CONF-771153-P2-4

THIRD GEOPRESSURED-GEOTHERMAL ENERGY CONFERENCE

University of Southwestern Louisiana
Lafayette, Louisiana

November 16-18, 1977

VOLUME II

Supported by the
U. S. DEPARTMENT OF ENERGY
under Contract No. EG-77-G-05-5557

Assistance provided by the
American Gas Association

CHEMICAL ANALYSES OF GEOTHERMAL WATERS FROM A SOUTH LOUISIANA WELL*

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INTRODUCTION

The Osborn-Hodges-Roberts-Wieland Engineering Firm of Bryan, Texas was responsible for reopening the abandoned Edna Delcambre #1 gas well, about 8 miles south of Delcambre, Louisiana, and collecting bottom-hole and flowing samples. McNeese State University, located in Lake Charles, Louisiana, was responsible for the analyses of the products of the well. Figure I shows the overall placement of the equipment. The drilling rig is seen 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 flow data and to dispose of the effluent in a disposal well drilled earlier. Most of the flowing samples were taken from stations on the test barge. Additionally, some in-line probes monitored certain characteristics of the water continuously as it flowed through the test barge equipment. The quarters barge is seen on the left of Figure I and housed a small laboratory, monitoring equipment and recorders for the in-line probes, as well as sleeping quarters for the crews.

*Work supported by the United States Energy Research and Development Administration.

DISCLAIMER

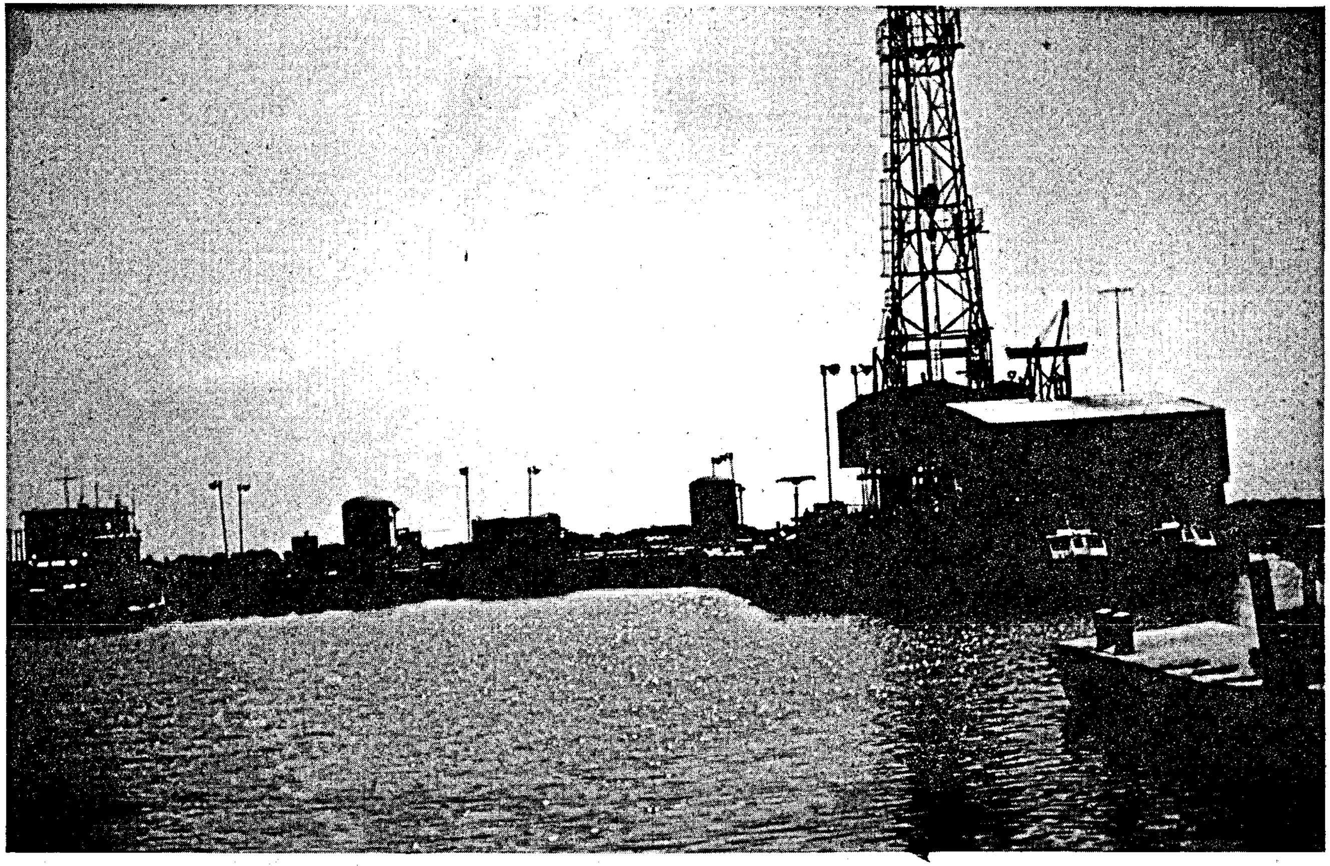


FIGURE I

EQUIPMENT ON LOCATION

TYPES OF SAMPLES AND ANALYSES

The following kinds of samples were collected for analyses from the #3 sand (perforated from 12,869' to 12,911') and the #1 sand (perforated from 12,573' to 12,605'):

