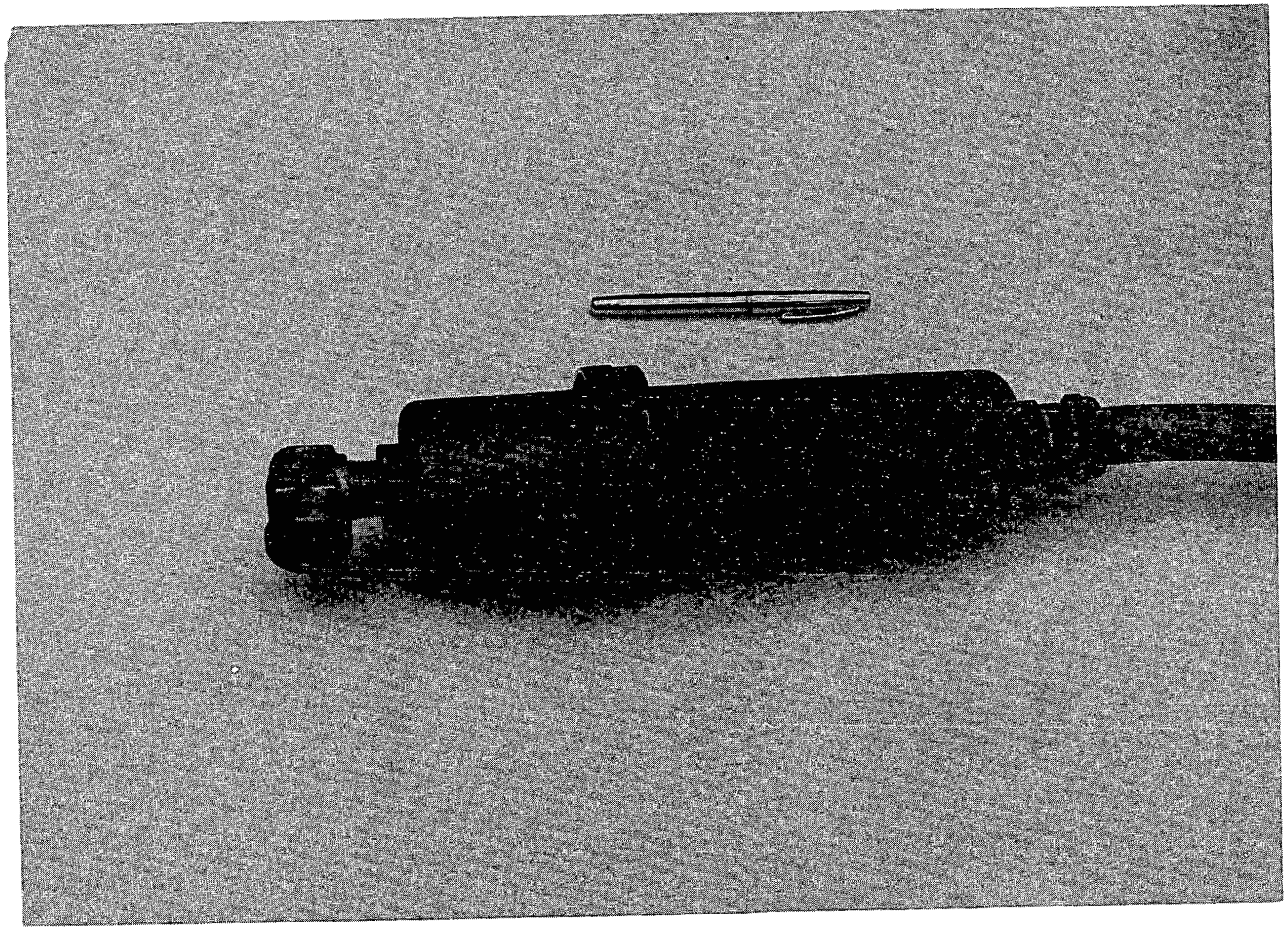


FIGURE 9

IN-LINE pH CELL (ASSEMBLED)

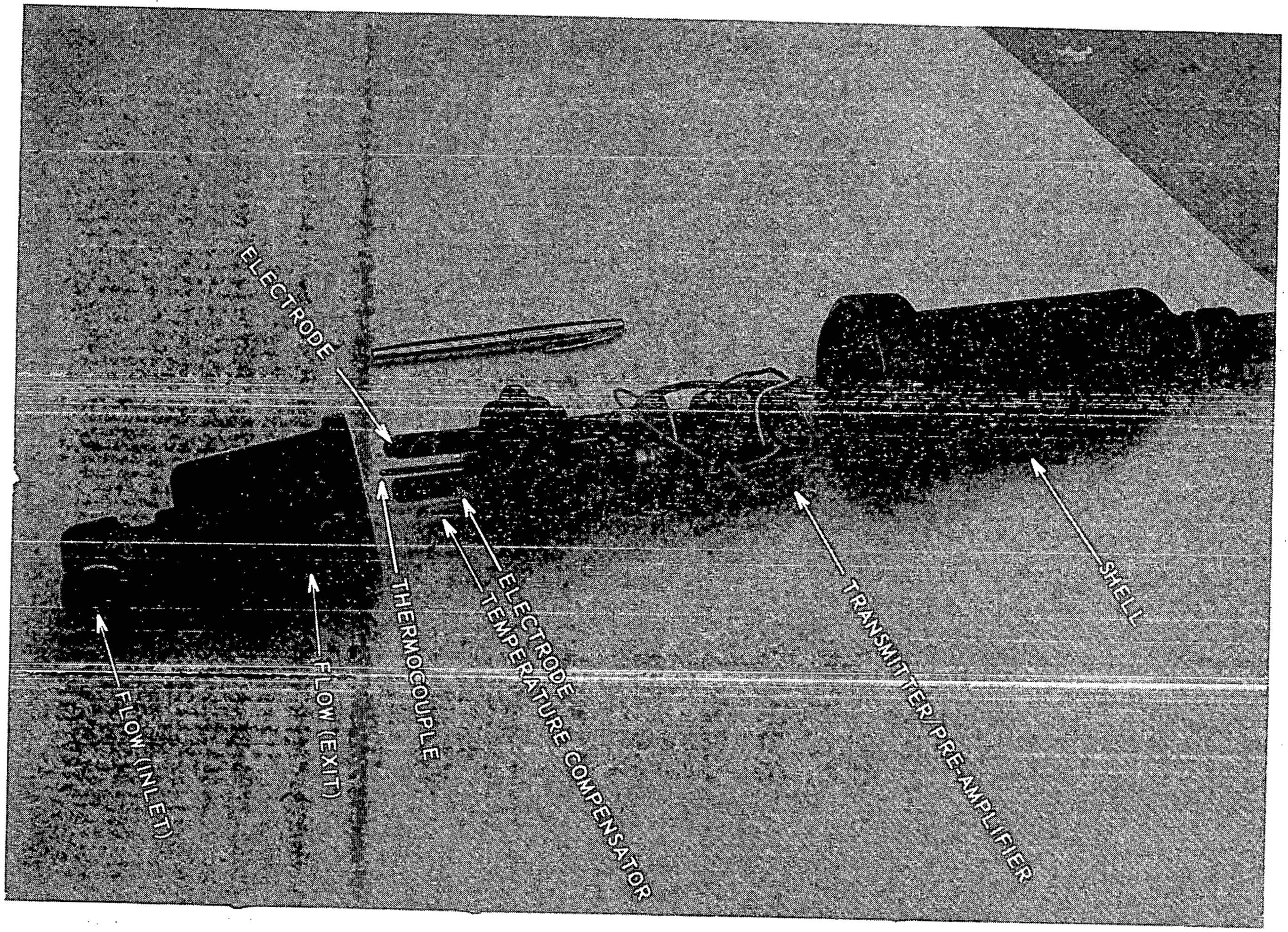


FIGURE 10

IN-LINE pH CELL (EXPLODED VIEW)

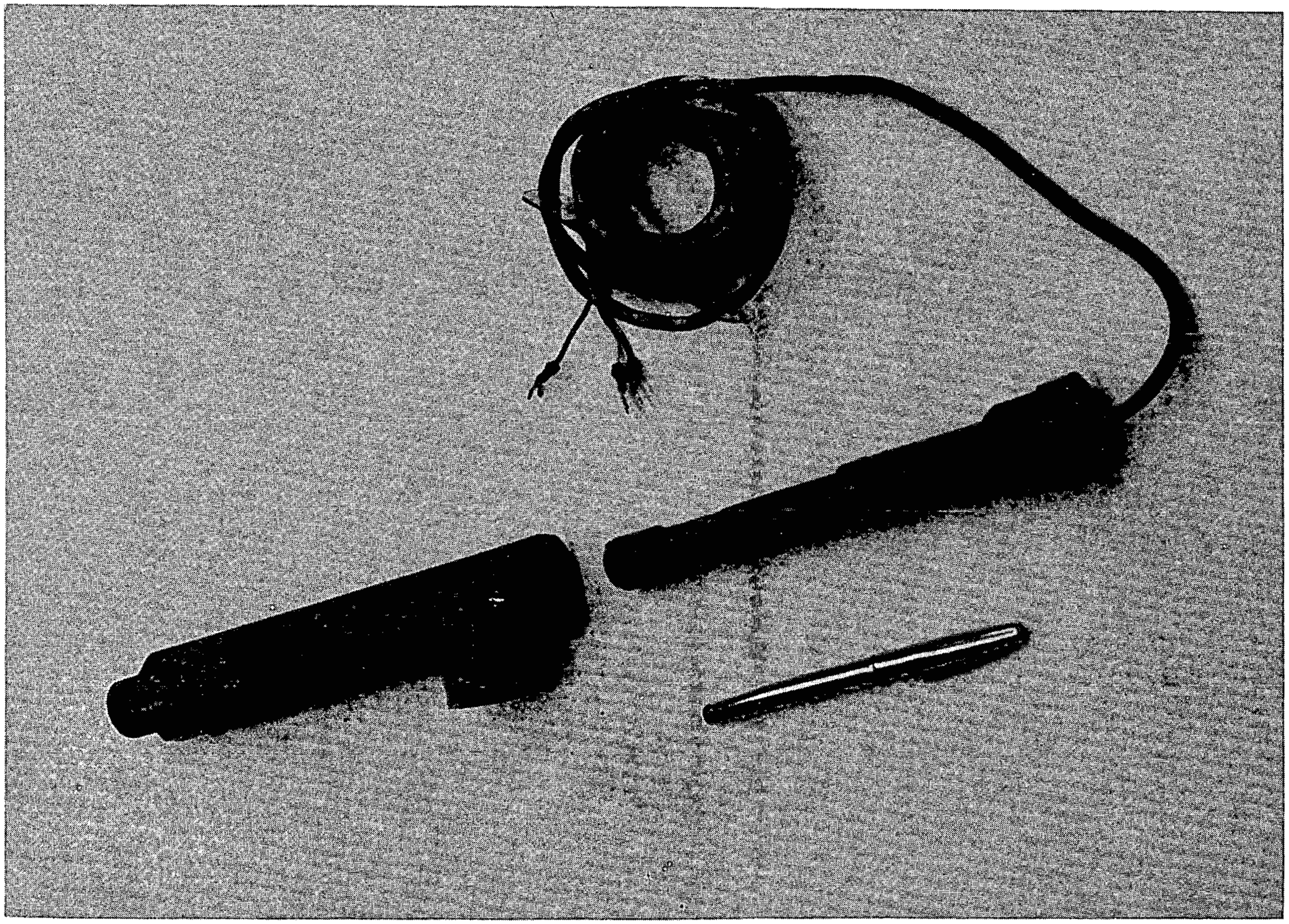


FIGURE 11

IN-LINE CONDUCTANCE CELL (DISASSEMBLED)

