Aromatic Hydrocarbons Associated With Brines From Geopressured Wells

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**HYDROCARBONS ASSOCIATED WITH BRINES
FROM GEOPRESSURED WELLS**

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**ANNUAL REPORT
FOR
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HYDROCARBONS ASSOCIATED WITH BRINES FROM GEOPRESSURED WELLS

Summary of Research Goals:

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

To monitor U.S. DOE geopressured design wells for the production of aliphatic oils and relate any such production with the cryocondensate yields.

To develop models of the geopressured reservoirs which are consistent with the data obtained.

To develop a harsh environment pH probe for use in well brines at surface temperatures and pressures.

Task 1:

SOLUBILITY AND DISTRIBUTION COEFFICIENT MEASUREMENTS

Background

The measurement of the basic physical chemical properties of the components of brine produced in the U.S.DOE geopressured wells is necessary to provide the fundamental data necessary for understanding 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.

The techniques we have developed during the course of this work allows us to make solubility 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.

Report Period

Solubilities, Henry's law constants, and aqueous/vapor partition coefficients of benzene, methylbenzene, ethylbenzene, 1,2-, 1,3- and 1,4-dimethylbenzene in aqueous sodium chloride solutions having ionic strengths of 0 to 5.00 have been completed at 25 °C.

Aqueous solubilities, Henry's law constants, and aqueous/vapor partition coefficients of benzene, methylbenzene, ethylbenzene, 1,2-, 1,3- and 1,4-dimethylbenzene have been determined at temperatures of 25.0, 40.0, 55.0 and 70.0 °C.

Solubilities, Henry's law constants and aqueous/vapor partition coefficients for benzene, methylbenzene, ethylbenzene, 1,2-, 1,3- and 1,4-dimethylbenzene in aqueous NaCl solutions with ionic strength, $\mu = 0$ to 5.00 at 25.0 °C are given in Tables I-VI.

Aqueous solubilities, Henry's law constants and aqueous/vapor partition coefficients for benzene, methylbenzene, ethylbenzene, 1,2-, 1,3- and 1,4-dimethylbenzene at 25.0 to 70 °C are given in Tables VII-IX. The data from Table VII is plotted in Fig. 4 as $\ln(\text{solubility})$ vs $1/T$. The linear correlation coefficient and slope for the benzene data are 0.987 and -1,029.8, respectively. Using this slope value, the salting out coefficient (computed from the data in Table 1), an ionic strength of 2.0 (salinity of approximately 120,000 ppm), and a temperature of 422 K (i.e., 300 °F) the calculated saturation concentration of benzene in geopressured brine would be of the order of 1,700 ppm.

Table I. Molar Solubilities, Henry's Law Constants, k and Partition Coefficients, K_p for Benzene in Aqueous Sodium Chloride at 25.00 °C

ionic strength	solubility mol/L $\times 10^3$	k torr $\times 10^{-6}$	K_p
0	21.7 $\pm$ 0.00	24.4 $\pm$ 0.0	4.23 $\pm$ 0.00
1	12.9 $\pm$ 0.00	40.9 $\pm$ 0.2	2.52 $\pm$ 0.02
2	9.21 $\pm$ 0.04	57.3 $\pm$ 0.5	1.80 $\pm$ 0.01
3	6.13 $\pm$ 0.01	116 $\pm$ 0.2	1.20 $\pm$ 0.01
4	3.69 $\pm$ 0.09	143 $\pm$ 1.0	0.720 $\pm$ 0.032
5	2.57 $\pm$ 0.02	205 $\pm$ 3.0	0.503 $\pm$ 0.007

Table II. Molar Solubilities, Henry's Law Constants, k and Partition Coefficients, K_p for Methylbenzene in Aqueous Sodium Chloride at 25.00 °C

ionic strength	solubility mol/L $\times 10^3$	k torr $\times 10^{-6}$	K_p
0	6.29 $\pm$ 0.03	25.2 $\pm$ 0.2	4.10 $\pm$ 0.03
1	3.86 $\pm$ 0.03	40.7 $\pm$ 0.5	2.52 $\pm$ 0.03
2	2.21 $\pm$ 0.00	71.2 $\pm$ 0.2	1.44 $\pm$ 0.01
3	1.50 $\pm$ 0.02	104.6 $\pm$ 2.0	0.975 $\pm$ 0.024
4	0.892 $\pm$ 0.02	174.6 $\pm$ 5.0	0.582 $\pm$ 0.017
5	0.638 $\pm$ 0.01	243.3 $\pm$ 9.0	0.416 $\pm$ 0.017

