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Petroleum Reservoir Characterization by Perfluorocarbon Tracers

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Abstract

Perfluorocarbon tracers (PFTs), a class of six compounds, were used to help characterize the Shallow Oil Zone (SOZ) reservoir at the Naval Petroleum Reserve in California (NPRC) at Elk Hills. The SOZ reservoir is undergoing a pilot gas injection program to assess the technical feasibility and economic viability of injecting gas into the SOZ for improved oil recovery. PFTs were utilized in the pilot gas injection to qualitatively assess the extent of the pilot gas injection so as to determine the degree of gas containment within the SOZ reservoir.

Four different PFTs were used, two were injected over a days duration (approximately 12 grams of each) into a well undergoing 250 MCFPD of gas injection and the other two tracers injected over a days duration in another well undergoing 75 MCFPD of gas injection. Samples were collected from at least eighteen sampling wells surrounding the injection wells; collected at the wellhead in 1 liter sampling bombs and transferred at the NPRC site to smaller Capillary Adsorbent Tracer Samplers (CATS) which were then shipped to Brookhaven National Laboratory (BNL) for tracer analysis. Up to six tracers can be simultaneously analyzed within fourteen minutes down to a detection limit of several femtoliters of tracer per liter of reservoir gas.

PFTs have been detected in at least thirteen of the sampling wells over several months of sampling. Results will be discussed in qualitative terms of reservoir characterization since the design of the experiment does not allow quantitative certainty in reservoir interpretation. The tracer program has suggested changes in the geological interpretation of the reservoir since faulting affects the movement of the tracer tagged injection gas.

This work demonstrates that a relatively simple tracer program can be used to improve reservoir characterization.

Introduction

Chemical tracers have their greatest utility in the determination of bulk flow transport and flow dispersion within both gaseous and liquid phases. In the past, perfluorocarbon tracers (PFTs) have amply provided this tracing utility in long-range atmospheric transport and dispersion experiments. PFTs have also been applied to subsurface petroleum reservoir experiments in the past (1) and are now being applied in several experiments at the Elk Hills Field, Naval Petroleum Reserve in California (NPRC). The purpose of these experiments is to apply the PFTs in transport and dispersion tests for the demonstration of their utility in these applications. The following is a report of the first demonstration experiment at NPRC, a qualitative tracer transport and dispersion test in the Shallow Oil Zone.

Perfluorocarbon Tracers

Perfluorocarbon Tracers are a family of fully fluorinated alkyl substituted cycloalkanes, a list of which is given in Table 1.

The PFTs are listed in order of chromatographic elution for the specific chromatographic column used in the laboratory analysis system. All PFTs except for the perfluoro indanes are currently available for use. The PTCH has several isomers of which only the two major isomers are simply designated as 1 and 2. Several of the PFTs cannot be used simultaneously, such as PECH and pc-PDCH or ot-PDCH, since they cannot be chromatographically resolved into separate peaks with the present chromatographic column.

The PFTs have the following advantages, i.e.,

1) There is a negligible background of the PFTs in the atmospheric and subsurface environments, due to very limited industrial use of the PFTs as heat transfer agents.

2) The PFTs are completely non-toxic, non-reactive and non-flammable and are totally environmentally safe.

3) The PFTs are sensitively detected by Electron Capture Detection (ECD) down to about a 0.1 femtoliters (10E-15) in the gas phase. This sensitivity is comparable to that for radioactive tracers, such as krypton-85 and tritiated methane. This sensitivity towards detection permits small quantities of PFTs to be used in petroleum reservoir experiments, of the order of tens of grams.

4) The perfluorocarbon tracer technology is a multi-tracer technology permitting up to six PFTs to be simultaneously deployed, sampled and analyzed which means a relatively low cost of use compared to the conventionally used tracers, such as the radioactive tracers.

The physical properties of the PFTs are given in Table 2.

