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**DEVELOPMENT OF MOBILITY CONTROL METHODS
TO IMPROVE OIL RECOVERY BY CO₂**

Final Report

Work Performed for the Department of Energy
Under Contract No. DE-AC21-79MC10689

Date Published—November 1983

New Mexico Institute of Mining and Technology
Socorro, New Mexico



**National Petroleum Technology Office
U.S. DEPARTMENT OF ENERGY
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TO IMPROVE OIL RECOVERY BY CO₂**

Final Report

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Abstract

The efficiency with which oil is recovered from known deposits is disappointingly low, and the object of this research program has been to improve it. The quantity of unrecovered oil in known reservoirs is so great that relatively small increases in recovery efficiency, even if applicable only to certain types of deposits, could make significant contributions to the Nation's energy supply.

In certain reservoir situations, highly compressed carbon dioxide (CO_2) has a great advantage over more common (and inexpensive) fluids as a displacement agent to force crude oil from the porous rock in which it's found. The advantage is that a much higher microscopic efficiency can be attained in the displacement process--at least in the laboratory.

This research aims to relieve a major difficulty that has so far prevented this high efficiency from being reached in field applications. The difficulty is that because CO_2 is much less viscous than oil or water, the injected fluid does not displace the oil uniformly. Instead, the CO_2 moves faster in some regions and directions than others, and "viscous fingers" are formed, through which most of the injected fluid flows. Some of these "breakthrough" into the production wells, lowering the effectiveness of both the injected CO_2 and of the production pumping capacity.

The aim of this project has been to develop ways to thicken the injected CO_2 , so as to forestall the growth of these parasitic flow patterns and the premature breakthrough that results from them. In this way the promise of greatly increased displacement efficiency can be fulfilled.

Two ways of thickening CO_2 have been investigated. Substantial progress has been made in both developments and both are promising. The first of the methods studied considers the use of polymer dissolved in the dense CO_2 to increase its viscosity by the needed extent. The results of this research include the development of instruments to measure solubility of polymers in condensed gases, and the viscosity of the resultant solutions at high pressures. In addition a large amount of data has been accumulated on available polymers. Although the CO_2 -soluble ones found do not increase the viscosity sufficiently, the research has produced promising information which could lead to the synthesis of novel polymers that would be well adapted to use as mobility control agents. Although these polymer types are not available commercially, they could be synthesized by known techniques; thus, further research in this direction could be very productive.

The second method to thicken the injected CO_2 is to combine it with aqueous surfactant solution in a " CO_2 foam." The higher pressure gradient required to force this composite fluid through the reservoir rock is equivalent, in retarding the growth of fingers, to the use of a viscous displacing fluid. Project effort has included development of a special

screening test to compare the suitability of surfactants for this purpose, and its use to test candidate surfactants from more than sixty commercially available products. In addition, a procedure was developed for evaluating the tendency of these materials to be adsorbed onto reservoir rock, and utilized to rate the most promising surfactants, relative to a rock sample from a particular oil field. Further tests on CO₂ foam gave measurements of the mobility of the foam in the same rock, under high-pressure conditions. A parallel effort was also made to calculate values of foam mobility from the published literature, in order to take advantage of the large amount of information and data gathered by other investigators.

The second of these methods is much nearer to field use than the other, particularly in lower temperature reservoirs. In fact, a companion project involving the same research team is assisting in a field trial of the method--the use of a "foam-like dispersion" of CO₂--in just such a reservoir, for which chemicals are currently available.

Work in this project has covered many details of the development of these thickening methods and has also considered the means by which they might be applied in the oilfield. These subjects, as well as a description of related work yet to be done are reported and discussed.

I. Introduction and Summary

A. Project Overview and Summary

This research project has been funded jointly by the U.S. Department of Energy (contract DE-AC21-79MC10689) and the State of New Mexico (New Mexico Energy Research and Development Institute (contract EMD 3307), and was designed in response to a Request For Proposal from the Department of Energy (DOE) on this subject in the summer of 1979. The Statement of Work in the original documents included a description of the major motivation for the project: although displacement of oil by CO₂ has very high potential efficiency - as demonstrated by laboratory experiments in "slim tubes" at pressures above the so-called "Minimum Miscibility Pressure" - its performance in a reservoir seldom fulfills this expectation. The general reason for this disappointing state of affairs is well known; the areal efficiency with which a reservoir is "contacted" is drastically lowered by the frontal instability caused by the displacing fluid's higher mobility than that of oil. This is a major difficulty that has frustrated most efforts to realize CO₂'s high potential. The purpose of the project has been to discover ways in which a greater portion of this potential for high displacement efficiency can be secured despite the difficulty.

The objectives of this research, as specified in the original Statement of Work, included the preparation of a literature review on the background, origin and proposed remedies for the "mobility ratio problem" as met in CO₂ displacements; the screening and selection of "potentially useful additives"; the conduct of laboratory experiments to determine cost effectiveness of such additives; and the recommendation of additives and of injection programs for use in field tests. Listed as "deliverables," in addition to the regular quarterly and annual reports, were the literature survey and an experimental plan to be proposed after preliminary work. Each of these sub-projects is summarized briefly in the paragraphs below.