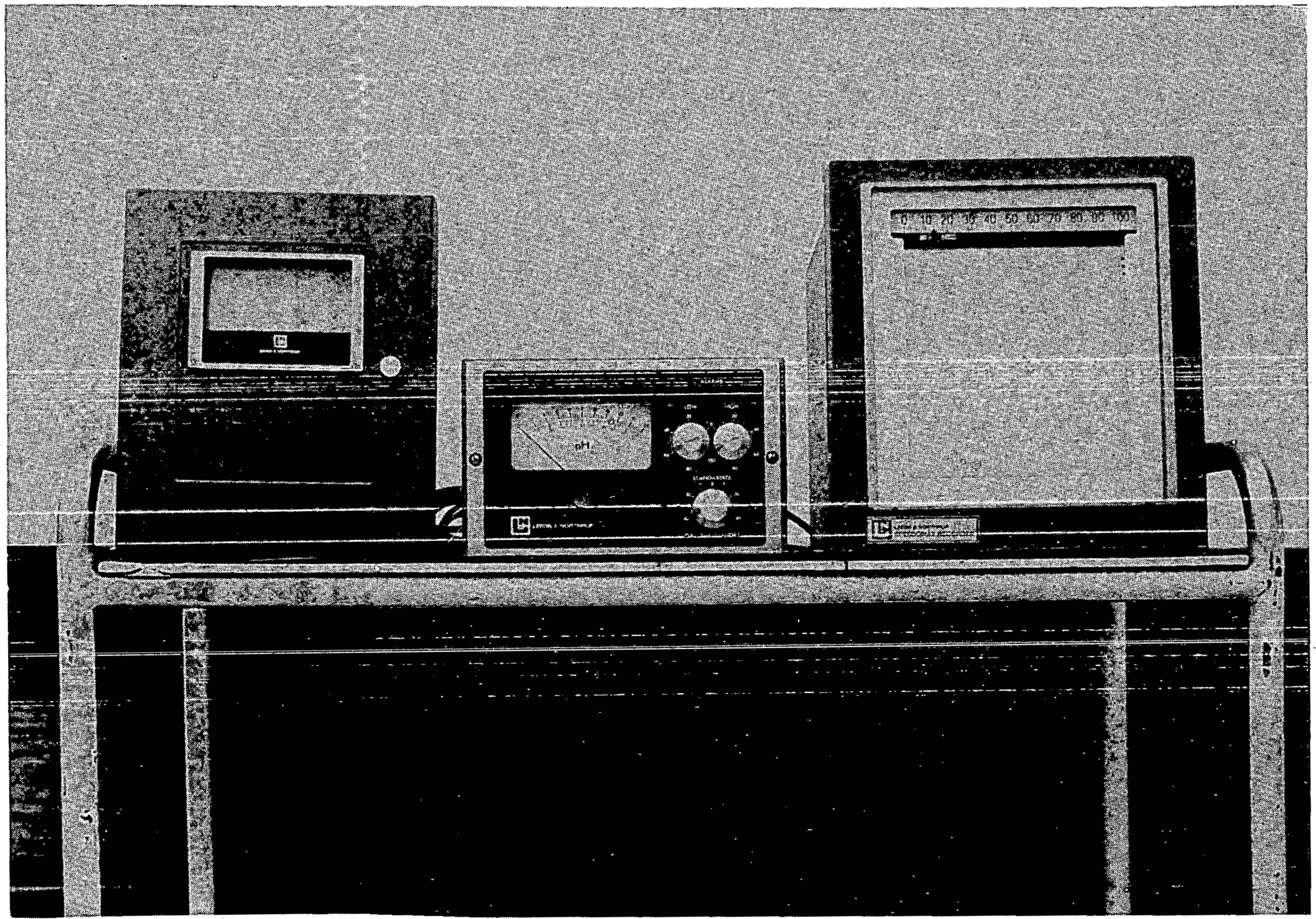


FIGURE 12

CONDUCTANCE & pH MONITOR & RECORDER

temperature and high pressure apparently was not available. The equipment was purchased and installed, therefore, with the knowledge that it would probably fail, but some useful information could possibly be obtained before failure.

The thermocouples worked well in measuring the temperature at the three points. The conductance, as measured from the recorder, gave almost identical values when compared to the laboratory measurements obtained on the same sample. It was necessary to adjust the in-line values to correct them for the constant of the conductivity cell because the constants supplied by the manufacturer were apparently nominal values. Each cell was calibrated at McNeese before it was used at the barge although the manufacturer claimed this procedure was not necessary.

The real surprise came in the recorded pH values, for they were considerably lower than the values obtained in the on-site laboratory. A recording obtained on 5-31-77 at Station #3 (Figures 3 and 4) showed a pH value of 5.4-5.5, whereas, the corresponding laboratory measurement (Sample #11 of Sand #3 in Table X) was 6.19. The well was shut-in to obtain bottom-hole samples, but the recorder continued to monitor the pH and temperature. Over a two- or three-hour period, the temperature decreased to 80°F (ambient temperature), and the pH increased slowly to 6.2, which was the same as the laboratory measurement noted above. The system was obviously not in equilbrium with respect to the gas, and the higher values obtained in the laboratory for the #3 Sand were apparently the result of a loss of carbon dioxide while the sample was being transported to the lab to make the measurement. In fact, any consistency in the lab measurement of the pH probably was the result of consistency in the time needed for transportation and measurement only and does not reflect the true pH of the solution.

Some of the in-line cells failed, as had been anticipated, and most of the spare parts had been used by the time tests started on Sand #1. Scale deposits on the electrodes were also a problem. It was decided to try to assemble enough parts to put one cell in working order for the Sand #1 test and locate it at Station #2 (Figures 3 and 4) in order to reduce the scaling problem. This was done and a recording was obtained on 6-25-77 that showed an in-line pH of 5.4; whereas, the corresponding lab measurement (Sample #6 of Sand #1 in Table X) was 6.19. The in-line pH continued to read 5.5 until the separator pressure started fluctuating and the flow was stopped. The thermocouple immediately began a decrease to about 96°F (ambient temperature), and the pH increased until it stabilized at approximately 6.0-6.1 which agrees with the lab measurement. Another recording from the same station was obtained the following day (6-26-77) after the flow had been increased. The in-line measurement fluctuated between 4.1-4.5 as the rate of flow changed. The valve was adjusted manually, as the flow became restricted, to keep the flow rate essentially constant. After shut-in, the pH increased to about 6.0, which corresponds to the lab measurement (Sample #8 of Sand #1 in Table X) of 6.16.

The in-line cells were calibrated both before and after these runs at ambient and elevated temperatures and were accurate to within 0.1 unit. As stated earlier, the in-line equipment was not intended for use under the conditions of temperature and pressure experienced in this test. Difficulties in maintaining the flow, pressure fluctuations, and equipment failures prevented continuous recording of the two sands.

One additional pH test was conducted by touching a piece of pH paper to the fluid from a zero-flashed bottom-hole sample as it emerged from the laboratory high pressure apparatus. The bottom-hole sample had been collected on 7-7-77 and was zero-flashed about a month later. The pH paper read 5.2 and an immediate pH measurement on a laboratory instrument read 6.62. The pH measurements are summarized in Table XLIV. It is apparent from the above discussion that the pH values obtained in the laboratory are too high. One can only speculate about the true pH of the geopressured water as it exists at in-situ conditions. It is almost certain that the actual value is lower than 5.4 on Sand #3 and 4.1 on Sand #1; how much lower is open to question.

TABLE XLIV

Comparison of In-Line and Lab pH Values

		In-Line		Lab
Sand	Date	Flowing	Shut-in	
#3	5-31	5.4	6.2	6.19
#1	6-25	5.4	6.0	6.19
#1	6-26	4.1-4.5	6.0	6.16
#1	Bottom-hole pH paper =		5.2	6.62

B. GAS SAMPLES FROM HIGH PRESSURE SEPARATOR

1. Collection Procedures

Separator gas samples were collected in 75 ml. stainless steel Whitey cylinders as described previously for the determination of radon (See section IV.A.4a and Figure 7). The separator operated at about 300 psig for Sand #3 but varied between 300 psig at the beginning to about 850 psig at the end of the flow test for Sand #1. The collection cylinders and valves were designed to hold a pressure of 2,000 psig.

2. Analyses Performed

The gas samples were sent to two outside laboratories for hydrocarbon analyses. Cities Service Oil Company, Lake Charles Operations, performed the mass spectrometric (MS) work and Weatherly Laboratories, Lafayette, La., performed the gas chromatographic (VPC) work. The MS data gave an analysis of C_1-C_{6+} while the VPC data gave C_1-C_{7+}. Both instrumental techniques also presented CO_2, N_2, H_2S, H_2, and He data.

3. Analytical Data and Discussion

Tables XLV and XLVI list the values obtained for separator gas samples from Sand #3 and Sand #1. The tables are arranged to compare the values obtained by MS and VPC techniques. The sample numbers used are the same ones assigned in Table VIII (Sand #3) and Table IX (Sand #1). The four samples for Sand #3 and seven samples for Sand #1 are spaced approximately equally, timewise, throughout the flowing portion of the tests. A dash in the space indicates the analysis was not performed for the component listed. Since the MS procedure gave C_{6+} but the VPC analysis gave C_6 and C_{7+}, the two apparently different sets of values may be compared in this region more easily by comparing the C_{6+} value in the MS column with the sum of the C_6 and C_{7+} VPC columns. All of the analyses have been normalized to 100 mol percent except those samples containing helium. The helium was determined in a separate analysis by VPC.

Generally, the values for methane gas are consistently higher, about 1-3%, by VPC for Sand #3. The values for ethane and carbon dioxide are about the same by both techniques, but the other values vary rather widely, certainly in relative percent variation, though not in absolute terms. The MS values most difficult to explain are those for the unsaturated compounds; i.e., the butylenes (C_{4-}) and amylenes (C_{5-}) in Sand #3.

Sample #	3		6		13		18	
Component (Mol %)	M.S.	VPC	M.S.	VPC	M.S.	VPC	M.S.	VPC
C_1	90.5	92.42	89.0	92.15	91.6	92.61		93.72
C_2-	0	0	0	0	0	0		0
C_2	4.1	3.90	3.9	3.88	3.5	3.34		3.19
C_3-	0	0	0	0	0	0		0
C_3	1.8	1.32	1.1	1.32	1.4	1.03		0.95
IC_4	1.5	0.50	0.7	0.52	1.2	0.38		0.34
NC_4	0	0.39	0.6	0.41	0	0.29		0.26
C_4-	0.3	0	0	0	0.3	0		0
IC_5	0.8	0.17	1.2	0.19	0.7	0.12		0.11
NC_5	0	0.12	0	0.12	0	0.08		0.06
C_5-	0	0	0.2	0	0	0		0
C_6	-	0.12	-	0.14	-	0.06		0.05
C_{6+}	0	-	1.7	-	0	-		-
C_{7+}	-	0.23	-	0.27	-	0.28		0.03
CO_2	0.06	0.68	1.0	0.85	1.3	1.10		1.15
CO	0	0	0	0	0	0		0
H_2	0.1	0	0	0	0	0		0
N_2	0.3	0.15	0.6	0.15	0	0.71		0.14
H_2S	0	0	0	0	0	0		0
He	-	-	0	-	0	-		-

M.S. = Mass Spectrometry

TABLE XLV

VPC = Vapor-phase chromatography

SEPARATOR GAS COMPOSITION -SAND #3

Sample #	2	9		15		21		23	28	29
Component (Mol %)	M.S.	M.S.	VPC	M.S.	VPC	M.S.	VPC	M.S.	M.S.	VPC
C_1	94.1	95.1	96.09	95.0	95.34	93.7	95.14	92.1	94.0	94.89
C_2-	0	0	0	0	0	0	0	0	0	0
C_2	1.1	1.2	1.11	1.2	1.15	2.3	2.24	2.2	2.1	2.40
C_3-	0.1	0	0	0	0	0	0	0	0	0
C_3	0.2	0.2	0.12	0.1	0.12	0.7	0.59	0.5	0.7	0.65
IC_4	0.2	0.1	0.02	0.1	0.02	0.6	0.16	0.2	0.5	0.17
NC_4	0	0	0.02	0	0.01	0	0.15	2.7	0	0.17
C_4-	0	0	0	0	0	0.1	0	0.1	0.2	0
IC_5	0.3	0	0.01	0	0.01	0.5	0.08	0.3	0.3	0.09
NC_5	0	0	0.01	0	0.01	0	0.05	0	0	0.06
C_5-	0	0	0	0	0	0	0	0	0	0
C_6	-	-	0.01	-	0.01	-	0.04	-	-	0.03
C_{6+}	0	0	-	0	-	0	-	0	0	-
C_{7+}	-	-	0.02	-	0.02	-	0.13	-	-	0.02
CO_2	2.6	2.6	2.43	3.0	3.19	1.5	1.28	1.05	1.3	1.24
CO	0	0	0	0	0	0	0	0	0	0
H_2	0	0	0	0	0	0	0	0	0	0
N_2	1.4	0.8	0.16	0.6	0.12	0.6	0.14	0.4	0.9	0.1
H_2S	0	0	0	0	0	0	0	0	0	0
He	0	0	0.01	0	-	0	0.01	0	0	0

M.S. = Mass Spectrometry
VPC = Vapor-phase chromatography

TABLE XLVI

SEPARATOR GAS COMPOSITION - SAND #1

Conditions of temperature and pressure in the reservoir are not conducive to olefin formation. The reported values of butylenes and amylenes are probably not accurate, and may be indicative of the presence of some hydrocarbon species not sought by mass spectrometry.

