"STUDIES OF CARBONATED WATER IMBIBITION USING MRI"

I. ABSTRACT

Oil recovery from naturally fractured, dual porosity reservoirs presents a special problem. Oil is easily produced from the fracture portion of the system. However, oil located in the matrix blocks is not readily displaced by either solution gas drive, natural water influx, or by any external drive displacement mechanism.

Spontaneous imbibition uses the effects of capillary forces to displace oil from low permeability matrix blocks but is usually very time dependent. CO_2-enriched water imbibition has been suggested as a method to accelerate and improve oil recovery from dual porosity reservoirs.[1] Spontaneous water imbibition and the effects of including CO_2 into the water being imbibed were studied using MRI techniques. Images of several processes taking place inside actual rock samples support facts that help to understand fluid movements due to water imbibition and the existence of preferential paths followed by oil in its way out to the rock surface. Dissolved CO_2 is carried into the rock porous spaces by the water being imbibed into the rock, alters rock and fluid properties, and after oil production has been completed a decrease in pressure -below the CO_2 mixing pressure- creates a gas drive that increases oil production. The location of dissolved gas, as well as the regions producing oil due to the localized gas drive were mapped. MRI allowed to observe that CO_2-enriched water imbibition is a process that prevails close to the rock-fracture face. Usually this distance is less than one inch. Drastic changes in oil saturation and fluid properties occur within a short distance of the rock-fracture surface. Conventional core analysis would have failed to identify these drastic changes, leading to erroneous conclusions. MRI has proven to be a very powerful core analysis tool. Oil from the rock matrix and oil that was adhering to the face of the rock was forced out by the localized gas drive. These amounts were quantified, and proven to be significant.

II INTRODUCTION

Naturally fractured reservoirs produce oil from two systems: the fracture system and the system of rock blocks associated to the fractures. Horizontal drilling has contributed to successfully intersect the fracture system. Oil production from the fractures is readily obtained, but oil production from the matrix blocks present a problem. Conventional waterflooding is inappropriate because any injected fluid follows the high permeability avenues, bypassing oil trapped inside the much lower permeability blocks.[2-5]

Spontaneous water imbibition is a mechanism driven by capillary forces that yields oil -the nonwetting phase- in exchange of water -the wetting phase-. Several tests on the Spraberrry[6] field, and other fractured reservoirs[7] have proven that spontaneous water imbibition can be an important oil producing mechanism. However, fractured reservoirs having low permeability matrix blocks require more time to achieve perceptible oil production from the matrix blocks.[8-11] Flow rates of oil being forced out of the matrix blocks by this mechanism is directly proportional to the square root of permeability times porosity.[12] Rocks with permeabilities in the order of 0.01 md and porosities below 5 % would require considerable time to produce any oil. Therefore, the process has to be accelerated to be economically applied to dual porosity reservoirs with low permeability matrix blocks.

Carbon dioxide has been used in the oil industry to enhance oil recovery for many years.[13-15] Several of is beneficial characteristics favor oil displacement, including:

References and figures at end of paper.

1) CO_2 becomes miscible with water and most crude oils,[16] 2) CO_2 might create swelling of oil,[17,18] 3) CO_2 has an acidic effect on calcareous rocks,[19] and 4) CO_2 creates a gas drive when pressure depleted below carbonation pressures.[1]

In order to apply the beneficial properties of CO_2, it has to be brought in contact with the oil in place. Water was sought as the carrier of CO_2 into the rock matrix. The inclusion of CO_2 in the imbibed water could not only accelerate but also increase oil recovery from the low permeability matrix blocks in a fractured, dual permeability reservoir.

The displacement test results presented in this paper were derived from conventional laboratory displacement measurements as well as NMR experiments.

Conventional laboratory studies furnished limited information because the data was obtained from effluent flow volumes and pressure change measurements and/or material balance calculations. The laboratory displacement tests easily lend themselves to high temperature experiments.

On the other hand, changing fluid saturations inside the rock sample caused by spontaneous water imbibition was visualized and quantified by NMR analyses.[20,21] The origin, inside the sample, of oil being produced may be located by monitoring the oil saturation changes along the core samples.

III. SAMPLE PREPARATION AND LABORATORY ARRANGEMENT

Displacement tests were divided into two phases: Conventional laboratory displacements and core displacements studied by NMR. Both sets of samples were prepared using the following procedure:

- The rock was cut to one inch in diameter, and three inches in length cylinders. The total length of the core sample being studied was restricted by the length of the homogeneous magnetic field being used. Therefore, longer samples could not be used.
- A drying period of 24 hours at 120 ^{0}F was chosen to eliminate water trapped inside the rock.
- Dry weight was obtained. The volumetric method was latter used to calculate porosity values.
- The samples were measured to obtain bulk volume.
- A nitrogen permeameter was used to measure permeabilities.
- Saturation of the cores with distilled water or Deuterium Oxide (D_2O) followed these measurements. Distilled water was used for the conventional displacements while D_2O for the displacements studied by NMR. The samples were submerged in distilled water / D_2O for 24 hours and vacuum was applied until complete saturation was obtained.
- Saturated weight was obtained. Porosity was calculated using the difference between the dry and saturated weight. The density of the liquid used to saturate the sample was used to convert weight differences to porous volumes.
- An initial oil saturation was obtained by forcing oil through the samples. At least 10 pore volumes were driven through the samples to reach the maximum oil saturation possible.
- The samples were weighted again to obtain average oil saturation values.

Conventional Laboratory Studies

A high pressure core holder was placed in a controlled temperature air bath to conduct experiments at elevated temperatures and pressures. A small reservoir was indented in the core holder spacer to simulate a fracture volume adjacent to a rock matrix block face, see Figure 1. An upper and lower fluid tap were connected to the indented volume to circulate water. Flow paths are shown in Figure 2. This design simulated the interaction between the fracture system and the block matrix. A flow rate of 0.3 cc/min through the lower fluid tap refreshed the water in the indented reservoir and at the same time carried away any oil expelled by the core to the upper fluid tap. No differential pressure was applied across the rock sample. The upper fluid tap was connected to a back pressure regulator to control the fluid pressure within the system. For the carbonated water case, a mixing cylinder was placed under pressure before entering the pump that circulated fluids through the simulated fracture/matrix system. Figure 3 shows a complete diagram of the laboratory equipment setup. Porosity values of the limestone samples used for these tests varied between 22 and 26 %, with permeability values changing from 7 to 12 md, respectively.

NMR Displacement Studies

Rock samples were completely saturated with D_2O instead of fresh or salt water. Deuterium Oxide do produce a Radio Frequency (RF) signal in the presence of a magnetic field but it is out of the RF range used to conduct the studies. Therefore, the intensity of the emitted NMR signals defines the presence of an oil volume in a particular region of the core. To confirm this fact D_2O and oil saturated samples were studied. The correlation of NMR signal vs. oil volume inside the samples is seen in Figure 4. The RF signals received are directly proportional to the oil volume inside the rock samples. Contamination of the core with regular water would cause the measurements to be incorrect. The oil volume inside the sample is a measure of porosity times oil saturation, ϕS_o. A normal core saturation sequence described earlier was followed to introduce the cores to a irreducible water and oil saturation. Kerosene as well as samples of Austin Chalk oil were used in the study of the characteristics of the imbibition process.

A recently developed fiberglass core holder was used to apply NMR techniques to high pressure experiments.[1] Experiments studied by NMR were conducted at 2,000 psi.

Reference samples of known properties and saturation values were included with the core to eliminate effects introduced by the shift in NMR responses over extended periods of time. The reference samples were small disks (1/8 " in length by 1" in diameter) of the same type of rock that was used for the experiments. Reference samples were saturated following the exact same procedure as the samples used during the experiments. An epoxy coat was applied to avoid any contact with oil or water that could change its saturation values. The reference samples provided a constant signal that was used to normalize NMR responses taken at different times. This normalization could be directly done because $T_{2\,ref} = T_{2\,sam}$. If they are different a different technique has to be applied.[22]

The pressure system was gradually increased to 2,000 psi by pumping oil at very low flow rates. Overburden pressure was also gradually increased to a maximum of 2,300 psi. After the system was pressured up, a small flow (0.30 cc/min) of D_2O or carbonated D_2O was used to start spontaneous imbibition by displacing oil from the indented reservoir adjacent to the rock face. There was no pressure differential applied across the core at any time during the imbibition experiments.

A typical NMR profile is shown in Figure 5. The saturated rock sample, reference sample, and areas of pure oil are clearly identified. A spatial oil volume distribution within the rock sample is obtained by this method.

Four different types of studies were conducted: 1) unadulterated water imbibition, 2) carbonated water imbibition, 3) cyclic imbibition - blow down process, and 4) combination of the these methods.

IV. UNADULTERATED
WATER IMBIBITION STUDIES

Conventional Laboratory Displacement Tests

Temperature was the only variable changed during this set of experiments. Oil recovery increased as temperature increased. At 70 °F 15.4 % of OOIP was recovered, at 110 °F 20.3 %, and at 150 °F 23.3 % of OOIP. Imbibition experiments were conducted at 550 and 950 psi. There was no significant change in oil recoveries as a function of pressure. The increase in oil recovery was attributed to a reduction in oil viscosity caused by the increase in the system temperature, see Figure 6.

NMR Studies

Spontaneous imbibition with countercurrent oil flow was initiated once oil in the indented reservoir at the core face was replaced by D_2O. The reservoir situation simulated at this time would be a fracture filled with water adjacent to a matrix block face. NMR profiles were taken every fifteen minutes to observe and monitor oil saturation profiles.

The use of proton profiles permitted oil saturation changes inside the rock samples to be monitored. MRI responses were translated to the oil volume inside the sample, (BV/L) ϕ S_o, based on the proportionality previously shown. Small shifts in the MRI response are observed when the profiles are plotted together. All the profiles had to be normalized before any comparison. The reference sample evidenced the small shifting of the signal. Figure 7 shows changes in the signal along the reference sample - signal shifting.

The integral of the signal from the reference sample was used to normalize all the experimental data. A constant oil volume from the reference sample evidenced unrealistic changes in RF signal -NMR shifting- superimposed to changes created by the displacement process being studied. Profiles were corrected by making the integral of the signal from the reference sample equal to that of the profile taken at initial conditions, $\int_{ref\,i} = \int_{ref}$.

Subtraction of normalized profiles taken at different times during the imbibition flooding allowed to construct oil saturation profiles that evidenced the displacement of the oil inside the sample by the water front moving into the rock, see Figure 8. Notice that the oil saturation profiles have a straight line trend. This trend shows that oil being produced comes from the complete length of the sample.