Table III. Molar Solubilities, Henry's Law Constants, k and Partition Coefficients, K_p for Ethylbenzene in Aqueous Sodium Chloride at 25.00 °C

ionic strength	solubility mol/L $\times 10^3$	k torr $\times 10^{-6}$	K_p
0	1.66 $\pm$ 0.04	31.8 $\pm$ 0.8	3.24 $\pm$ 0.08
1	1.01 $\pm$ 0.05	52.1 $\pm$ 2.6	1.98 $\pm$ 0.09
2	0.549 $\pm$ 0.02	95.7 $\pm$ 3.9	1.07 $\pm$ 0.05
3	0.387 $\pm$ 0.007	135 $\pm$ 2	0.755 $\pm$ 0.014
4	0.202 $\pm$ 0.007	215 $\pm$ 8	0.473 $\pm$ 0.018
5	0.148 $\pm$ 0.015	353 $\pm$ 36	0.289 $\pm$ 0.029

Table IV. Molar Solubilities, Henry's Law Constants, k and Partition Coefficients, K_p for 1,2-dimethylbenzene in Aqueous Sodium Chloride at 25.00 °C

ionic strength	solubility mol/L x 10^3	k torr x 10^{-6}	K_p
0	2.09 ± 0.05	17.9 ± 0.6	5.69 ± 0.16
1	1.17 ± 0.05	31.4 ± 1.4	3.28 ± 0.16
2	0.637 ± 0.004	57.5 ± 0.3	1.70 ± 0.01
3	0.419 ± 0.012	86.9 ± 2.9	1.18 ± 0.03
4	0.241 ± 0.030	154 ± 21	0.673 ± 0.096
5	0.121 ± 0.021	314 ± 36	0.341 ± 0.059

Table V. Molar Solubilities, Henry's Law Constants, k and Partition Coefficients, K_p for 1,3-dimethylbenzene in Aqueous Sodium Chloride at 25.00 °C

ionic strength	solubility mol/L x 10^3	k torr x 10^{-6}	K_p
0	1.58 ± 0.02	29.2 ± 0.3	3.53 ± 0.04
1	0.923 ± 0.032	49.8 ± 1.7	2.06 ± 0.07
2	0.567 ± 0.011	80.9 ± 1.5	1.27 ± 0.03
3	0.294 ± 0.015	155 ± 9	0.659 ± 0.033
4	0.179 ± 0.007	254 ± 9	0.401 ± 0.015
5	0.0957 ± 0.002	472 ± 10	0.214 ± 0.005

Table VI. Molar Solubilities, Henry's Law Constants, k and Partition Coefficients, K_p for 1,4-dimethylbenzene in Aqueous Sodium Chloride at 25.00 °C

ionic strength	solubility mol/L x 10^3	k torr x 10^{-6}	K_p
0	1.63 ± 0.02	29.8 ± 0.4	3.46 ± 0.05
1	0.846 ± 0.019	57.2 ± 1.3	1.79 ± 0.04
2	0.512 ± 0.010	94.4 ± 1.9	1.09 ± 0.02
3	0.288 ± 0.006	168 ± 3	0.611 ± 0.012
4	0.152 ± 0.005	316 ± 11	0.322 ± 0.011
5	0.109 ± 0.015	456 ± 35	0.223 ± 0.017

Table VII. Solubilities in mmol/L at 20.0 to 70.0 °C

	25.0 °C	40.0 °C	55.0 °C	70.0 °C
Benzene	21.7	24.5	28.1	34.4
Methylbenzene	6.28	6.46	7.75	9.20
Ethylbenzene	1.64	1.98	2.91	3.68
1,2-Dimethylbenzene	2.15	2.47	3.08	4.07
1,3-Dimethylbenzene	1.70	2.12	2.87	
1,4-Dimethylbenzene	1.70	2.39	2.92	

Table VIII. Aqueous/Vapor Partition Coefficients at 20.0 to 70.0 °C

	25.0 °C	40.0 °C	55.0 °C	70.0 °C
Benzene	4.23	2.61	1.76	1.33
Methylbenzene	4.10	2.20	1.45	0.97
Ethylbenzene	3.29	1.80	1.34	0.93
1,2-Dimethylbenzene	6.05	3.14	1.95	1.38
1,3-Dimethylbenzene	3.81	2.18	1.49	
1,4-Dimethylbenzene	3.60	2.34	1.45	