As can be seen in Table 2, the PFTs are liquids at normal temperatures and have solubilities in hydrocarbon fluids. This indicates that the PFTs will not be transported conservatively in petroleum reservoirs, i.e., the PFTs will not be transported at the bulk flow rate of the subsurface medium, but rather at a rate retarded with respect to the bulk flow rate. This degree of retardation is dependent on the composition of the hydrocarbon phases in the reservoir and the reservoir pressure and temperature. This retardation can be calculated for each of the PFTs by standard models and in turn this retardation can be used to determine additional information about the reservoir, such as the average residual pore oil saturation along the path of transport in a gas injection experiment. Thus a multi- PFT experiment can be designed not only to determine the reservoir transport and dispersion properties but also the degree of pore oil saturation along the path of transport. More details about the PFT technology is available in reference 2.

The Shallow Oil Zone (SOZ) Reservoir at NPRC

The SOZ is a multilayered reservoir which originally contained more than 1,250 million barrels of oil. It is estimated that the primary recovery efficiency in the SOZ will be less than 50%. Cumulative production to date is 439 MMBO. The SS-1 is one of nine oil producing intervals in the (SOZ). The SS-1 represents a large portion of the remaining 150-200 MMBO left to be produced by primary production methods. The SS-1 also has the lowest reservoir pressure, less than 50 psig, of any of the intervals in the SOZ. The low reservoir pressure provides the opportunity to increase the economic value of its remaining primary reserves by implementing processes which increase reservoir pressure and productivity, thereby accelerating recovery.

Gas injection is a potentially viable means to increase the economic value of the remaining oil-in-place by supplementing the natural gravity drainage mechanism. A pilot gas injection project was initiated in April 1991 to gather production and injection data to assess the technical feasibility and economic viability of injecting gas to increase reservoir pressure and productivity. Pilot results will be used to determine the potential for expanding this process to other portions of the SOZ.

The area for gas injection was selected for the following reasons:

1) The pilot area appears to be contained by five normal faults, with displacements of 20 to 100 feet to the southeast. The faults form a fault block elongated in a NE-SW direction. The two larger faults are labelled "V" and "W". Three smaller faults between "V" and "W" subdivide the pilot area into four sections.

2) Production characteristics in the area indicate that a secondary gas cap has formed in the SS-1 interval south and east of the fault "V" while most of the wells north and west of the fault "V" are within the oil band.

3) There is good areal distribution of wells with mechanical integrity that can be used for injection, production and monitoring. The wells in the project area are completed only in the SS-1.

4) The primary drive mechanism is gravity drainage. There is an oil band approximately 500 feet thick in contact with a secondary gas cap which had an initial reservoir pressure of about 4 psig. The absence of natural water influx and the small number of wells has facilitated the establishment of a base performance prediction and provides the means to identify changes in production caused by gas injection.

Based on the preceding characteristics, the selected location meets the criteria needed to assess, in a timely manner, the incremental increase in production due to gas injection.

Gas Injection Sites

Wells 34-10G and 44-10G, (the pilot injection wells) are 75-100 feet above the gas/oil contact and are separated from each other by a normal fault with 20 to 40 feet of throw to the southeast. A map of the pilot area is given in figure 1. Well 34-10G is completed in sublayers Pa, A, A1 and B of the SS-1, with an average net thickness of 45 feet, a project area of 7421 NAF and an average gas saturation of 60% in the gas cap. Well 44-10G is completed only in sublayer D, with an average net thickness of 15 feet, a project area of 1331 NAF and an average gas saturation of 60%.

These completions present the opportunity to evaluate both vertical and areal effect that gas injection will have on SS-1 sublayers and the faults surrounding the injectors. Gas injection started in 34-10G on April 24, 1991 and in 44-10G on May 26, 1991.

Experimental Procedures

Tracer Injection

The PFTs were specifically utilized to qualitatively determine the direction of migration of the injected gas and possible gas migration across the faults. PMCP and PMCH were simultaneously injected into 34-10G on June 18, 1991 over a 28 hour period when the well was injecting 250 MCFPD of gas. The PFTs were introduced into the reservoir in the gas phase by injecting a small flow of PFTs from a high pressure cylinder flowing through a regulator into the injection well. The regulator was used to ensure a constant injection rate over the 28 hour injection period. The high pressure cylinder contained approximately 0.05% of gaseous PMCP and 0.06% of gaseous PMCH in nitrogen. The resulting PFT concentration in the 34-10G injection gas was 89,330 picoliters of PMCP per liter of injection gas and 97,000 picoliters of PMCH per liter of injection gas. Likewise, oc-PDCH (64,700 pL/L) and ot-PDCH (139,000 pL/L) were injected into 44-10G on June 19, 1991 over a 24 hour period when the well was injecting 75 MCFPD. Approximately 12 grams of each PFT was used in this experiment.