B. Sub-project Descriptions

1. Preliminary Efforts

After an initial period in which relevant literature references were gathered and studied, a topical report¹ was prepared which described and classified these publications. This document consisted of descriptive survey of the field as discussed in 151 references to the petroleum engineering and related literature. All subjects deemed relevant to the mobility control problems of CO₂ floods were included, and the status of engineering information described. The study and analysis of these papers provided further background for the definition of the outstanding problems, and for the design of properly directed laboratory efforts. The Literature Survey was followed by a proposed Experimental Plan that was submitted as the Third Quarterly Report of the Project.² This Plan, reflecting the results of work done for the Literature Survey, included

certain changes from the ideas originally proposed about what should be the course of the research. One of these modifications consisted of the recognition that polymeric materials might be found which could dissolve in and viscosify dense CO₂, and the inclusion of the explicit search for such chemicals as an experimental objective. A second identifiable modification of the plan was to emphasize direct measurement of mobility during displacement of oil by both unprotected (no mobility control) and by mobility-controlled CO₂.

The project's activities thus fell into the three categories of laboratory work corresponding to the objectives identified in the Experimental Plan, and a further goal concerning reservoir application.

2. The Instrumented Core Flood

This activity consisted of the design, construction and testing of a core flow system in which the effectiveness of mobility control agents and additives in CO₂ floods could be evaluated. Means were developed by which CO₂ floods with several mobility control additives were to be compared with each other, and also with unprotected CO₂ floods performed in the same equipment using CO₂ alone. The instrumented core is about 29" long, and 2" by 2" in cross section. It was cut from a large piece of a quarried dolomite of a type described by J.J. Meister³ that was purchased from the J.E. Baker Company of York, PA and was coated with epoxy. In use, it is enclosed in a steel, high-pressure container and surrounded by oil for the transmittal of overburden pressure. The core was designed to test flooding effectiveness in three separate ways. The first is, of course, the direct measurement of displacement efficiency by collecting oil displaced at reservoir pressure for different CO₂ floods starting from similar waterflooded initial states. In addition, there are also two methods by which the longitudinal profile of the frontal region can be assessed. One enables the direct measurement of flow mobility at four equally-spaced locations along the core. At each location, two pressure taps separated by one centimeter in the direction of flow were affixed to provide access to the core fluids. A pair of tubes led from each such pair out through the pressure wall to a differential pressure transducer, which was then able to measure the pressure gradient at that part of the rock.

A second method also measures the longitudinal variation of properties during a flood and so provides information about the effectiveness of mobility control agents. This method utilizes electrical measurements: the voltage differences between adjacent electrodes along a line of closely spaced pins piercing the epoxy coating on one side of the core. A "conductivity profile" is calculated from the voltages read while current flows through the core, between two current electrodes which are each in contact with the whole cross section at the input and output ends of the rock sample. The self-potentials, observable when no current is flowing, can also be measured, and are of interest in assessing ion concentration and the condition of the electrodes.

3. "CO₂ Foams"

The second objective of laboratory work has been the development of "foam-like dispersions" of CO₂ and surfactant solutions. It has long been observed, and is the subject of an early patent⁴, that a surfactant-stabilized foam of gas and water has a very low mobility to flow through porous media.

There are many literature references to measurements of the associated pressure drop and of oil recovery during "foam floods." These support the idea that a "CO₂ foam" could be an effective mobility controlled displacement fluid. Development of the idea in this research project has required additional work on several outstanding problems. One such problem is concerned with the effectiveness of foam-like dispersions when the non-aqueous fluid is not a gas but rather a "dense fluid" (such as liquid or supercritical CO₂) and is thus more capable of influencing the surfactant distribution. A second problem has been to determine the role played by compressibility in decreasing mobility, and a third is concerned with the need to control the extent of the mobility decrease in the reservoir. A very large number of different surfactants are available commercially, and many are quite effective in stabilizing foams in the laboratory, but experiments to predict reservoir performance are also necessary. These have included high pressure measurements of mobility of the foam-like dispersion with CO₂, and its ability to displace the particular crude oil from the formation rock in question. Other tests were also performed to examine surfactant adsorption, so that due allowance for these losses could be made in the reservoir. Especially if high temperatures were involved, it would be necessary to examine the chemical stability of the surfactant in contact with reservoir brine. Development of "foam-like dispersions" has entailed both the measurement of surfactant performance in these tests as targeted for one particular reservoir, and the consideration of the general question of designing efficient tests for other situations. Even with all of this laboratory work, it must remain for field-scale experiments to verify that a "CO₂ foam" can be propagated for reservoir distances, preserving during that time the ability to displace oil uniformly.

4. Direct Thickeners

The third objective of our laboratory work has been to explore the possibility of "direct thickeners" as mobility control additives for CO₂. The use of such polymeric materials, soluble in dense CO₂ and capable of raising its viscosity sufficiently, would have the great advantage that no additional water would need to be introduced into the reservoir along with the primary displacement fluid "slug." This absence of additional water would eliminate the corrosion caused by the combination of water and CO₂ in the injection well. It would also allow better contact within the reservoir rock between residual oil and the CO₂--thereby lowering the risk that the microscopic displacement efficiency would be decreased by trapping of residual oil.

The search for direct thickeners has included the development of special apparatus and procedures to measure the solubility of substances. This measurement involves use of a high pressure observation and mixing cell in which the solution of a polymer in dense CO₂ can be formed. The method also utilizes a transfer means by which a measured volume of the solution can be moved out of the mixing cell and into an assay vessel for measurement of the quantity of solute transferred. A second apparatus development modified the above device so that it could also be used for viscosity measurements.