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

The separator gas data will be reported by Dr. O.C. Karkalits in a later presentation at this conference. The bottom-hole samples were zero-flashed to obtain the volume of gas dissolved in the water and these values will be reported by Dr. Karkalits also. The separator water samples and the zero-flashed bottom-hole water samples were analyzed chemically at the on-site lab as well as at the McNeese labs in Lake Charles.

Figure II shows the physical placement of the equipment on the test barge. Sample collection stations for flowing water samples were located at the box marked "sample point" and at the two "monitoring stations". Some of the raw sample was collected and some was filtered through a 0.4μ nucleopore membrane filter. Portions of each were acidified so that a total of four samples were collected at the box marked "sample point" in Figure II. A 500 ml stainless steel Whitey cylinder, fitted with valves, was used to collect a sample at the box marked "monitoring station". The metal cylinder assured collection of a sample that would retain the pressure of the system.

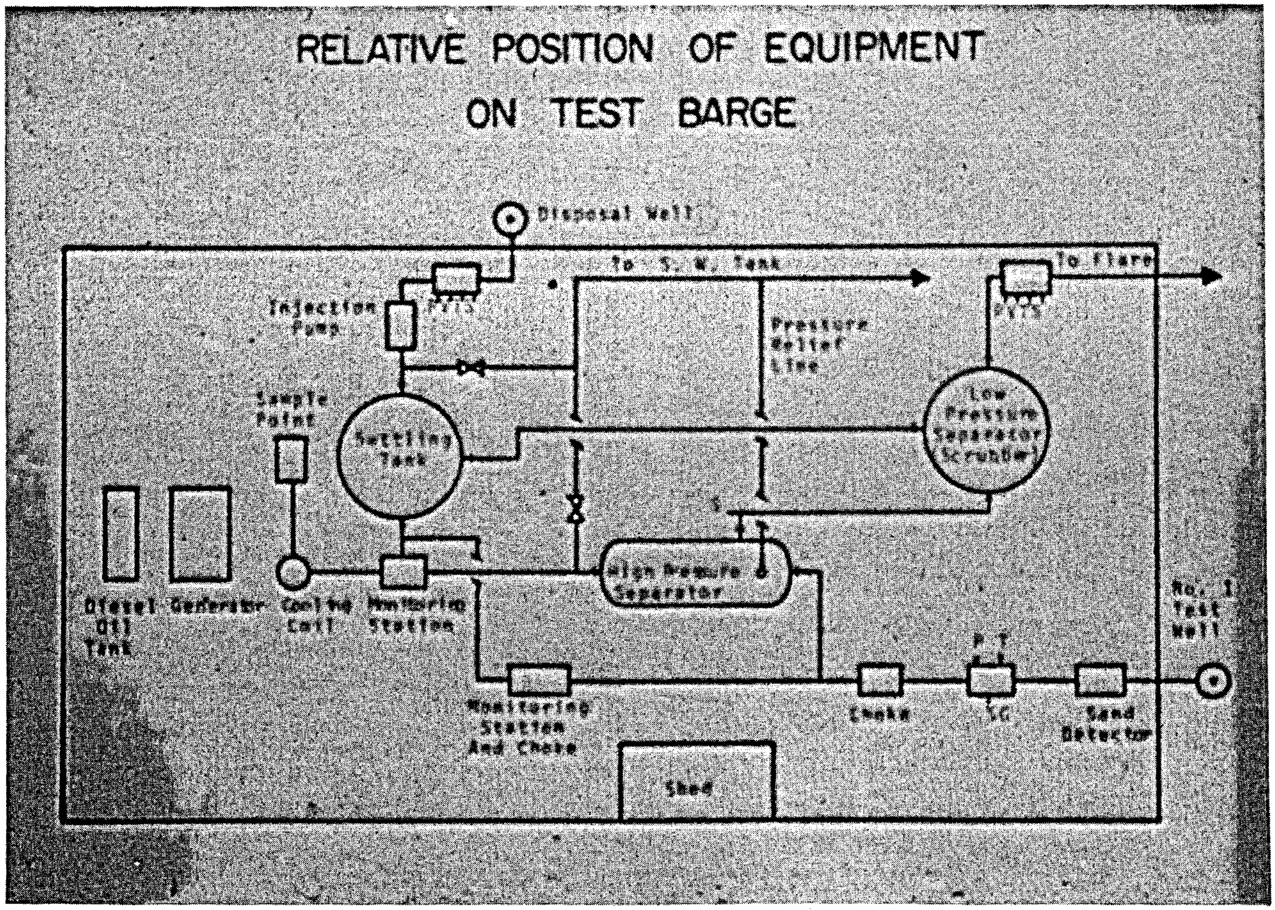


FIGURE II

RELATIVE POSITION OF EQUIPMENT ON TEST BARGE

Figure III shows the determinations that were conducted on-site.