Subtraction of the integral underneath the NMR profiles taken at a given time from the profile obtained under original conditions allowed to construct cumulative oil production curves. It is important to note that this method measured the amount of oil remaining in place instead of the amount of oil being produced. This fact eliminates errors introduced by counting oil adhering to the rock surface as oil still in place. The approach used to calculate changes in oil saturation and produced oil as % of OOIP is as follows:

The volume of oil inside the core sample, Oil Vol_{sam}, can be calculate from:

$$Oil\ vol_{sam} = \frac{\int_{sam} \times Oil\ vol_{ref}}{\int_{ref}}$$

Notice that Oil Vol_{sam} can be found with this technique because $T_{2\ ref} = T_{2\ sam}$. At initial conditions:

$$Oil\ vol_{sam\ i} = \frac{\int_{sam\ i} \times Oil\ vol_{ref\ i}}{\int_{ref\ i}}$$

Produced % of OOIP can be calculated from:

$$\%\ of\ OOIP = \left(\frac{Oil\ vol_{sam\ i} - Oil\ vol_{sam}}{Oil\ vol_{sam\ i}}\right) 100$$

By substituting the expressions of Oil vol_{sami} and Oil vol_{sam}, and noting that Oil $vol_{ref} =$ Oil vol_{refi}, we obtain:

$$\%\ of\ OOIP = \left[\left(\frac{\int_{sam\ i}}{\int_{ref\ i}} - \frac{\int_{sam}}{\int_{ref}}\right)\middle/ \frac{\int_{sam\ i}}{\int_{ref\ i}}\right] \times 100$$

After normalization, which means that:

$$\int_{ref\ i} = \int_{ref}$$

$$\%\ of\ OOIP = \left(\frac{\int_{sam\ i} - \int_{sam}}{\int_{sam\ i}}\right) 100$$

The proportionality of $\int_{sam}$ to ϕS_o allowed the usage of NMR profiles to calculate changes in oil saturation:

$$\Delta S_o = \frac{\phi S_{oi} - \phi S_o}{\phi S_{oi}}$$

Figure 8 shows oil saturation changes due to unadulterated water imbibition over a 900 minute span, at room temperature. Although not all the obtained profiles were plotted for clarity purposes, it is clear from Figure 8 that most of the oil is recovered at early times. The exponential trend of the water imbibition process has been discussed by other authors.[8,23-26]

V. CARBONATED WATER IMBIBITION STUDIES

The solubility of CO_2 in water is a function of pressure and temperature. Solubility of CO_2 in D_2O and the oil used for the majority of of experiments was measured. Figure 9 shows results of the solubility measurements. Solubility of CO2 in oil is significantly higher than it is in water[27] or D_2O. Salinity is also an important factor.[28-31] These changes are quite dramatic at low pressures. Water carbonation varied from 1 % to 5.5 % by weight, that is to a maximum carbonation pressure of 500 psi. Solution of CO_2 in oil creates swelling.[32] Oil expansion was also measured. Figure 10 shows the results of the test performed. Oil expands as much as 200 % of its original volume at only 500 psi carbonation pressure.

Conventional Laboratory Displacement Tests

Studies conducted at elevated pressure and temperature indicated not only increased recovery but increased recovery rate. Figure 11 represents a plot of recovery at 70, 110 and 150 °F cumulated to 48 hours. These recoveries were 26.9 %, 34.6 % and 38.0 % of OOIP respectively using 2.3 % (by weight) carbonated water. Figure 11 also shows that there is a more pronounced effect on recovery at higher temperatures, because the reducing viscosity effects of temperature and the beneficial effects of CO_2 [17] are combined.

Comparison of Figures 12 and 13 shows a considerable increase in recovery rate when the temperature of the tests was increased from 70°F to 110°F. The difference in recoveries is also pronounced when the temperature of the tests was changed from 110°F to 150°F, see Figure 14. The increase in recovery at early times is quite apparent when oil production due to unadulterated water imbibition is compared to that caused by carbonated water imbibition.

Tests were also conducted at room temperature to compare the temperature dependent effect to the carbonated water effect. The effect of carbonated water as the imbibed fluid affects ultimate recovery to a much greater degree than does temperature.

The amount of oil produced by bringing the system pressure below the carbonation pressure induced a localized gas drive which caused substantial increases in oil production.

Figures 12 and 13 also show the effect on recovery when the operating pressure is reduced below the bubble point of the carbonated water. A solution gas drive effect was installed. Although the increase in temperature diminishes the ability of water to dissolve CO_2, increases in temperature provided enhanced oil recoveries. Figure 15 summarizes all the beneficial effects for unadulterated and 2.3 % carbonated water. It is important to note that although gas availability for the blow down effect decreases as temperature increases, oil recovery slightly increased at high temperature. Less viscous oil requiring less driving gas to be expelled could cause this effect. Oil recovery by the induced solution drive method is seen to be proportional not only to the amount of CO_2 dissolved into the imbibing water but also to the temperature.

A slow pressure depletion was attempted with no increase in oil recovery. Gas being evolved by this method forces oil, and water, out of the porous space only if the amount of gas evolving exceeds the maximum escaping velocity of the gas. Pressure decline rate is an important factor in establishing the number of gas bubbles formed.[33] It is reasonable to believe that the minimum speed of depletion would be directly proportional to the ability of the matrix rock to conduct gas -relative permeability to gas.

Other important factor was permeability increase due to the acidic nature of the CO_2 - enriched mixture. Carbonated water enlarged the existing pores and pore throats, increasing rock permeability as much as 20.33 % over the original permeability values.

NMR Studies

The same experimental procedure used for unadulterated water imbibition was applied to the carbonated water imbibition tests. Oil saturation profiles of initial and after imbibition conditions are shown in Figure 16. Subtraction of oil saturation profiles showed that oil located near the rock surface was being more easily produced. Cumulative oil production due to water imbibition follows an exponential trend.[7,23-26] Conventional and NMR observations suggest that cumulative oil production caused by carbonated water imbibition also follows an exponential trend that can be fitted by Aronofsky's equation[23] and the dimensionless equation introduced by Kazemi.[24]

The system pressure (2,000 psi) was reduced to atmospheric pressure in order to force the dissolved gas to evolve out of solution. Comparison purposes required repressurization of the system to its original value. Compressibility effects would had mask possible results should it had been done otherwise. Figure 17 compares the oil saturation profiles before and after the blow down was induced. Comparison of the two profiles evidences that the origin of the oil produced by the induced solution gas drive is from a region very close the the imbibing face. Figures 17 and 18 evidence other important factor: oil swelling. Behind the gas drive swept region, when CO_2 dissolved into the indigenous oil was discharged by the blow down effect, oil swelled by CO_2 absorption returned to its original volume and the created void space was filled by oil, and water, being driven from the front of the sample. This effect provided an indirect measurement of oil swelling. Production due to oil swelling was not nearly as high as that due to solution gas drive.

Gas produced through the face of the sample also had the beneficial effect of removing oil adhering to the surface of the sample. Figure 17 shows the disappearance of the spike created by the oil droplets adhering to the surface of the sample. Oil production caused by this effect was not considered to construct the presented cumulative oil production curves, but it is significant when total production is calculated. Removed oil from the face of the rock -fracture cleaning- was not quantified, but oil produced due to fracture cleaning reached similar proportions to that produced from the rock matrix by water imbibition.

Subtraction of NMR profiles obtained during the run permits the changes in the oil saturation values over time to be compared. Note in Figure 18 the dramatic change in saturation when blow down was instituted and also the near face change as compared to the imbibition process itself.

Samples of Austin Chalk oil were also used in a series of experiments. Oil recovery increased from 10 % to almost 16 % of OOIP even before concluding production when a 38.9 °API Austin Chalk oil was used. Figure 19 shows an increased oil recovery from 7 % to 20 % when a 39.6 °API Austin Chalk oil was used.

The substantial increase in oil recovery at the end of the carbonated water imbibition due to the induced solution gas drive effect led in an attempt to use of this convenient property in a cyclic manner.

Carbonated water imbibition was allowed for a period of time to establish a definite trend in the cumulative oil recovery curve. The system pressure was instantaneously dropped below the CO_2 mixing pressure and brought back to the initial 2,000 psi.

Subtraction of oil saturation profiles from the original conditions profile allowed the movement of oil relative to its original position in the core to be observed. The time needed to recover similar amounts of oil was reduced to nearly one third of the time required when unadulterated water imbibition was applied. Figure 20 compares rate of recovery by different displacement processes for a particular rock sample.

Gas evolving inside the sample and forcing oil out of the sample left an additional oil bank close to the surface of the rock. Figure 21 evidences this fact, which is especially evident after the second gas expansion cycle. CO_2 tends to strip the light components of the oil, leaving the heavier ends in place. Less mobile oil, could create the oil bank seen in Figure 20. Composition analysis of the produced oil and the oil forming the observed oil bank is being continued.

A carbonated water imbibition flood was also attempted after an adulterated water imbibition had taken place. A 39.6 °API Austin Chalk oil was used. Oil production due to unadulterated water imbibition reached 7 % of OOIP. After oil production was negligible, water in contact with the rock was substituted by CO_2 - enriched water. Rate of recovery and ultimate oil recovery were drastically increased, see Figure 22. Although the complete exponential trend was not obtained, oil recovery was increased from 7 to 24 % of OOIP. Two short blow down cycles were also attempted, oil production increased from 24 % to 28 % of OOIP during the first cycle, and from 28 to 31 % of OOIP during the second cycle. It is important to note that after these cycles are attempted, the production rate is drastically decreased or nullified, and the cyclic manner has to be used afterwards if any additional oil is to be produced.

VI. CONCLUSIONS

- NMR imaging has shown that there are significant changes in oil saturation within short distances from the imbibing face. This fact is specially apparent after the blow down effect. Therefore, the superficial nature of carbonated water imbibition prevent small rock samples imbibing from all faces to be representative of any reservoir situation.

- Decrease in the system pressure bellow the CO_2 mixing pressure creates a gas drive that contributes significantly to oil production.

- Cumulative oil production due to carbonated water imbibition can be described by an exponential equation of the form suggested by Aronofsky and Natanson, and Kazemi and Gilman.[22,23]

- The laboratory studies suggest that most of the CO_2 is being kept close to the rock face and dissolved into the indigenous fluids. Produced oil may carry some of the dissolved CO_2 out of the sample. At the present time it appears that only marginal quantities of CO_2 are being carried deep into the rock sample.