These measurements have been made on about forty polymers. Most of them are commercially available and were obtained from the manufacturers, but some are small samples sent to us by other investigators from the industrial or academic laboratories where the polymers had been synthesized. Of these polymers, which are presumed to be representative of most commercially available products of their type, more than a dozen have been found to be soluble in the parts-per-thousand range or greater in dense CO₂. Generally these are also soluble in light hydrocarbons and are completely insoluble in water. They are mostly based on straight-chain hydrocarbons, are of relatively low molecular weight, and atactic in their molecular structure. Unfortunately for the purposes of this project however, none of the tested CO₂-soluble polymers are nearly effective enough in raising the viscosity of the resulting solution, so no direct thickener for CO₂ floods has been developed. But there is a positive result, in addition to the successes in apparatus development for the measurements of solubility and viscosity in high pressure fluids. This success lies in the information that dense CO₂ is indeed a solvent, though not a very powerful one, and that certain types and structures of polymers are much more soluble in CO₂ than others. Based on the information presented in this report, the probability is high that some polymers suitable for use as direct thickeners for mobility control of CO₂ floods can be synthesized. It can be expected that such materials will be cost effective for use in many CO₂ floods, especially where mobility control methods involving the use of water would lead to severe corrosion or loss of displacement efficiency.

5. Reservoir Considerations

One further, continuing activity of this research project has been the consideration of the practical reservoir engineering, operational and economic problems in the application of mobility control in CO₂ floods. Some of this activity has been in conjunction with the companion DOE project 81MC16426 and specifically directed towards the design of an injection program in a mini-pilot area of the Rock Creek field of West Virginia. The more general aspects of these mobility control application problems, however, are properly part of this project: such efforts have been directed toward the formulation of criteria which will be of wider use.

This introductory section has briefly summarized the activities and accomplishments of the project. More detailed discussions about each of

these are given in subsequent major sections of the report. Prior to these discussions, however, sections are presented to give more detail on the general reservoir considerations involved in the need for mobility control in CO₂ floods, the methods by which the goal can be pursued, and the results which might be expected.

II. Need For Mobility Control

The principal advantage of dense CO₂ as a displacement fluid in enhanced oil recovery (EOR) projects is the demonstrably high microscopic efficiency (close to 100%) with which it can displace crude oil from porous material. This efficiency is obtained in the laboratory in long "slim tubes," packs of initially oil-saturated glass beads or sand, operated at pressures above the so-called minimum miscibility pressure (MMP). Extensive research performed at the Petroleum Recovery Research Center (PRRC)⁵ and many other laboratories⁶⁻⁸ has shown that although only hydrocarbons of low enough molecular weight are miscible in all proportions with liquid or dense supercritical CO₂, high displacement efficiencies are attained in slim tubes even with black oils. These crudes are not "first contact miscible" with CO₂, and contain significant quantities of high molecular weight "heavy ends" that have very low solubility in CO₂. The reason for the high displacement efficiency in this case is that crude oil is a mixture containing low as well as high molecular weight components. During the early stages of a one-dimensional displacement by CO₂ at high enough pressure, the dynamic processes of extraction and flow combine (in a way first described by Hutchinson and Braun)⁹ to develop a transition region between the crude oil and the CO₂. This zone of graded composition is fully miscible in both fluids. After its development this miscible zone, if it remains intact, can displace essentially all of the oil along its remaining distance of travel.

Because actual oil reservoirs are more complex in structure than sand packs, it was never expected that the miscible zone could maintain its integrity everywhere, or that displacement efficiencies in the field could approach those observed in these laboratory experiments. However, in addition to less-than-ideal displacement caused by heterogeneities in the rock, there is another difference between the reservoir and the slim tube. This difference stems from the multi-dimensional geometry of the oil-bearing formations, which affords the opportunity for non-uniform displacement velocities. Flow velocities in the oil field are in fact extremely variable from place to place, due both to the natural heterogeneities of permeability and porosity, and to the fact that the fluids enter and leave through wells whose radii are generally very small in comparison to the distances between them.

The flow pattern is also influenced by the fluid properties themselves.¹⁰⁻¹² The frontal region is subject to an instability when the displacing fluid is more mobile in the formation rock than the displaced fluid.¹³⁻¹⁶ If the mobility ratio is large, as it is in an unprotected CO₂ flood, any irregularities on the front grow rapidly into "fingers" which bypass reservoir oil.¹⁷ The resulting degradation of the frontal

region causes early breakthrough of CO₂ into the producing wells and decreases the achievable displacement efficiency. This latter result occurs both by the bypassing of oil and by the breakup of the Hutchinson-Braun⁹, developed-miscibility zone.

In a vertical displacement the frontal instability caused by an unfavorable mobility ratio can often be counteracted by taking advantage of the gravitational forces operating on the density difference between the displacing and displaced fluids.¹⁸⁻¹⁹ However, in most reservoirs the flow is predominately horizontal so that this is impossible. If the mobility ratio is larger than five or ten (depending on the extent of the previously cited geometrical factors), the resulting non-uniformity of displacement becomes a very serious obstacle to the efficient and economic production of oil. The expected results of a large mobility ratio, as exists in most CO₂ floods, are early breakthrough of CO₂ to the production wells, and a rapid subsequent decline of the rate at which oil is swept from that region ordinarily considered to be in the production well's drainage area. Even such an unprotected CO₂ flood can be economically successful--particularly if the produced CO₂ can be recycled. The performance of any such flood could be considerably improved, however, if means were available to control the growth of viscous instability patterns.

