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CARBON DIOXIDE FOR THE RECOVERY OF (RESIDUAL)
CRUDE OIL

Final Report

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FINAL REPORT

March 1983

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FIGURES 1 THROUGH 16 FOLLOW IN SEQUENCE.

I. INTRODUCTION

This is the final report for the United States Department of Energy Contract EY-76-S-03-0113, "Carbon Dioxide for the Recovery of Crude Oil" at the University of Southern California under the direction of Professor Todd M. Doscher.

The original plan of the work was altered with the agreement of the various contract officers from that of emphasis on the use of additives in improving the efficiency of carbon dioxide to a plan for developing a thorough understanding of the mechanism and basic efficiency of carbon dioxide as a recovery agent for residual crude oil.

It is the residual crude oil, the oil remaining after waterflooding, which is the valid target for enhanced oil recovery processes. High fractions of the original high gravity oil in place in a reservoir can be economically produced by the application of good conventional primary and secondary (primarily, waterflooding) operating practices. It is for the recovery of the residual oil after waterflooding for which there is a need for new technology.

As this program proceeded, the results obtained from the physical model studies were not those anticipated from prior theoretical studies and laboratory experiments which had not been physically scaled. This required that the work be continued to no more than define and establish as unequivocally as possible the actual mechanism by which carbon dioxide might recover some of the reputed hundreds of billions barrels of residual oil in reservoirs in the United States. Only in this way could a proper evaluation of the potential of the process be defined and hopefully, subsequently, improved.

The work has now been completed and leads to the conclusion that the recovery of residual oil by carbon dioxide depends on solution of the carbon dioxide in the oil and the displacement of the resulting solution by the continuing gas drive, or, alternately, a substitute water drive. The efficiency of the process will depend on the diffusion of carbon dioxide into the residual oil prior to the breakthrough of the latter and the residual oil phase saturation to the concurrent gas drive.

II. SUMMARY

The results of these studies indicate that carbon dioxide displaces residual crude oil as a result of solution of the carbon dioxide, and the continuing gas drive.

Solution of the carbon dioxide results in a volumetric expansion of the oily phase. Its resulting higher pore volume saturation renders it mobile. This, together with the fact that the solution of carbon dioxide in crude will have a lower viscosity than that of the crude, enables it to be displaced down to a new residual saturation by the continuing gas drive. In the scaled physical models that were employed, there is evidence that the residual saturation of crude, or of the solution of carbon dioxide in crude, is less than the initial residual saturation of the crude to a water drive. Thus, in gravity stabilized models it was found that carbon dioxide is only equivalent to nitrogen in the absolute recovery of residual crude. In terms of the efficiency of the gas, barrels recovered per thousand standard cubic feet of gas injected, carbon dioxide was actually inferior to nitrogen because of its lower specific volume

The injection and subsequent flow and distribution of carbon dioxide into a reservoir, as in the case for the injection of any relatively highly mobile and low density fluid, was found to be governed by viscous fingering and gravity segregation. The viscous fingering, rather than being a disadvantage, is necessary in order for the required interphase area (between the residual crude and the carbon dioxide) for diffusion to occur and carbon dioxide thus transferred into the oil.

In the absence of solution of the injected gas, the results obtained depend exclusively on the reduction in the residual oil saturation, remaining after a water drive, to a gas drive. In the models used in this project, stabilizing an inert (nitrogen) gas drive by inclining the model resulted in recoveries comparable to when using carbon dioxide and at lower ratios of the mass (SCF) of injected gas to recovered barrel of oil.

The physical model studies are limited in their capability of modeling all the parameters that can be listed as possible determinants of the recovery of residual oil by carbon dioxide. Those which were deduced to be of prime importance were explicitly scaled. The omission of some and the softening of the scaling rules for others only contributed to rendering the model results more favorable than could be achieved in real reservoirs, and the reader is warned that this is so. The one correlation that can be made between these experimental results and field performance is by comparing the results of the Little Creek (Mississippi) pilot project on the recovery of waterflooded oil by injection of carbon dioxide. Over 25 MSCF of carbon dioxide (continuously injected) were required to recover a barrel of residual crude in that project¹⁷ whereas the results of this work suggest that 20 to 30 MSCF of carbon dioxide would be required to recover a barrel of oil from a reservoir containing a residual oil saturation of 20%. Thus, even though the results of this model study leads to optimistic results, in comparison to what might be anticipated in field operations, the results do not suggest that the continuous injection of carbon dioxide to recover residual crude oil will prove to be a highly economic process.