- Oil swelling contributes to oil production but its contribution seems to be small compared to the mechanism of enhancing oil mobility by mobilizing the light components of the oil. Previous work shows the more moveable oil bank is created when CO_2 strips the light components of the original oil in place.[34]

- The creation of an oil bank by the induced gas drive suggests that: 1) the oil not removed might have a different composition, 2) additional evolving gas is needed to remove the oil left behind, or 3) a combination of the two previously mentioned

effects. This fact would confirm that CO_2 is striping the light ends of the hydrocarbon present, leaving the less movable components behind. More detailed studies are needed in order to clarify this effect.

- Loss of CO_2 entrained in the carrier water moving into the sample prevented complete utilization of its beneficial effects to maximize oil recovery efficiency. A decrease in oil saturation was obtained along the complete core, but the most drastic decrease was observed only close to the surface of the rock.

- A combination of CO_2 - enriched water imbibition and pressure depletion created a cyclic type of recovery. This method combined the beneficial effects of CO_2 at early times of the process, and the increase in oil production due to the localized gas drive observed after pressure depletion.

VII. NOMENCLATURE

BV	=	Bulk volume
D	=	Rock sample diameter
ϕ	=	Rock porosity
k	=	Absolute permeability
K_o	=	Oil permeability
L	=	Rock sample length
Oil vol$_{sam}$	=	Volume of oil inside the rock sample
Oil vol$_{ref}$	=	Volume of oil inside the reference sample
OOIP	=	Original Oil In Place
q_w	=	Water flow rate
S_o	=	Oil saturation
S_{oi}	=	Oil saturation at initial conditions
$T_{2\ ref}$	=	Spin-spin relaxation time of the reference sample
$T_{2\ sam}$	=	Spin-spin relaxation time of the sample
V_o	=	Oil Volume
$\int_{ref}$	=	Integral underneath NMR profile of reference sample
ΔS_o	=	Change in oil saturation
$\int_{sam}$	=	Integral underneath NMR profile of sample
$\int_{sam\ i}$	=	Integral underneath NMR profile of sample, at initial conditions

VIII. ACKNOWLEDGEMENTS

IX REFERENCES

1   Perez, J., Poston, S.W., and Sharif, Q: "Carbonated Water Imbibition Flooding - An Enhanced Oil Recovery Process for Fractured Reservoirs," paper SPE 024164

presented SPE/DOE Eighth Symposium on Enhanced Oil Recovery held in Tulsa, Oklahoma, April 22-24.

2. Kleppe, J., and Morse, R.A.: "Oil Production from Fractured Reservoirs by Water Displacement," paper SPE 5084 presented at the 1974 SPE-AIME Annual Fall Technical Conference and Exhibition, Houston, TX, October 6-9.

3. DeSwaan, A.: "Theory of Waterflooding in Fractured Reservoirs", *SPEJ* (April 1978) 117-122.

4. Davis, G.B., and Hill, J.M.: "Some Theoretical Aspects of Oil Recovery from Fractured Reservoirs," *Trans., I. Chem. E.* (1982) **60**, 352-358.

5. Sonier. F., Souillard, P., and Blaskovich, F.T.: "Numerical Simulation of Naturally Fractured Reservoirs," *SPERE* (Nov. 1988) 1114-1122.

6. Brownscombe, E.R., and Dyes, A.B.: "Water-Imbibition Displacement... Can it Release Reluctant Spraberry Oil?," *Oil and Gas J.* (Nov. 17, 1952) 264-265.

7. Beliveau, D and Payne, D.A.: "Analysis of the Waterflood Response of a Naturally Fractured Reservoir," paper SPE 22946 presented at the 66th Annual Technical Conference, Dallas, October 6-9, 1991.

8. Graham, J.W., and Richardson, J.G.: "Theory and Application of Imbibition Phenomena in Recovery of Oil," *Trans.*, AIME (1959) **216**, 377-381.

9. Blair, P.M.: "Calculation of Oil Displacement by Countercurrent Water Imbibition," paper SPE 1475-G presented at the 1960 SPE Fourth Biannual Secondary Recovery Symposium, Wichita Falls, TX, May 2-3.

10. Parsons, R.W., and Cheney, P.R.: "Imbibition Model Studies on Water-Wet Carbonated Rocks," *SPEJ* (March 1966) 26-34.

11. Kyte, J.R.: "A Centrifuge Method to Predict Matrix-Block Recovery in Fractured Reservoirs," *SPEJ* (June 1970) 164-70.

12 Graham, J.W., and Richardson, J.G.: "Theory and Application of Imbibition Phenomena in Recovery of Oil," *Trans.*, AIME (1959) **216**, 377-381.

13. Pirson, S. J.: "Tertiary Recovery of Oil," Paper presented before the Central Appalachian Section, AIME (June 26, 1941)

14. Whorton, L. P., Brownscombe, E. R., and Dyes, A. B.: "A Method for Producing Oil By Means of Carbon Dioxide," U.S. Patent No 2,623,596 (1952).

15. MacFarlane, R. M., Breston, J. N., and Neil, D. C.: "Oil Recovery from cores When flooded with Carbonated Water and Liquid Gas," *Producers Monthly* (Nov. 1952) **17**, 23-25.

16. Holm, L, W., and Josendal, V. A.: "Mechanism of Oil Displacement by Carbon Dioxide," *Trans.*, AIME (1974) 1427.

17. Miller, J. A., and Jones, R. A.: "A Laboratory Study to Determine Physical Characteristics of Heavy Oil after CO_2 Saturation," paper SPE 9789 presented at

the 2nd Joint SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, April 5-8, 1981.

18. Chung, F.T.H, Jones, R.A., and Nguyen, H.T.: "Measurements and Correlations of the Physical Properties of CO2-Heavy Crude Oil Mixtures," paper SPE 15080 presented at the 56th Regional California SPE Meeting, Oakland, April 2-4, 1986.

19. Latil, M.: *Enhanced Oil Recovery*, Gulf Publishing, Houston, TX (1980).

20. Vinegar, H.J.: "X-RAY CT and NMR Imaging of Rocks", *JPT* (March 1986) 755-60.

21. Edelstein, W.A., Vinegar, H.J., Roemer, P.B., and Mueller, O.M.: "NMR Imaging for Core Analysis", paper SPE 18272 presented at the Annual Technical Conference and Exhibition, Houston, TX, Oct. 1988.

22. Chang, C.T., Robinson, J.W., and Edwards, C.M.: "An Agarose Gel Reference Standard For Use In MRI Determination of Porosity and Fluid Saturations in Porous Media", *Engineering Imaging Laboratory Research Report 90-01*, Texas A&M University, College Station, TX, Feb. 1991.

23. Aronofsky, J.S., Masse, L., and Natanson, S.G.: "A Model for the Mechanism of Oil Recovery from a Porous Matrix Due to Water Invasion in Fractured Cores," *Trans.*, AIME (1958) **213**, 17-19.

24. Kazemi, H., Gilman, J.R., and El-Sharkaway, A.M.: "Analytical and Numerical Solution of Oil Recovery from Fractured Reservoirs Using Empirical Transfer Functions," paper SPE 19849 presented at the 1989 SPE Annual Technical Conference and Exhibition, San Antonio, TX, Oct. 8-11.

25. Mattax, C.C., and Kyte, J.R.: "Imbibition Oil Recovery from Fractured, Water-Drive Reservoirs," *JPT* (June 1962) 177-184.

26. Scheidegger, A.E.: *The Physics of Flow Through Porous Media*, The Macmillan Co., New York, N.Y. (1960)

27. Dodds, W. S., Stutzman, L. F., and Sollami, B. J.: "Carbon Dioxide Solubility in Water," *J. Ind. and Eng. Chem.* (1956) **1**, 92-95

28. Holm, L. W.: "CO_2 Requirements in CO_2 Slug and Carbonated Water - Oil Recovery Processes," *Producers Monthly* (Sept. 1963) 6-28.

29. Crawford, H. R., Neill, G. H., Bucy, B. J., and Crawford, P. B.: "Carbon Dioxide - A Multipurpose Additive for Effective Well Stimulation," *JPT* (March 1963) 237-242.

30. Johnson, W. E. MacFarlane, R. M., and Breston, J. N.: "Changes in Physical Properties of Bradford Crude Oil When Contacted with CO_2 and Carbonated Water," *Producers Monthly* (Nov. 1952) 16.

31. Martin, J. W.: "Additional Oil Production through Flooding with Carbonated Water," *Producers Monthly* (July 1951) 18-23.

32   Miller, J. A., and Jones, R. A.: "A Laboratory Study to Determine Physical Characteristics of Heavy Oil after CO_2 Saturation," paper SPE 9789 presented at the 2nd Joint SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, April 5-8, 1981.

33.   Stewart, C.R., Hunt Jr., E.B., Scheneider, F.N., Geffen, T.M., and Berry Jr.,V.J.: "The Role of Bubble Formation in Oil Recovery by Solution Gas Drive in Limestones," paper presented at the Fall Meeting of the Petroleum Branch, American Institute of Mining and Metallurgical Engineers, in San Antonio, Texas, October 17-20, 1954.

34.   Bahralolom, I.M., and Orr Jr., F.M.: "Solubility and Extraction in Multiple-Contact Miscible Displacements: Comparison of N_2 and CO_2 Flow Visualization Experiments," paper SPE 15079.presented at the 56th Regional California SPE Meeting, Oakland, April 2-4, 1986.