Even before dense CO₂ was proposed as a displacement fluid in oil reservoirs, the general nature of the problem described above as familiar to reservoir engineers and the need for their solution was evident. This was a result of the serious consideration given in the late 1950's and early 1960's to "miscible flooding," using light hydrocarbon mixtures as displacement fluids. These fluids, whether they are "first contact miscible" or dependent on extraction for the development of a miscible front, also have low viscosities. The displacement patterns in those floods were thus also subject to severe frontal instability. These instabilities were in many cases aggravated by a larger density difference between solvent and crude oil than is common in most CO₂ floods. In consequence, the several horizontal displacement projects which were operated with hydrocarbon solvents in those years yielded very disappointing results. (On the other hand the lower densities of Liquified Petroleum Gas (LPG) and of "enriched gas" has enabled several very successful gravity-stabilized solvent floods to be designed and operated in formations with sufficient vertical relief).²⁰

III. Methods of Control

In general, the methods used or proposed for the control of frontal instability all entail the increase of flowing pressure gradient behind the front--that is, the decrease of the displacing fluid's mobility. Three such methods are described briefly in the paragraph below.

A. WAG

Efforts to decrease or eliminate the fingering in horizontal floods by water injection are discussed in the literature and cited in our Literature Survey.¹ All of these efforts are based on the attempt to decrease the effective mobility of the displacing fluid, so as to increase the pressure gradient in the regions it occupies. The first of these methods came in the era of interest in hydrocarbon floods. It was proposed in 1958 by Caudle and Dyes,²¹ and two years later, with a somewhat different theoretical justification, by Blackwell and his co-workers.²² The method is based on the markedly decreased relative permeability of the rock to solvent caused by only a small increase in water saturation. Thus with the addition of water to the injection fluid, it was expected that the uniformity and efficiency of solvent floods could be increased. This method has been used in many hydrocarbon solvent floods as well as in several CO₂ projects. Known as WAG, for Water Alternated with Gas,²³ from the operational procedure which was suggested by Fitch and Griffith, it has been adopted in most applications of both CO₂ and hydrocarbon miscible floods. It is convenient, both for control purposes, and also to minimize corrosion, to inject the solvent and water alternately rather than simultaneously. The cycle time used in WAG projects has varied from one up to six months or more.

Unfortunately, there are two major unanswered questions about the effectiveness of the WAG process. These concern the influence of added water on the microscopic displacement efficiency, and the mobility control effectiveness of increases in water saturation, unless these increases are themselves very uniform in space and time. Early experiments by Raimondi and Torcaso^{24,25} established the great increases in the applicable "dispersion coefficient" during the displacement of oil by solvent in the presence of high water saturation. More recent work^{26,27} has verified this large effect of water in "trapping" oil and preventing its contact with the (solvent) displacement fluid. A second difficulty with WAG is in its performance as a mobility control procedure. Although not as severe as in continuous CO₂ floods, early breakthrough of displacement fluid has unfortunately been a common occurrence in flood programs that incorporate WAG procedure.

B. Thickeners

Because past efforts to control the mobility of CO₂ have not fulfilled expectations, it has seemed important in this project to seek different methods of mobility control. These should be based on more lasting and uniform means of increasing the pressure gradients in the zone occupied by the displacing fluid. In addition, they should not interfere with the high microscopic displacement efficiency that made miscible displacements attractive in the first place. Such mobility control methods must be based on a controllable thickening of the displacement fluid, and also must not involve the addition of much water or any other agent which might interfere with the extraction of hydrocarbons and the development of a miscible displacement front. Although these objectives

would be generally desirable for any high mobility ratio solvent flooding process, it is particularly useful to consider the needs of EOR projects utilizing CO₂, because (domestically, at least) these projects comprise almost all of the "miscible gas" floods which are potentially profitable today.

1. CO₂ Foam

Two means of thickening CO₂ have been investigated in this project. The first method is the use of a foam-like dispersion of dense CO₂ in a surfactant solution. The decreased mobility of such a composite fluid through porous rock is apparently a consequence of the formation and migration of the aqueous films in which most of the water is transported. These films separate the CO₂ into cells or "packages," preventing it from moving freely through the pore space. Because the "foam" is a composite fluid with structure comparable in size to the average pore, the mobility in the rock cannot be assumed to be simply calculable as the ratio of rock permeability to a fluid viscosity. Despite this difficulty, however, the mobility reduction can be measured under reservoir conditions in the laboratory and the measurements utilized for prediction of behavior in the field. A recent SPE paper²⁸ supplements this report in describing the "foam" work of the project.

2. Direct Thickeners

A second method of thickening CO₂ has also been considered. This has consisted of the search for polymers which are directly soluble in dense CO₂. Such a solution is homogeneous on a molecular scale, and its flow properties can be characterized by a viscosity--though possibly non-Newtonian. Calculation of the mobility of such a solution could be performed confidently by the usual formulas. Unfortunately, our experiments indicate that there are no commercially available polymers that are soluble in CO₂ and raise its viscosity sufficiently. Nevertheless, continued search for novel polymers for use as "direct thickeners" seems justified by our results so far and by the probability that they would be more trouble-free than "foams" in application. This aspect of our project has also been reported separately.²⁹

C. Slug Design Considerations

In application, it would be economically impractical to inject a thickened, miscible displacement fluid for too long a time. To fill all of the reservoir pore space with even such a relatively inexpensive solvent as CO₂ would be too costly. Instead, only a "slug" of the solvent is used which is then followed by a less expensive fluid like water. The successful engineering design of a slug process must combine the advantage of displacement by an expensive, but presumably very effective fluid, with the economy of using it only in smaller quantities. Whether this can be done will depend not only on the cost and displacement effectiveness of

the solvent, but also on the slug's ability to resist those processes which degrade it during its passage through the reservoir.