According to the results of this work, the usefulness of carbon dioxide for recovering residual oil will increase if gravity segregation can be mitigated, say by high velocity and small interwell spacing, and if its solution in the residual oil, before it breaks through into production wells can be enhanced by optimizing the extent of viscous fingering and the size of the slug used before following the carbon dioxide with water. A more detailed exposition of the conclusions reached from this project will be found in Sections IV, V, and VI.

III. CONCEPTUAL BASIS FOR SCALING A PHYSICAL MODEL OF CARBON DIOXIDE DISPLACEMENT OF RESIDUAL OIL

A. INTRODUCTION

This work was conducted using scaled physical models to study the basic mechanism for the displacement of residual crude oil, following water flooding, by both miscible solvents and carbon dioxide. The description of the physical models and the earlier results of this study have already been presented^{1,2,3,4,5}, and will not be repeated herein. A schematic diagram depicting the apparatus which was used for the high pressure experiments is shown in Fig. 1.

The prototype reservoirs were uniform, low permeability reservoirs with a porosity of the order of 30% and permeabilities ranging from 25 mds. to 100 mds. The prototype flood pattern was that of a simple linear flood. However, the geometry was idealized in that the cross section was circular. This was dictated by the fact that to build a properly scaled, high pressure model with flat sides would have required the expenditure of several hundred thousand dollars, well beyond the means of a University study. Since the primary goal of the work was to study the mechanism of the displacement rather than the performance of any particular field operation, such idealization was acceptable.

B. THE SCALING METHODOLOGY

Although the theory and methodology for scaling physical phenomena have been in use for over a century, and Geerstma, et. al.⁶ presented the mathematical basis for its application to reservoir processes some two decades ago, many questions continue to be raised as to just what the experimentalist is doing when a reservoir process is so scaled. Rather than resort herein to a resume of the mathematical arguments for physical scaling, a heuristic account based on the principles of fluid flow might be more readily accepted by the reader.

The models used in these studies scale the physical dimensions of the prototype, the absolute permeability of the reservoir, the viscosity of the fluids, the velocity of fluid flow due to the imposed pressure gradient, diffusion, and the differences in density between the reservoir and injected fluids. Proper scaling can be shown to be achieved if the ratio of the prototype length to the model length has the same value as the ratio of the velocity of fluid flow due to an imposed pressure gradient to the velocity caused by the difference in density between the injected and reservoir fluids, and to the ratio of the latter to the velocity of fluid flow caused by molecular diffusion, etc. Capillary pressure, relative permeability, and convective diffusion were not scaled because they could not be scaled in the same experiment in which other parameters, believed to be far more important in affecting the process, were scaled. A discussion of the necessity for scaling certain parameters in laboratory experiments follows.

1. Mobility Ratio

The macro-process governing the recovery of residual oil has frequently been conceived of as frontal displacement of the non-mobile residual oil by the injected fluid which is propelled only by the applied (external) pressure gradient. Several other parameters also affect the course and efficiency of the displacement. First of all, there is the matter of the mobility ratio; the ratio of the mobility of the displacing fluid to that of the displaced fluid. The effect of this factor in affecting the efficiency of fluid displacement is well known⁷.

A fluid with a higher mobility will have a higher velocity under the same pressure gradient as the less mobile phase. Therefore, starting at any interface between the two, the former will race ahead of the latter. The phenomenon of viscous fingering results. Even in the most uniform of porous media, local perturbations in lithology provide the loci for the initiation of such fingers. Care needs to be taken that the width of any model is sufficient so that the thickness of any one finger of the more mobile phase does not approach that of the model. Were this to occur, an erroneous result would be obtained suggesting frontal displacement in the prototype.

When the actual reservoir fluids are used in the laboratory model the matter of the viscosity ratio is automatically handled. When using a compressible fluid, such as carbon dioxide, it follows that it is necessary to use a pressure and temperature level that is the same as that of the prototype.

2. Heterogeneity

The heterogeneity of the prototype must also be matched in the construction of the model. It is feasible to match macro-heterogeneities, such as two or three layers of differing permeability, and even changes in sand thickness. However, it is extremely difficult to match small scale heterogeneities. For the purpose of studying mechanism and generalized behavior of a recovery process an idealized, uniform model is acceptable.

3. Applied Pressure Gradient and Gravity Gradient

The applied pressure gradient is only one of the gradients which imparts velocity to the reservoir fluids. In a flat reservoir, this gradient is the one causing horizontal (longitudinal) flow. The difference in density between fluids also generates a pressure differential which imparts a vertical (transverse) component to fluid flow.