Oil $\longrightarrow$ **Water**
$\longleftarrow$

q_w
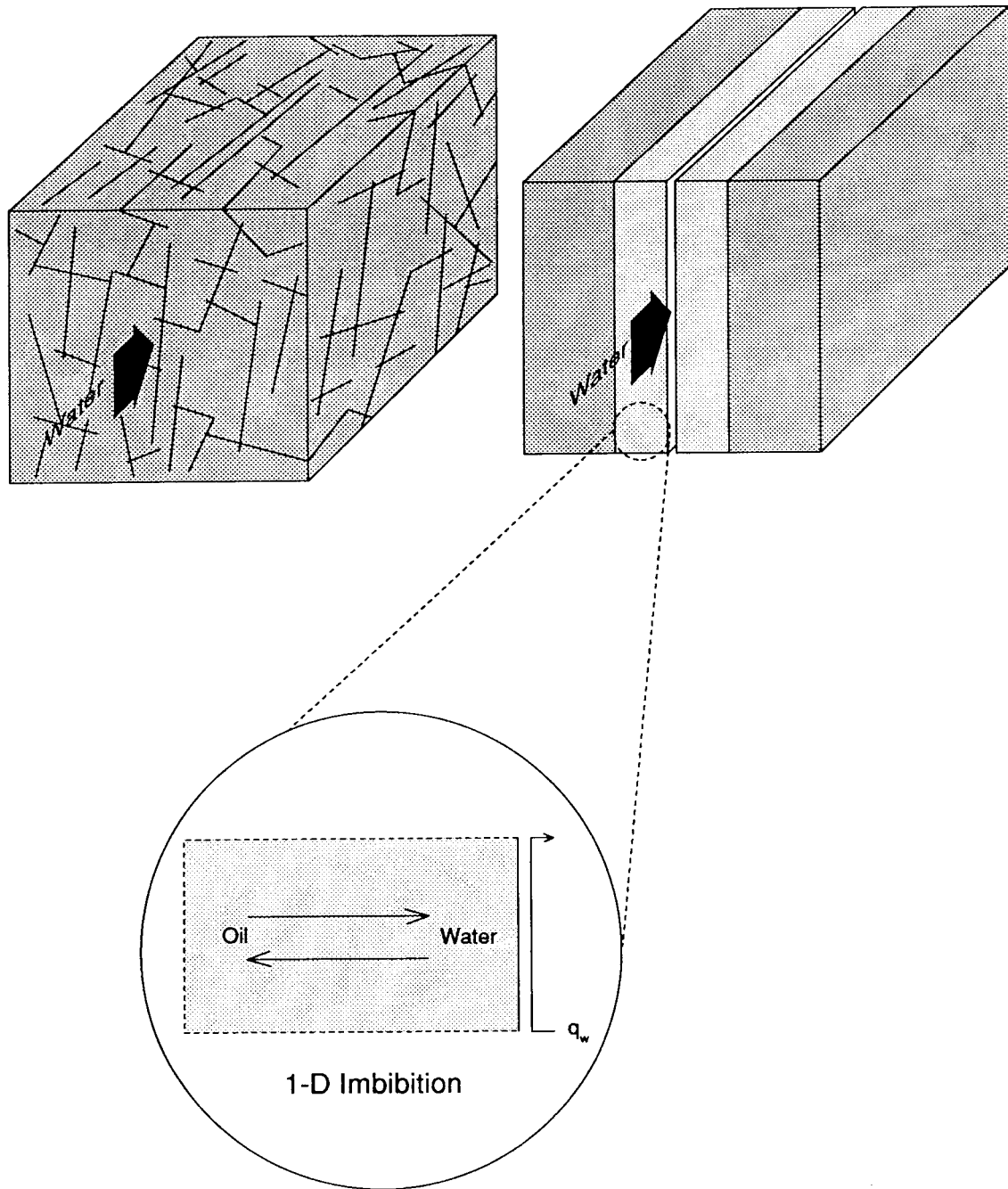
1-D Imbibition

Figure 1. A one - dimensional imbibition process can be visualized within a short distance from the water imbibing surface.
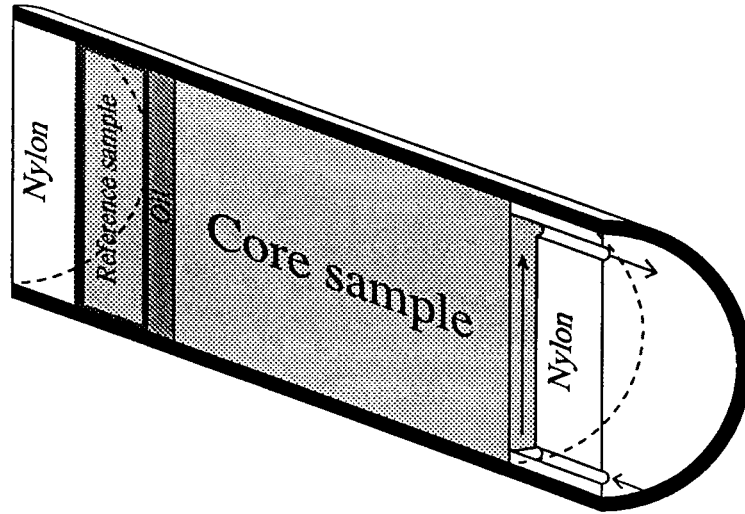
Figure 2 Layout of the core sample and flow path.
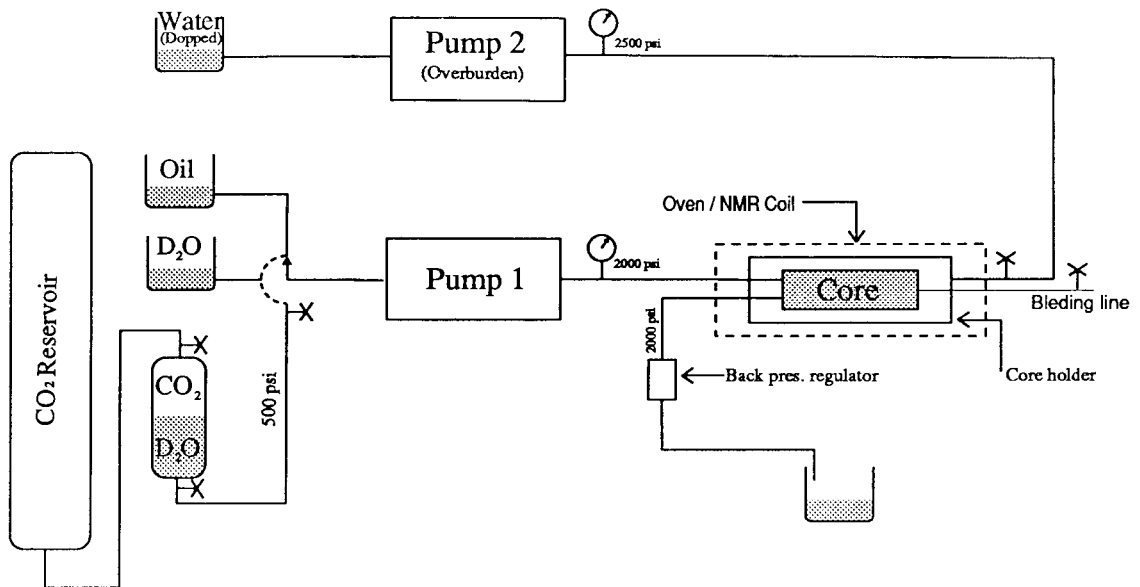
Figure 3 Laboratory diagram of the system used to run conventional laboratory and MRI imbibition experiments.
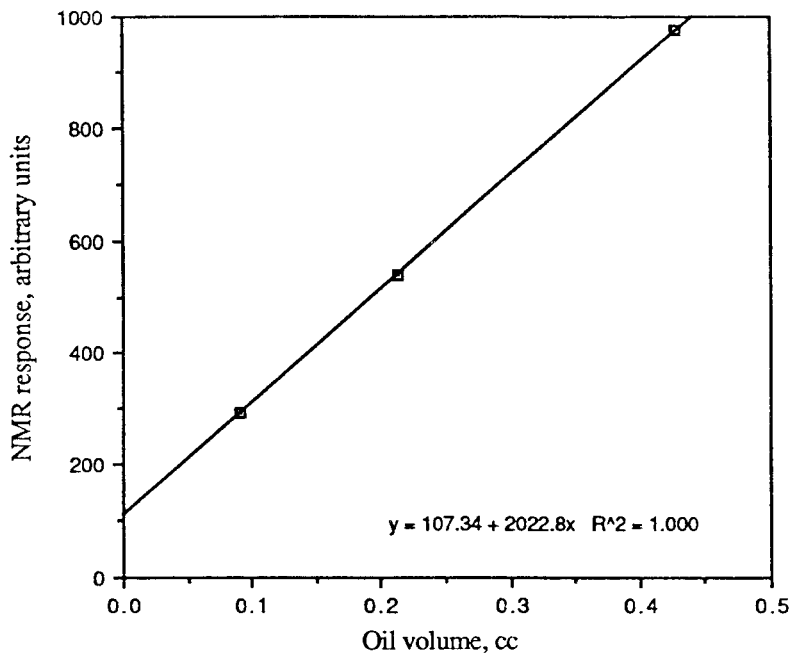
Figure 4. NMR correlation for different samples tested.