For Sand #1, the values for methane are consistently higher by VPC but not as much as for Sand #3. The values for ethane and carbon dioxide agree between the two techniques for Sand #1 also. The other values vary between MS and VPC methods but apparently not as much in Sand #1 as in Sand #3. Again, the MS values for unsaturated components in the #1 Sand; i.e., propylenes (C_{3-}) and butylenes (C_{4-}), are hard to explain, and are probably incorrect.

Some of the RUSS samples collected at Station #2 (See section IV.A.1, Figure 3 and Figure 7) were zero-flashed, and the volume of gas measured in a procedure described later in Section IV.C.3. A volume of 0.5-3.5 SCF gas/Bbl water, depending upon separator pressure, was obtained. This gas was analyzed by mass spectrometry for some of the Sand #3 samples; the data are presented in Table XLVII. The sample numbers refer to those assigned earlier in Table VIII for Sand #3. The methane content is lower and the carbon dioxide content is higher in the separator water than in the separator gas, but that would be expected because the lighter fraction should be concentrated in the gas

Sample #	7	12	18
Composition (Mol %)			
C_1	78.9	75.2	70.0
C_2-	0	0	0
C_2	2.9	2.8	2.8
C_3-	0	0	4.4
C_3	0.4	0.7	1.2
IC_4	0.3	1.5	0
NC_4	0	0	0.3
C_4-	0	1.2	0
IC_5	0	1.9	0
NC_5	0	0	1.6
C_5-	0	0	0
C_{6+}	0	0	10.7
CO_2	13.6	12.0	3.0
CO	2.9	3.5	3.7
H_2	1.0	1.2	2.3
N_2	0	0	0
H_2S	0	0	0
He	0	0	0

TABLE XLVII

ZERO-FLASHED GAS FROM SAND #3 SEPARATOR WATER SAMPLES

(ANALYSIS BY MASS SPECTROMETRY)

and the heavier fraction should be concentrated in the water. Additionally, the carbon dioxide forms a chemical bond with the water, which would help hold that component in water solution. The results of Samples #12 and #18 are mystifying with regard to the butylene and propylene values. Likewise, the carbon monoxide content in the samples cannot be explained. It would have been expedient to compare these MS values with VPC values, but insufficient sample was available for a VPC analysis. Some RUSS samples from Sand #1 were zero-flashed with the intention of determining the composition of the gas by VPC, but too little gas was available for an analysis.

C. BOTTOM-HOLE SAMPLES

1. Sampling Equipment and Collection Procedures

The collection of bottom-hole samples was carried out under the contract issued to OHRW, who in turn, subcontracted to other firms. A Reyburn fluid sampler, a wire-line device developed by S. Reyburn and operated by Camco, was used to collect the bottom-hole samples from both sands. A schematic of the sampler is shown in Figure 13, and a photograph is shown in Figure 14. The unit is about 6 feet long, about 1-3/4 inches in diameter, and is made of stainless steel. Originally, the flow-through device included a clock mechanism that could be set to close the upper and lower valves at a predetermined time. The clock mechanism failed on many of the early attempts to

Length: 6'   Diameter: 1 3/4"   Volume: Approx. 650 ml

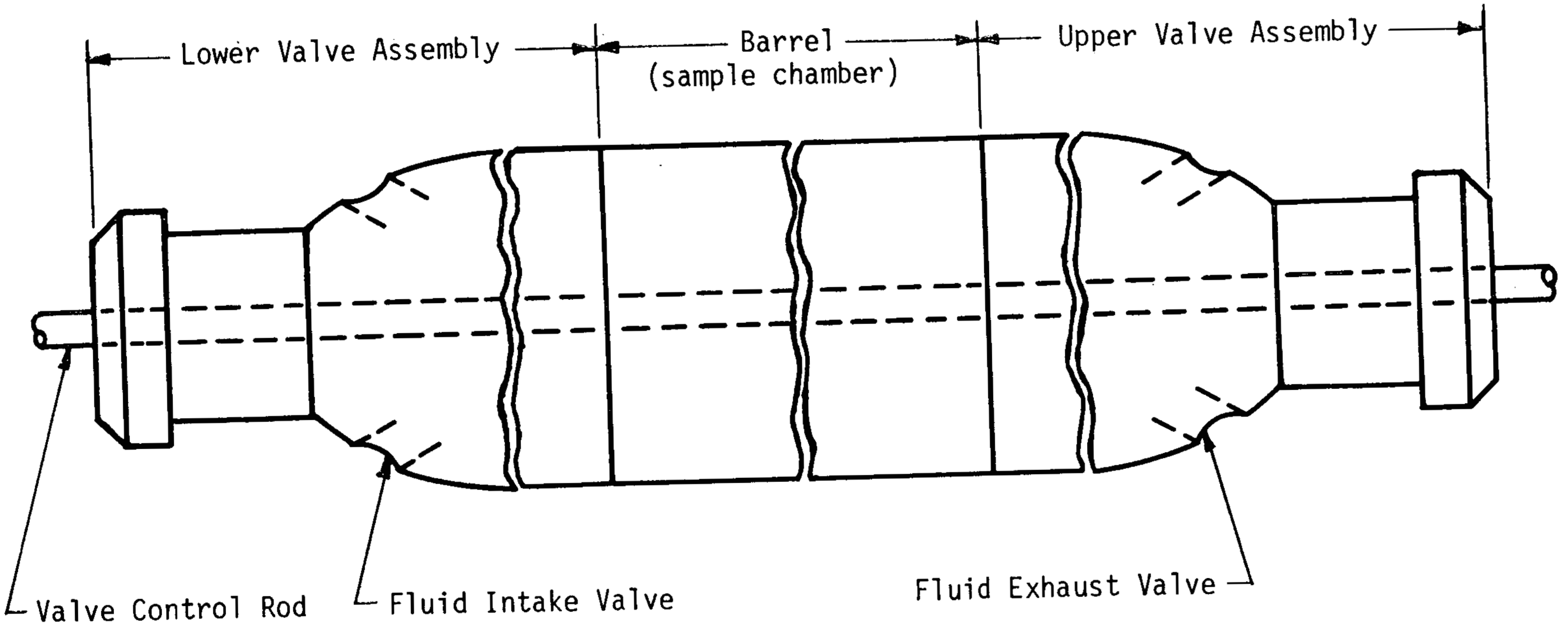


FIGURE 13

SCHEMATIC OF REYBURN BOTTOM-HOLE SAMPLER

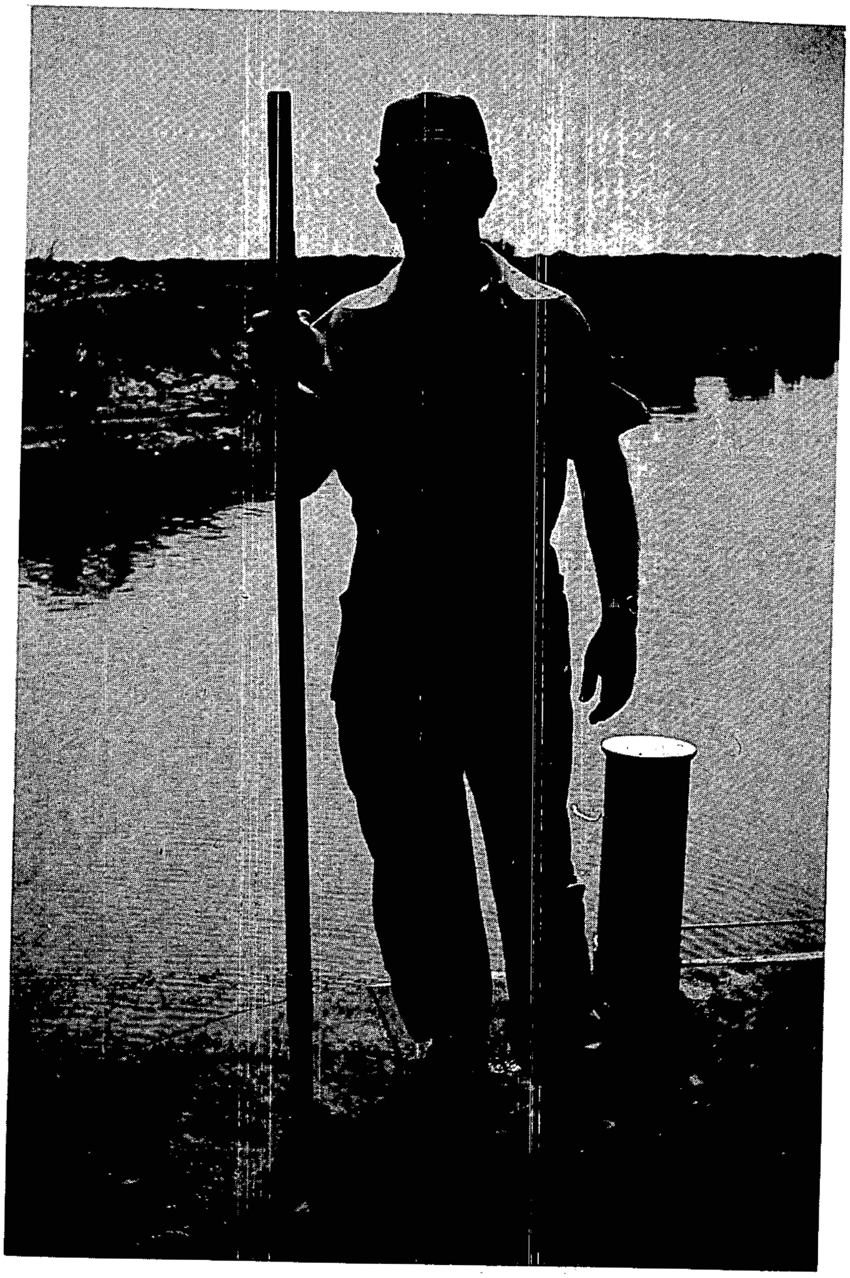


FIGURE 14

PHOTOGRAPH OF REYBURN BOTTOM-HOLE SAMPLER collect bottom-hole samples, however, and it was replaced with a shear-pin mechanism. The shear-pin mechanism performed in a satisfactory manner.

Two samplers with a capacity of about 650 ml. were available at the start of the test. One had been disassembled and cleaned thoroughly with nitric acid by McNeese personnel. Both units were to be lowered, in tandem, and returned with the bottom-hole fluid. In theory, the previously cleaned sampler was to be opened on-site and the fluid used to obtain an analysis of the various chemical constitutents (particularly mercury) while the contents of the other sampler were to be transferred to high pressure containers for gas analysis at a later date. In practice, however, the uncleaned sampler failed to deliver fluid under pressure, (the "O" rings failed to hold, the clock mechanism failed to close the valves, the threads on some of the parts galled, etc.) and it was necessary to collect both kinds of bottom-hole samples with the cleaned sampler, which was the only one available. The transfer procedure, described in the next section, used a mercury hydraulic pump, which contaminated the cleaned sampler during the first transfer. For that reason, the values for the trace metals on the bottom-hole fluid are questionable, but they are included for completeness (see Tables LII & LIII).

The first bottom-hole samples were collected from Sand #3 on 5-27-77, but the sampling devices failed to hold the pressure.