A mean value for the externally applied pressure gradient within a reservoir undergoing fluid injection is probably no more than 1 psi./ft., after allowing for the steep gradients around the injection and production wells. The gradient due to the density difference between injected and reservoir fluid is 0.45 g/ft. For a density difference of 0.2, say when waterflooding a high gravity crude, the gradient is only about 0.1 psi./ft., substantially less than the applied gradient. Nevertheless, if the reservoir thickness is only 10% of the effective interwell distance, a water

particle entering at the top of the injection well will exit at the bottom of the reservoir, barring the interplay of other factors. Such a ratio of thickness to spacing is not an uncommon one in many reservoirs in the United States. However, when the capillary pressure is high, as it is when waterflooding water wet reservoirs, the segregation of the water is mitigated to some extent by the resulting imbibition.

When flooding a watered out reservoir with carbon dioxide, the density difference between reservoir water and the carbon dioxide reaches or exceeds values of the order of 0.5. Consequently, the ratio of the gravity gradient to the applied pressure gradient can reach a value of 0.25. Now, a fluid particle of carbon dioxide entering at the base of injector would reach the top of the same reservoir, cited above, well before it reached the production well. Actually, the situation is even more favorable for gravity segregation since in radial flow the applied pressure differential varies inversely with the radial distance from the injection well; the variation can be by a factor of over 20 from a radius of 10 feet to the mid-point of a 20 acre pattern. Over a significant segment of the reservoir, the applied pressure gradient may fall to values which are comparable to and even less than the vertical gradient. Also, if carbon dioxide is presumed to be the non-wetting phase in comparison to water then its accumulation at the top of the reservoir will not be checked by imbibition.

From the foregoing discussion it is apparent that when scaling a recovery process like the one under discussion, carbon dioxide injection for the recovery of residual oil, it is very important to scale the ratio of the fluid velocity due to the applied pressure gradient to the fluid velocity due to the innate gravity differential produced by the fluids themselves.

4. Molecular Diffusion

When considering the displacement of a reservoir fluid by one which is soluble in it (which may or may not be accompanied by significant solubility of the reservoir oil in the injected fluid) another important parameter must be scaled, i.e., the molecular diffusion of the solute into the reservoir oil.

Regardless of the fact that an injection fluid is soluble in the reservoir crude, it's role as a displacement agent must not be precluded from consideration. If the residual crude is at a high, mobile saturation then the injection of the solvent will result in the same kind of gravity segregation and viscous fingering which develops in an immiscible displacement^{8,9}. Therefore, it is still necessary when studying the use of solutes and solvents for the recovery of oil to scale the viscous and gravity gradients as described above.

However, a significant difference between immiscible and solvent displacement may occur because of solution. The attainment of solution equilibrium is driven by diffusion and convective mixing. Dispersion is the term usually applied to the sum of the two effects. The mass transfer of solvent into crude oil and vice versa can of course only occur where the two make contact. At a still interface, the transfer is effected only by molecular diffusion from within the solvent through the interface between

the solute and crude oil, and then into the bulk of the crude.

The need for considering diffusion is not limited to tertiary oil recovery studies. A recent study¹⁰ has revealed how mathematical simulations lead to erroneous results when the combined effect of diffusion and injected fluid distribution are not explicitly and properly included.

When dealing with residual oil, the matter is somewhat more complex. Water is the only mobile phase when injection of the solute or solvent occurs. The residual oil is trapped and occluded by the mobile water. There are now two mechanisms by which the injected solvent (or solute) can diffuse into the residual oil: 1) the mobile water in an element of the reservoir must flow ahead of the solvent (or solute), i.e., be displaced, for the latter to be able to contact the residual oil; or, 2) carbon dioxide dissolves in the mobile water, then diffuses through it to the water-oil interface, through the latter and then on into the crude oil.

It is obvious that molecular diffusion must be properly scaled when a solute or solvent fluid is used for displacement of reservoir oil.