Table IX. Henry's Law Constants $\times 10^{-5}$ at 20.0 to 70.0 °C

	25.0 °C	40.0 °C	55.0 °C	70.0 °C
Benzene	2.44	4.15	6.45	9.20
Methylbenzene	2.51	4.97	8.07	12.56
Ethylbenzene	3.13	6.08	8.64	13.53
1,2-Dimethylbenzene	1.73	3.48	5.93	8.80
1,3-Dimethylbenzene	2.72	5.03	7.74	
1,4-Dimethylbenzene	2.87	4.72	7.95	

Fig. 1 is a plot of the solubilities for benzene, methylbenzene, ethylbenzene, 1,2-, 1,3- and 1,4-dimethylbenzene as a function of molar volume. The linear correlation coefficients of the Fig. 1 plots at ionic strength, $\mu = 0$ to 5 are 0.999, 0.998, 1.000, 0.997, 0.997 and 0.992, respectively. While such plots are popular they suffer from the objection that while molar volumes computed from solute densities and molecular weights may be proportional to the effective volume of solute molecules in the pure solutes, they are not necessarily true indicators of the effective volumes of solute molecules in other solvents.

More recently the use of molar volume has been replaced by molecular surface area (MSA), originally suggested by Langmuir (1) in connection with solution free energies, as a more appropriate variable. While molecular surface areas are theoretically more appealing they are not easily computed. Fig. 2 is a plot of solubility values from this study as a function of MSA. The MSA values used are those of Amidon et al.(2). Linear correlation coefficients for the Fig. 2 plots for ionic strength, $\mu = 0$ to 5 are 0.999, 0.998, 0.998, 0.998, 0.998 and 0.990, respectively.

Figure 1

Figure 2

Benzene and its C_1 and C_2 substituted analogs are all liquids at room temperature. With the exception of ethylbenzene these substances may be viewed as rigid molecules in which a benzene hydrogen has been replaced by a methyl group. To a first approximation, the molecular volumes (MV) or molecular surface areas (MSA) of such a series can be represented by a sum of group contributions

$$\Sigma GC = B - nH_B + n(M - H_M) \quad (1)$$

where n is the number of methyl groups, B is the benzene value and M the methane values for the appropriate property and H_B and H_M are the corrections to the value corresponding to the removal of one hydrogen atom from benzene and methane, respectively.

Equation 1 may be simplified to

$$\Sigma GC = B + nS \quad (2)$$

where $S = M - H_B - H_M$. Fig. 3 is a plot of the aqueous solubility of benzene, methylbenzene and 1,2-, 1,3-, and 1,4-dimethylbenzene as a function of ΣGC as computed from equation 2 in which B and S have been assigned arbitrary values of one. The linear correlation coefficients of the aqueous solubility data plotted in this fashion are for $\mu = 0$ to 5, 0.995, 0.994, 0.998, 0.994, 0.992 and 0.997, respectively. Since such plots find their greatest use in estimating solubilities, the authors feel that when conditions and available data justify it such a simple approach as equation 2 gives a useful first approximation. Estimated solubilities based upon extrapolations of the data in Figs. 1-3 are given in Table X.

Figure 3

Table X. Estimated Aqueous Solubilities of tri-, tetra-, penta-, and hexamethylbenzenes in mmol/L at 25.00 °C from Extrapolation of Least Squares Fit of Figs. 1-3 Data

	Trimethylbenzenes *			Tetramethylbenzenes		
	1,2,3-	1,2,4-	1,3,5-	1,2,3,4- *	1,2,3,5-*	1,2,4,5-**
Molar Volume	0.833	0.587	0.417	0.238	0.197	0.0961
MSA	0.688	0.557	0.487	-----	-----	-----
Σ GC (Eq. (2))	0.498	0.498	0.498	0.141	0.141	0.141

Pentamethylbenzene**		Hexamethylbenzene**
Molar Volume	0.0308	0.171
MSA	-----	-----
Σ GC (Eq. (2))	0.0400	0.0113

* liquid at 25.00 °C

** solid at 25.00 °C

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 ft³ 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 (June, 1989) 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.

Report Period

The only well continuously in operation during the past year has been the Pleasant Bayou. The well was cryogenically sampled as follows:

<u>Date</u>	<u>Flow Rate</u> (bbls/day)
1-11-90	16,040
2-16-90	16,570
3-30-90	15,790
4-27-90	16,570
5-29-90	16,220
8-30-90	18,440
9-27-90	22,800
10-18-90	24,810
11-30-90	13,000
12-28-90	12,260

Samples were taken each month that the well flowed for a significant period of time. With few exceptions the scrubber operated each day that the well flowed during the entire year.