Figure III

Analyses Conducted On-Site

pH

Temperature - ^{o}C	Chloride - as mg Cl^{-}/l
Conductance - µmhos/cm	Dissolved silicate - as mg SiO_2/l
Turbidity - j.t.u.	Density - g/ml
Bicarbonate - as mg $CaCO_3/l$	Total dissolved solids - mg/l
Carbonate - as mg $CaCO_3/l$	Total hardness - as mg $CaCO_3/l$

Figure IV lists the determinations that were performed in the McNeese Labs in Lake Charles. The on-site density, total dissolved solids, and viscosity determinations were repeated because a constant temperature water bath was impractical in the lab on the barge; also vibrations were too severe to use an analytical balance. The 0.4µ filter papers used to collect the filtered samples on the test barge were weighed at McNeese to give the amount of suspended solids. The volume has been normalized to one gallon, in all cases. All of the other determinations, except boron, were made using atomic absorption or flame spectrometry and the concentration is expressed in mg/l of the metal.

Figure IV

Analyses Conducted at McNeese Labs in Lake Charles

Density - g/ml @ 20°C
Total dissolved solids - mg/l
Suspended solids - mg/gallon
Viscosity - centipoise @ 20°C
Calcium - mg/l
Magnesium - mg/l
Iron - mg/l
Zinc - mg/l
Strontium - mg/l
Boron - mg/l
Sodium - mg/l
Potassium - mg/l

ANALYTICAL DATA AND DISCUSSION

Figure V lists selected data obtained from the #3 sand. Whenever possible, standard methods adopted by the U.S. Geological Survey were used. A total of 18 samples were collected from 5-22-77 to 6-07-77 and, although all samples were not subjected to every determination, some trends are readily apparent. All of the samples are not listed in the table, of course, but the listed ones are representative of the group. Typical values are listed in the last column. These are the averages of all of the samples run and includes data not listed in Table V. Using the average assumes, of course, that all of the values should be the same which is not necessarily a valid assumption. No statistical treatment of the data has been made at this time but it will be included in the final report.

In general, the pH decline is from a value near 7 to a value near 6. This decrease is probably caused by the increased flow rate.

Figure V

Selected Data from #3 Sand

Flowing Water Samples

Collection Date	05-22-pm	05-26-am	05-27-pm	05-28-am	05-28-pm	05-29-am	05-30-pm	05-31-am	06-07-pm	Typical Value
Collection Point	flare	flare	separator	separator	separator	separator	separator	separator	separator	
pH	6.83	6.87	6.60	6.56	6.28	6.50	6.24	6.19	6.19	
Turbidity	very high	very high	45	35	14	22	26	28	65	
Conductance (corrd to 25°C)	142,000		143,000	146,000	144,000	144,000		146,000	143,000	144,000
Density @ 20°C	~ 1.06		1.070	1.071			1.071	1.072	1.071	1.071
Total Dissolved Solids	~115,000		113,200	113,300			113,400	113,400	113,200	113,300
Suspended Solids			55.2	24.2	29.9	20.0		1.0	0.80	
Total Hardness	6140	6100	6120	6040	6130	6120	6080	6030	6120	6050

TABLE CONTINUED ON NEXT PAGE

Figure V (cont'd)

Collection Date	05-22-pm	05-26-am	05-27-pm	05-28-am	05-28-pm	05-29-am	05-30-pm	05-31-am	06-07-pm	Typical Value
Collection Point	flare	flare	separator	separator	separator	separator	separator	separator	separator	
Chloride	79,400	79,200	67,200	67,000	67,300	67,000	67,000	67,000	66,800	78,400 67,100
Dissolved Silicate		56	54		56	56	57	56	59	58
Bicarbonate	1090	1320	1110	1110	1050	1070	1030	1030	1070	1060
Calcium		1800	1600	1700	1600	1600	1700	1600	1700	1700
Magnesium			160	160	160	160		160	160	160
Iron		5.8	4.9	9.0	8.7	9.2	8.3	7.9	7.5	
Zinc		15	5.2	3.0	1.7	1.2	0.79	0.40	0.13	
Strontium		300	290	280	290	300	310	290	300	290
Boron		58	60	59	62	61	57	61	61	60
Sodium		47,000	42,000	43,000	43,000	40,000	44,000	40,000	43,000	43,000
Potassium		290	300	300	290	290	290	300	290	290
Viscosity @ 20^{o}C			1.197	1.190		1.188	1.197	1.196	1.190	1.194