Tracer Sampling

Ten monitoring wells (including both inactive gas cap wells and active producers) were sampled daily starting on June 19, 1991. The gas cap wells were produced at low rates, about 1 MCFPD, to ensure turnover of the gas in the wellbore. Sampling was accomplished by collecting directly at the wellhead into pre-evacuated one liter pressure bombs by the field operator. The field operator also recorded the wellhead pressure which was needed in the calculation of the final PFT concentration. The pressure bombs containing the samples were then transported to the field laboratory where they were further processed. The pressure was measured in each sample bomb and if it was less than 5 psig it was diluted with helium to raise its pressure to 5 psig. Then a 50 mL sample was withdrawn by a syringe and injected onto a Capillary Absorbent Tracer Sampler (CATS). The CATS was developed as part of the PFT technology as a convenient sampler for PFTs. The CATS is a two inch long, 1/4 " O.D. glass tube containing 60 milligrams of Ambersorb, a form of activated carbon. The Ambersorb physically adsorbs the PFTs from the 50 mL sample as it flows through the CATS. The CATS tubes were then mailed to Brookhaven National Laboratory (BNL) for analysis. The CATS samplers have the advantage of not having to ship sampling bombs to the analysis site. Once the bombs were sampled for PFTs, the bombs were then occasionally sampled for their hydrocarbon gas content, especially in latter stages of the program, to verify effective sampling of the reservoir. Several sample bombs occasionally contained air indicating the presence of casing leaks or that the monitoring well was no longer in connection with the reservoir. Before the sampling bombs were returned to the field for the next days samples, they were steam cleaned, dried in a stream of helium and pre-evacuated.

The CATS were shipped in 30 glass tube mailers by express mail to BNL. Once received, the CATS were thermally desorbed through a catalytic processing system to remove any adsorbed hydrocarbons, especially the higher molecular weight hydrocarbons which would interfere with the further analysis of the sample. The samples were then recollected on another set of CATS for analysis of their PFT content. Further details on the catalytical processing of the sample is given in reference 3.

The CATS samples were then analyzed chromatographically in a specially modified gas chromatograph and detected using electron capture detection. Specific details on the analysis technique are given in reference 2. A sample chromatograph showing the results of an analysis is given by Figure 2, Well 25-10G, January 7, 1992 showing all four PFTs used in this experiment.

Sampling at the monitoring wells continued on a daily basis through July 4, 1991. Due to anticipated tracer dispersion in the reservoir, sampling frequency was reduced to every other day until August 15, 1991. Sampling was again reduced to every three days on August 18 and changed to every week on September 7, 1991. At that time, the number of monitoring wells was increased to 18 due to the detection of PFTs in wells across the "V" fault. In early November the number of monitoring wells was decreased to four (wells 81-10G, 25-10G, 35-10G, and 45-10G) as the final stages of the tracer study were designed to monitor movement of PFTs across the "W" fault and their continued movement in the updip direction.

On several occasions, duplicate bomb sampling (two sample bombs taken at each monitoring well) and duplicate CATS sampling (two CATS samples per bomb sample) was undertaken to assess the precision of the PFT sampling and analysis procedures. Based on eight duplicate samples, it was determined that the measured PFT concentrations had a precision of about 26%. The largest contribution to this relatively poor sampling and analysis precision (compared to a laboratory analysis precision of about 5%) is due to the possible casing leaks in some of the monitoring wells or the method of physically obtaining the sample which introduced variable amounts of air into the samples. This was evidenced (after the duplicate sample study) by the variablity of the hydrocarbon gas present in the bombs as diluted by air and shown by the hydrocarbon gas analysis of the samples. This variable dilution also diluted the tracer concentrations in the sample bomb thus decreasing the overall precision of the sampling and analysis methods. No correction to the tracer concentrations have been made based on the later hydrocarbon analyses, since this was intended to be a qualitative tracer experiment.