Camco personnel redesigned the sampler after flowing tests had begun and several bottom-hole samples were collected later on 5-31-77 and 6-01-77. Samples that had apparently lost part of the pressure were used as analytical samples, and those that were brought to the surface under 2,000-3,000 psig were transferred to high pressure containers for gas analysis at a later date. Calculations indicated that a sample collected at bottom-hole conditions would be under 2,400-4,600 psig at surface temperatures (see discussion in Appendix C). At an evaluation meeting in Lafayette, La., on June 6-7, 1977, OHRW was directed to collect as many bottom-hole samples as possible in a 24 hour period of operation. Three additional samples were collected under this plan on 6-11-77. Table XLVIII shows the bottom-hole samples collected from Sand #3; other pertinent information is included.

All of the bottom-hole samples from Sand #1 were collected on 7-06-77 and 7-07-77, and information regarding these samples is shown in Table XLIX. Original plans called for bottom-hole samples to be collected at the beginning, middle, and end of the test for each sand, but that was not practical considering the collection and transfer problems encountered by Camco personnel.

2. Transfer Equipment and Procedures

The bottom-hole samples that had 2,000-3,000 psig pressure when they were brought to the surface were transferred to high

Date and Collection Time	Sample	Remarks
05-27-0130	1	Seals leaked. No pressure at surface. Saved liquid for on-site analysis.
05-31-1915	2	Some leakage. Low pressure at surface. Collected in cleaned sampler. Saved liquid and sent to MSU labs.
05-31-2115	3	* Good pressure at surface. Camco lost pressure in transferring to high-pressure container. Liquid saved for on-site analysis. Remainder sent to MSU labs.
06-01-1245	4	* Good pressure at surface. Transferred and sent to Weatherly Labs for zero-flash. Gas from zero-flash to Cities Service for gas analysis by mass spectrometry and liquid from zero-flash to MSU.
06-01-1715	5	* Good pressure at surface. Transferred and sent to Core Labs for zero-flash. Gas from zero-flash analyzed by gas chromatography at Core Labs. Liquid from zero-flash analyzed on-site. Remaining liquid given to U.S.G.S labs in Menlo Park, California.
06-01-2155	6	* Good pressure at surface. Transferred and sent to Weatherly Labs for zero-flash. Gas from zero-flash to Cities Service for gas analysis by mass spectrometry and liquid from zero-flash to MSU.

TABLE XLVIII

SAMPLE COLLECTION SCHEDULE - SAND #3

BOTTOM-HOLE SAMPLES

Date and Collection Time	Sample	Remarks
06-11-0745	7	Lost pressure. Liquid sent to MSU labs.
06-11-1030	8	*Good pressure at surface. Transferred and sent to Weatherly Labs for zero-flash. Gas to Cities Service and liquid to MSU labs.
06-11-1330	9	*Good pressure at surface. Transferred and sent to Core Labs. Sample container arrived with end caps removed. Container opened at low pressure and precipitation had occurred.

*"Good" indicates pressure above 2000 psig.

TABLE XLVIII (CONT'D)

SAMPLE COLLECTION SCHEDULE - SAND #3

BOTTOM-HOLE SAMPLES

Date and Collection Time	Sample	Remarks
07-06-1545	1	*Good pressure at surface. Transferred and sent to Weatherly Labs. Opened at low pressure and precipitation had occurred. Analyzed liquid on site.
07-06-1740	2	*Good pressure at surface. Camco lost pressure in transferring and allowed liquid to stand too long before on-site analysis commenced. Analysis questionable.
07-06-2030	3	*Good pressure at surface. Camco lost pressure in transferring. Liquid saved for on-site analysis and MSU labs. Good on-site analysis.
07-06-2245	4	*Good pressure at surface. Transferred and sent to Core Labs. Opened at low pressure. Liquid analyzed on-site. Remainder of liquid to U.S.G.S. Labs in Menlo Park, California.
07-07-0005	5	*Good pressure at surface. Transferred and sent to Weatherly Labs. Opened at low pressure.
07-07-0430	6	*Good pressure at surface. Transferred and sent to Weatherly Labs. Opened at low pressure. Some precipitation.
07-07-0730	7	*Good pressure at surface. Transferred and sent to Core Labs. Sample zero-flashed. Gas analyzed by gas chromatography. Liquid analyzed on-site and remainder sent to MSU labs.
07-07-0900	8	Sampler failed. Contents contaminated with oil and grease. Liquid to MSU but not analyzed.

*See Table XLVIII

TABLE XLIX

SAMPLE COLLECTION SCHEDULE - SAND #1

BOTTOM-HOLE SAMPLES

pressure stainless steel containers, manufactured by Ruska Instrument Co. and shown in Figure 15, with a mercury hydraulic pump shown in Figure 16. The bottom-hole sampler was connected to the pump and the pressure was raised in increments while the sampler was rocked. Pressure-volume readings were taken, in an analogous manner to the treatment of gas-oil samples, until the PV curve showed a sharp break indicating that the contents of the sampler were in a single phase. Unfortunately, the gas-water mixtures did not behave similarly to gas-oil mixtures, and a sharp break in the PV relationship never occurred. There is no doubt that the gas-water mixture is a two-phase system at the well-head due to the decrease in temperature (238°F to ambient) as the sampler is brought from the depths of the well (see Appendix C). It is imperative that this system be returned to a single phase before transferring to the high pressure containers; otherwise, correct gas/water ratios will not be obtained, for a small error at bottom-hole conditions will be magnified at STP. Camco personnel transferred Sand #3 samples at various pressures ranging from 4,600 psig to 9,000 psig. Sand #1 samples were transferred at 10,000 psig, the maximum working pressure of the Camco system, although there was no assurance that the components were in a single phase. The gas data presented in the next section strongly suggest that representative bottom-hole samples were not collected (due to the failure of the sampling

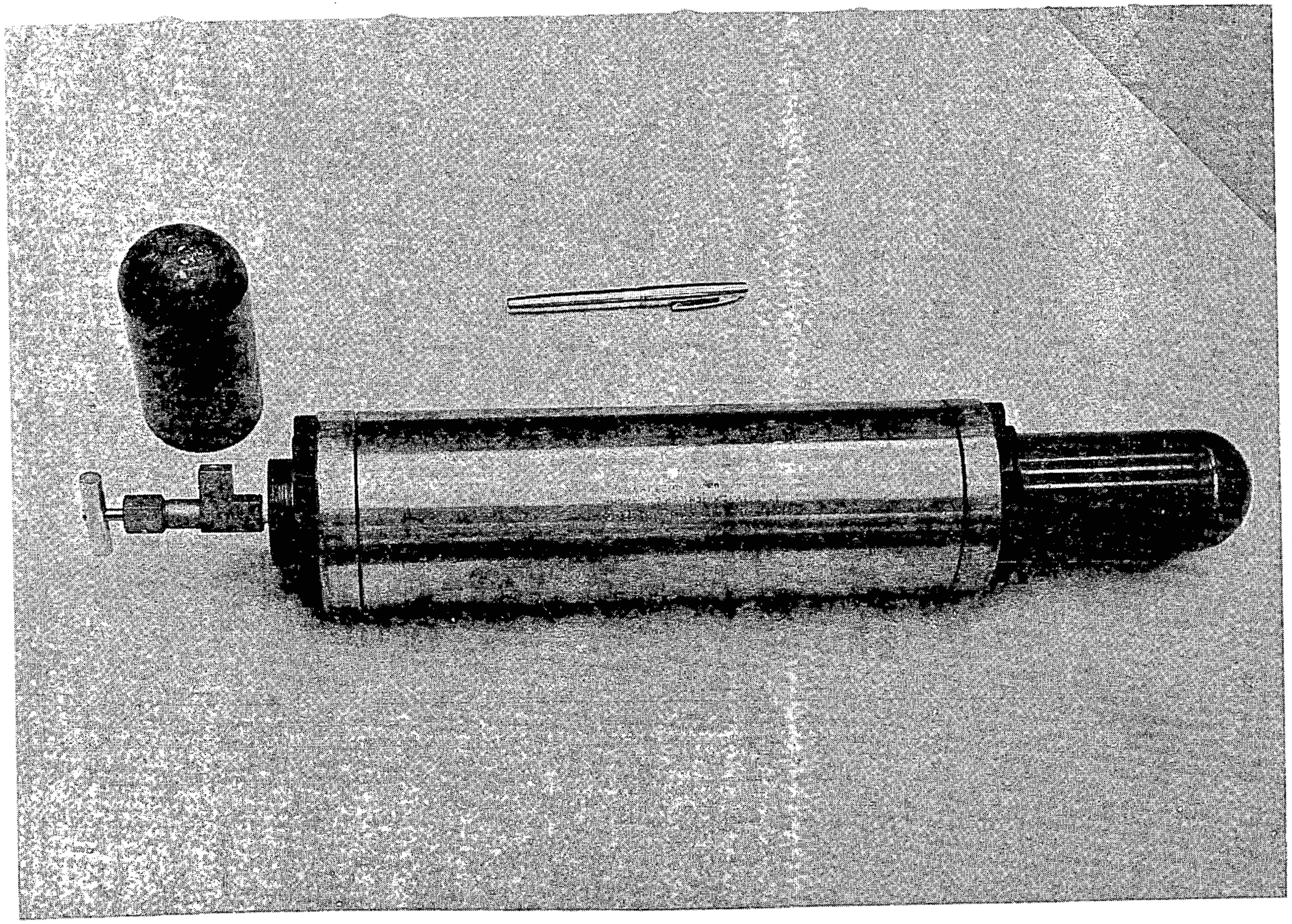


FIGURE 15

HIGH-PRESSURE BOTTOM-HOLE FLUID CONTAINER

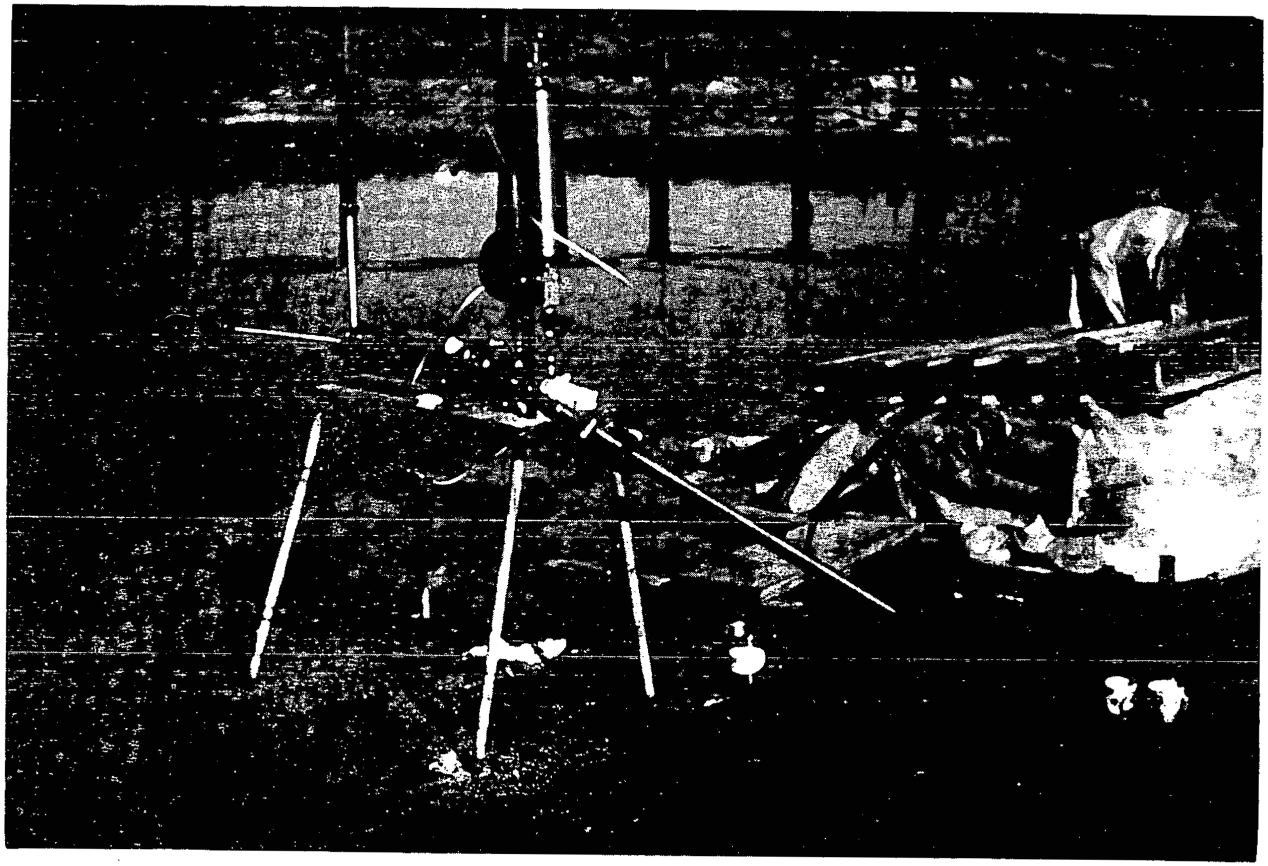


FIGURE 16

BOTTOM-HOLE SAMPLE TRANSFER EQUIPMENT

device), or that some of the gas was lost while attempting to place the system in a single phase and transfer it to the high pressure containers.