There is some question concerning the accuracy of these values, however, and the ramifications of this will be discussed in detail later. The value of 6.50 measured on 5-29 seems somewhat out of line with the trend and is probably caused by sample collection prior to the system reaching equilibrium after separator shut down. The turbidity decreases, as expected, as the well is flushed. The high value on June 7 may be the result of increased sand production near the end of the flow tests. That sample was the last one taken before the well was shut-in to obtain bottom-hole samples and considerable sand had accumulated in the separator. The suspended solids also show a decrease from the first samples obtained. There is a significant change in chloride after 5-26. This may be caused by a chloride gradient. The well was first perforated between 12,894' and 12,911'. A few days later it was perforated between 12,869' and 12,893' and the lower chloride values persisted after clean-up following the second perforation. The 78,400 mg Cl^-/1 shown in Figure V is the average of 5 samples and 67,100 reflects the average of 13 samples after clean-up following the second perforation. The randomness of the iron is probably real and reflects the amount picked up from the tubing and the separator. The sodium values vary somewhat, probably because of the large dilution factor (1:10,000) used and any small error is greatly magnified. The higher value of 5-26, however, is probably real as a result of the chloride gradient mentioned above. The trend in zinc is unmistakable and is probably the result of cleaning out the system from start up. After stabilization, the limits were about 0.1 - 0.2 mg Zn/l. The pipe dope used during installation of various units on the test barge contained relatively large amounts of zinc. As will be seen later, the results of the upper sand are rather constant with regard to zinc which is consistent with this reasoning. Note that the density and total dissolved solids determinations on the samples from the flare line are approximate because the vibrations on the barge precluded use of an analytical balance.

Figure VI lists selected data obtained from the #1 sand. A total of 29 samples were collected from 6-23-77 to 7-13-77. The last two samples (7-12-am and 7-13-pm) have been included only because they were the last samples taken from the well. They are not useful in correlating values as a function of time because the pressure of the separator was changed, chokes were being changed frequently, and certain equipment and/or connections failed during the latter stages of the test. For these, and probably other reasons, the samples were collected at times which were dictated by expedience rather than any planned operations; however, the remainder of the samples in Figure VI show trends for several of the determinations.

The pH tends to decrease as a function of time in sand #1, probably for the same reason stated in sand #3. As indicated for the #3 sand, the accuracy of the pH measurement is questionable and will be discussed later. The turbidity tends to decrease with time as it does in sand #3 and the higher values near the end are probably caused

Figure VI

Selected Data from #1 Sand

Flowing Water Samples

Collection Date	06-23-pm	06-25-pm	06-27-pm	06-29-pm	07-01-pm	07-07-pm	07-10-pm	07-12-am	07-13-pm	Typical Value
Collection Point	flare	separator	separator	separator	separator	separator	separator	separator	separator	
pH	6.26	6.19	6.09	5.96	6.15	6.02	6.06	6.28	6.17	
Turbidity	70	42	12	21	44	10	71	54		
Conductance (corrd to 25°C	166,000	163,000	164,000	164,000	165,000	163,000	152,000	166,000	162,000	162,000
Density @ 20°C	~1.08	1.086	1.085	1.086	1.085	1.084	1.084			1.085
Total Dissolved Solids		133,800	133,400	133,400	133,000	133,800	133,000			133,400
Suspended Solids			2.5	1.0	1.0					
Total Hardness	6740	6760	6880	6900	6910	6890	6860	6980	6850	6840

TABLE CONTINUED ON NEXT PAGE

Figure VI (cont'd)

Collection Date	06-23-pm	06-25-pm	06-27-pm	06-29-pm	07-01-pm	07-07-pm	07-10-pm	07-12-am	07-13-pm	Typical Value
Collection Point	flare	separator	separator	separator	separator	separator	separator	separator	separator	
Chloride	80,800	80,400	80,500	80,600	81,100	80,500	80,700	79,300	78,900	80,400
Dissolved Silicate		57		58	55					55
Bicarbonate	1170	1060	1020	1020	970	1200*		970	1020	
Calcium		2100	2100	2000	2000	2100	2100	2100	2100	2100
Magnesium		180	180	180	190	180	190	180	180	180
Iron		24	19	14	8.7	12	11	10	10	
Zinc		1.3	1.0	1.0	1.1	1.0	1.1	1.0	1.0	1.1
Strontium		400	430	330	430	430	430	370	400	400
Boron		64	66	60	60			65	65	63
Sodium		45,000	45,000	45,000	45,000	47,000	46,000	45,000	43,000	46,000
Potassium		290	290	280	290	290	290	290	280	290
Viscosity @ 20°C		1.249	1.248	1.249	1.247	1.249	1.244			1.248

*First flowing sample collected after bottom-hole sample. Note value agrees with flare sample of 6-23-pm and bottom-hole shown in Figure X for Sand #1.

by increased sand production. The chloride is rather constant in this sand as opposed to the earlier one. The bicarbonate ion shows a clear decrease with time in the #1 sand which is probably caused by precipitation of carbonate at higher temperatures as a result of higher flow rates. This was seen in sand #3 also but the change was not as pronounced. The iron decreases but reaches a limiting value approximately equal to that found in sand #1. The higher initial values are probably a result of the much slower flow rates used (and therefore longer contact time with the separator) at the beginning of the test on sand #1. The zinc is remarkably constant in this sand as opposed to the #3 sand; presumably, all of the pipe dope was cleaned out of the system during testing of the first sand. The remaining determinations in Figure VI do not exhibit any marked changes and the two sands may be compared with the aid of the last columns in Figures V and VI. The value found for a determination in sand #1 is almost always higher than the corresponding number for sand #3. As expected, silicate is slightly lower in sand #1 because the temperature, and therefore the solubility, is lower than in sand #3.