The frontal instabilities which have been described previously were considered in the somewhat artificial situation where a large amount of displacing fluid was injected. In the more realistic circumstance of a slug injection followed by a chase fluid, the finger growth rate depends also on the mobility of the following fluid and on the finger spacing (or wavelength) perpendicular to the average flow direction. Whereas closely spaced fingers at the front of the slug grow rapidly without being much affected by the chase fluid, longer wavelength disturbances draw much of the energy for this parasitic growth from regions further from the front, and are thus more dependent on the large-scale variations of mobility in the flow direction.

Degradation of a slug, when either the solvent or the chase fluid is more mobile than the oil by a factor of five or more, will be dominated by frontal instabilities. With such mobility ratios, the solvent slug can be expected to break up into disconnected regions of high solvent saturation, with the largest size determined by the rate of instability growth and the volumetric size of the slug. These CO₂-rich regions will migrate rapidly toward the production wells and will separate into still smaller units as they proceed. Although these moving CO₂-rich regions can displace all or most of the oil in their paths, large areas out of their reach remain untouched. Thus an unprotected CO₂ flood can reduce the oil saturation in much of the reservoir to a value no lower than the waterflood residual--particularly if the slug volume is small.

In the case considered here, however, the mobility of the CO₂ will be decreased enough to prevent the rapid growth of instability fingers. Although mobility control is the first and most important step needed to increase the efficiency of a CO₂ flood, it is not the only one. In addition, the injected slug volume must be great enough so that the slug will remain effective throughout the displacement process. Even with potential instability growth controlled by thickening the CO₂, there will remain other slug degradation mechanisms. The most serious of these is caused by the fact that the dense CO₂ itself is not completely displaced by an immiscible chase fluid like water. After the slug of mobility-controlled CO₂ has been displaced through the reservoir by the water chase fluid, it will leave behind a residual saturation of CO₂. This residual saturation will extend over all of the swept region of the reservoir, and the associated volume thus constitutes the amount of CO₂ needed for the slug. This simple criterion is based on the design principle that the slug should exhaust itself just as it reaches the end of its planned travel through the reservoir. Actually, because the front of a CO₂ slug (where it is displacing the oil bank) is also subject to some degradation (in this case, by dispersive mixing with the oil), it would probably be worthwhile to overdesign the slug volume by ten percent or so as a safety margin, in order to displace all of the oil available in the pattern.

IV. Benefits from Mobility Control

Four principal advantages can be expected from the use of mobility control in CO₂ floods. These are discussed and, to the extent possible, evaluated in this section. The first of these advantages is that more oil can be recovered--the reservoir will be swept to a lower overall residual. Second, the oil cut will be higher (after the arrival of the oil bank at the production wells), and third, it can be expected that the oil production can be sustained economically for a longer time. These three benefits can be considered to be aspects of the same situation as modified by the central economic fact that the oil field's operational expenses must be paid for by the proceeds of selling the oil. The field must be shut down if, at the current oil price, the rate of production sinks below the threshold value. The use of mobility control can thus prolong the economic life of an oil field. A fourth, and more independent benefit, is that less CO₂ will be needed than in an unprotected CO₂ flood, thus enabling a limited CO₂ supply to be used more effectively.

The extent and economic value of these benefits will vary from reservoir to reservoir, depending on a number of parameters. Of particular influence on the timing of the benefits will be the saturation state of the reservoir at the time at which a mobility controlled CO₂ injection pattern is begun. It will be more attractive if the waterflooding which commonly precedes a CO₂ flood has not been carried to an economic end-point. This has to do with the timing of the additional oil production to be expected. If the oil saturation of the reservoir had been everywhere reduced to waterflood residual, then no immediate response could be expected to the injection of mobility-controlled CO₂. Production could only be expected to commence after the oil bank formed around the injector had expanded and been displaced outward, to reach the production wells. Other important reservoir engineering variables are the total oil remaining in place, the well spacing and condition, and the permeability. The manner in which these factors are related to the economic outcome is based on the physical processes by which the oil is displaced.

From the mechanistic point of view of the processes occurring within the reservoir, a major change in the displacement pattern is expected to be induced by the use of mobility control. The frontal region separating the injected, thickened CO₂ from the displaced water and oil behaves differently because of the reduction in mobility ratio. In an unprotected CO₂ flood, there is a large positive growth rate of the irregularities that are continually produced on the iso-composition surfaces by flow through inhomogeneous rock. If the CO₂ is thickened, however, this growth rate is reduced or even, if the mobility ratio M is lowered to less than one, made negative. (ie., in this case inhomogeneity-produced "bumps" or "ripples" on the iso-saturation surfaces will decay, rather than grow larger, as the flow proceeds.) Without mobility control, the unrestricted instability growth causes a large fraction of the reservoir to be bypassed by the injected CO₂. With sufficient thickening, on the other hand, the frontal region is not broken up into fingers, and a contiguous oil bank can be developed in front of it. In addition, because of the mobility control, the CO₂-rich displacing fluid can be injected as a slug, rather

than continuously, without being degraded by the growth of instability fingers which can penetrate through the frontal region. Less CO₂ is then required for the displacement program.

A key parameter in predicting the magnitude of the expected benefits from mobility control is the mobility ratio M. The value of this ratio, together with some geometrical factors, determines the relative speed with which fingers grow on an uncontrolled displacement front. It was first pointed out by Van Meurs and Van der Poel³⁰ 1958 that the displacement velocities in parallel paths occupied by two different fluids must be, at least approximately, in the ratio of their mobilities. A thoroughgoing application of this general principle to reservoir flow is not yet possible because of many complications. These center around questions of effective finger width and of transport phenomena at their lateral boundaries. Because these phenomena are very dependent on distance and on the finely scaled heterogeneity of the rock, it is not yet clear how to treat these important details, or to scale laboratory results to the field. Thus a precise calculation of the economic benefits from mobility control is not yet possible. This is primarily because the details of the displacement pattern of the unprotected flood are unknown.