Task 3: WELL SAMPLE ANALYSIS

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.

Report Period

The regular cryocondensate samples and the scrubber samples were returned to the laboratory and analyzed by gas chromatography and the yield of the

products determined. Table XII summarizes the total cryocondensate concentration as well as the concentrations in the brine and the gas after passing the separator system. Figure 4 displays the total cryocondensate yield, from the cryogenic measurement, as a function of production volume. The graph includes data from the beginning of the current long-term test on the Pleasant Bayou Well. The daily cryocondensate yield determined from the scrubber samples up to late December of 1990 is shown in Figure 5. The filled circles indicate dates on which the daily samples were normalized to the cryosamples.

Table XI. Cryocondensate Concentrations as a Function of Production Volume.

<u>Date</u>	<u>Cumulative Brine Volume (Mbbbl)</u>	<u>Cryocondensate</u>		
		<u>Total</u> uL/L	<u>Gas</u> uL/L	<u>Brine</u> uL/L
1-11-90	8.49	31.59	19.49	12.10
2-16-90	9.08	28.21	17.28	10.93
3-30-90	9.73	31.16	20.06	11.10
4-27-90	10.17	35.11	24.25	10.86
5-29-90	10.65	29.84	20.02	9.82
8-30-90	11.25	30.69	16.97	13.73
9-27-90	11.84	40.16	22.01	18.15
10-18-90	12.29	40.11	23.78	16.34
11-30-90	12.94	32.57	18.68	13.89
12-28-90	13.29	29.76	16.16	13.61

gr

Figure 4

Figure 5

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.

Report Period

None of the phases in the separator at the Pleasant Bayou Well have yielded aliphatic oils during this past year. Until June, flow rates from the well have been restricted to accommodate the Hybrid Power System and very little stress has been placed on the reservoir. After the extended shutdown from June to August, the flow rate was steadily increased until October. We had hoped this would begin a high flow rate and high stress on the reservoir. According to our model of a geopressured reservoir, oils should not be extracted from the adjacent shale unless there is a significant pressure gradient across the shale-sandstone interface. Unfortunately, the rate was reduced again during the last two months of the year. This

reduced flow was required because of the some sand production. We are hopeful that the new year will again bring higher flow rates.

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. CHEM-FET, 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.

Report Period

Milestones achieved during the past year include:

1. The construction of the high pressure test cell was completed and
2. The test instrumentation was acquired and installed (Figure 6).
3. The probe containing the ISFET and its reference electrode was designed and constructed.
4. pH measurements have been made at all pressures and ionic strengths expected in the geopressured program.
5. Elevated temperature measurements have begun, but significant problems have been encountered.

In preparing to test the probe (3 above) at elevated pressures, we encountered a technical difficulty. The electrical leads from the probe pass through the walls of the pressure vessel that we designed. The leads must be sealed in such a way as to withstand the pressure gradient across the walls; our early attempts to do this were not successful. We began using flexible silicone potting compounds which would allow for the simple replacement of the ISFET elements. Several attempts with several materials resulted in several brine irrigations of the lab floor.

We have now turned to a different design in which the ISFET and its Ag-AgCl reference are sealed with epoxy resin into a stainless steel shell. The epoxy encompasses a guide plate for the wires and bonds to the walls and to an internal supporting shoulder in the shell. This seal has proved quite strong and has been tested to just over 6,000 psig. In Figure 7, one can see an over view of the entire probe. The ISFET and the reference electrode can be seen at the end of the shell. The shell widens to a heavy structure (the inside diameter is but 0.1") which has an O-ring seal, threads and wrench surface. The entire unit with its standard weather-tight connector can be screwed into either a fitting in our a test cell or into a field

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unit which we are now designing.

Our test data indicates that the ISFET pH probe is quite stable and yields good response at high pressures. The test cell containing the probe and a pressure transducer is placed in a laboratory press. The force applied to the piston in the test cell pressurizes the contents of the cell. The pressure is maintained and controlled by a hydraulic feedback system. The electric potential difference between the ISFET and the reference electrode is proportional to the pH of a brine solution contained in the cell. Figure 8 displays the output of the probe as a function of the pH of the brine at a constant pressure of about 6000 psig. The linearity of the graph is the mark of a potentially good instrument because as a calibration curve it allows the measurement of an unknown pH. The stability of the probe output as a function of pressure is shown in Figure 9.