$y = 107.34 + 2022.8x \quad R^2 = 1.000$
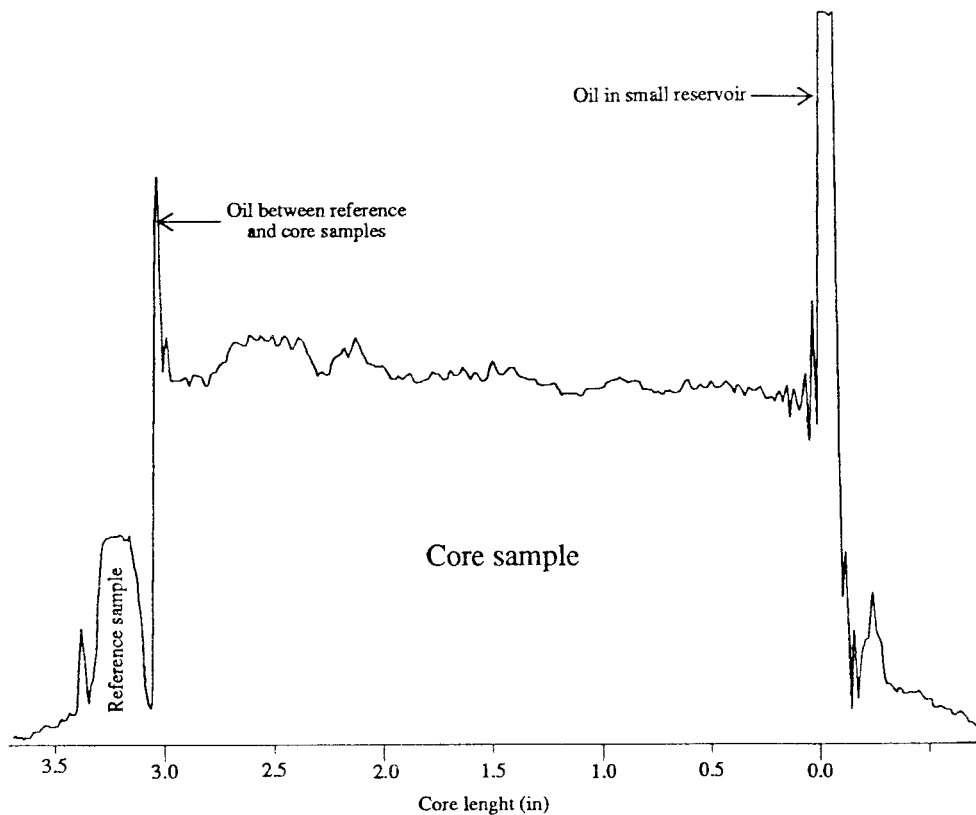
Figure 5. Typical proton profile obtained from MRI. Reference and core samples are clearly identified.
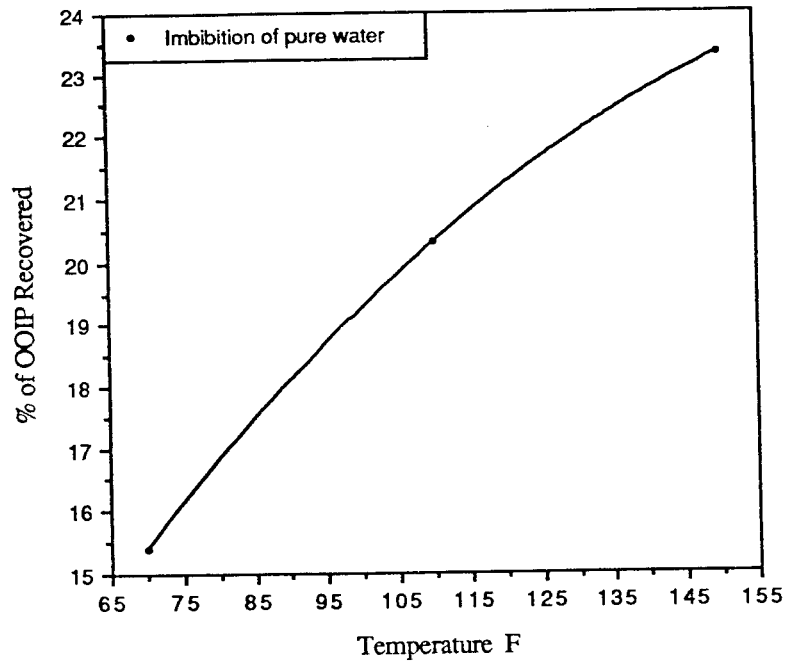
Figure 6. Unadulterated water imbibition. Oil recovery increase caused by increase in temperature.
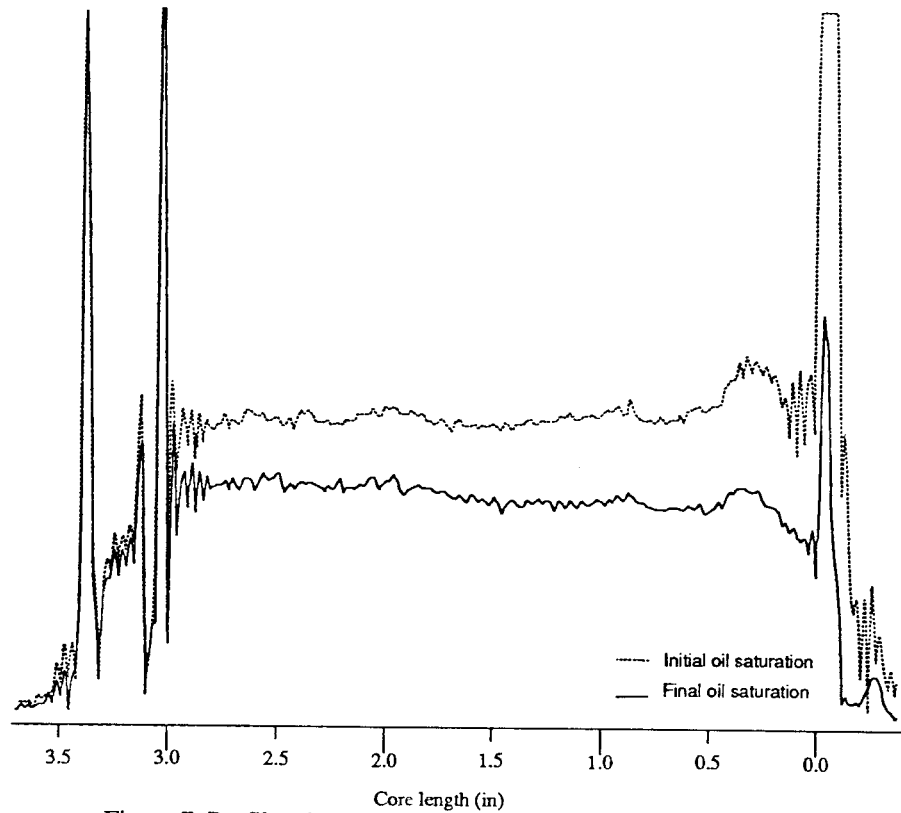
Figure 7 Profile taken at initial and final oil saturation. The use of a reference sample evidenced the small shifting of the signal.
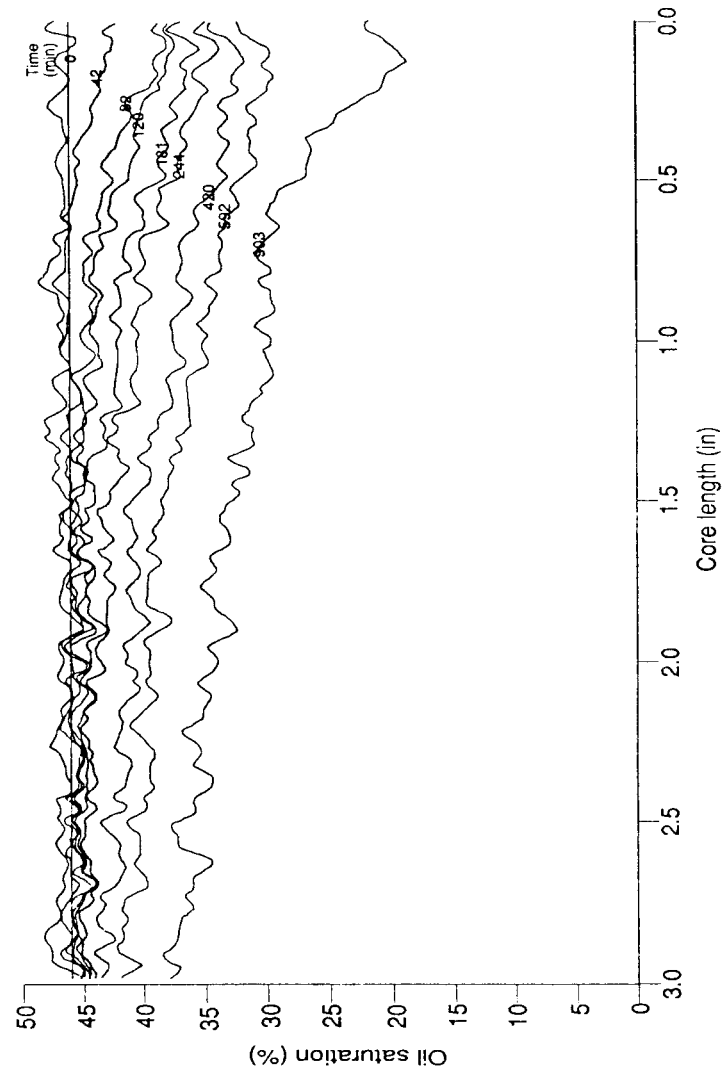
Figure 8. Oil saturation changes as a function of time. Unadulterated water case.
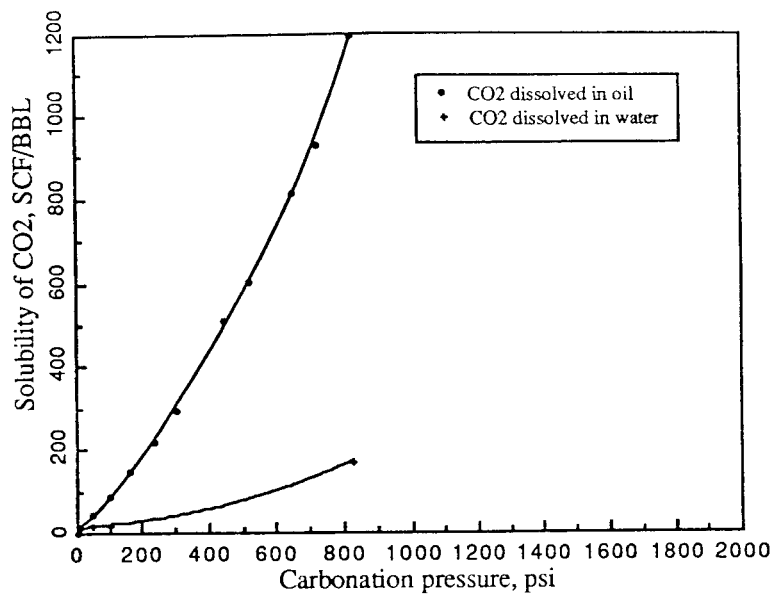
Figure 9. Solubility of carbon dioxide in oil and D_2O.
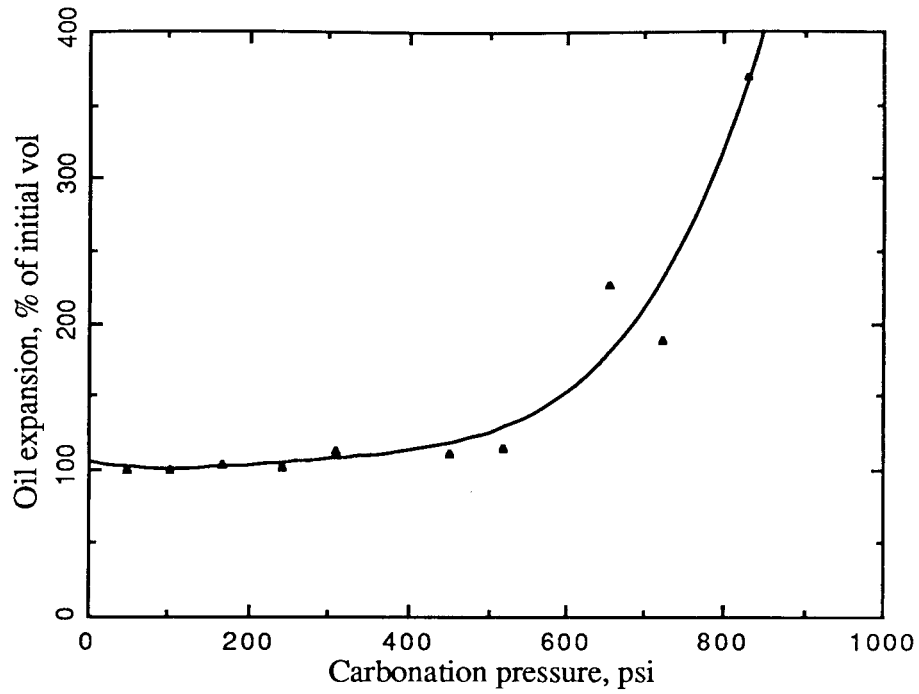
Figure 10. Oil expansion due to the solution of carbon dioxide.
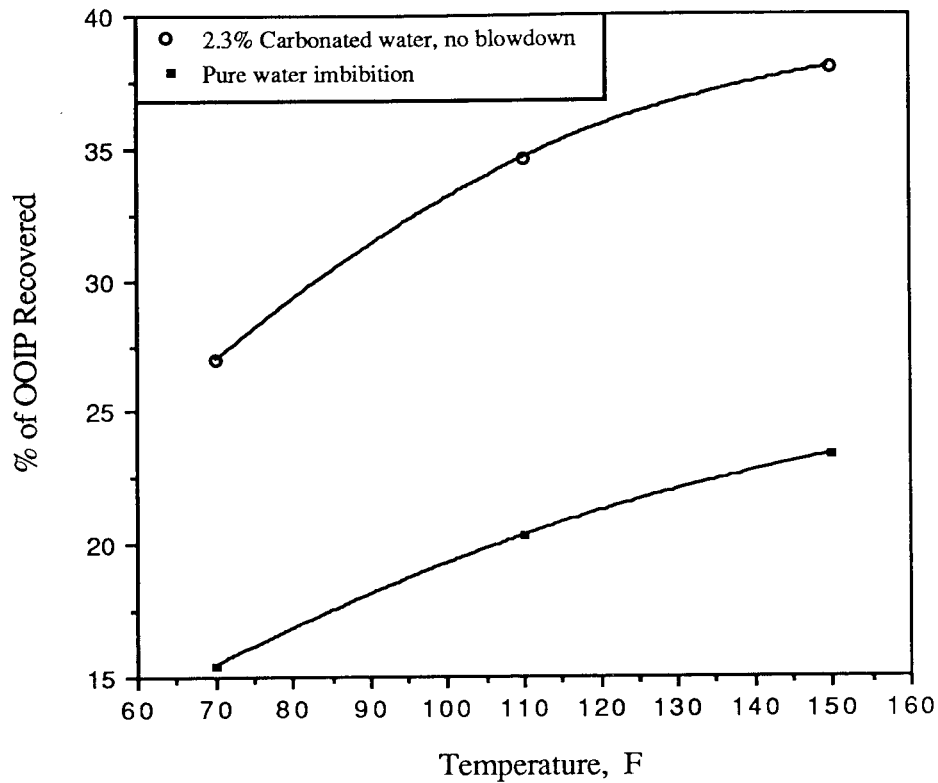
Figure 11. Comparison of oil recovery due to pure and carbonated water imbibition as a function of temperature.