Oil samples were obtained from several producing wells in the oil zone. These oil samples, about 0.5 liters each, were sent to BNL for PFT analysis. The PFT was extracted from the oil samples by heating the oil and collecting the vapor onto CATS. The CATS was then processed per the standard procedure.

Results

Results of the PFT study will be discussed according to individual monitoring wells:

24-10G PFTs injected at 34-10G were detected in this monitoring well five days after the tracer injection. This well is located about 770 feet to the west of 34-10G implying a flow velocity of about 150 feet per day. The PFT concentrations measured at 24-10G are given in figure 3 as a function of time since injection. Note the persistance of the PFTs for almost 100 days after injection indicating pooling of the injected gas at 24-10G with subsequent migration away from 24-10G. A minor degree of retardation exists between PMCP and PMCH as observed at this well. The observation of tracer at this well is consistent with increasing wellhead pressure.

78-3G This well located 3600 feet to the northeast of the injection wells showed no tracer after almost five months of monitoring.

16-10G This well located 1850 feet to the southwest of the injection wells showed PFTs (from 34-10G) 105 days after injection implying an average transport velocity to this well of 17.5 feet per day. Tracer retardation between PMCP and PMCH is observed at this well with the latter PFT arriving 28 days later.

63-10G Tracer was never detected in this well after five months of sampling. However, the hydrocarbon analyses indicated that almost all of the samples taken from this well contained only air implying that this well was not in connection with the reservoir.

45-10G PFTs were detected in this well 126 days after injection in 34-10G. This well is 940 feet to the southeast of 34-10G and across the "W" fault. A transport rate of 7.2 feet per day can be calculated.

81-10G This well located 3660 feet to the northeast of 34-10G showed PMCP 140 days after injection. PMCH, the second PFT also injected at 34-10G, appeared 161 days after injection indicating retardation. This is shown in figure 4. The PFT concentrations detected at this well are almost comparable to those detected at 24-10G implying almost an equal portion of injected gas being transported to 81-10G as to 24-10G. Further analysis will be performed on the observed retardation to estimate a residual pore oil saturation along this path. A velocity of 26 feet per day can be calculated. The observance of PFT at this well is corroborated by the increasing wellhead pressure.

52-10G This well located 1800 feet to the northeast of 34-10G showed PFTs (from 34-10G) 84 days after injection. However, this occurred after the well had undergone an injectivity breakdown procedure to reestablish reservoir communication. The PFT concentrations are comparable to those seen at 81-10G.

33X-10G No or negligible amounts of PFTs were detected at this well suggesting the injected gas does not cross the "V" fault at this location.

35-10G PFTs (from 34-10G) were detected 24 days after injection at this well located 690 feet to the south of 34-10G. The PFT concentrations are about a factor of 100 lower at this well compared to 24-10G suggesting that only a small portion of the injected gas is being transported to 35-10G.

15-10G PFTs were detected at this well 47 days after injection in 34-10G. This well is located 1600 feet to the southwest of 34-10G. PFTs continued to be detected at this well for two months until the end of the sampling program.

25-10G PFTs (from 34-10G) were detected 34 days after injection at this well located 1000 feet to the southwest of 34-10G. As seen in figure 5, the PFTs persisted about 35 days at this well. Note also the retardation in arrival times between PMCP and PMCH. PFTs injected at 44-10G were detected at 120 days after injection as seen in figure 6. This is the only well in which the PFTs injected in 44-10G have to date been detected. The chromatogram shown in figure 2 is from a gas sample from this well showing all four PFTs being simultaneously detected.

14-10G PFTs (from 34-10G) were detected at this well when this well was added to the monitoring program at 22 days after injection. This well is located 1300 feet to the west of 34-10G across the "V" fault. The PFT concentration is a factor of 10 lower compared to 24-10G suggesting that the "V" fault is only partially sealing at this location.

