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HYDROCARBONS ASSOCIATED WITH BRINES FROM GEOPRESSURED WELLS

Technical Progress Report

Fourth Quarter 1990

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DISCLAIMER

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THE UNIVERSITY OF SOUTHWESTERN LOUISIANA (USL)

DE-FC07-90ID12945

3 Mar 1990 - 31 Dec 1991

Summary of Research Goals:

To determine the concentration of the cryocondensates in fluids of the various USDOE Geopressured wells a function of production volume. To correlate the production of these compounds with reservoir and well production characteristics. To precisely measure solubilities of cryocondensates components in water and sodium chloride solutions (brines) as a function of ionic strength and temperature and the component's distribution coefficients between these solutions and oil. To develop models of the reservoir which are consistent with the data obtained.

To monitor the wells for the production of aliphatic oils and relate any such production with the cryocondensate yields.

To develop a harsh environment pH probe for use in well brines.

Contract Tasks:

Task 1: ***SOLUBILITY AND DISTRIBUTION COEFFICIENT MEASUREMENTS***

Background

An understanding of the basic physical chemical properties of the brine components produced in the U.S.DOE geopressured wells is necessary to provide the fundamental data necessary for an understanding of the mechanisms by which constituents of petroleum migrate and are partitioned into different phases in various geologic strata. The cryocondensate materials, which we sample, are present in the geopressured brines of all the wells observed to date. These materials are a complex mixture of aromatic compounds ranging in complexity from benzene to highly substituted anthracenes. A review of the literature concerning the solubility and thermodynamic distribution coefficients (see for example Keeley, Hoffpauir & Meriwether, J of Chem and Eng Data, 33: 87-89, 1988) reveals that while data is available for room temperature and for solutions of pure water, there is little earlier information on these compounds in solutions of higher salinity *and at elevated temperatures. Our work, reported in the reference noted above, extended the basic solubility data for benzene and toluene (two of the major aromatic constituents of the geopressured brine) to higher sodium chloride concentrations. A new paper, currently in the peer review process, extends the available data on ethylbenzene and the three isomers of xylene. A preprint of this paper was attached to the July, 1989, monthly report.*

The techniques we have developed during the course of this work allows us to make these measurements with precision and to make major contributions to the basic literature. It is important to realize that reliable data on these fundamental quantities comes only with great attention to detail and an insistence on consistency and reproducibility. To determine the solubility of one compound at one set of conditions requires the manual injection of a minimum of 45 samples into a gas chromatograph and an analysis of each chromatogram.

Current Reporting Period

The research on the most abundant cryocondensate components: benzene, methylbenzene, ethylbenzene, 1,2-, 1,3-, 1,4- dimethyl benzene has been completed. A final summary report was submitted and attached to the 15 July 1990.

Task 2: DOE WELL SAMPLING

Background

The various operational wells are sampled on a monthly basis for the yield of the cryocondensate hydrocarbons. The hydrocarbons of interest are distributed, in the separator, between the gas and liquid phases, both phases are sampled to obtain a quantitative analysis. A portion of the gas stream passes (60 ft^3 over about a three hour period) through a cryogenic system and removes all materials which have partial pressures that allow for their condensation at -78.5 C: hence the term "cryocondensates" to distinguish them from "condensates", a term commonly used in the oil and gas industry. A second procedure is used to recover the cryocondensate which was not exolved from the brine with the gas. This is accomplished by slowly passing brine from the separator through a coiled tube in an ice/water bath at 0 C. The lower temperature is used to prevent the loss of the volatile components. In the laboratory the brine is extracted with hexane and the cryocondensate content determined by gas chromatography. From this data the cryocondensate content of the original well brine is determined and the yield corrected to oil field standard conditions: 1 atm pressure and 60 F.