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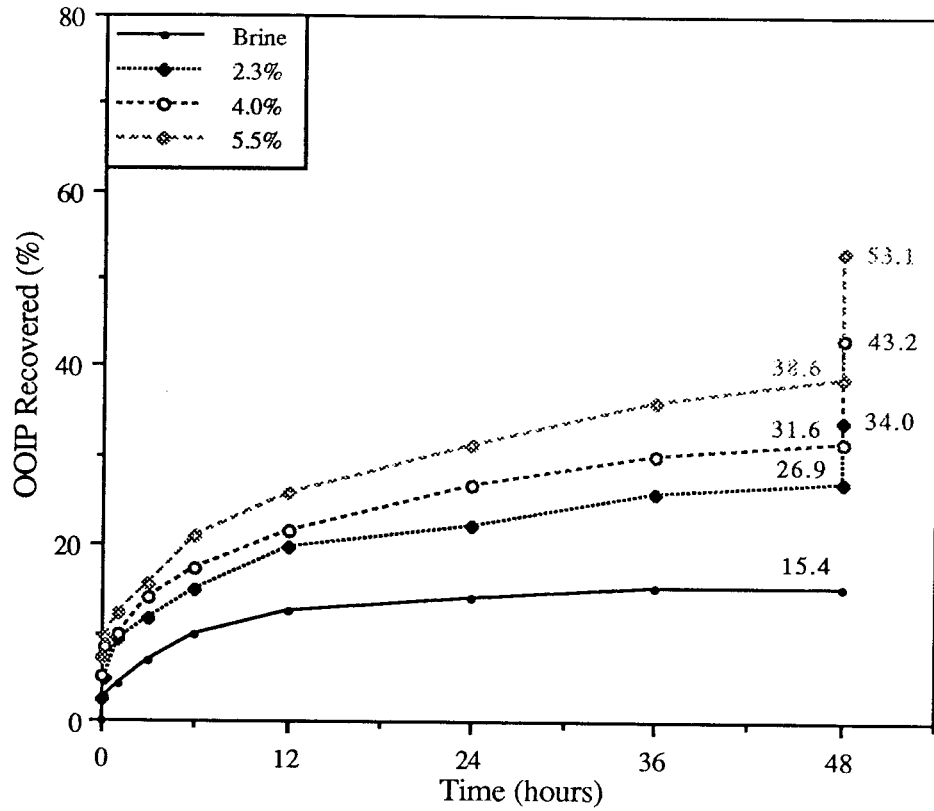
Figure 12. Oil recovery increases due to carbonated water imbibition at 70 °F.
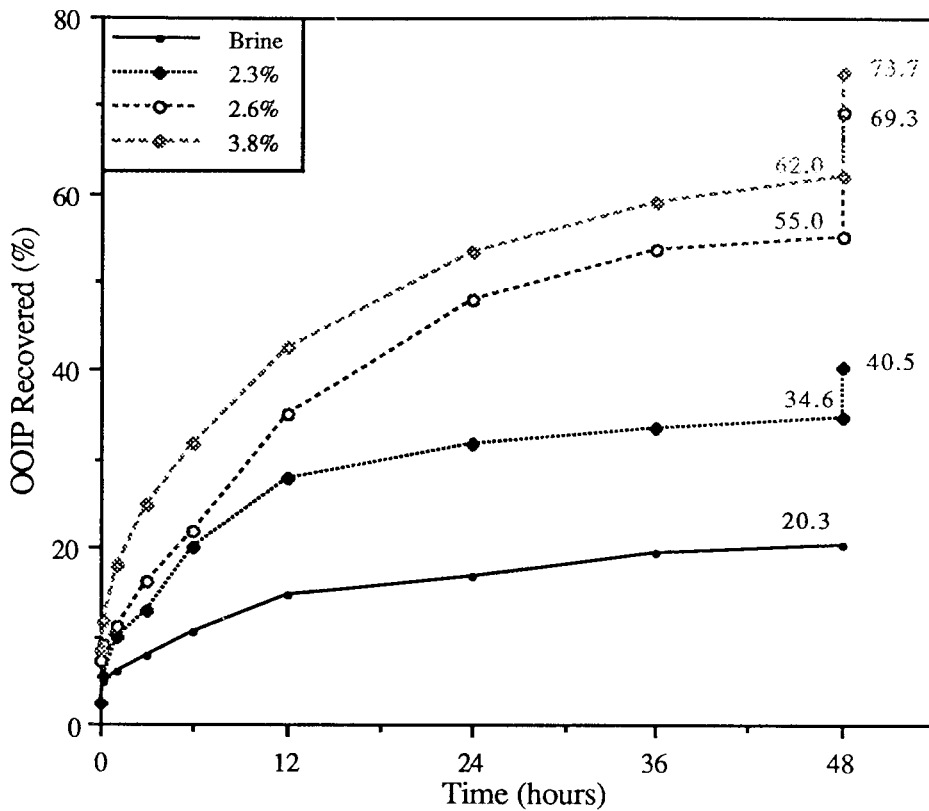
Figure 13. Oil recovery increases due to carbonated water imbibition at 110 °F.
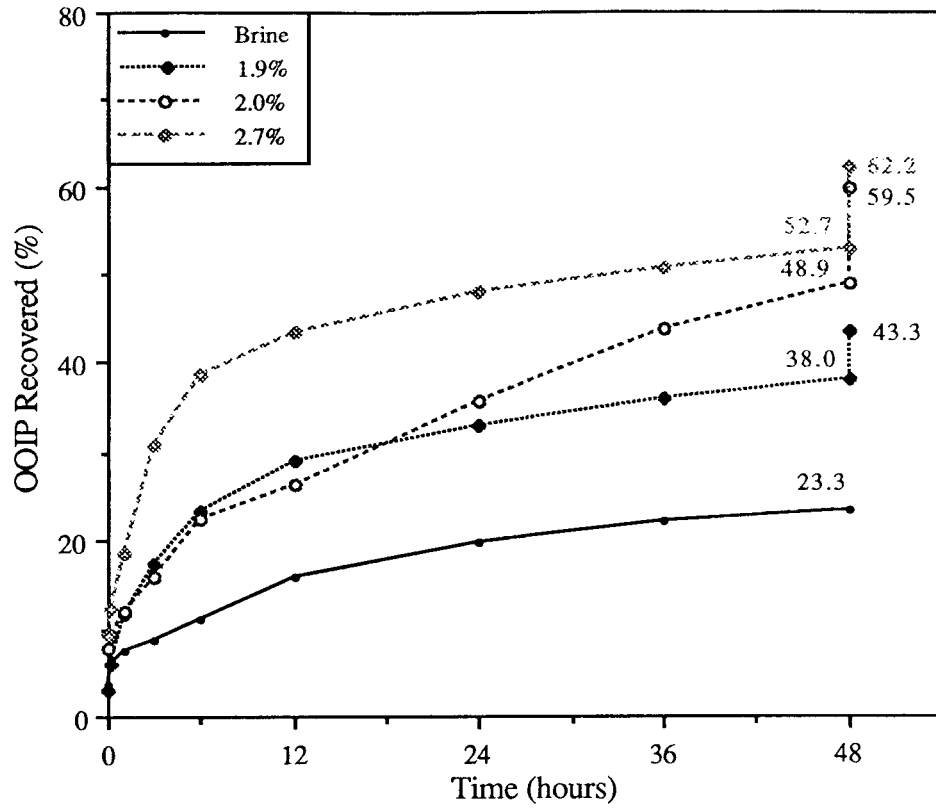
Figure 14. Oil recovery increases due to carbonated water imbibition at 150 °F.
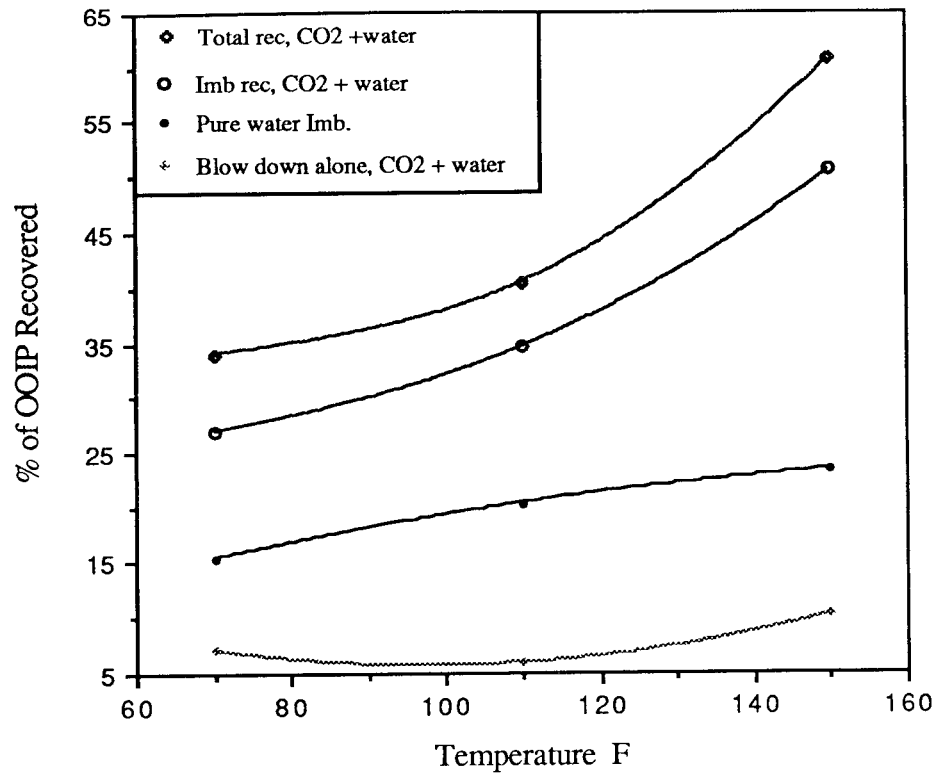
Figure 15. Comparison between pure water and carbonated water imbibition.
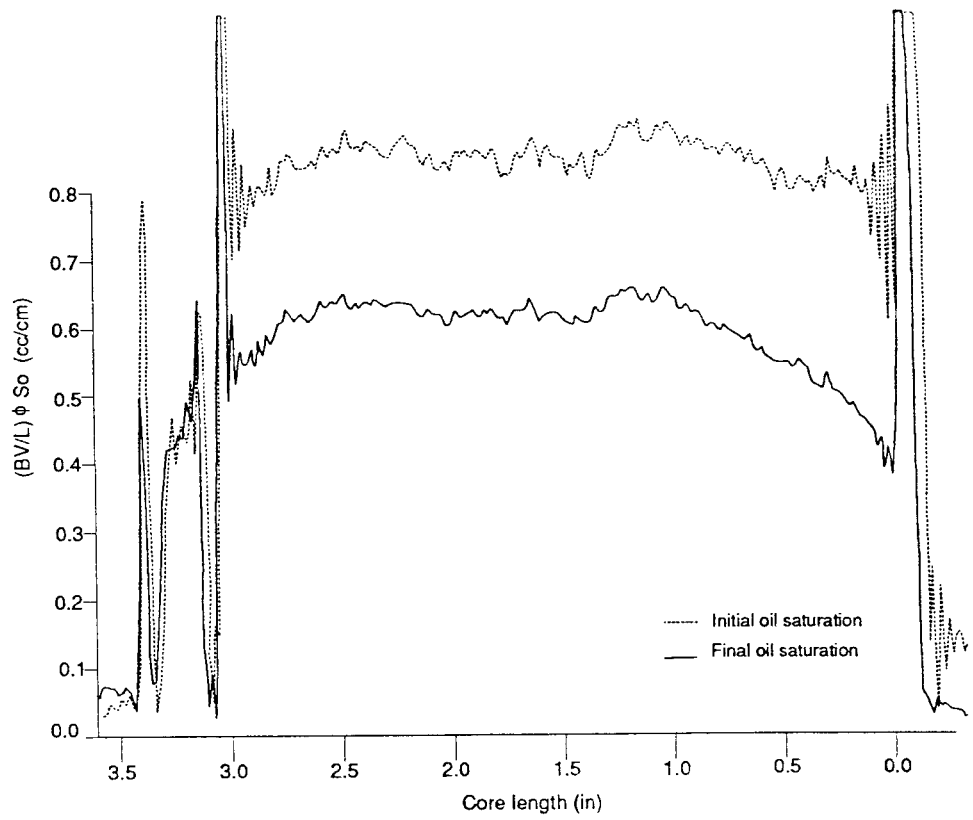
Figure 16. Oil saturation profile taken at initial and after 835 minutes of imbibition conditions. After normalizing the signal, comparisons of the profiles can be done.
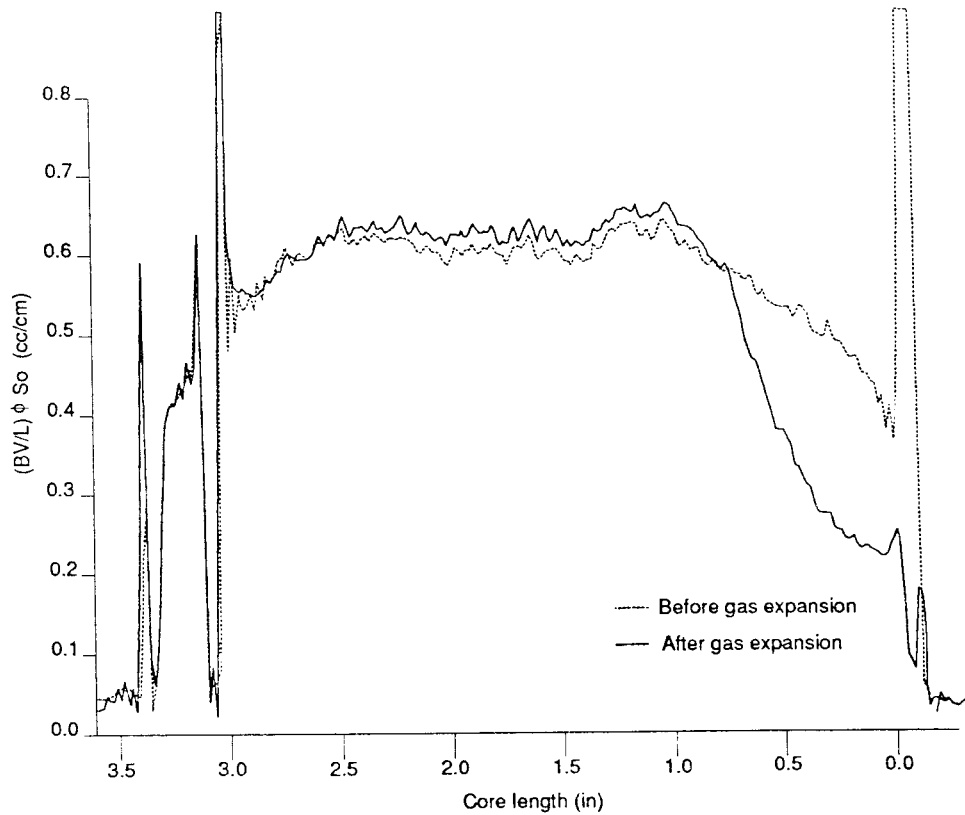
Figure 17. Oil saturation profile taken before and after the expansion of the CO_2 dissolved into the imbibed water.