A number of samples were sent to outside laboratories as shown in Figure VII. Dr. Kreitler is measuring istopic ratios of oxygen, nitrogen, and carbon. Dr. Kraemer is interested in the uranium levels. Dr. Kharaka has obtained both bottom-hole and flowing samples for an extensive analysis of each. McNeese submitted samples to Dr. Laseter for a determination of trace organics. The Bureau of Mines asked to measure the amount of helium in the flowing samples. Dr. Fruchter

Figure VII

Outside Laboratories

A. Kreitler - UTA - Austin, Texas

B. Kraemer - USGS - Bay St. Louis

C. Cairns - Freeport Sulphur - New Orleans

D. Kharaka - USGS - Menlo Park, California

E. Janzer - USGS - Denver

F. Fruchter - Battelle Pacific Northwest, Richland, Washington

G. Laseter - UNO - New Orleans

H. Bureau of Mines - Amarillo, Texas

came to the site and collected analytical samples for mercury, arsenic, and other heavy metals. At McNeese's request, Dr. Janzer measured the radioactivity and the results are shown in Figures VIII and IX. Some of these values are about a factor of ten higher than those observed in surface waters; consequently, the radioactivity of the water probably should be investigated further. The total potassium values shown in Figure IX agree rather well with those determined at McNeese.

Figure X lists the analyses for the bottom-hole samples. The lower viscosity for sand #3 is caused almost completely by the lower density which is used in the viscosity calculation. The iron is about an order of magnitude higher 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 bottom-hole sampling and the amount of iron is

Figure VIII

Radioactivity

USGS - Denver

Sand #3

Collection Date	05-24-pm	05-31-am	06-03-pm	06-07-pm
Rn in gas, pCi/l	15	100	61	64
Rn in solution pCi/l	-	-	540	300
^{137}Cs, pCi/l	1400	1100	1900	1800
Gross α as μg 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, μg/l	0.10	0.11	0.2	0.06

Figure IX

Radioactivity

USGS - Denver

Sand #1

Collection Date	6-24-pm	6-27-pm	6-28-pm	6-30-pm	7-03-pm	7-11-pm
Rn in gas, pCi/l	41	50	59	55	31	24
Rn in solution pCi/l	-	-	150	330	140	190
^{137}Cs, pCi/l	440	1200	1200	800	1100	1300
Gross α as μg U/l	1700	11000	6400	4100	6400	10,000
Gross β as pCi^{90}Sr/l	400	1100	1100	700	960	1200
^{226}Ra, pCi/l	86	140	230	240	360	370
U, μg/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

Figure X

Bottom-Hole Samples

Typical Values

Determination	#3 Sand	#1 Sand
pH	5.90	6.33
Turbidity	17	30
Conductance (corrd to 25°C)	142,000	
Density @ 20°C	1.075	1.084
Total Dissolved Solids	114,100	134,600
Total Hardness	5830	6940
Chloride	67,100	80,000
Dissolved Silicate	59	45
Bicarbonate	1300	1200
Calcium	1600	
Magnesium	160	
Iron	100	
Zinc	1.2 - 8.4	
Strontium	300	
Boron	59	
Sodium	44000	
Potassium	270	
Viscosity, 20°C	1.208	1.243

increased due to dissolution of the tubing. The remainder of the bottom-hole values track the values obtained from the flowing samples.

IN-LINE MEASUREMENTS

The in-line equipment was meant to measure the pH, conductance, and temperature, continuously. Initially, one set of the probes was placed at each of the three sampling stations; i.e., at the box marked "sample point" and the two "monitoring stations" shown in Figure II. The probes were connected with cables to appropriate amplifiers and monitors located in the on-site laboratory on the quarters barge. A multipoint recorder with six inputs monitored any two of the three sets continuously. 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 temperature and high pressure apparently was not available. The equipment was purchased, 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.

The real surprise came in the recorded pH values for they were considerably lower than the values obtained in the on-site laboratory. Figure XI shows the actual tracing obtained on 5-31-77 at the station preceding the separator. The pH is obtained by dividing the brown colored line (labelled pH #3) by 10 and adding 2. (The left hand side of the paper is zero.) Note that the lower part of the recording gives an average value of about 5.5. The cell was shut-in at a point noted by the arrow but the recorder continued to monitor the pH and the temperature. The pH changed to 62, which is about the same as the values measured in the on-site laboratory, while the temperature (labelled temp #3) decreased from 212°F to 80°F. The system is obviously not in equilibrium with respect to the gas and the higher values obtained in the lab for the #3 sand are apparently the result of a loss of carbon dioxide while the sample is being transported to the lab to make the measurement. Any consistency in the lab measurement of the pH is probably the result of consistency in the time of transportation and measurement only and does not reflect the true pH of the solution.