We have designed and installed a gas scrubbing system at the Pleasant Bayou Well to collect a daily sample of the benzene and toluene components of the cryocondensates. The device is usually *simply referred to as the "scrubber". This is not a quantitatively complete sample, but should be relatively correct on a day-to-day basis.*

Current Reporting Period

The only one of the US DOE design wells that was flowing during the reporting period was the Pleasant Bayou #2. This well was cryogenically sampled as follows:

Date	*Flow rate (bbl/day)*
18 Oct	*24,800*
30 Nov	*13,000*
28 Dec	*12,250*

Task 3: ANALYSIS OF WELL SAMPLES

Background

The regular cryocondensate samples and the scrubber samples (one for each day since the last visit to the well) referred to above are returned to the laboratory and analyzed by gas chromatography and the yield of these products determined. The monthly cryogenic result is reported in terms of the cumulative brine production. A daily quantitative result is obtained by normalizing the scrubber sample data to the monthly quantitative sample taken as described above.

Current Reporting Period

The analysis of the well samples taken during the current period are given and all results to date are discussed in Attachment 1.

REVIEW OF THEORETICAL MODELS OF GEOPRESSURRED RESERVOIR HYDROCARBONS

Background

This is a new task assigned to us under the new cooperative agreement. The review of the literature is to serve as a basis for the development of theoretical models of the reservoir.

Current Reporting Period

The bibliographic data base which forms the basis for theoretical models has been established with the aid of computer searches of the Chemical Abstracts Service (CAS).

Task 5: ALIPHATIC HYDROCARBON MONITORING

Background

Both the L. R. Sweezy and the Gladys McCall wells produced a heavy aliphatic oil after a large initial brine production (~ 8 million barrels in the case of Gladys McCall). During this induction period, the concentration of the cryocondensates determined as part of Tasks 3 and 4 above increased. These observations led to our proposal of a model of the geopressured reservoir in which brine production drew heavy hydrocarbons from the neighboring shales in the production formation. These heavy hydrocarbons were considered to be the source of additional aromatics extracted into the water phase of the reservoir. A complete review of this model can be found in our paper published in the Journal of Energy Resources Technology (Vol. 110 pp. 177-182, 1988). Each month we monitor the various fluid phases from the separators at the production wells for aliphatic oils. Thus far the Pleasant Bayou well has shown no signs of aliphatic oils. The behavior of the Pleasant Bayou has differed from the earlier wells in that the cryocondensate concentration has not systematically increased as a function of cumulative brine production.

Current Reporting Period

None of the phases from the separators at Pleasant Bayou yielded aliphatic oils during the reporting period.

Modeling: Our dynamic model of the geopressured reservoir is, we believe, a good one. As with all models, it is one to be challenged, added to, revised or discarded on the basis of experimental data. Unfortunately for us, the Pleasant Bayou well, the only one available to us in recent years, had been operated primarily as a source of brine for the HPS. To assure a reliable brine source, the well had been flowing at conservative rate of around 16,000 bbl/day. This rate did not stress the reservoir, and in terms of our model, does not draw fluids as readily from the neighboring shales. With no new fluids, there is little or no oil from which to extract new cryocondensate (aromatic hydrocarbons) and no oil to produce. During the third quarter of 1990, the flow rate from the Pleasant Bayou was increased in steps to over 22,000 bbls/day. This rate and the higher rates projected, would provide the basis for a test of our model. Unfortunately the rate has again been lowered, and as of our last measurements was at just over 12,000 bbl/day. When Hulin flows at high rates, we will be watching with great anticipation to see what its behavior portends. The long-delayed Hulin project will be an opportunity to test our model in a new environment.

Task 6: HARSH ENVIRONMENT pH PROBE

Background

The U. S. Department of Energy has in the past sponsored several *attempts to develop a device to measure the pH in the brine stream of geothermal wells and in other harsh environments. (for example, see Taylor and Phelan, PNL-3593). As recently as January, 1988, DOE solicited, through its Small Business Innovation Research (SBIR) program, proposals for the development of a similar device. This did not result in funding. Such a device is desirable so as to provide in-situ data for general analysis of brines (and other chemical streams) and in particular to provide data for the understanding of scaling and corrosion.*

We became aware of a new device that was being marketed by the CHEMFET Corporation (Bellvue, WA) to measure pH under normal laboratory conditions and were encouraged by Mr. Ray Fortuna (DOE - Wash) to pursue this possibility.. This device was based on the ISFET - the Ion Sensitive Field Effect Transistor. Under this Task, we are studying the application of these devices under conditions corresponding to those found in typical geopressured brines. CHEMFET, Corp has been cooperating with us in this effort by donating the ISFETs for tests.