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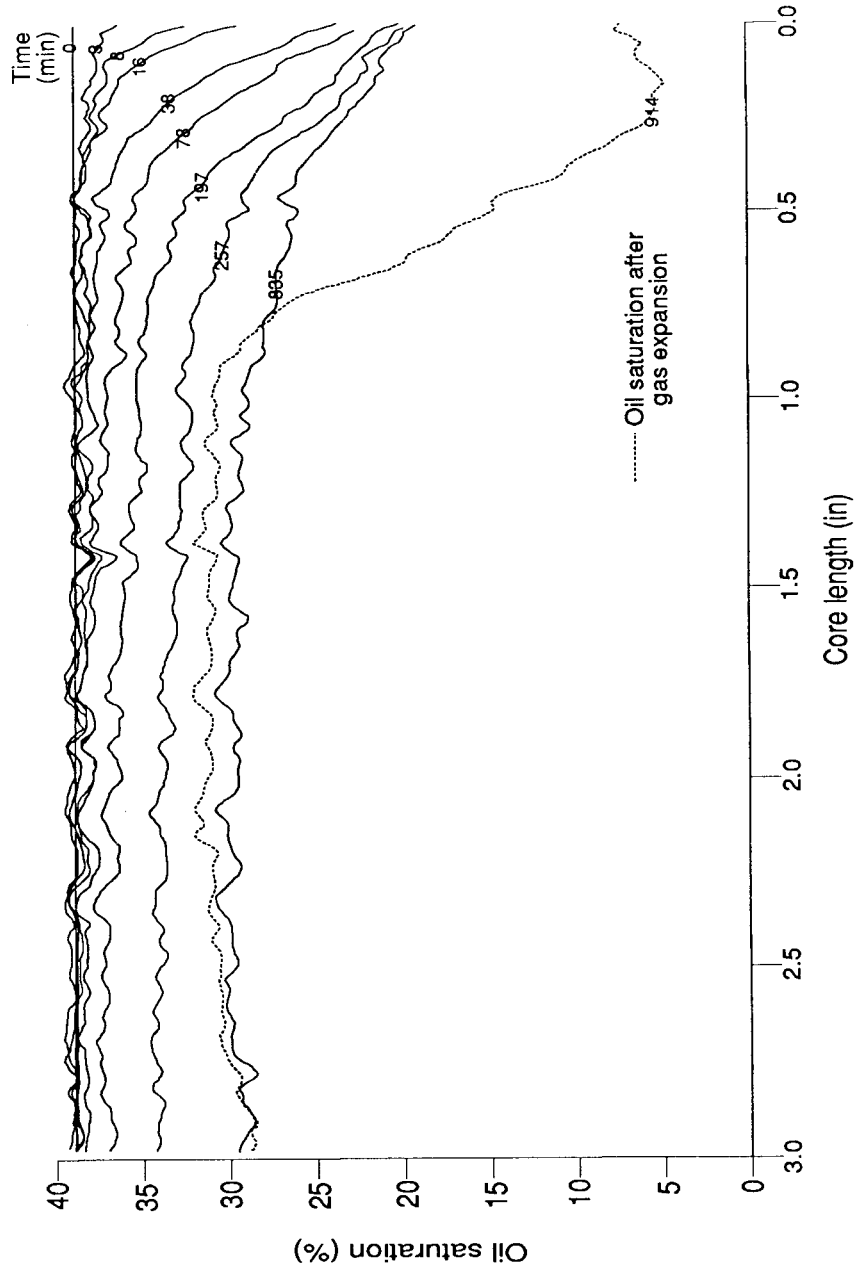
Figure 18. Oil saturation changes as a function of time. Carbonated water case.
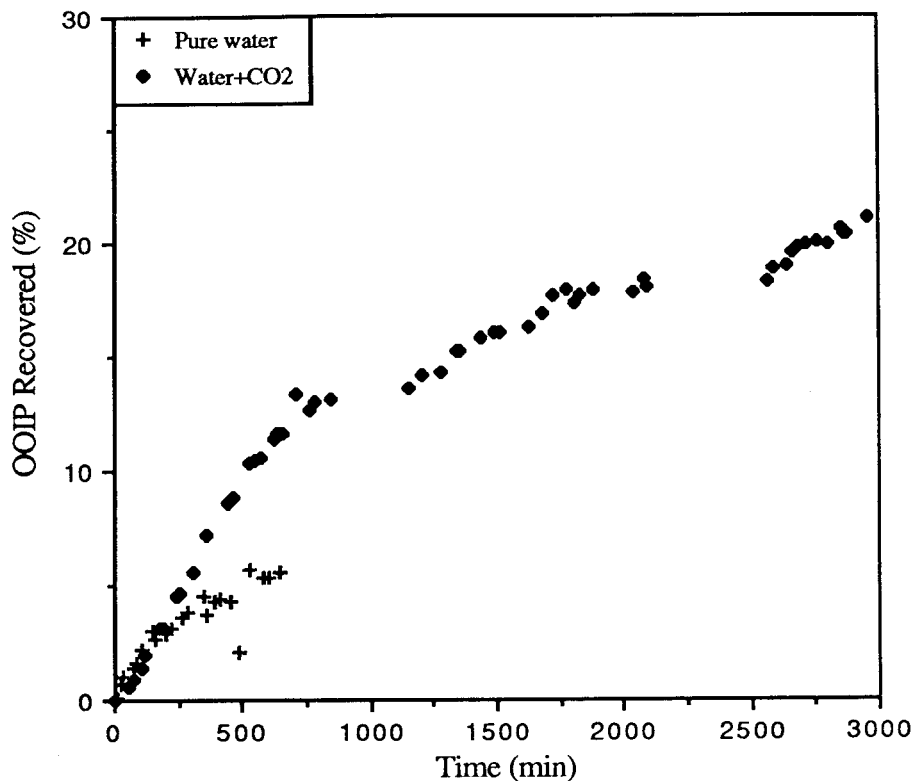
Figure 19. Comparison of cumulative oil production due to unadulterated and carbonated water imbibition. A 39.6 °API Austin Chalk oil was used.
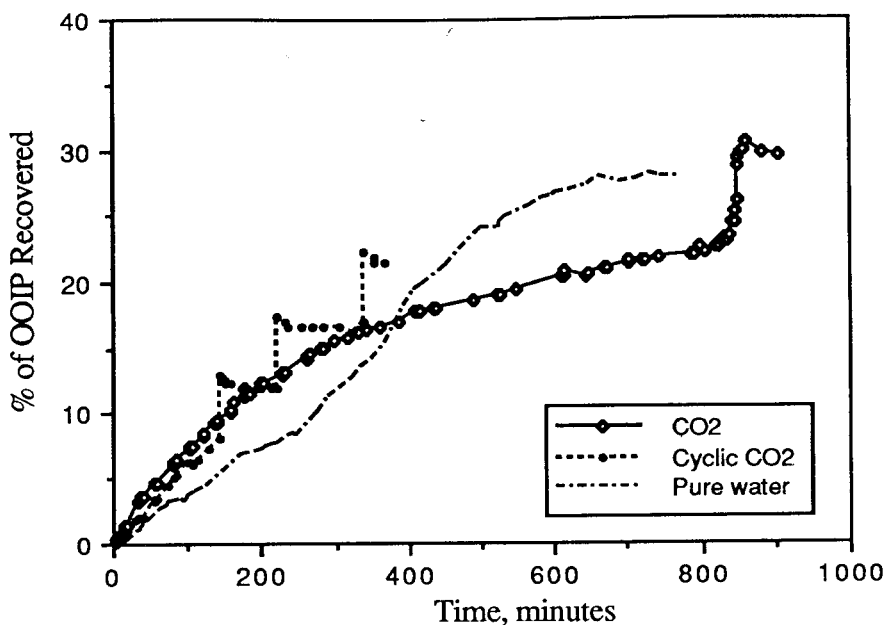