5. Convective Dispersion

Most reservoir processes occur at flow rates which are in the laminar region therefore convective mixing is generally not considered to be an important feature of oil recovery operations. Exceptions are near the well bore of high gas rate wells, and in the steam zone of reservoirs being produced by a steam drive. Nevertheless, for whatever such convective mixing contributes it should be scaled. It is impossible to do so while honoring the overwhelming need to scale the flow due to density differences, applied pressure and diffusion. As a result, the convective dispersion is probably exaggerated in the models. This was deduced by considering the factors governing such dispersion and their indicated values from studies which have appeared in the literature^{9,11}. The much higher fluid velocities that must be used in the model and the large pore dimensions will contribute to a greater degree of convective dispersion in the model since the (ratio of) dispersion (to molecular diffusion) is a function of $a(r_p \cdot v)^{1,20}$, where r_p is the pore radius and v is the fluid velocity¹². On the other hand, the coefficient "a", apparently a measure of tortuosity, is much higher for a real reservoir than it is for the glass bead models. It is nevertheless unlikely that the lower value of "a" for the model can fully offset the higher value of the exponential term. The fact that convective dispersion is probably enhanced in the model means that the viscous fingering and gravity segregation will be somewhat mitigated. The model results will be superior in mobilizing the residual crude to those of the prototype.

No discussion of dispersion in relation to flooding with carbon dioxide would not be complete without reference to "slim tube" experiments which have been so frequently referred to in the literature as a way for determining the so-called "minimum miscibility pressure". The slim tube is a long, 25 to 75 feet, 1/4" to 1/2" diameter tube packed with sand. The usual experiment is to fill the tube with crude oil and displace it with carbon dioxide at various pressures. The amount of crude oil recovered prior to breakthrough is recorded, and the pressure at which the recovery

is 85 to 95% of the oil originally present in the tube is defined as the minimum miscibility pressure.

In point of fact the recovery increases steadily with increasing pressure because the density of the carbon dioxide is progressively increased with increasing pressure. The attainment of a high recovery reflects having attained a maximum density of the carbon dioxide, see Fig. 2. The high recovery displacement efficiency observed in the slim tubes is due to the fact that viscous fingering of a sufficiently dense fluid is completely inhibited in a sufficiently small diameter system. In mathematical terms, the time required to develop a finger is proportional to L/v , the length the fluid interface has travelled at the velocity, v ; whereas the time required to wipe out a finger is d^2/D , where d is the diameter of the system and D , the effective diffusion (dispersion). A small diameter will be prone to prevent viscous fingers from becoming established. (Of course, the low density of the carbon dioxide at low pressures will promote gravitational instability, and will result in a higher velocity at the same mass flow rate.)

6. Capillary Pressure

There is always some concern as to just how the capillary pressure must be scaled in model experiments on fluid displacement. However, before discussing the methodology for such scaling it is well to examine just what phenomenon is controlled by the capillary pressure in studying the recovery of residual oil by carbon dioxide.

In the preceding section, it was deduced that if carbon dioxide is to dissolve in the residual crude it must either (1) diffuse through the water that occludes the residual oil, or (2) the water surrounding an element of residual oil must be displaced by carbon dioxide so as to be able to contact the latter. Since the solubility of carbon dioxide in water is so much less than that in crude oil, ultimate saturation of crude via (1) would be a very slow process. Therefore, mechanism (2) must be the dominant one if carbon dioxide is going to saturate the crude. It is not apparent that capillary pressure will affect this presumed step in the mobilization and ultimate displacement of residual oil by carbon dioxide. Therefore, if indeed this mechanism is the dominant one in the recovery of residual oil by carbon dioxide, there does not seem to be any overwhelming reason for capillary pressure to be considered for precise scaling.

On the other hand, if carbon dioxide causes a reduction in interfacial tension (capillary pressure), which, per se, contributes to the mobilization and displacement of residual crude oil, then scaling capillarity is important. The pressure gradient due to capillarity, $\frac{\sigma \cos \theta}{rL}$, where σ is the interfacial tension, r is the pore radius, and L the length over which the capillary pressure is acting. When L is taken to be the radius of the pore, i.e., the capillary pressure is exerted only over the dimension of a pore, the ratio of capillary pressure to applied pressure differential is $\frac{\sigma \cos \theta}{\Delta P r}$ which is a very large number; 10,000 or greater in waterflooding. Were the capillary pressure gradient to act in series with the applied pressure gradient then the overall fluid rates in reservoirs would be far lower than observed. It may be concluded therefore that the effect of the capillary pressure gradient is primarily limited to isolated

loci in porous media. In other words, it primarily affects local pore saturation and desaturation in two phase flow.