The goal of this task is to produce and field test an operational probe on a geopressured well.

Current Reporting Period

One of the concerns in the development of a reliable instrument for any purpose is the stability of the instrument over time. In order to measure the stability of an ISFET probe we set up a long term measurement of the voltage output as a function of time. Figure 1 shows the very encouraging results. The output changes only very slowly over time. The small time dependence of the output is quantified by the slope of the line which is the first term in the equation on the figure.

We are still faced with the problem of availability of new ISFETs to work with and test. As noted in the last quarterly report, CHEMFET, Inc is under going financial reorganization. They had first hoped to be operational by late Fall, but now hope for January. They did however arrange for the purchase of some ISFETs through the Trustee in Bankrupcy. We have submitted a purchase order and hope they will soon be forthcoming. We have thus far been unable to discovery a new source of ISFETs. Until we have a new supply in hand, we will be unable to proceed with tests at higher temperatures.

ACTIVITIES NOT COVERED UNDER THE REGULAR TASKS

1. Dr. Keeley attended the Advisory Council meeting in Idaho Falls. He presented and defended the research program we proposed for 1991.

2. Dr. Meriwether attended and presented material at the Geo-pressured Energy Program Review in Washington in December.

Dean F. Keeley
Professor of Chemistry
Principal Investigator

John R. Meriwether
Professor of Physics

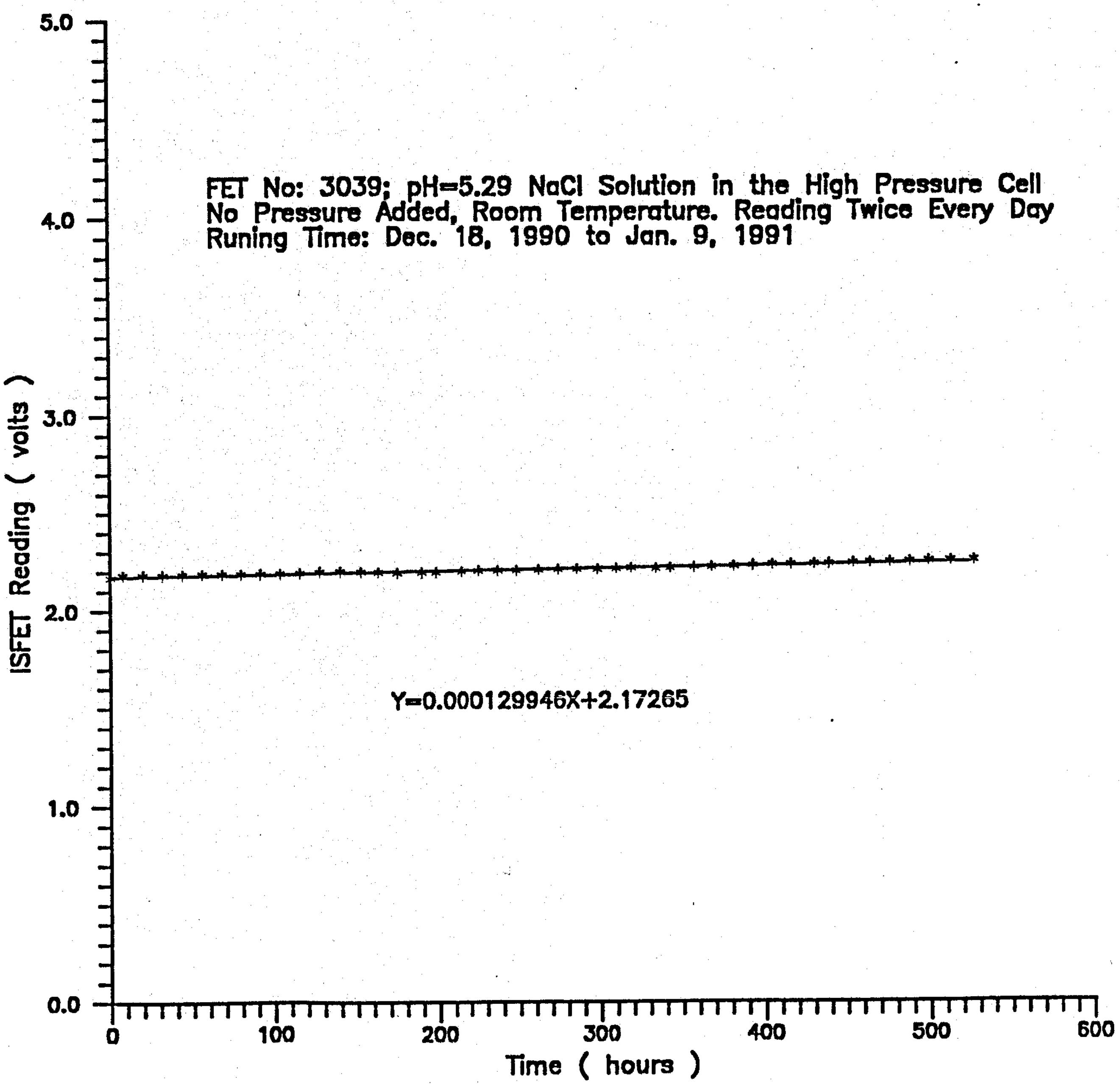

FET No: 3039; pH=5.29 NaCl Solution in the High Pressure Cell
No Pressure Added, Room Temperature. Reading Twice Every Day
Runing Time: Dec. 18, 1990 to Jan. 9, 1991
Y=0.000129946X+2.17265
ISFET Reading (volts)
Time (hours)
0.0
1.0
2.0
3.0
4.0
5.0
0
100
200
300
400
500
600

Figure 1

ATTACHMENT 1

Attachment 1

The Pleasant Bayou well was sampled during the quarter on 10/18/90, 11/30/90, and 12/28/90. The results for the analyses of the cryocondensate sample collected on these dates and other pertinent data are as follows:

Date	Cumulative Brine Volume (Mbbl)	Flow Rate (kbbl/d)	Cryocondensate Total uL/L	Gas uL/L	Brine uL/L
10-18-90	12.29	24,810	40.11	23.78	16.34
11-30-90	12.94	12,993	32.57	18.68	13.89
12-28-90	13.29	12,259	29.76	16.16	13.61