3. "Zero-Flash" Treatment of Samples

a. Equipment and Procedures Used

The bottom-hole samples that were transferred to high pressure containers were transported to one of two laboratories where they were flashed at room pressure and room temperature. Weatherly Laboratories, located in Lafayette, Louisiana, pumped the container to some pressure higher than the original transfer pressure and rocked the sample until a single phase was obtained. Several hundred rockings were usually necessary. The sample was then allowed to expand at constant pressure into a collection system which had previously been purged with helium or nitrogen. The gas from the sample was collected in a 500 ml. graduated gas buret and the liquid was collected in a graduated separatory funnel. The standard cubic feet of gas at 60°F (SCF) per barrel of water at 60°F was calculated. At least two gas samples were collected; i.e., one in a gas buret containing helium and the other in a gas buret containing nitrogen. This procedure was used to calculate percent by volume since it was anticipated that the samples would contain both helium and nitrogen. In practice, however, the helium content was too low to be measured by mass spectrometry and the dual collection procedure was abandoned after the first few runs. The gas buret was transferred to Cities Service laboratories in Lake Charles, where the composition was obtained by mass spectrometry, and the zero-flashed liquid was transferred to the MSU labs. The standard method of reporting gas composition in mol percent (normalized to 100 mol percent) was used.

The samples sent to Core Labs in Dallas were treated similarly except that no provisions were available for purging the system with an inert gas; therefore, the sample was zero-flashed at constant pressure (10,000 psig was used in all cases at Core Labs) and the gas and fluid were collected in an air atmosphere. The gas/water ratio was calculated, and the composition of the gas was determined by vapor phase chromatography using values normalized to 100 mol percent.

b. Gas Analyses and Discussion

(1) Volume of Gas

Table L lists the volume of gas obtained for bottom-hole samples from Sand #3 and Sand #1. All of the samples were not zero-flashed, of course, as many of them lost pressure while coming out of the well and these were used for analysis of the water. Note that many of the values for the gas/water ratio are inordinately low. Reference to Tables XLVIII and XLIX will help in understanding Table L. The gas/water ratio for Sand #3 varies from 14.7-19.2 for four samples. The value of 2.6 for

SAND #3

Sample	Lab	SCF/Bbl	Remarks
4	Weatherly	15.2 14.9	Each value is average of two runs.
5	Core	18.7 18.7	Opened at 675 psig
6	Weatherly	19.2 17.1	Opened at 660 psia. Each value is average of two runs.
8	Weatherly	15.1 14.7	Opened at 1390 psia. Each value is average of two runs.
9	Core	2.6	Opened at low pressure.

SAND #1

Sample	Lab	SCF/Bbl	Remarks
1	Weatherly	2.2	Opened at 25 psia
4	Core	4.9	Opened at 0-1 psig
5	Weatherly	5.9	Opened at 13 psia
6	Weatherly	0.7	Opened at 53 psia
7	Core	16.9 16.0	Opening conditions unknown.

TABLE L

SCF GAS/BBL WATER

Sample #9 is obviously low since the container had lost some of the pressure. All but one sample from Sand #1 mysteriously lost pressure after they were transferred to high pressure containers; therefore, only one good determination is available on that sand. There does not seem to be a significant difference in the amount of gas dissolved in the water from either sand, assuming the value for Sample #7 on Sand #1 is representative.

(2) Composition of Gas

The gas collected during the zero-flash treatment at Weatherly Labs was analyzed by mass spectrometry and the gas collected at Core Labs was analyzed by vapor phase chromatography. The gas collected from the containers that had lost pressure was not analyzed. Table LI gives the composition of the zero-flashed gas from both sands. No comparison between techniques in Table LI should be made as Sample #5 was zero-flashed at Core Labs about two months after Samples #4 and #6 were zero-flashed at Weatherly Labs. Any hydrogen contained in Sample #5 would have escaped more easily than heavier components, and this would have affected all of the other values somewhat because of normalization.

(3) Comparison with Recombination Data

Pure methane has a solubility of about 37 SCF/Bbl of pure water at the reservoir conditions of Sand #3 of 238^{0}F and 11,000 psig (2) (14). The volume of gas found in the first bottom-hole samples was near 15 SCF/Bbl, but the gas was not pure methane nor

Sand #	3	3	3	3	1
Sample #	4	5	6	8	7
Technique	MS	VPC	MS	MS	VPC
Lab**	W	C	W	W	C
Component					
C_1	91.8	93.41	93.4	92.0	94.42
C_2	0.9	0.92	1.1	1.7	1.56
C_3	0	0.03	0.1	0.3	0.16
IC_4	0	0	0	0.1	0.01
NC_4	0	0	0	0	0.01
IC_5	0	0	0	0	0
NC_5	0	0	0	0	0
C_6	-	0	-	-	0
C_{6+}	0	-	0	0	-
C_{7+}	-	0	-	-	0
CO_2	7.1	4.70	4.0	3.1	2.73
CO	0	0	0	0	0
H_2	0.1	0	1.2	2.3	0
N_2	0.1	0.94	0.2	0.5	1.11
H_2S	0	0	0	0	0

*MS = Mass Spectrometry
VPC = Vapor phase chromatography

**W = Weatherly Labs
C = Core Labs

TABLE LI

COMPOSITION OF BOTTOM-HOLE GAS SAMPLES IN MOL PER-CENT

SAND #3 AND SAND #1

was the fluid pure water. A lower solubility would be expected, of course, because of the large amount of dissolved solids and a "salting out" effect, but no comparison data were available on the solubility of gas in saline waters. In order to obtain such data, recombination and differential liberation studies were made on fluids and gases from both sands. Additionally, recombination and differential liberation studies were performed on pure methane and "stock tank" water from Sand #3 and Sand #1. The complete experimental procedure and discussion of results for these studies are given in the report by OHRW.

The early results obtained by differential liberation were about 18 SCF/Bbl for the gas/water ratio, but later determinations gave higher values near 23-24. The pure methane-"stock tank" water gave ratios of 24.6 for Sand #3 and 22.8 for Sand #1. There does not appear to be any significant difference in the solubility of pure methane gas vs. separator gas. Assuming the first, and lower, gas/water ratios were caused by inexperience with these differentially liberated samples and assuming the last, and higher values, were more accurate as a result of more sophistication gained with experience, the suggestion must be made that the bottom-hole samples obtained were not representative or that the fluid was not saturated with gas.

The problems associated with obtaining bottom-hole samples have been mentioned earlier and need not be repeated here but there is a definite possibility that these problems prevented a representative sample from being obtained. Conversely, the gas/water ratios obtained from recombination and differential liberation studies are imprecise and firm conclusions from these data are not warranted. Additional recombination and differential liberation studies should be performed in order to determine the best technique to use and the precision that can be expected.

A volume of 45-88 SCF gas/Bbl water was obtained at the well-head during flow tests. This is considerably larger than the volume obtained from either bottom-hole samples or recombination studies which suggests that some free gas may have been available in the formation. The report by OHRW discusses this possibility in greater detail.

c. Water Analyses and Discussion

The fluid from the zero-flashed samples was collected for chemical analysis. McNeese established a temporary analytical unit at Core Labs (Dallas) for analyzing Samples #5 and #9 of Sand #3 and Samples #4 and #7 of Sand #1. Total hardness, bicarbonate, chloride, and pH were measured on those samples immediately after they were zero-flashed, unless the sample containers had lost pressure and precipitation had occurred. Table LII gives the analysis of the bottom-hole fluid from Sand #3, and Table LIII gives data for the Sand #1 bottom-hole fluid. The tables reflect all of the analyses that were done although some of them are

	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7	Sample #8	Sample #9
pH	5.90		6.39		6.65				6.68
Turbidity	17		41						
Conductance	147,000		142,000						
Density			1.0784						
Dissolved Solids			113,700						
Viscosity			1.212						
Total Hardness	6050		5830		5780				
Calcium Hardness	4350		4140						
Chloride	67,700		66,600		67,000				
Silicate		59							
Bicarbonate	1150 1190		1300		1310				
Calcium		1600	1600	1630			1630		
Magnesium		163	159	165			159		
Cadmium		0.72	0.35	0.32		0.33	0.43	0.29	
Iron		117	107	60			90		
Zinc		2.2	8.4	1.8		6.5	1.30	1.40	
Barium		6.0 6.5							
Strontium		290	310	320			320		
Boron						59		56	
Sodium		42,000	43,000	44,000		44,000	43,000	44,000	
Potassium		310	270	260		270	260	270	
Sulfate		212 210							

TABLE LII

ANALYSIS OF BOTTOM-HOLE FLUID FROM SAND #3

(ALL UNITS DEFINED EARLIER; SEE TABLES II, III, IV)

	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7
pH	6.84	6.50	6.33	6.71	6.62	6.73	6.62
Turbidity		65	30				
Conductance							
Density						1.0879	
Dissolved Solids						134,170	
Viscosity						1.247	
Total Hardness	6680	6740	6940	6640			6710
Calcium Hardness							
Chloride	79,500	80,500	80,400	79,500			79,500 79,700
Silicate			45*				
Bicarbonate	1190	1200	1120	1430			1220
Calcium			2090				2030
Magnesium			180				177
Cadmium			0.30				0.32
Iron			17.7				35.0
Zinc			1.70				1.13
Barium							6.3 6.4
Strontium			330				330
Boron			58				58
Sodium			47,000				47,000
Potassium			310				320
Sulfate							150

TABLE LIII

ANALYSIS OF BOTTOM-HOLE FLUID FROM SAND #1

(ALL UNITS DEFINED EARLIER: SEE TABLES II, III, IV) clearly questionable. The decision to include all of the numbers was made in order to allow the reader to establish a relationship between the values in Table LII and LIII and the causes for some of the fluctations that may be found in Tables XLVIII and XLIX.

The determinations affected most by the amount of time samples are allowed to stand before analysis begins are: pH, turbidity, conductance, total hardness, calcium hardness, and bicarbonate. Others are affected also, but the original sample can be treated appropriately to preserve the integrity of those determinations. Close examination of Table XLVIII (sample schedule) will show that Samples #1, #2, and #3 of Sand #3 (Table LII) should present the most reliable values for those determinations affected by time. The other determinations were made on the remaining samples as a matter of thoroughness, and the values for some, such as cadmium, zinc, and iron, vary somewhat. The variability of cadmium and zinc may be caused by contamination with mercury (that may contain these metals) during transfer of fluid from the bottom-hole sampler to the high pressure containers. Iron is higher, by a factor up to about 10, in the bottom-hole samples when compared to the flowing samples. This is probably caused by the fact that the well is shut-in during the bottom-hole sampling period, and the amount of iron is increased due to dissolution of the tubing.