In establishing the residual oil saturation to a waterflood and in the subsequent carbon dioxide flood, the same fluid velocity was used. The only change in capillary number between the waterflood and the subsequent carbon dioxide flood would be due to changes in the interfacial tension affected by the presence of the injected carbon dioxide. The fractional change in the capillary number in the model would therefore be equal to the fractional change in the prototype. However, depending upon the value of the capillary number, a proportional change in it may have a different absolute effect on the residual oil saturation; see Reference 13, and note that the independent parameter therein is the inverse of the capillary number as herein described. In the prototype, the capillary number is high and in the model it is much, much lower. The available evidence indicates that a much smaller change in residual oil saturation occurs at large capillary number than occurs at small capillary numbers. Therefore, it should be expected that if the carbon dioxide lowers the interfacial tension affecting pore oil saturation, the effect would be greater in the model than in the prototype; the model results should be optimistic.

(A recent study¹⁴ has shown that carbon dioxide causes profound changes in wettability of sandstones by affecting clay hydration and other properties of the mineral surfaces; in effect drastically alters the wettability of the mineral surfaces. The overall effect was shown to result in a marked increase in residual oil saturation. The same effect was not observed when glass beads were substituted for actual reservoir rocks. The conclusion, already expressed, that the model experiments will provide optimistic results in comparison to what may be expected in field operations is fortified by the results of this study.

In the high pressure model studies that were conducted as part of this investigation, residual oil saturations at a consistent value of the order of 20% were obtained. Considering only the parameters that have already been discussed, it can be concluded that the optimistic results that were obtained do apply to a prototype with a residual oil saturation of the order of 20%, and probably to any prototype with a non-mobile, residual saturation, except for the absolute amount of oil recovered. Additional experiments were also done at mobile oil saturations, achieved by simultaneous injection of oil and water or at connate water saturation, in order to evaluate the specific effect of oil saturation on the process.

7. Phase Behavior

Much has been said of the potential of carbon dioxide to develop a truly miscible solvent for crude oil as a result of the separation of such a phase by the interaction of the carbon dioxide and the crude oil¹¹. Carbon dioxide itself is not miscible with crude oils, but exhibits a miscibility gap. A typical pseudo-two component phase diagram is shown in Fig. 3.

There is little question that such a miscible phase is theoretically capable of being developed. Should it develop in the reservoir, a very basic question is whether it would in fact be capable of efficiently mobilizing and displacing the residual oil.

The argument usually presented is that a diffusion zone, or transition zone would develop between a developing oil bank and the miscible composition. Such an argument overlooks the secondary conclusions of an early work¹² on miscible displacement. The reported experiments clearly revealed an astounding rapid breakthrough of the injected miscible fluid as soon as the mobility ratio moved above unity. Of course, this should not have been unanticipated in view of earlier work⁸ which pointed to the same qualitative conclusion. In other words, since the density of the experimental fluids were matched, the results of these experiments indicated no transition zone being developed but instead indicated the dominance of viscous fingering. As far as can be determined all calculations on the development of a transition zone are based on a stable, frontal displacement. Such stability just cannot occur when injecting highly mobile fluids into an oil reservoir. Hence, even if the interaction of carbon dioxide and crude oil within a reservoir can lead to the development of a miscible composition, it is not at all apparent that the formation of such a composition of matter could lead to a high recovery of residual oil.

It has already been indicated that the most likely way by which carbon dioxide contacts the crude is dependent on the displacement of water from around the element of residual oil in question. The molar ratio of carbon dioxide to crude in that element rises rapidly, see the calculated results of one of the scaled models in Fig. 4. (It is noted that a GOR of 4000 is tantamount to a carbon dioxide mol fraction in excess of 0.9.). As a result the phase behavior, if equilibrium is established, is at a high system carbon dioxide concentration. The "gaseous" phase is virtually pure carbon dioxide containing a small fraction of volatile constituents of the crude oil. If the system is below the critical point the equilibrium liquid will be a relatively dilute solution of carbon dioxide in crude. If the system is above the critical point, the equilibrium "liquid" would again contain an overwhelming proportion of carbon dioxide. Because of the low concentration of the crude oil, or some of its components in the mobile, rich carbon dioxide compositions that are seen to develop as a result of attaining thermodynamic equilibrium, large quantities of carbon dioxide would have to be injected to recover a significant amount of reservoir crude oil. A recovery scheme based on this is in fact not much different than any gas recycling operation for recovering volatile fractions of the crude. It does not appear to be a viable scheme for recovering residual oil.