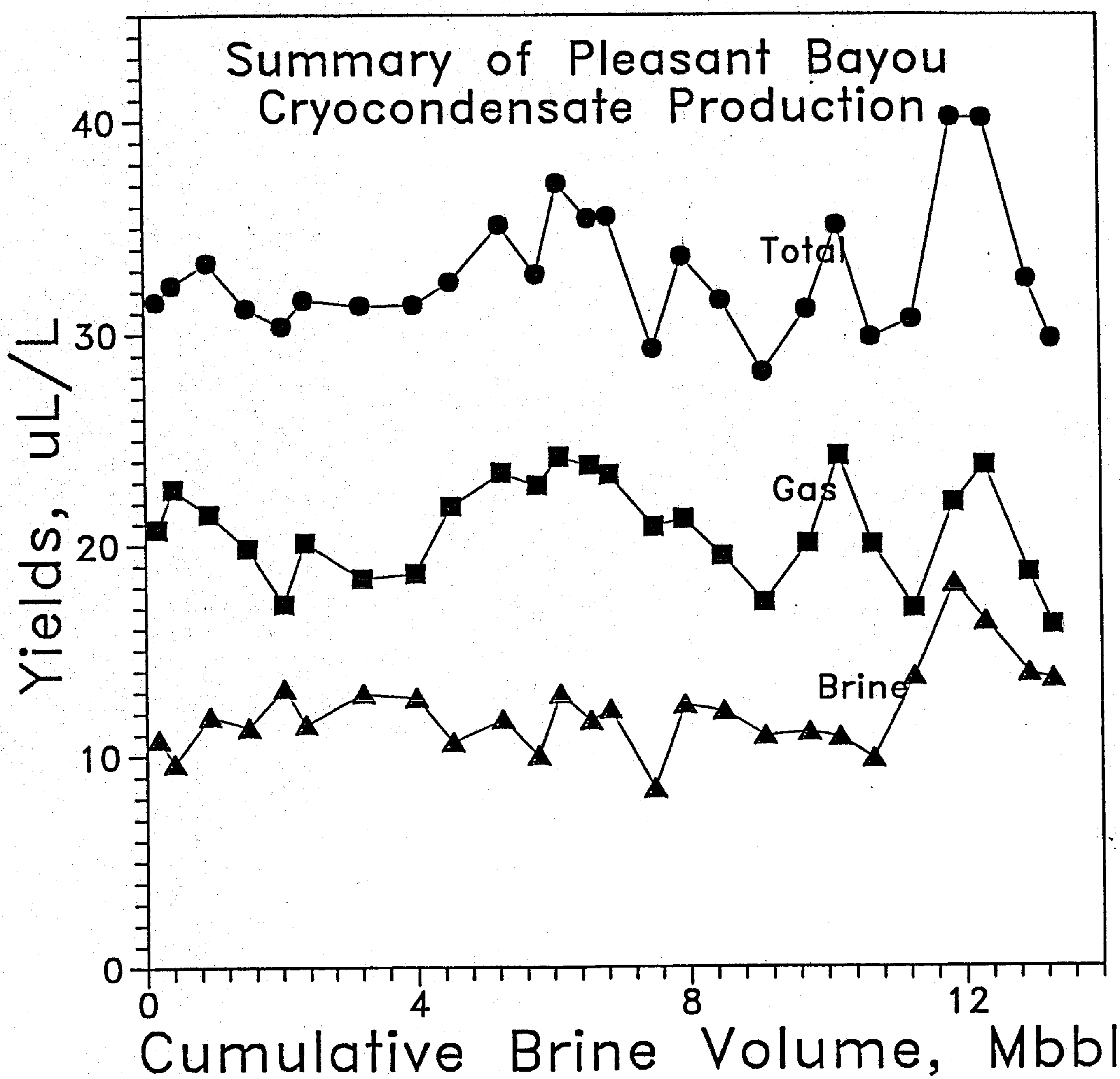
This data (the last three points) as well as all cryocondensate data collected from cite visits to date are shown in Figure 1.

The total cryocondensate value of 40.11 uL/L for the sample collected on 10-18-90 is consistent with the earlier value of 40.16 uL/L for the sampled collected on 9-27-90. In both cases the well was flowing at an elevated flow rate, 22.8 kbbls/d on 9-27 and 24.8 kbbl/d on 10/18. When the flow rate was reduced the values for the total cryocondensate decreased accordingly to values similar to those observed prior to the high rate flow test. As mentioned earlier (see 3rd quarter 1990 report) this behavior is consistent with the model we proposed in which fresh aromatic rich oil is being drawn from the adjacent shale in an amount that is proportional to the difference in the pressure between the sand and shale formations.

The daily concentration of cryocondensate from 4/22/89 through 12/28/90 as computed from the data obtained from the gas scrubber samples is shown in Figure 2. The agreement for the latter part of 1990 is good considering that during that period the flow rate from the well went from 16 kbbl/d in May up to nearly 25 kbbl/d in October and down to 12 kbbl/d in December and in addition the gas separation employed two separators until early in November when the large separator was taken off line and again in mid-December when flow only occurred through the large separator. Since the gas scrubber analyses require constant operation between cite sampling visits for optimum results the parallel agreement between the cite visit data (Figure 1) and the daily scrubber sample data (Figure 2) is really quite remarkable.

Attachment 1

Figure 1



Attachment 1 Figure 2