All of the bottom-hole samples from Sand #1 were not subjected to all of the determinations, partly as a matter of availability of the time and quantity of sample and partly because the analysis of Sand #3 bottom-hole samples showed that a complete analysis of every sample was not necessary. An examination of Table XLIX (sample schedule) indicates that Samples #3 and #7 of Sand #1 (Table LIII) should provide the most accurate values for those determinations subject to time. Cadmium values and zinc values for bottom-hole and flowing samples are in closer agreement for Sand #1 than Sand #3. Iron is not quite as high for Sand #1 bottom-hole samples. The value of 45 for dissolved silicate in Table LIII is probably in error. This determination was not made until sometime after the sample was collected. Another determination about two months later gave a value of 30; therefore, it is rather obvious that some of the silicate had precipitated. Comparisons between flowing and bottom-hole samples for other determinations listed in Tables LII and LIII were made in the discussion of flowing samples and will not be repeated here.

V. SUMMARY AND CONCLUSIONS

A. SUMMARY

McNeese collected almost 250 separate flowing and bottom-hole water samples and a considerable number of gas samples. The separator gas samples were analyzed by mass spectrometry and vapor phase chromatography. The separator water samples were subjected to certain determinations in an on-site laboratory and the remaining determinations were performed in the MSU labs. Some separator gas and water samples were sent to the U.S.G.S. Laboratories in Denver for the determination of radioactive constitutents. Trace organics were determined in the Center for Bio-Organic Studies at the University of New Orleans. Bottom-hole samples were collected and transferred to high pressure containers by Camco, Inc. These samples were zero-flashed at Weatherly Labs (Lafayette, La.) and Core Labs (Dallas, Tex.) to determine the volume of gas dissolved in the fluid. The composition of the gas and fluid was then determined. An average value of 16.4 SCF gas/Bbl water was obtained for Sand #3 on 14 determinations. The gas/water ratio was 16.4 SCF/Bbl for Sand #1 on two determinations. Recombination and differential liberation studies were performed on the separator gas and separator water. An average of five determinations on Sand #1 gave 21 SCF/Bbl with the last determinations giving 23 SCF/Bbl. Three determinations for Sand #3 gave values of 18.1, 17.9, and 23.3 SCF/Bbl, but the trend in both sands was toward higher values as more experience was gained by the labs involved. A hydrocarbon-water mixture behaves differently than an all-hydrocarbon system, and it is believed that the later data may be more reliable than the earlier data as a result of the more refined techniques gained through experience. Additional experimental data are needed to clarify this question.

Recombination and differential liberation studies were also carried out on pure methane and "stock tank" water from the separator. Sand #1 gave 22.8 SCF methane/Bbl of stock tank water and Sand #3 gave 24.6 SCF methane/Bbl of stock tank water. The recombination studies suggest that the bottom-hole samples either were not representative or that they were not saturated with hydrocarbon gas. The variability in the volume of the gas found in the <u>in-situ</u> samples; i.e., from 14.7 to 19.2 SCF/Bbl, suggests that the <u>in-situ</u> samples may not have been representative with regard to the amount of gas found. This is not difficult to envision considering the trials and tribulations of the company assigned the task of collecting and transferring bottom-hole samples. These data do not allow any conclusions as to whether pure methane or separator gas is more soluble in reservoir (stock tank) water.

Although all of the water samples were not subjected to every determination, about 1,000 separate determinations were made. In the future it probably will not be necessary to collect as many samples and be as thorough in their analyses, but that was not known for the first geopressured well until all of the samples had actually been collected and analyzed.

Most of the trends discussed in the various sections of this report would have been missed if only a few samples had been collected. The number of samples collected in the future will be dictated, of course, by the kinds of information, including trends, which may be desired.

B. CONCLUSIONS

Some general conclusions about the water analyses are as follows:

1. The pH and bicarbonate values (measured in the laboratory) tend to decrease with increased flow rate through the separator.
2. Turbidity and suspended solids values generally decrease with time in the flowing samples as the well becomes cleaner.
3. The dissolved silicate concentration decreases as the temperature of the aquifer decreases.
4. Correct <u>in-situ</u> values cannot be obtained for all determinations by analyzing bottom-hole samples.
5. Concentration gradients apparently occur within zones of an aquifer for certain ionic species.
6. The values for most of the analytical determinations remained rather constant throughout the test on any one sand.
7. The flow rate affects the pH measurement in an in-line cell and the pH generally decreases with increasing flow rates through the separator.
8. The in-line pH measurement appears to be affected by the pressure of the separator and the composition of the gas.

9. In-line measurements for pH, conductance, and temperature are often erratic, which may be the result of plugged chokes, excessive gas evolution, and/or adsorption of gas bubbles on the electrodes.

10. The hydrogen ion concentration of the flowing samples is at least an order of magnitude lower than the laboratory measurements. The value of the hydrogen ion in-situ must certainly be even lower. Both values should be known; the first is needed for practical operation of surface equipment and the latter is needed for theoretical purposes.

VI. RECOMMENDATIONS

The chemical equilibria involved in the geothermal water play an important role in an economic sense. Many geopressured-geothermal wells contain carbon dioxide which is quite soluble under in-situ conditions. The acidic nature of the water saturated with carbon dioxide may require the use of special alloys for tubing, pumps, separating vessels, and test equipment. The Delcambre well fluids contained a large amount of salts which are quite corrosive to mild steel in water solution and the combination of salts with an acid produces a very reactive environment which cannot be ignored when surface equipment is being considered. Work should continue in developing generators, turbines, heat exchangers, and other equipment that can withstand these waters.

The solubility of carbon dioxide in geothermal water is a function of pressure, temperature, and the amount of dissolved solids. The gas is released from solution as the water is brought from the geopressured zone to the well-head. Release of carbon dioxide from solution increases the pH, shifts the bicarbonate-carbonate equilibrium, and decreases the solubility of certain salts. This results in an increased probability of the precipitation of carbonates and silicates; thus scaling is another economic factor to be considered in surface equipment. The scaling problem could be reduced, however, by applying conventional pre-treatment procedures.

Some of the elemental determinations show that water of this type almost certainly must be disposed of by injection into a disposal well; the presence of radioactive material may complicate the disposal problem, indicating the need for attention to this possibility.

Bottom-hole collection and transfer procedures seem poor, at best, and must be improved if representative samples and reliable quantitative data are to be obtained. Traditional procedures used by the petroleum industry in collecting and transferring bottom-hole samples with a wire-line device are not suitable for geopressured-geothermal samples. The sampler itself needs to be improved with regard to "O"-rings and similar sealing materials. The method of transferring geopressured water from a wire-line sampler to a separate container as used here is quite inadequate. It must be emphasized that the transfer should be made at a pressure *no lower than* the reservoir pressure and even this is not adequate if the wire-line sampler is not vigorously agitated such that the gas and water phases are thoroughly mixed. Once the gas phase has separated from the liquid, it is *very difficult* to re-establish equilibrium as a single phase. Unless these difficulties can be overcome, recombination and differential liberation studies should replace the bottom-hole sampling procedures.

In-line measurements are desirable, but conductance and pH cells capable of withstanding more heat and pressure must be developed if accurate measurements are to be made for even a short period of time. Some equipment construction and sampling procedures should be modified to avoid contaminating samples prior to analysis; e.g., pipe dope contaminates the flowing samples with zinc while mercury, containing other trace metals and used in the hydraulic transfer pump, contaminates the bottom-hole samples.

Priorities should be established for obtaining flowing samples so that analytically consistent data useful in establishing trends may be obtained. This could be done without sacrificing engineering or geological data, but in this test at least, the engineering data were obtained in a start and stop operation, and the analytical samples were taken as a matter of expedience rather than as a planned operation. Finally, some of the "standard" analytical procedures require modifications, and it is essential that sampling and analysis be done by personnel with some geothermal experience.

Some specific recommendations for future geopressured-geothermal projects are as follows:

1. Avoid excessive use of pipe dope in pipe connections during the construction and assembly of surface equipment. The use of Teflon tape may avoid, or at least minimize, contamination from the pipe dope or similar materials.
2. Improve wire-line samplers with regard to seals.
3. Transfer material from the wire-line sampler to the high pressure container at a pressure <u>no lower than</u> the reservoir pressure.
4. The material in the wire-line sampler must be in a single phase before it is transferred to the high pressure container.

Agitate the wire-line sampler vigorously in order to attempt to return the materials to a single phase before the transfer step. It is desirable to develop a thermostatically controlled jacket for the wire-line sampler to keep the samples at bottom-hole temperature so that phase separation will not occur.

5. Avoid the use of mercury as a confining liquid in bottom-hole transfer equipment because mercury contains other trace materials, particularly "heavy metals"; therefore, bottom-hole samples obtained via a mercury hydraulic pump and analyzed for trace heavy metals have no value for analytical purposes. A procedure using distilled water, or some other metal-free liquid for the hydraulic fluid, is desirable, provided the mechanics of the problem can be solved.
6. In-line conductance cells and in-line pH cells capable of withstanding high pressure and high temperature should be developed. A down-hole pH probe is very desirable.
7. Use chemists with some geothermal experience for sampling and analysis.
8. Establish priorities for obtaining engineering data and chemical data so that analytically consistent samples, useful in establishing trends, may be obtained.
9. Investigate the radioactivity problem in depth, both with regard to the amount of each isotope present and to the possibility of fractionation of the uranium chain.

10. Continue research in developing metals that can withstand the highly saline water found in this well and that can be used in surface equipment in developing the geopressured-geothermal resource.
11. Connect heat exchangers, pumps, and other critical equipment in such a way that they may be cleaned easily. It may be economically feasible to connect two similar units in parallel so that one may be cleaned while the other one is in use.
12. Monitor the composition of the water fed to the disposal well. In view of the high concentration of salts in some wells, it is conceivable that the sands in the disposal well accepting the spent fluid may become partially plugged with solids. If this occurs, some acidizing may become necessary. Monitoring temperature, pressure, and salt concentration of the effluent fed to the disposal well is advisable.
13. Perform additional recombination and differential liberation studies in order to establish the correct solubility for "natural gas" in geothermal water.

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VIII

APPENDICES

APPENDIX A

Summary of Analytical Procedures

Determination	Sample	Procedure
Arsenic	FA	Extraction of solution (made highly acid with HCl) with benzene, evaporation of solvent, and neutron activation analysis (9).
Barium	FA	Neutron activation analysis.
Bicarbonate (alkalinity)	RU	Electrometric titration to pH=4.5.
Boron	FU	Carmine-spectrophotometric method. Prepare standards containing proper amount of silicate.
Cadmium	FA	Atomic absorption (direct).
Calcium	FA	Atomic absorption (direct) or flame emission. Use $LaCl_3$ to suppress interferences.
Carbonate (acidity)	FU	Electrometric titration to pH=8.3.
Chloride	FU	Mohr method.
Chromium (+6)	FA	Complexation with APDC* at pH=2.8, extraction with MIBK*, and 1. atomic absorption spectrometry on MIBK layer or 2. evaporation of MIBK in vacuum oven and neutron activation analysis (slow neutrons) on solid.
Conductance	RU	Wheatstone bridge method.