However it is possible, for most secondary or tertiary prospects, to estimate the amount of oil accessible to a mobility controlled flood. Primary data for this calculation will come from the records of oil production and from a study of the flow patterns from injection to production wells. With proper design, a thickened CO₂ slug can be expected to move essentially all of the oil from the portions of the reservoir it traverses. Of course, not all of this mobilized oil can be economically displaced into production wells. The mobility ratio between the mobility-controlled CO₂ slug and the crude oil should be kept at less than about three to prevent extensive intrusion of instability fingers into the oil bank. Additionally, the slug should be large enough in volume so that its unavoidable degradation by the driving fluid behind it will not dissipate the slug entirely before the displacement target is reached. This flood design procedure itself can thus provide an estimate of the amount of oil recoverable by a mobility-controlled CO₂ flood. Detailed comparison with the results of unprotected CO₂ floods will require better information on the course of such displacements, however.

V. Project Activities and Accomplishments

This major section of the final report is divided into four parts: three are devoted to laboratory activities and one further sub-section describes auxiliary efforts involved in the project. As discussed briefly in the Introduction and Summary, auxiliary activities are also vital in the development of technology for mobility control of oil displacement by CO₂. The first of these tasks was the preparation of the project's Literature Survey."¹ More recently, substantial effort has been expended on the creation of flood design procedures for field application of mobility control. Much of this latter activity was in conjunction with a companion project, "Mobility Control for CO₂ Injection," DE-AC21-81MC16426

whose purpose is to lend support to a field trial of mobility control procedures in the Rock Creek field of Roane County, West Virginia. The details of that part of the work applicable specifically to operations at the West Virginia oil field are described in the reports of that project. On the other hand many of the results of that effort are of general applicability and are properly part of this project. Such general features of the reservoir engineering of mobility controlled floods are reported in sub-section D below.

A. The Instrumented Core

1. Objectives and Constraints

The goal of the work described in this section has been to test mobility control agents for effectiveness, by actual displacement experiments. Although many variations of the basic core flooding test have been reported in the petroleum literature, it was felt that some specialized apparatus and procedures were needed for this work. These special needs, and the development of the apparatus and procedures used to satisfy them, are described here.

The effectiveness of a particular mobility control agent for increasing the oil production from a particular reservoir could only be determined directly by a time-consuming and expensive field test. Furthermore, because there are so many economically unresolvable questions about the detailed geometry and environment of any oil field, the results of field experiments are not always definitive. Laboratory testing can thus be very useful to evaluate mobility control agents and procedures for CO₂ floods. These tests can save both money and time, and in addition they have the potential for providing useful comparisons between different procedures. Practical considerations therefore dictate that as much information as possible be learned from laboratory tests about the effectiveness and operating characteristics of proposed mobility control techniques before their field use. Because of this practical need, not in spite of it, the limitations of such information must be borne in mind.

It would be convenient to regard the laboratory flow system as a miniature reservoir, the observation of which could answer important operational questions directly. Indeed many literature reports of displacement experiments seem to have been designed and operated under this assumption. Thus, in many of the experiments on the effectiveness of "foam," a linear flow system is initially saturated with surfactant solution (with some residual oil in some cases). After injection of the CO₂ or other displacing fluid begins the output or "produced" fluid from the other end is observed as a function of the injected volume. It is understandable that the reader, and perhaps the experimenter, may be tempted to regard the system as a speeded-up model of an entire reservoir. The author's evaluation of a procedure's effectiveness may often be given in terms of the fraction of the initial liquid contents which is displaced from the core system. Similarly, the end point of the experiment may also be decided by analogy with the gas-oil ratio of a field flood--the proportion of displacing to displaced fluid in the effluent.

These experiments have been very useful--they convincingly demonstrated that this use of surfactants (as "foam" stabilizers) is very effective in improving the uniformity of both water and oil displacement in laboratory floods. They have also provided useful comparisons of different surfactant formulations. Particular reference is made to recent work of Bernard, Holm and Harvey³¹ where the tests were performed at high enough pressure to keep the CO₂ in a dense state throughout the flow system.

Nevertheless, it must be pointed out that the reservoir is not accurately modelled in its entirety in such tests. In particular--and with particularly confusing effect--distance is not scaled. For instance, the water saturation profile from the input end must have substantial influence on the course of the experiment. The distance and time scales of this variation, though, are related primarily to the detailed processes of the laboratory flood which are not necessarily duplicated in the field. In fact, because of the multitude of physical and chemical mechanisms of importance (in both laboratory and field displacements), and their different dependence on time and distance, it is generally not possible to design a "scale model" of the oil field which will behave like the prototype in all respects. Such a model would be quite acceptable, of course, if it merely behaved like the reservoir in a few "simple" matters like the output efficiency of a flood or the pattern of displacement. But these matters are unfortunately not simple; they involve the interaction of many processes and mechanisms that are not directly observable in the oil field or even in a laboratory flow system.