8. Relative Permeability

No attempt was made to scale the relative permeability of reservoir rocks when constructing the models. Relative permeability, as a quantity capable of measurement, is a concept that applies to the diffuse flow (constant saturations of all fluids across the entire, planar interface between displacing and displaced fluids). In carbon dioxide flooding, the flow is stratified. In the absence of layering, the viscous fingers will eventually meld into a gross overlay of carbon dioxide. The relative flow of carbon dioxide and water, and the expansion, if any, of the carbon dioxide (overlay) zone will depend only on end point values of the relative permeability of (1) carbon dioxide at very high saturation displacing mobile water, and (2) mobile water being depleted from the water saturated zone (beneath the carbon dioxide) as a result of the pressure differential

maintained by injection of carbon dioxide.

If the reservoir is layered, then each layer - unless so thin that frontal displacement does occur therein - can be assumed, as a first approximation, to perform much as a single uniform reservoir. Of course, the overall performance of the reservoir will be much poorer because of the preferential breakthrough in the most conductive layers, of a single uniform layer.

Therefore, for the prototype having a uniform lithology, the results of the model experiment will differ from those expected in the prototype only by the differences in end point permeabilities. If anything, the breakthrough of carbon dioxide will be earlier in the model since the end point relative permeabilities to water in most real reservoirs are quite low - probably lower than that in glass beads - because of hydration of the mineral surfaces and their higher degree of tortuosity.

Again, the conclusion is reached that the results of the model experiments examining the potential of carbon dioxide for recovering residual crude oil will be optimistic on the count that the relative permeability of real reservoirs was not scaled.

The breakthrough of the injected mobile fluid is primarily a function of the particular way it segregates and fingers through a particular reservoir, the micro- and macro-heterogeneities in the lithology of that reservoir, and the resistance to flow of the fluid being displaced in the "channels" through which the injected fluid is coursing. The only way to derive a "relative permeability" for the system is to calculate it from the results of the very same experimental or field operation to which such measures are to be applied.

The assumption made in this study is that the lithology of the prototype is as uniform as the glass bead packing in the models. Regardless of relative permeability considerations, breakthrough of the injected carbon dioxide will be slowed in the models because of the absence of any gross heterogeneities in absolute permeability. And, regardless of relative permeability, gravity segregation will be greater in the experimental models than in real reservoirs which have permeability barriers and/or extremely low values of the vertical permeability. However such layering, if not of uniform lithology, absolute permeability, and fluid saturation, will only exacerbate the breakthrough problems.

IV. SUMMARY OF RESULTS OF EXPERIMENTS REPORTED EARLIER

The principal results of experimental work reported earlier^{1,2,3,4,5} led to the following conclusions:

1. Water, the continuous mobile phase, following water flooding, is displaced prior to residual oil. Residual oil begins to be produced virtually concurrently with the breakthrough of carbon dioxide. Typical results are shown in Figures 5 and 6. The carbon dioxide does not bank the crude oil ahead of it. It is not certain from this performance, per se, whether a concentrated solution of carbon dioxide is being produced, or the carbon dioxide is merely transporting the oil, or whether both mechanisms are active.

2. The inverse of the efficiency of the carbon dioxide, thousands of standard cubic feet of carbon dioxide required to displace a barrel of residual crude oil, is in the range of 20,000 to 30,000 at pressures of 1000 psi. and higher. The efficiency of carbon dioxide in displacing crude oil increases markedly as the saturation of mobile crude oil increases. Typical results are shown in Fig. 7.

3. The efficiency of carbon dioxide increases rapidly up to a pressure of about 1000 psi. and then much more slowly, see Fig. 8. This was at first attributed solely to increase in solubility of carbon dioxide with pressure, but with subsequent experimentation much of the effect had to be attributed to a decrease in gravitational segregation.

4. The effect of pressure can be offset by an increase in temperature. Adjusting the pressure at different temperatures so as to maintain a constant density results in the carbon dioxide performing identically at the varying temperatures, see Fig. 9.

5. No change in gravity of the produced crude oil is observed until oil production has declined to a very low rate, Fig. 10. This performance indicates little if any effect on the performance of the carbon dioxide due to the enrichment of the carbon dioxide by volatile components of the crude. Nitrous oxide, having physical properties, including that of solution in organic liquids, very similar to those of carbon dioxide performed equally well in recovering residual crude oil.