Determination	Sample	Procedure
Copper and Lead	FA	Complexation with APDC* at pH=2.8, extraction with MIBK*, and 1. atomic absorption spectrometry on MIBK layer or 2. evaporation of MIBK in vacuum oven and neutron activation analysis (slow neutrons for lead) on solid.
Density	FU	Gravimetric
Dissolved solids	FU	Residue on evaporation at 180°C
Gas Samples		Mass spectrometry or gas chromatography
Hardness (calcium)	FU	Titration with Na_2EDTA using murexide as indicator
Hardness (total)	FU	Titration with Na_2EDTA using Eriochrome Black T as indicator
Iron	FA	Atomic absorption (direct)
Lead (See Copper)	FA	
Magnesium	FA	Atomic absorption (direct). Use $LaCl_3$ to suppress interferences.
Manganese	FA	Neutron activation analysis
Mercury	FA	Neutron activation analysis
pH	RU	pH meter
Potassium	FA	Flame emission. Prepare standards containing proper amount of sodium.
Radioactivity	Gas RA	Counting Procedures

Determination	Sample	Procedure
Silica	FU	Molybdenum blue spectrophotometric method. Prepare standards containing proper amount of chloride.
Sodium	FA	Flame emission.
Strontium	FA	Atomic absorption (direct). Use $LaCl_3$ to suppress interferences.
Sulfate	FU	Purification by column chromatography (3), then gravimetry.
Suspended solids	RU	Pass through 0.40 µm membrane filter
Trace organics	RU	Collected and stored in glass containers. Extracted with hexane, 40% benzene-60% hexane and methanol and those fractions run by GC-MS (8)(10)(11)(15).
Turbidity	RU	Nephelometry
Viscosity	FU	Ostwald method
Zinc	FA	Atomic absorption (direct)

*APDC = Ammonium pyrollidine dithiocarbamate

MIBK = Methy isobutyl ketone

APPENDIX B

ANALYSIS OF FLOWING WATER SAMPLES---SAND #3

SAMPLE	1F	2	3	4F	5F	6	7	8	9	10	11	12	13	14	15	16	17	18
ARSENIC (mg/l)						<0.05				<0.05				<0.05				<0.05
BARIUM (mg/l)						2.7 2.4				3.0 2.9								2.5 2.7
BICARBONATE (mg $CaCO_3$/l)						1110	1110	1050	1070	1030	1030	1030	1030	1080	1060	1100	1050	1070
BORON (mg/l)				58		61 60 60	59	62 62	61 61	57	61	61	62	57 61	56	57 61	57	61 62
CADMIUM (mg/l)				0.39		0.57	0.43	0.56	0.42	0.60	0.38	0.31	0.44	0.48	0.45	0.50	0.30	0.41
CALCIUM (mg/l)				1830* 1770		1630	1670	1630	1630 1630 1630	1720 1670	1630	1600	1650	1770 1560* 1670	1710 1670	1630	1650 1670	1700 1680
CHLORIDE (mg/l)	79,400	78,800	77,200	79,200	67,000	67,200	67,000	67,300	67,000	67,000	67,000		67,000	67,100	67,400	67,100	66,900	66,800
CHROMIUM (mg/l)				0.007* 0.007*		0.008 0.003*	0.009* 0.005*	0.008* 0.005*	0.002*	0.008 0.007*	0.008* 0.005*	0.002* 0.002*	0.005* 0.006*	0.008 0.002*	0.007* 0.004*	0.002*	0.002*	0.025 0.006*
COPPER (mg/l)						0.016 0.014				0.017 0.017				0.017 0.034*				0.018 0.018
DENSITY (g/ml)						1.0700	1.0709			1.0708	1.0719		1.0710	1.0721	1.0715			1.0711
HARDNESS, TOTAL (mg $CaCO_3$/l)	6140	6030	6000	6100	6000	6120	6040	6130	6120	6080	6030	5980	6040	5960	6000	6020	5960	6120
IRON (mg/l)				5.8		4.9	9.0	8.7	9.2	8.3	7.9	7.1	7.6	7.8	8.0	7.8	8.2	7.5
LEAD (mg/l)						< 0.2				<0.2				<0.2				< 0.2
MAGNESIUM (mg/l)						163	163	160	160 161		163	160 161 163 161	157	161 158	159	167 165	163 160 158	159
MERCURY (mg/l)						< 0.02				<0.02				<0.02				< 0.02
pH	6.83	6.98		6.87	6.45	6.60	6.56	6.28	6.50	6.24	6.19	6.42	6.17	6.27	6.12	6.33	6.24	6.19
POTASSIUM (mg/l)				290		300	300	290	290	290	300	290	280	290	290	280	290	290
SILICATE, DISSOLVED (mg SiO_2/l)				56		54		56 56	56	57	56	58 56		60		61 59	61	59 57
SODIUM (mg/l)				47,000		42,000	43,000	43,000	40,000	44,000	40,000	43,000 43,000	41,000	45,000	44,000	45,000	44,000	43,000
SOLIDS, DISSOLVED (mg/l)						113,180	113,320			113,400	113,410		113,280	113,480	113,330			113,230
SOLIDS, SUSPENDED (mg/gallon)						55	24	30	20		1.0	0.65		0.15	0.30	0.35	0.55	0.30
SPECIFIC CONDUCTANCE (μmhos/cm)	142,000		145,000		145,000	143,000 149,000	146,000	144,000	144,000 146,000		146,000	148,000	147,000	143,000	145,000	141,000	143,000	
STRONTIUM (mg/l)				300		290	280	290	300	310	290	300 290	280	310	310	280	290	300
SULFATE (mg/l)						210 214 208				203 208 196				200 204 206				182 179 188
TURBIDITY (J.T.U.)		63				45	35	14	22	26	28	35	27	28	34	33	28	65
VISCOSITY (centipoise)						1.197	1.190		1.188	1.197	1.196		1.197	1.197	1.197			1.190
ZINC (mg/l)				15.		5.2	3.0	1.7	1.2	0.79	0.40	0.10	0.20	0.16	0.14	0.10	0.20	0.13

APPENDIX B

ANALYSIS OF FLOWING WATER SAMPLES---SAND #1

SAMPLE	1F	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
ARSENIC mg/l x 10^3		< 50								<50								<50											<50
BARIUM mg/l		2.2 2.3								3.8 4.1								3.0 2.8											2.8 2.9
BICARBONATE mg $CacO_3$/l	1170	1130	1130		1070	1060	1030	1030	1010	1020	1040	1000	1010	1020	1080	980	990	970	970	960	970	1200*	990	1010			970	1020	1020
BORON mg/l		64				64				66				60				60					60				65		65
CADMIUM mg/l		0.29	0.31	0.29	0.28	0.26	0.28	0.27	0.31	0.28	0.29	0.30	0.31	0.31	0.31	0.28	0.27	0.31	0.29	0.27	0.30	0.32	0.33	0.32	0.32	0.32	0.30 0.32	0.31	0.32 0.30
CALCIUM mg/l		2030	2100	2000	2030	2070	2070	1770*	2030	2100	2070	1970	2030	1970	1930	2070	2070	2030	2100	2070	2070	2070	2030	2100	2100	2100	2130	2070	2100
CHLORIDE mg/l x 10^{-3}	80.8	80.4	80.4	80.5	80.6	80.4	80.4	80.4	80.5	80.5	80.7	80.6	80.7	80.6	80.4	80.4	80.0	81.1 81.2	80.0 80.4	80.7	80.7	80.5	80.4	80.4	80.7		79.3*	81.1	78.9*
CHROMIUM mg/l x 10^3		6 7								<2 2								8 7											13 14
COPPER mg/l x 10^3		38 34								22 22								16 15											10 11
DENSITY g/ml	See Table XV, page 33																												
HARDNESS, TOTAL MG $CaCO_3$/l	6740	6750	6740	6820	6800	6760	6870	6750	6790	6880	6730	6880	6880	6900	6890	6800	6700	6910	6910	6930	6970	6890	6880	6840	6860		6980	6840	6840
IRON mg/l		21.4 22.5	25.2 24.6	27.0 28.7	24.1 25.4	23.5 24.3	16.3 17.9	14.8 16.8 17.4	16.3 18.0	17.2 19.0	14.9 15.8	14.0 15.2	14.9 16.0	12.2 13.6	11.1 12.1	11.4	9.5	8.7	9.8	10.3	11.3	11.8	11.0	10.8	10.8	10.0	10.1	11.1	10.0
LEAD mg/l		< 0.2								<0.2								<0.2											< 0.2
MAGNESIUM mg/l		183	183	183	183	183	180	143*	177	183	183	177	180	177	177	183	187	187	183	187	187	183	187	187	187	183	183	180	183
MERCURY mg/l x 10^3		< 20								< 20				< 20				< 20											< 20
pH	6.26	5.95	6.16	6.32	6.20	6.19	6.17	6.16	6.14	6.09	6.01	6.14	6.13	5.96	6.19	6.29	5.92	6.15	6.13	6.28	6.18	6.02	6.04	6.10	6.06		6.28	6.12	6.17
POTASSIUM mg/l		290 310	280	280	270	290 310	290	280	280	290 310	270	290	290	280 320	300	290	290	290 310	290	290	290	290	280 310	290	290	260*	290 320	300	280 320
SILICATE, DISSOLVED mg SiO_2/l		60	60	60	58	57	58	56	57			56	56	58	57	56	55	55	55	55									
SODIUM mg/l x 10^{-3}		46 46	47	45	45	46 45	47	45 47	47	45 49	50 50	42	45	46 45	47	50	45	45 45	43	43	45	48	44 46	46	46	47	45 47	47	43
SOLIDS, DISSOLVED mg/l	See Table XIV, page 31																												
SOLIDS, SUSPENDED mg/gallon	—						2.6	1.1	0.4	2.5	1.0	0.8	1.2	1.0	0.8	2.1	0.7	1.0	0.1	0.1									
SPECIFIC CONDUCTANCE µmhos/cm x 10^{-3}	166	155	164	161 164	162	163	162	159	159	164	153*	163	157	164	173*	161	158	165 166	161	162	158	163	161	161	152*		166	162	162
STRONTIUM mg/l		370	400	370	400	400	430	330	400	430	370	370	400	330	330	400	400	430	400	400	430	430	500*	430	430	430	370	400	400
SULFATE mg/l (range)		148 155								141 146								138 145							142 146				134 135
TURBIDITY J.T.U.	70	55	55	42	28	42	13	7	18	12	28	17	8	21	11	20	42	44	11	8	25	10	30	22	71		54	31	
VISCOSITY (centipoise)	See Table XVI, page 35																												
ZINC mg/l		1.0	1.2	1.1	1.3	1.3	1.1	1.1	1.1	1.1	1.0	1.0	1.0	0.98	0.90	1.0	1.1	1.1	1.1	1.0	1.1	1.0	1.1	1.1	1.1	1.0	1.0	1.0	1.0

APPENDIX C

CALCULATION OF PRESSURE IN BOTTOM-HOLE SAMPLES @ AMBIENT TEMPERATURE

STATEMENT OF PROBLEM

Bottom-hole water samples were taken for laboratory testing and analyses. The pressure at the bottom of the well was estimated to be 11000 psi, however, by the time the samples were opened at the laboratory, the pressure of the samples had dropped to inconsistent values far below the estimated bottom-hole pressure.

An explanation of the pressure difference was needed in order to ascertain if the bottom hole sampler had leaked and how much leakage may have occurred.

APPROACH TO SOLUTION OF PROBLEM

In order to obtain a quick answer to the problem, several assumptions were made for the conditions existing at the bottom of the well and at the laboratory. These conditions were then applied to an approximate method for calculating the sampler pressure after the contents and the sampler itself had cooled from the bottom-hole temperature to the temperature of the laboratory. These assumptions and conditions are stated as the calculation method is developed.

DATA AND SYMBOLS USED

Bottom-hole conditions

P_b - Pressure in sampler = 11000 psi

T_b - Temperature of sampler contents = 238^oF

V_{sb} - Volume of sampler contents

V_{wb} - Volume of water and dissolved gas

V_{Gbs} - Volume of saturated gas at standard temperature and pressure

Top (laboratory) conditions

P_t - Pressure in sampler

T_t - Temperature of sampler contents = 75°F

V_{st} - Volume of sampler contents

V_{wt} - Volume of water and dissolved gas

V_{Gf} - Volume of free gas

V_{Gts} - Volume of saturated gas at standard temperature and pressure

Material constants

α_s - Coef. of linear expansion for sampler = 8.4E-6 in/in/°F

B_s - Bulk modulus of sampler = 28.8E6 psi

β_w - Coef. of volume expansion for water = 0.002 $in^3/in^3/{}^oF$

B_w - Bulk modulus of water = .3E6 psi

CALCULATION METHOD

To begin the development of a method of calculation, first assume that the sampler is completely filled with water at the bottom of the well. This gives

$$V_{sb} = V = V_{wb}$$

Next assume that at the laboratory the sampler contains water and free gas which has effervesced from the water. The volume of free gas is the difference in the gas saturation value at the bottom (from curves of gas volume at standard temperature and pressure vs. temperature at various pressure levels) and the gas saturation value at the laboratory (from the same curves). Neglect the change in water volume due to the gas that left solution. Thus

$$V_{st} = V_{wt} + V_{Gf}$$

The volume of the sampler changes by the relation

$$V_{st} = V_{sb}\,(1 - \Delta V_{s\Delta T} + \Delta V_{P_t})$$

where $\Delta V_{s\Delta T} = 3\,\alpha_s\,(T_b - T_t)$ Change in volume due to temperature