84-9G PFTs (from 34-10G) were detected at this well as soon as it was added to the monitoring program 38 days after injection at 34-10G. This well is located 1925 feet to the west of the injector. The PFT concentration detected at this well is comparable to that detected at 14-10G, suggesting a rapid, albeit minor westerly transport of injected gas from 34-10G.

14NE-10G A small breakthrough of PFTs (from 34-10G) occurred 112 days after injection at this well, located 1025 feet to the west of 34-10G across the "V" fault. The PFT concentration is comparable to that from wells located to the west of the "V" fault where PFT was detected.

65-9G No or negligible amounts of PFT were detected at this well. This well is located to the west of well 75-9G and is not on figure 1.

74-9G PFTs (from 34-10G) were detected at 84 days after injection at this well located to the west of 84-9G. The PFT concentration are comparable to those seen at wells west of the "V" fault. PFTs were also detected in the oil sample from this well.

85-9G PFTs (from 34-10G) were detected at this well as soon as it was included in the sampling program 62 days after tracer injection. As before, the PFT concentrations are consistent with those detected at wells west of the "V" fault.

55-9G No PFTs detected at this well. This well is located to the west of well 75-9G and is not on figure 1.

On several sampling dates a uniform concentration of PFTs was detected at the majority of the monitoring wells, even at those shown by hydrocarbon gas analysis not to be in connection with the reservoir. On examination, the cause was found to be tracer backflow when the primary vacuum compressor malfunctioned. However, it was found that the backflow problem could be clearly identified by tracking compressor downtime. As such, samples were not obtained when the compressor was not operational.

Conclusions

The inclusion of PFTs in this pilot study aided in the delineation of injected gas transport in the SS-1 layer of the Shallow Oil Zone. Presently, the PFT experiment is still ongoing and the analyses of the results is not yet complete. However, some conclusions can tentatively be drawn from the results of the PFT study:

1) Detection of PFT in wells outside of the pilot project area confirmed that the faults bounding the pilot project are not absolutely sealing, but are restrictors to the migration of injected gas at low reservoir pressures (10 to 20 psig). Analysis of incremental reservoir pressures in the pilot indicates the bounding faults are leaking approximately 10% of the injected gas.

2) Explanation of the observed PFT migration patterns in the reservoir may require reinterpretation of the current fault patterns. The detection of PFT in well 81-10G, but not in well 78-3G, and the confirming reservoir pressure data, indicates that a potentially different fault orientation exists.

3) Areas of production response are consistent with increasing detection of PFTs.

4) The observed retardation between the arrival of the two PFTs at 81-10G and 25-10G may possibly provide an estimate of residual pore oil saturation along the path from the injection wells to these monitoring wells.

Other presently on-going PFT experiments at NPRC

There are two other PFT experiments at NPRC which are presently ongoing. The first consists of a six PFT experiment in the 24Z reservoir undergoing gas and water injection and the second is also a multi-PFT experiment in the 26R reservoir undergoing gas injection. Results of these experiments will be available at a later date.

Acknowledgement

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Table 1

Current and Future Potential Perfluorocarbon Tracers

Name	Abbreviation
Perfluorodimethylcyclobutane	PDCB
Perfluoromethylcyclopentane	PMCP
Perfluoromethylcyclohexane	PMCH
Perfluoro cis 1,2-dimethylcyclohexane	oc-PDCH
Perfluoro trans 1,3-dimethylcyclohexane	mt-PDCH
Perfluoro cis 1,4-dimethylcyclohexane	pc-PDCH
Perfluoroethylcyclohexane	PECH
Perfluoro trans 1,2-dimethylcyclohexane	ot-PDCH
Perfluoro cis 1,3 dimethylcyclohexane	mc-PDCH
Perfluoro trans 1,4 dimethylcyclohexane	pt-PDCH
Perfluoro cis indane	1-PI
Perfluoro trans indane	2-PI
Perfluoro trimethylcyclohexane	1-PTCH
Perfluoro trimethylcyclohexane	2-PTCH