In light of the above, we have not tried to model a complete reservoir in the experiment designed for this project. To attempt the assessment of mobility control agents in CO₂ floods, it has instead been decided simply to see how effective these agents are in retarding the formation and growth of instability fingers. Their performance in this respect will determine the overall reservoir performance of mobility control agents. To measure this retardation of instability growth, a flow system is required which is large enough in cross section so that the finger growth is not significantly impeded by transverse dispersion between parallel flow paths. Tests of a mobility control agent in a slim tube could not yield the information needed, for instance, simply because oil recoveries in such a geometry are already high in a CO₂ flood. The high relative importance of transverse dispersive processes in the small cross section of a slim tube prevents the formation and growth of any significant instability patterns in such systems. Along with the need for a large enough cross section, there are also other geometrical requirements on a rock sample to be used in floods for evaluating mobility control methods. The length of the flow system should be sufficient to permit reasonably extensive development of frontal instabilities when favored by the mobility gradient in the particular test. Even though the flow system is not a scale model, and can at best be considered to behave like a small piece of the reservoir, the measured growth of fingers in it can be of great assistance in calculating the analagous phenomena in the field.

A system designed to satisfy these requirements is naturally subject to experimental constraints. The major constraint, which dramatically opposes the above considerations, concerns the size of the flow system. The costs both of construction and day-to-day operation, and the duration of individual experiments, increase much faster than linearly with size. These factors place a firm ceiling on the physical dimensions of the laboratory experiment. It is most important (and unfortunately all too unusual) that their effect should be thoroughly considered early in the design of a laboratory flow system.

A further constraint deals with the needs of observation, expressing the original reasons for the performance of the experiments. In this case, we wish to observe, as directly as possible, the internal events accompanying fluid displacement from a sample of permeable rock. During the test, furthermore, the rock, the sides of which are covered with a fluid-impermeable coating to define the flow, is necessarily also contained in a length of thick-walled pipe. This combination enables the absolute pressure level to be maintained at about 2500 psi. Under these circumstances, direct observation of the three-dimensional flow field in the rock does not seem possible, especially because the means of observation are also subject to constraints of time and money. The details of design and operation of the present experimental system which resulted from consideration of these matters are given in subsequent sub-sections. Prior to their further discussion, however, some remarks on the status of these experiments are appropriate here.

As might be expected, the laboratory experiment which was designed, constructed and operated for this project incorporates many compromises of conflicting requirements. The reader may detect a reflection of this fact in the results of this segment of the experimental work. Although the instrumented core was brought to operational condition and several experimental floods were performed with it, it has not yet been used to assess the utility of a mobility control agent. There are several causes for not using the instrumented core for its designed purpose. One is the simple fact that the development of agents worthy of testing in it did not occur until late in the project. The agents which became available then--all of them foam-like dispersions of CO₂ in surfactant solutions--were successfully tested in other ways. Second, the development of many of the measurement and operational sub-systems of the "instrumented core" took more time than anticipated. In addition, the complications of the interactions were great enough to make operation and maintenance of the system difficult. For instance, apparently insignificant changes in pressure and temperature--possibly combined with chemical deterioration--produced small cracks in the epoxy coating on the sides of the rock. Leakage of overburden fluid through these cracks ruined several experimental runs, and the cracks were difficult to locate and repair.

Despite the difficulties, however, the instrumented core has proved itself as a useful tool for this research. It is able to provide data which will be of importance in the assessment of mobility control additives and procedures. Several modifications of the core system,

designed to make it less troublesome and more reliable in use, are planned in ongoing studies. These modifications are generally based on lessons learned from experience with the flow system as built. They represent improvements or corrections of unforeseen deficiencies of the first design and are discussed below.

2. Experimental Design

The flow system selected for this experiment was intended to simulate, in broad outline, a portion of the most nearly marginal of the reservoir rock systems in which CO₂ is used as a displacement fluid. Thus, the initial experiments were designed to assess the utility of mobility control agents in tertiary floods of carbonate reservoirs. The porous medium chosen was cut from a quarried rock rather than from an actual oilfield core, in order to obtain a larger sample. It was considered essential that the longitudinal dimension of the laboratory rock sample be parallel rather than perpendicular to the bedding planes. In this way the flow pattern would not be primarily dependent on the continuity of low permeability layers in the rock. A low-to-medium permeability dolomite rock with fine-grained vug structure was chosen for the experiments, in the hope that it would be somewhat similar to the carbonate formations of west Texas and eastern New Mexico. The rock selected is described briefly in Table I. Because the initial displacement experiments were to represent tertiary CO₂ floods, the necessary rock preparation consisted of a series of brine and oil displacements to leave the rock brine-saturated except for an irreducible residual oil saturation (irreducible, that is, by further waterflood).

Table I
Core Dimensions and Characteristics

| | |
|---------------|----------------------------|
| length | 29. inches (74 cm) |
| cross section | 1.90 x 2.10 (4.8 x 5.3 cm) |
| material | Baker* Dolomite |
| porosity | 0.20 |
| permeability | 35 md |
| pore volume | 370 cm ³ |

To maintain sufficient density of the CO₂ during the designed displacement runs, it was necessary to maintain in the rock an absolute pressure above 1000 psi. To this end, the output fluids are led through an electronic back pressure regulator (BPR) which consists of a servo motor-driven needle-valve operated automatically in response to the

*The 'core' sample was cut from slab purchased from J.E. Baker³ quarries, York PA. The rock is described by J.J. Meister in reference.

difference between a set point and the measured core output pressure. It is quite similar to a BPR described recently by VanEgmond and Lease.³² By this means, the absolute pressure throughout the rock could be maintained at necessary operating levels independent of the input flow rate.

As noted previously, the high internal pressure necessitates a balancing high pressure around the outside of the core. One traditional way in which this has been done in many experiments has been to use a rubber sleeve around the sides of the core, with a liquid (usually water) in the annulus between it and a heavy-walled containing vessel. This "overburden" liquid could then be pumped to a high pressure to keep the rubber sleeve pressed tightly enough against the rock. This method could not be used here because of certain additional measurement constraints and was accordingly modified in two major respects. Instead of a rubber sleeve to contain the internal fluids and define the flow through the rock, a layer of epoxy was used. A second modification was to use oil instead of water as the overburden fluid to eliminate any electrical conductivity that would interfere with the electrical measurements described below.