$\Delta V_{P_t} = P_t / B_s$ Change in volume due to pressure

The volume of the water changes by the relation:

$$V_{wt} = V_{wb}\,(1 - \Delta V_{w\Delta T} + \Delta V_{w\Delta P})$$

$\Delta V_{w\Delta T} = \beta_w\,(T_b - T_t)$ Change in volume due to temperature

$\Delta V_{w\Delta P} = (P_b - P_t)/B_w$ Change in volume due to pressure

The volume of free gas is given by the difference in saturation values at the bottom and at the laboratory which is corrected with Boyles' law.

$$V_{GF} = \left[V_{wb}\left[\frac{V_{Gbs}}{V_{wb}}\right]_{STP} - V_{wt}\left[\frac{V_{Gts}}{V_{wt}}\right]_{STP}\right]\frac{(15)}{(460+60)}\;\frac{(460+T_t\,{}^{o}F)}{P_t}$$

$$= V_{wb}\left[\left[\frac{V_{Gbs}}{V_{wb}}\right]_{STP} - \frac{V_{wt}}{V_{wb}}\left[\frac{V_{Gts}}{V_{wt}}\right]_{STP}\right]\frac{15}{520}\;\frac{(T_t\,{}^{o}R)}{P_t}$$

$$= V_{wb}\left[\left[\frac{V_{Gbs}}{V_{wb}}\right]_{STP} - (1 - \Delta V_{w\Delta T} + \Delta V_{w\Delta P})\left[\frac{V_{Gts}}{V_{wt}}\right]_{STP}\right]\frac{15}{520}\;\frac{(T_t\,{}^{o}R)}{P_t}$$

Applying the relation $V_{sb} = V = V_{wb}$ gives:

$$V_{st} = V(1 - \Delta V_{S\Delta T} + \Delta V_{SP_t}) = V(1 - \Delta V_{W\Delta T} + \Delta V_{W\Delta P}) +$$

$$+ V \left[\left[\frac{V_{Gbs}}{W_{wb}}\right]_{STP} - (1 - \Delta V_{W\Delta T} + \Delta V_{W\Delta P}) \left[\frac{V_{Gts}}{V_{wt}}\right]_{STP} \right] \frac{15}{520} \frac{(T_t\,{}^{o}R)}{P_t}$$

Rearranging the equation gives:

$$\left[(\Delta V_{W\Delta T} - \Delta V_{S\Delta T}) + (\Delta V_{SP_t} - \Delta V_{W\Delta P}) \right] \frac{520}{15} \frac{P_t}{T_t\,{}^{o}R} - \left[\frac{V_{Gbs}}{V_{wb}}\right]_{STP} =$$

$$(1 - \Delta V_{W\Delta T} + \Delta V_{W\Delta P}) \left[\frac{V_{Gts}}{V_{wt}}\right]_{STP}$$

Substituting the relations for the changes in volume gives:

$$\frac{\left[(\beta w - 3\alpha s)(T_b - T_t) + \left(\frac{1}{B_s} + \frac{1}{B_w}\right) P_t - \frac{P_b}{B_w}\right] \left[\frac{520}{15}\right] \frac{P_t}{(T_t\,{}^{o}R)} - \left[\frac{V_{Gbs}}{V_{wb}}\right]_{STP}}{\left(1 - \beta w\,(T_b - T_t) + \frac{P_b - P_t}{B_w}\right)}$$

$$= \left[\frac{V_{Gts}}{V_{wt}}\right]_{STP}$$

The simplest method for obtaining the solution for the preceding equation was to plot curves for the left hand side for varying values of P_t at a constant temperature T_t. The intersection of the curves obtained, P_t vs. $(V_{Gts}/V_{wt})_{STP}$, with the saturation curves, P + vs. $(V_{Gf}/V_w)_{STP}$, gives the P_t for a given temperature T_t.

CALCULATION RESULTS

The results of the calculations are illustrated in the curves shown for 60%, 80%, and 100% gas saturation values. The intersection of the curves show for:

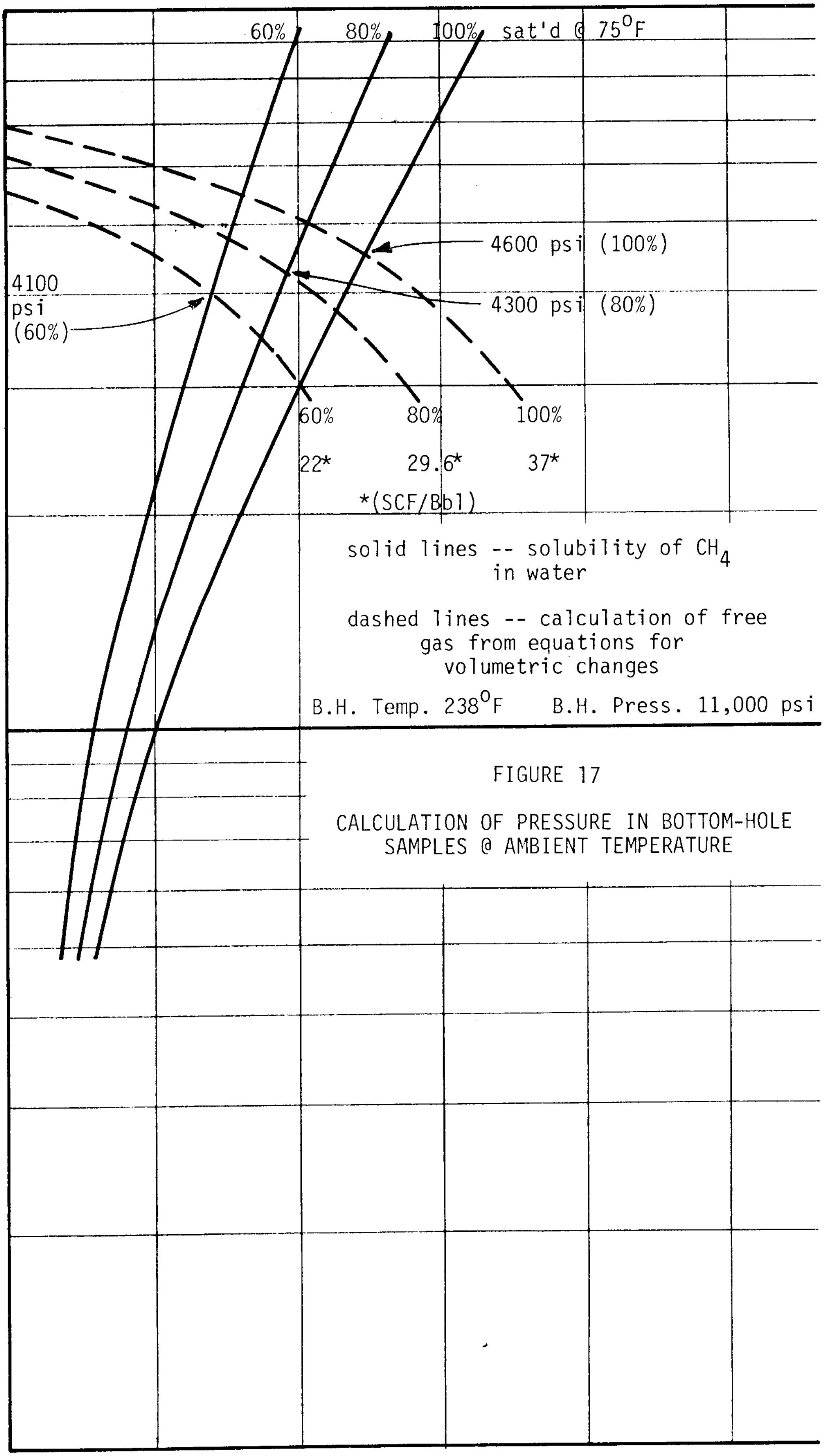

FIGURE 17

CALCULATION OF PRESSURE IN BOTTOM-HOLE SAMPLES @ AMBIENT TEMPERATURE

100% gas saturation at top and bottom P_t = 4,600 psi

80% gas saturation at top and bottom P_t = 4,300 psi

60% gas saturation at top and bottom P_t = 4,100 psi

The results of a second calculation for a pure water sample show that the pressure at the laboratory would be P_t = 2,430 psi.

These data show that the larger portion of the pressure variations is due to the cooling of the sampler and its contents during the period between the time the sample was taken and the time laboratory tests were initiated. Since the pressures measured in.the laboratory were usually lower and inconsistent, leakage from the sampler cannot be ruled out completely. Other assumptions made for this approach may be variable, further complicating the problem.

APPENDIX D

Equipment Used at Well-Site

pH was measured with a pH meter, Beckman Model 4500.

Conductance measurements were made with an Industrial Instruments Model RC-16B2 bridge.

Turbidity was measured with a Hach Turbidimeter.

Suspended solids were trapped using a Gelman Instrument Co. stainless steel pressure filter, 47 mm. diameter, Model 4280.

Colorimetric measurements for silicate were made using a B & L Spectronic 20 spectrophotometer.

Density and dissolved solids were estimated with a triple beam balance.

Hot plates and stirrers were Corning, Model PC-351.

Ovens were Thelco, Model 16.

A Honda, Model E-3500, 110 V.A.C., 3.5 KVA generator powered the onsite laboratory.

Bottom-hole samples were transferred to high pressure fluid sample bottles manufactured by Ruska Instrument Corp., Cat. # 2343.1.

In-line pH equipment consisted of L & N 10136 electronic transmitter, 7773 mounting (with thermocouple) and 7075-3 pH receiver (monitor).

In-line temperature thermocouple built in to pH housing, and additionally used L & N Century temperature/multivolt transmitter.

In-line conductivity used L & N 4905 series, flow through type, cell constant of 50.0, and L & N 7073-17 receiver (monitor).

Recorder for in-line equipment was an L & N Speedomax H, 6 inputs, 4-20 mv recorder.

Portable eye wash fountains manufactured by Vallen Corp., Model 1003, were used for safety.

APPENDIX E

Equipment Used at McNeese Laboratories

A constant temperature bath was provided with a Blue M Model PCC-13A cooling coil, Blue M Model MW 117255A control unit, and a Sargent-Welch Cat. # S-84873 heater and control unit.

Balances were Mettler, Model H-10W.

pH was measured with a Beckman Model 4500 pH meter.

Colorimetric measurements for boron and silicate were made with a B & L Spectronic 20 spectrophotometer.

Ovens were Blue M, Model OV-185A.

Muffle furnaces were Thermolyne, Model F-A1730, with CPS-4032P controller.

Powdered samples were mixed with a Spex Industries mixer mill, Cat. # 8000.

A Philips Electronics Instruments x-ray diffractometer, and x-ray spectrograph provided x-ray analysis. (Purchased in 1968, no Model number.)

Emission spectrographic results were obtained using a Jarrell-Ash 3.4 meter Ebert Spectrograph, which incorporated a 30,000 LPI grating. Plates were developed with a J-A model 34-300 film processor and read on a J-A model 21000 microphotometer.

Metals were measured by flame or atomic absorption spectrophotometry using a Perkin-Elmer, Model 370A, unit.

Slow neutrons for neutron activation analysis were provided by the reactor at Texas A & M. A flux up to $\sim 10^{16}$ neutrons/cm^2 was available.

Fast neutrons for neutron activation analysis were provided by a unit at McNeese manufactured by Accelerators, Inc. A flux up to $\sim 3 \times 10^{11}$ total neutrons/cm^2 was available.

APPENDIX F

GLOSSARY

j.t.u. = Jackson Turbidity Units.

RU = raw, untreated (plastic storage).

RUSS = raw unfiltered (stainless steel storage).

FU = filtered, untreated (plastic storage).

RA = raw, acidified (plastic storage).

FA = filtered, acidified (plastic storage).

Mg/l = milligrams per liter.

U.S.G.S. = United States Geological Survey.

md = millidarcy (a permeability unit).

MS = mass spectrometry.

VPC = vapor-phase chromatography.

OHRW = Osborn-Hodges-Roberts-Wieland Engineering.

MSU = McNeese State University.

SCF = standard cubic feet.

STP = standard temperature and pressure (1 atmosphere and 60°F).

W = Weatherly Laboratories of Lafayette, La.

C = Core Laboratories of Dallas, Tex.

Stock tank water = the water remaining after the effluent from the separator was "zero" flashed.