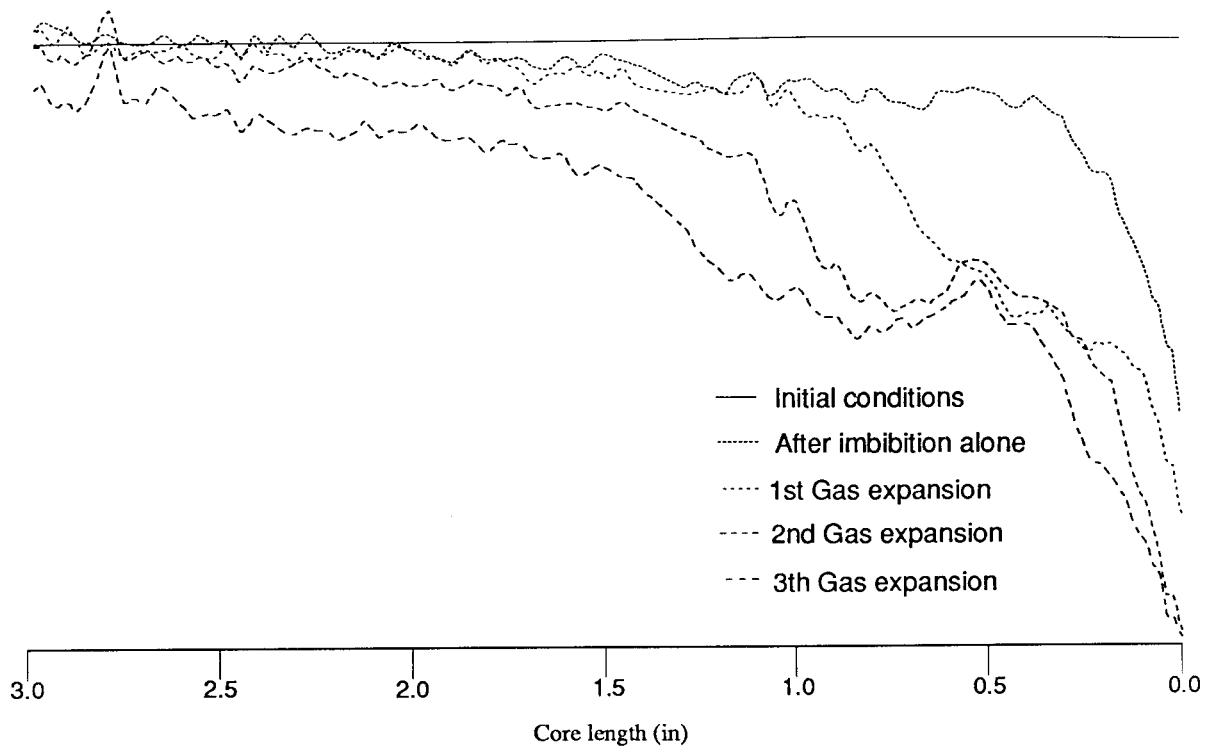Figure 20. Comparison of cumulative oil production using pure and carbonated water.

Figure 21. Oil saturation profiles showing conditions at different stages relative to the initial conditions.
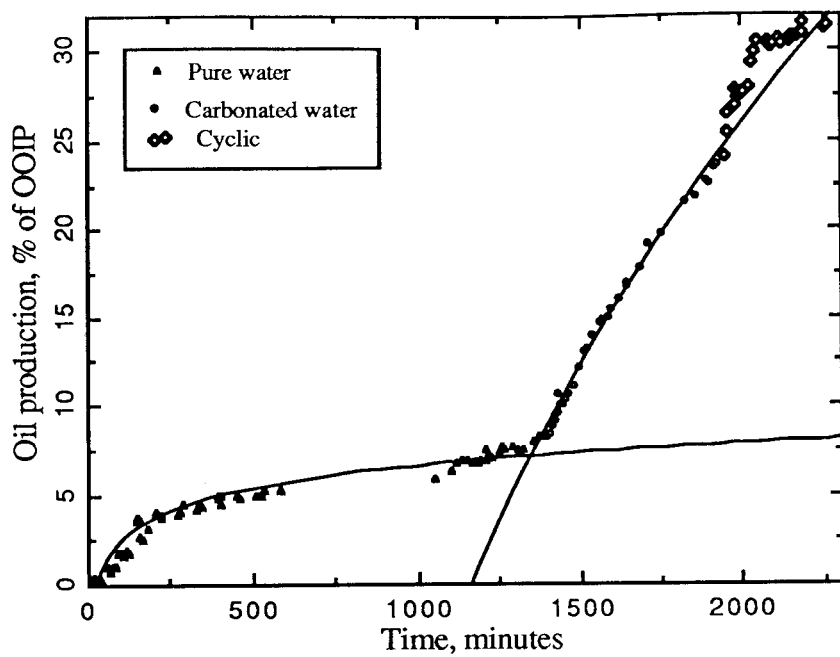

Figure 22. Oil recovery caused by different imbibition methods.