Figures XII and XIII give similar conclusions from recordings on the #1 sand on 6-25-77 and 6-26-77 respectively. Some of the in-line equipment failed after tests on the #3 sand. The in-line cells were then relocated to a point immediately after the separator for the tests on the #1 sand although they were located immediately preceding the separator for the tests on the #3 sand.

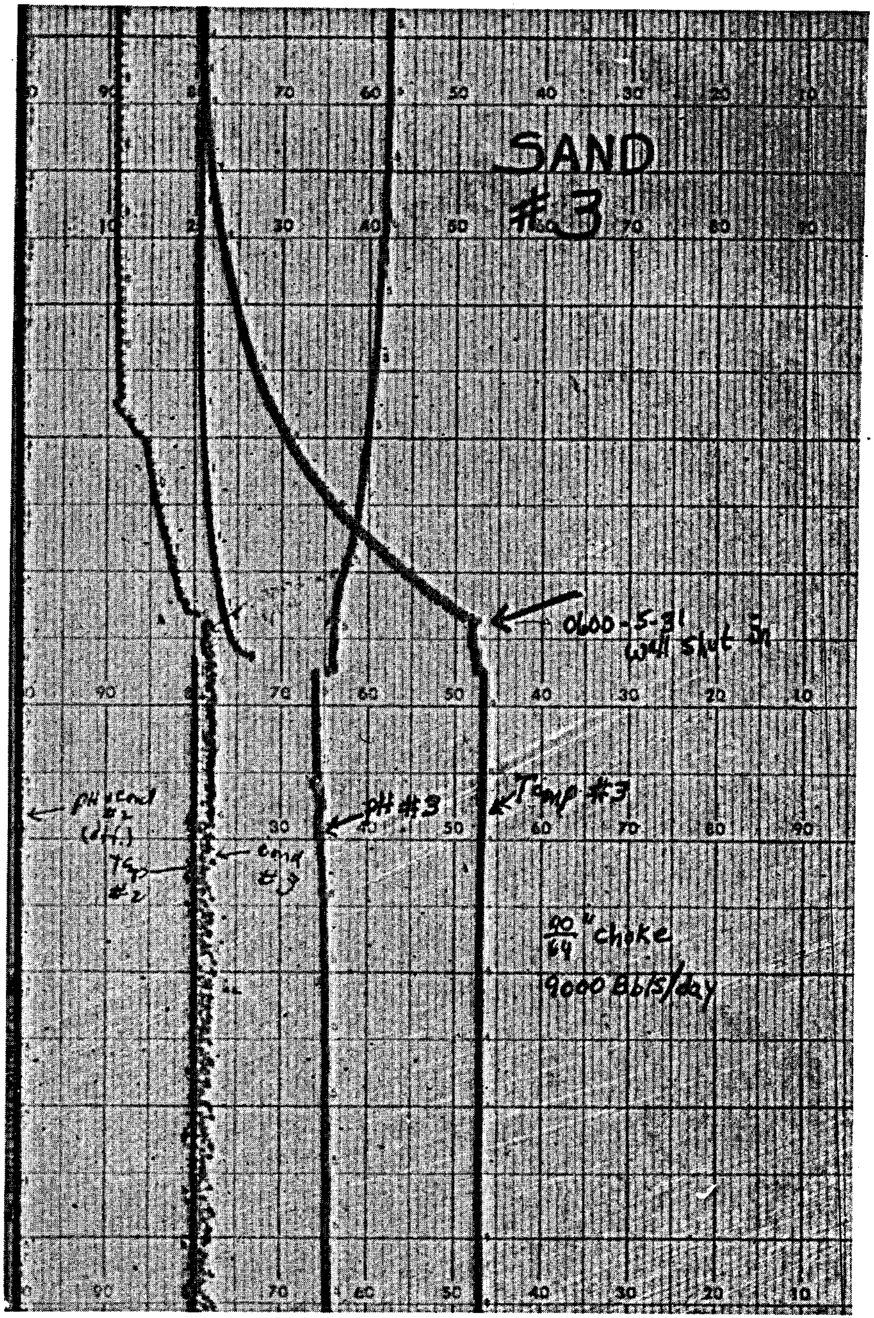


FIGURE XI

IN-LINE RECORDING FOR #3 SAND

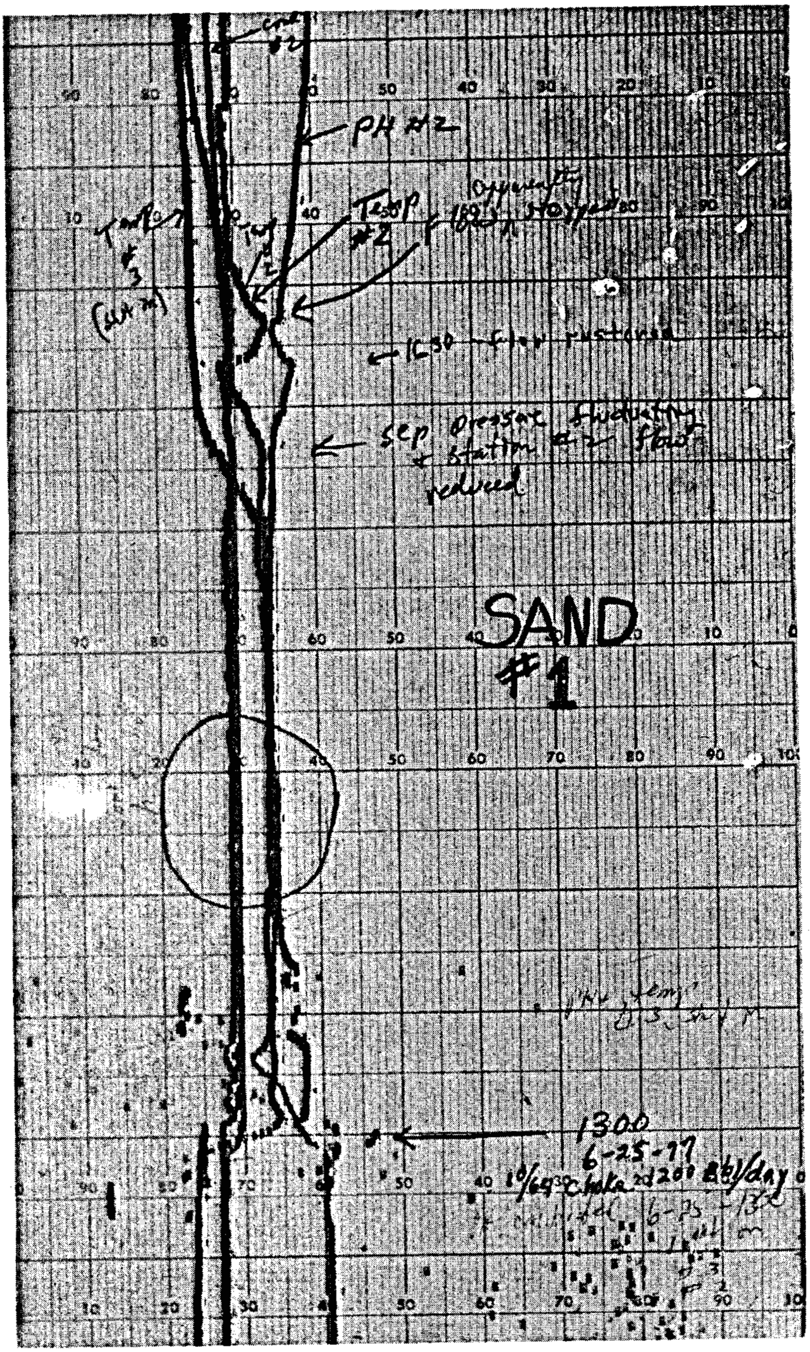
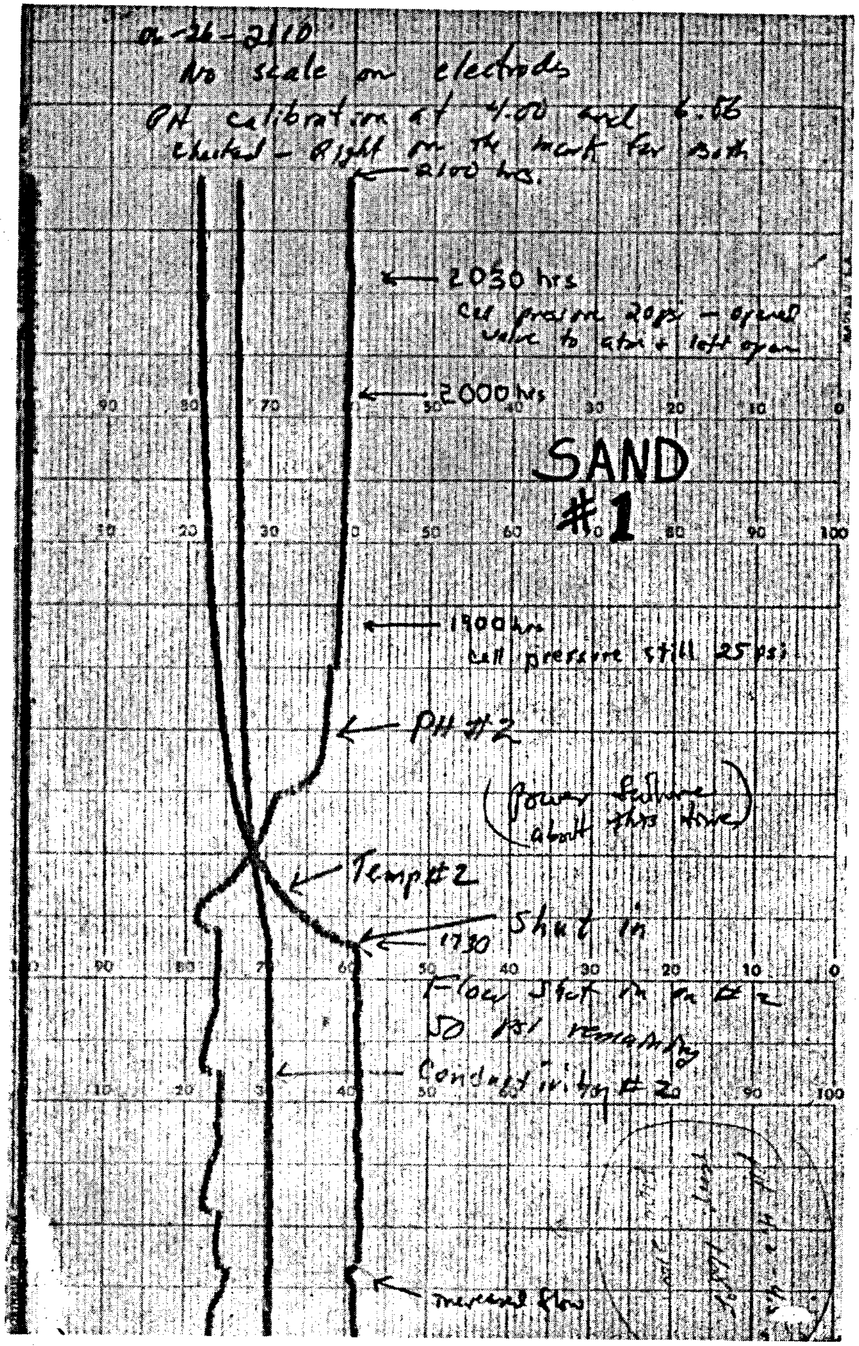