6. When a slug of carbon dioxide is injected and then followed by water, there is an optimum size of the slug for minimizing the quantity of carbon dioxide required to produce a barrel of residual crude (maximizing efficiency) although more crude oil will probably be eventually produced for larger slugs (experiments were not always continued far enough to unequivocally prove the latter), see Figs. 11 and 12. The hypothesis presented for this behavior is that of each successive increment of carbon dioxide injected, a greater fraction goes to establishing a free "gas" saturation rather than into solution of the crude oil. Once a free gas saturation is established, the transmissibility of the system to carbon dioxide will increase rapidly, see Fig. 13. A similar effect of decreased efficiency of incremental slugs of carbon dioxide was noted in the Sacroc Unit (Kelly-Snyder Field, Texas)¹⁵ secondary recovery operation, see Fig. 14. Using several smaller slugs demonstrated a somewhat poorer efficiency

than injecting a single large slug equal to the sum of the smaller ones. Optimum slugs in uniform, low permeability prototypes of the experimental models used in this study would recover residual oil at quite favorable ratios of injected carbon dioxide per barrel of recovered oil. Such prototypical reservoirs with no disturbing heterogeneity are not common.

V. RECENT EXPERIMENTS

The preceding results suggested that the solubility of carbon dioxide in crude oil is the key to its ability to mobilize and displace residual oil. The solution of the carbon dioxide is hypothesized to result in sufficient volumetric expansion of the oil to render it mobile. Subsequently, the mobilized oil is displaced by the continuing gas drive, or a waterdrive if a slug of carbon dioxide is followed by water injection.

It follows from this analysis that viscous fingering, which leads to the development of an extensive interfacial area through which diffusion of carbon dioxide can occur, is desirable. A gross gravity overlay is undesirable since the area through which diffusion will occur is much more limited for the same amount of carbon dioxide injected.

The experiments that had been done, however, had not addressed the matter of the significance of any decrease in residual oil phase saturation to the gas drive, per se. A study on residual oil saturation to gravity drainage¹⁶ revealed that in many instances the residual oil saturation to gas was lower than the residual oil saturation to water. Therefore it was suspected that some of the increased recovery of crude oil due to the injection of carbon dioxide might be merely due to this phenomenon. In an attempt to obtain a perspective on this matter, experiments were carried out in dipping models, using both nitrogen and carbon dioxide.

The results of a pair of experiments which were carried out in models that were inclined at an angle of 18° to the horizontal and starting at a very low oil saturation so as to eliminate as much as possible the potential for any mobile oil being present are shown in Figs. 15 and 16.

The flow rate and inclination of the model were chosen so that both the nitrogen and carbon dioxide would stably displace the denser, more viscous mobile water in the models. That the advancing gas front was indeed stable is convincingly demonstrated by the absence of any gas production until some 0.6 p.v. of gas had been injected. The two experiments yielded virtually identical results.

The fact that there was no early gas breakthrough indicates the absence of viscous fingering and gravity override. Although the reliability of any single point has to be qualified because of the possibility of fluid hold-up in the network of valves and tubing of the experimental set-up, the results suggest less mixing of the nitrogen and displaced oil than of carbon dioxide and the oil it has displaced. However, the absolute amount of oil recovered is virtually identical in each experiment. This result is strongly supportive of a conclusion that in these model experiments the mechanism for displacement of residual oil is merely a reduction in residual oil saturation by a gas drive. The much higher efficiency of the nitrogen, the inverse of the MSCF/B plotted as the ordinate in Fig. 16, in comparison to the efficiency of carbon dioxide, is in direct proportion to their specific volumes at the pressure and temperature of the experiments.

The results of the experiments and the resulting conclusion must not be allowed to lead to any misunderstanding. In experiments in horizontal models at identical temperatures and pressures, with the density of the

nitrogen significantly less than of the carbon dioxide, the nitrogen breaks through much earlier and recovers much less oil. The higher density of the carbon dioxide, in a horizontal model, promotes a greater sweep of the model (as a result of a lowered rate of gravity segregation). However, in view of the results in the inclined models it is not possible to unequivocally separate the contribution due to gas drive in reducing residual saturation from that due to solution and volumetric expansion.