One of the necessary requirements of a good instrument is the stability of its output of a function of time. The results of our measurements are quite encouraging. Figure 10 presents a measurement of the output of the probe as a function of time for over 500 hours. The small positive slope of the curve is quite acceptable.

Figure 8

Figure 9

Figure 10

ACTIVITIES NOT COVERED UNDER THE REGULAR TASKS

1. Both Dr. Keeley and Dr. Meriwether met regularly with Dr. Jane Negus-de Wys to review the technical progress on the contract.
2. Dr. Keeley worked with Dr. Negus-de Wys and with industrial contacts to develop and plan the activities of the **Industrial Consortium for the Utilization of the Geopressured-Geothermal Resource**. We have assisted in distributed information concerning the Consortium to local industry and to interested members of the Louisiana Congressional delegation.
3. Dr. Meriwether attended the Geothermal Review meeting in San Francisco in April. He participated in the meeting to develop long-range plans for the geopressured program.
4. Dr. Meriwether attended and participated in the meeting held in Houston to develop long-range plans for the geopressured program.
5. Dr. Keeley attended the Advisory Council meeting in Idaho Falls. He presented and defended the research program we proposed for 1991.
6. Dr. Meriwether attended and presented material at the Geopressured Energy Program Review in Washington in December.
7. Dr. Keeley wrote and circulated a Topical Report: *Observation of an Unknown Material Collected at the Pleasant Bayou Geopressured Well Commencing in December, 1989 to Date* to the Geothermal-Geopressured research groups. A copy follows.

Topical Report on Observation of Unknown Material

Collected at Pleasant Bayou Geopressured Well

Commencing in December, 1989 to Date

by

**Dr. Dean F. Keeley, Professor of Chemistry
Dr. John R. Meriwether, Professor of Physics
The University of Southwestern Louisiana
Lafayette, LA 70504**

September 27, 1990

Background: Since April 22, 1989 samples have been collected daily at the Pleasant Bayou geopressured well by saturating an oil (Mobil-1) with gas from the well's large gas/brine separator. The gas that is sampled is conducted from the top of the large separator through 3/8" stainless steel tubing to the rear of the well cite sampling building and from there through the back wall of the building into a sampling station specifically designed and built for the purpose of obtaining oil samples which are saturated with each of the components in the gas stream. The distance of the sampling equipment from the separator is estimated to be close to 50 feet.

The samples are picked up on a monthly basis when USL personnel are at the well to collect samples used to quantify the amount of aromatic hydrocarbons in the exsolved gas. The monthly quantitative analysis of the aromatic hydrocarbons in the gas stream and the values of the benzene and toluene in the oil samples are used to estimate the daily concentration of aromatic hydrocarbons in the gas.

From the end of April, 1989 till the end of December, 1989 nothing unusual was observed. Beginning with the last week of December, 1989 several of the oil samples, which are normally crystal clear, were observed to be cloudy. Pleasant Bayou well personnel indicated in the sample log book that the cloudiness was due to water. When we saw what was apparently a white solid material in several of the sample bottles our scientific curiosity dictated that we should investigate further even though such an investigation was not one of our assigned tasks.

The white solid was recovered from one of the sample bottles and a routine characterization attempted. The following is a summary our findings concerning the recovered material to date.

Color: white, apparently crystalline solid

Melting point: 79.8-81.5°C

Solubility characteristics:

Mobil-1 oil	insoluble
Hexane	insoluble
HCl (dil)	insoluble
Acetone	insoluble
NaOH (dil)	insoluble
H ₂ O	insoluble
Benzene	insoluble
H ₂ SO ₄ (conc)	insoluble
HCl (conc)	insoluble

Mass spectrographic data:

Molecular weight	274
Parent peak	255
Possible splits	propyl butyl pentyl

Infra-red spectroscopic examination results:

Examination shows primarily carbon-hydrogen stretching frequencies.

Electron microscopic examination: underway

C, H, and N analysis: underway

We are preparing this report since the events of December, 1989 have reoccurred beginning on 8/2/90, reaching a maximum on 8/6/90, and ending 8/9/90 and a second although much less occurrence on 8/22/90 and 8/23/90 and 8/25/90. Photographs of these two events are included on the following page.

As scientists we would be remiss in our duty if we did not report these events so that those in charge of the DOE Geopressed Energy Program are aware of them and can asses for themselves their possible significance, if any, to the program.

Upper: Samples from 8/1/90 to 8/10/90
Lower: Samples from 8/21/90 to 8/26/90