FIGURE XII

IN-LINE RECORDING FOR #1 SAND (6-25-77)



6-26-2110
No scale on electrodes
PH calibration at 4.00 and 6.86
Checked – Right on the mark for both
← 2100 hrs.
← 2030 hrs
cell pressure 20psi – opened valve to atm + left open
← 2000 hrs
← 1900 hrs
cell pressure still 25 psi
← PH #2
(power failure about this time)
← Temp #2
← Shut in
← 1730
Flow shut in on #2
50 psi remaining
← Conductivity #2
← increased flow

FIGURE XIII

IN-LINE RECORDING FOR #1 SAND (6-26-77)

Note that the pH value is about 5.4 (circled area) for the 6-25 sample and about 4.2 - 4.5 for the 6-26 sample. The pH is in red, the temperature is in brown, and they are labelled pH #2 and Temp #2. After the well was shut-in, the pH increased to about 6.0 - 6.1 which, again, is the value of the laboratory measurement. The temperature on all of the figures is obtained by multiplying the chart reading by 4 (the left side is zero) and shows the cooling of the cell to ambient temperature after shut-in.

The pH 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 last test for pH was made 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 paper showed the pH to be 5.2 and an immediate pH measurement on a laboratory instrument read 6.62.

SUMMARY AND RECOMMENDATIONS

Some observations, made after an examination of all of the data collected to date, 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 decrease with time in the flowing samples.
3. The dissolved silicate concentration decreases as the temperature of the aquifer decreases.
4. Correct _in situ_ values probably cannot be obtained for all determinations by analyzing bottom-hole samples.
5. Concentration gradients apparently occur within certain zones of the 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 is affected by the pressure of the separator.
9. The in-line pH measurement may be affected by the composition of the gas and/or a streaming potential.
10. Erratic in-line measurements may be the result of plugged chokes, excessive gas evolution, and/or adsorption of gas bubbles on the electrode.
11. The hydrogen ion concentration of the flowing samples is _at least_ an order of magnitude lower than the laboratory measurement. The value of the hydrogen ion _in situ_ may be even lower. Both values should be known accurately,

the first for practical operation of surface equipment and the latter for theoretical purposes.

McNeese collected almost 250 separate flowing and bottom-hole water samples. Although all samples were not subjected to every determination, about 1000 separate determinations, excluding gas analyses, have been made. A few determinations still remain but the analytical portion of this project should be completed soon. 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 done. The number of samples collected in the future will be dictated, of course, by the kind of information, including trends, which may be desired.

Some of the elemental analyses show that water of this type must almost certainly be disposed of by deep-well injection. The radioactivity problem should be investigated further. Corrosion from highly saline geothermal wells will almost certainly be a problem to surface equipment. Bottom-hole collection and transfer procedures seem to be poor, at best, and must be improved if representative samples are to be obtained. Conductance and pH cells capable of withstanding more heat and pressure are desirable 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 and mercury, used in the hydraulic pump, and containing other trace metals, contaminates the bottom-hole samples. Finally, consideration should be given to more coordination between the engineering data and the chemical information desired and how it is to be acquired. The start and stop operation used to obtain some engineering data precludes obtaining consistent analytical data useful in showing trends.