Presently only perfluoro indane is not available

Table 2

Physical properties of the PFTs

Tracer	Melting Point (C)	Boiling Point (C)	Density at 20 C (gm/cc)	Critical Properties Tc (C)	Pc (atm)
PDCB	-40	44.5	1.67	170.1	21.0
PMCP	-45	48	1.72	177.9	22.5
PMCH	-39	76	1.80	210.2	21.1
PDCH (ot+oc)	-22	102.6	1.87	235.2	18.7
PDCH (mt+mc)	-70	102.1	1.86	235.5	18.7
PDCH (pt+pc)	-70	100.9	1.85	235.5	18.7
PECH	-60	101.0	1.77	234.1	18.7
PI	-8 to -15	117.8	1.89	--	--
PTCH	-56	125.2	1.90	257.5	17.2

Individual values for the cis/trans isomers of PDCH, PI and PTCH are not available.

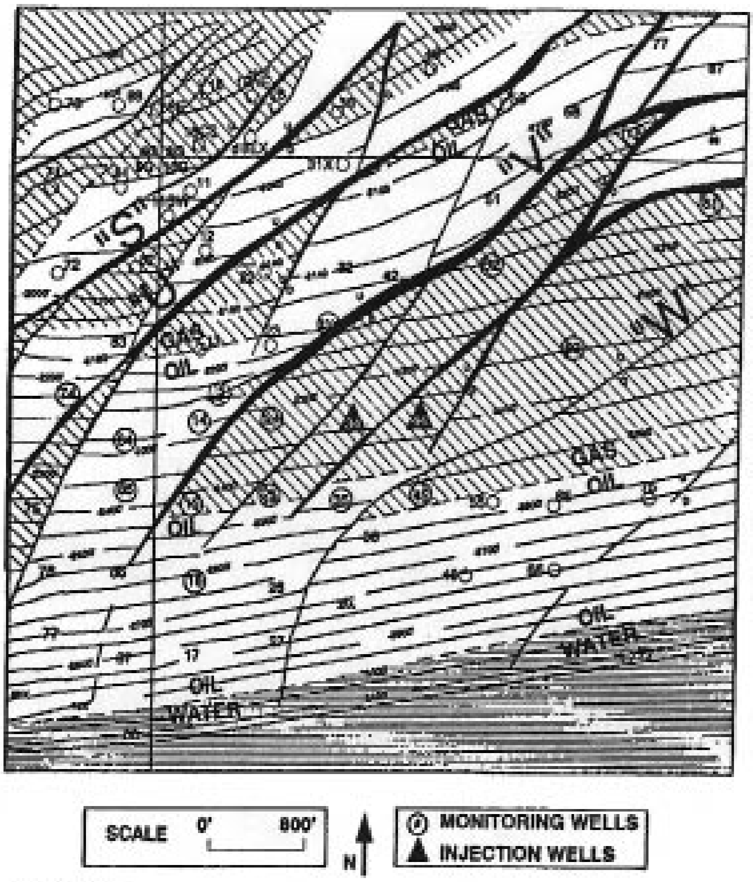

FIGURE 1

MAP OF THE SS-1 INTERVAL OF THE SOZ

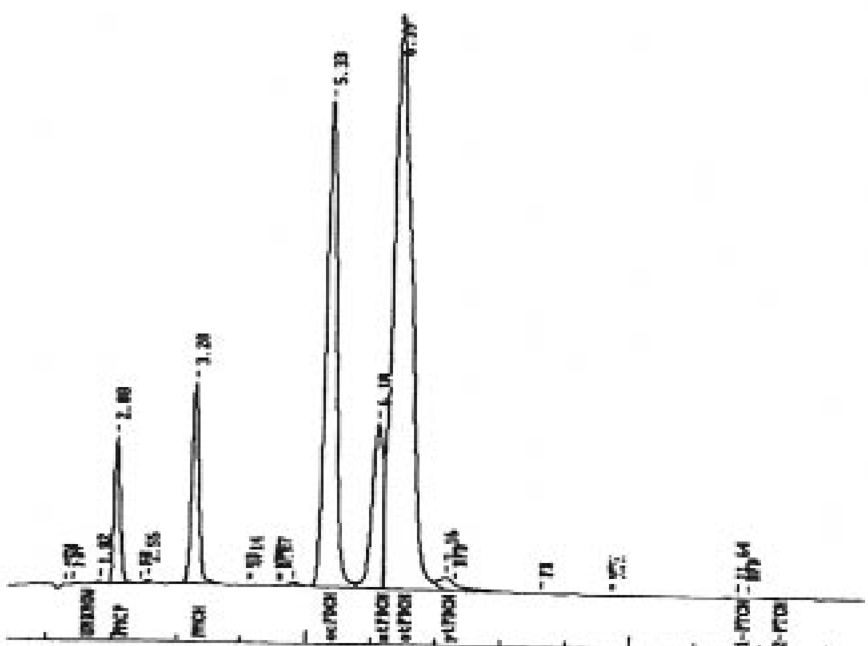

FIGURE 2

CHROMATOGRAPH OF ALL FOUR PFTs PRESENT AT WELL 25-10G.
JANUARY 7, 1992 SAMPLE

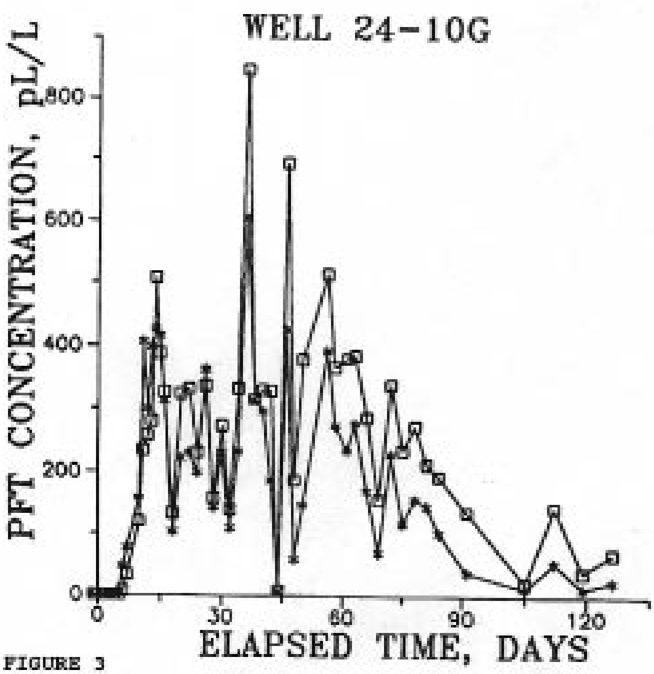

FIGURE 3

MEASURED PFT CONCENTRATION AT WELL 24-10G, STARS ARE PMCP, SQUARES ARE PMCH

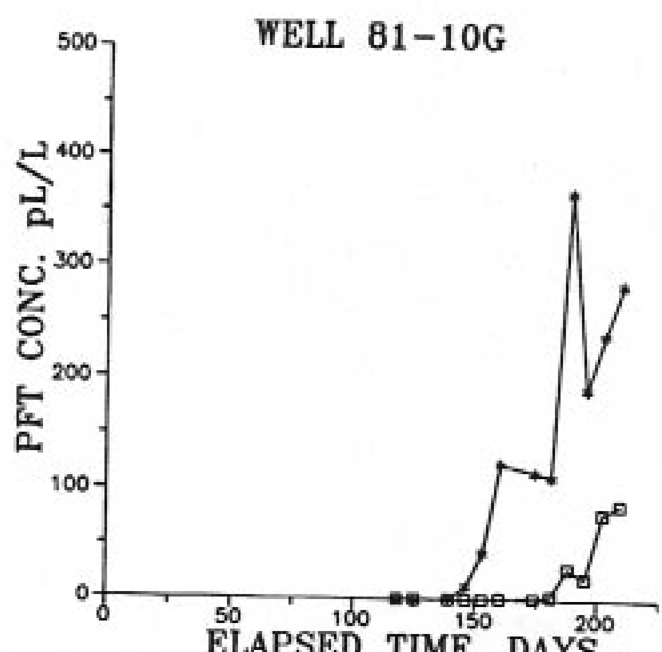

FIGURE 4

MEASURED PFT CONCENTRATION AT WELL 81-10G, STARS ARE PMCP, SQUARES ARE PMCH