In so far as the reduction in residual oil saturation to a gas drive might provide a significant contribution to the recovery, the model results may or may not be comparable to the recovery that would be achieved in a real reservoir. This is so because the factors surrounding the establishment and/or changes in residual saturation were not scaled in these experiments. The particular factors are, of course, the distribution of pore sizes and the rugosity and wettability of the mineral surfaces. However, as noted in the discussion under Sec. 6 of Part III a recent study has indicated that when carbon dioxide reaches a mineral surface changes in wettability were observed to occur which led to a dehydration of the surfaces and a greater retention of crude oil. Also, as noted earlier in that section, the capillary number is much lower in the model and any changes in it resulting from the presence of carbon dioxide would tend to cause a greater change in residual saturation than that caused by changes in capillary phenomena in the prototype. Although the conclusion is moot, the authors of this work have concluded that any contribution of a reduction in residual oil saturation, per se, will be greater in the model than in the prototype. The model experiments are believed to be optimistic on this and the several other accounts already referred to in this report. A positive answer can be generated only by undertaking a series of experiments in which the determination of residual oil saturation to inert and soluble gas drives is the primary goal of the work.

V. CONCLUSIONS

The results of this study point to the conclusion that the recovery of residual oil by carbon dioxide injection is due to both solution of the carbon dioxide in the crude oil, and its consequent volumetric expansion and viscosity reduction, and a reduction in the absolute residual saturation of the oil phase to a gas drive.

During the injection of carbon dioxide for the recovery of residual oil, a pressure should be maintained in the reservoir such that at the temperature of the latter the density of the carbon dioxide is at least of the order of 0.3 to 0.4

In so far as solution of carbon dioxide is required to mobilize the residual oil, viscous fingering is actually necessary for the successful use of carbon dioxide to recover residual oil. Only in this way can there be developed the extensive interfacial area through which diffusion of carbon dioxide can occur.

In so far as the reduction in residual oil saturation to a gas drive, per se, may be the dominant factor in effecting the recovery of the residual oil then a stable displacement is desirable. However, if this factor is dominant, then less compressible gases, such as nitrogen, should give almost equivalent results in terms of absolute recovery if a stable displacement can be achieved. Indeed, a smaller mass of nitrogen, fewer standard cubic feet, would be required than of carbon dioxide to recover a barrel of residual crude.

A very large quantity of carbon dioxide, in excess of 20 MSCF will be required to recover a barrel of residual crude oil by continuous injection of carbon dioxide. The efficiency of the carbon dioxide can be greatly increased by limiting the injection to an optimum-sized slug and then following the latter with a water flood.

The efficiency of the carbon dioxide will also be increased if gravity segregation can be minimized, but without destroying the development of extensive fingering of carbon dioxide into the reservoir.

Finally, it should be noted that the results of this study show that a large amount of the mobile water in the reservoir, following a waterflood, will have to be displaced and produced ahead of and/or simultaneously with the residual oil.

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Fig. 1 -- High Pressure Apparatus Cell is 3 ft x 2.5"

- BPR - Back pressure regulator
- CFP - Constametric feed pump
- CO₂ - Carbon dioxide tank
- D - Differential gauge
- F - Filter
- FC - Fraction collector
- FWV - Five-way valve
- GB - Gas booster
- GC - Gas chromatograph
- HS - Electromechanic heater and stirrer
- OP - Overburden pump
- PG - Pressure gauge
- RR - Reducing regulator
- S - Solenoid valve
- SC - Solenoid valve controller
- SEP - Gas liquid separator
- TC - Thermocouple
- TR - Multichannel temperature readout (digital)
- V - Miniature ball valve
- VP - Vacuum pump
- WTM - Wet test meter

RESULTS OF TYPICAL SLIM TUBE EXPERIMENTS AND RELATIONSHIP TO DENSITY AND VISCOSITY OF CO₂

FIG. 2

FIG. 3 -- TYPICAL CO₂-CRUDE OIL PHASE DIAGRAM

**INSTANTANEOUS GAS OIL RATIO FOR THE
DISPLACEMENT OF BOTH HIGH AND RESIDUAL
OIL SATURATION OF THE APPALACHIAN
CRUDE AT 1,400 PSI AND 73°F**

**FRACTIONAL FLOW CURVE (ON MOLAR BASIS)
OF CARBON DIOXIDE FOR THE DISPLACEMENT
OF RESIDUAL OIL AT 1,400 PSI AND 73°F**

FIG. 4

FIG. 5

FIG. 6

**TYPICAL EFFICIENCY RELATIONSHIPS AS
A FUNCTION OF INITIAL SATURATION,
45°API CRUDE - CONTINUOUS INJECTION**

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

**ADDITIONAL CO₂ INJECTION AND PRODUCTION
PER BARREL OF ADDITIONAL OIL VS. CUMULATIVE
CO₂**

SACROC

FIG. 14

Experiment 26: CO_2

Experiment 29: N_2

FIG. 15: STABLE DISPLACEMENT IN INCLINED MODELS

FIG. 16

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