In order to maintain the proper pressure in the overburden fluid, a high pressure pump was used to transfer oil from an external reservoir into the heavy-walled container surrounding the epoxy-coated core. To provide a means by which the pressure could be relieved, an outlet allowed oil to leak from the system, through a nearly-closed needle valve, and back into the external reservoir. The pump was switched automatically in response to the appropriate pressure transducer signals to maintain the overburden or "sleeve" pressure above that of the internal fluid by a margin of about 50 psi. The arrangement permitted the system to adjust automatically to changing experimental conditions during different displacement runs.

For the purpose of assessing the characteristics of tertiary floods with CO₂, three aspects of the experiments with the "instrumented core" were designated as measurement objectives. These aspects were based on three different measurement systems and are discussed in the next three sub-sections.

3. Fluid Measurements

The first measurement objective was to evaluate the efficiency of CO₂ floods--that is, to measure the fraction of remaining oil recovered by the displacement. Standard laboratory methods are quite suitable for this determination. The effluent is led through the electronic BPR, downstream of which it separates into gas (assumed to be predominately CO₂ at atmospheric pressure) and liquid. The liquid is then collected in standard test tubes on a fraction collector, thus giving a convenient record of produced oil/water fraction. Although, as noted above, no CO₂ floods with mobility control were attempted in this flow system, one "uncontrolled" flood--of a waterflooded core, by CO₂ alone--was performed. The volumetric results of this displacement test, while not directly

analogous to those expected from a reservoir, do indicate qualitatively similar behavior. For instance, at the commencement of the CO₂ flood, the produced fluid was initially composed of water alone. This results from the fact that water was initially the only mobile phase even though the waterflood residual oil fraction was 37.6%. However, breakthrough of CO₂ and oil occurred after only 44 cc (or 11.9% of the pore volume) of CO₂ had been injected. This was much sooner than would have resulted from a uniform displacement and, in fact, indicates that the velocity of the tips of the fingers was about 8.5 times as great as the "displacement velocity" $Q/A\phi$.

Shortly, after breakthrough, the water production rate was reduced to zero. Whereas the previous result of the core flood is similar to that which occurs in field CO₂ floods, this reduction-to-zero of the water rate is not. In a reservoir, much of the flow into the production well is from directions other than that of the injection wells, so that even after major breakthrough of the oil-and-CO₂ fingers, some water continues to be produced.

The fraction of CO₂ in the non-aqueous production is appreciable at breakthrough and continues to rise. This qualitative feature is again common to both laboratory models and to uncontrolled CO₂ displacements in the field. Unfortunately the rate at which this rise takes place is not directly scaled, since it depends on factors which differ greatly between field and laboratory displacements. One of these factors is simply the gross geometrical shape of the porous flow system. Here the difference in dimensionality of the field and the laboratory systems is critical. Another factor leading to difference in behavior is the size. Because entrainment of hydrocarbon components into the moving CO₂ proceeds by molecular diffusion, the rate of the process is very sensitive to distances and concentration gradients at many scales, from pore size up to that of the fingers. There seems to be no reason to presume that the average microscopic geometry would be the same even between one part of the reservoir and another, and certainly not between the average field behavior and that of a linear core flood.

Thus, as was expected in the laboratory displacement, the proportion of CO₂ in the produced fluid continued to increase after breakthrough. In this experiment the oil fraction had been reduced to a value so close to zero that the run was terminated after a total of 336 cm³ of CO₂ had been injected. The produced fluid during this time included 82 cc of oil. These numerical results cannot be taken to indicate any reservoir behavior, but would be of interest for comparison with later runs performed with mobility controlled floods. The results of this uncontrolled CO₂ flood are summarized in Table II.

Table II
CO₂ Flood of "Instrumented Core"

| | |
|--|-------------------|
| Initial oil saturation (waterflood residual), | 139 cc (37.6% pV) |
| CO ₂ injection rate (at 1008 psig 25°C; =0.72 g/cc) | 15 cc/hr |

At Breakthrough

| | |
|--------------------------------------|------------------|
| Cumulative CO ₂ injection | 44 cc |
| Cumulative brine produced | 44 cc (11.9% pV) |

At Conclusion of Flood

| | |
|--------------------------------------|-------------------|
| Cumulative CO ₂ injection | 337 cc (91.1% pV) |
| Cumulative brine produced | 45 cc (12.2% pV) |
| Cumulative oil produced | 82 cc (22.2% pV) |
| Cumulative CO ₂ produced | 210 cc |

The effectiveness of mobility control agents can thus be assessed, to some extent at least, from the results of a laboratory core flood in a rock of large enough dimensions. The particular results of interest are the time until breakthrough, the rate of decrease of produced oil fraction after breakthrough, and, of course, the proportion of the waterflood residual oil which is recovered. Caution is again urged in the interpretation--these results are not directly indicative of the quantitative behavior of reservoir displacements. It is wise to include the measurements of certain other aspects of the laboratory flood, in order to strengthen the overall comparisons made between uncontrolled CO₂ displacements and different types of mobility-controlled floods. An ideal measurement situation would be one in which major features of the oil saturation distribution could be sensed and recorded in three dimensions. This would enable growth of the instability patterns--both their length and their lateral distribution--to be followed in detail. Such an ideal measurement technique would make possible a very convincing and informative assessment of a mobility control agent's effectiveness.

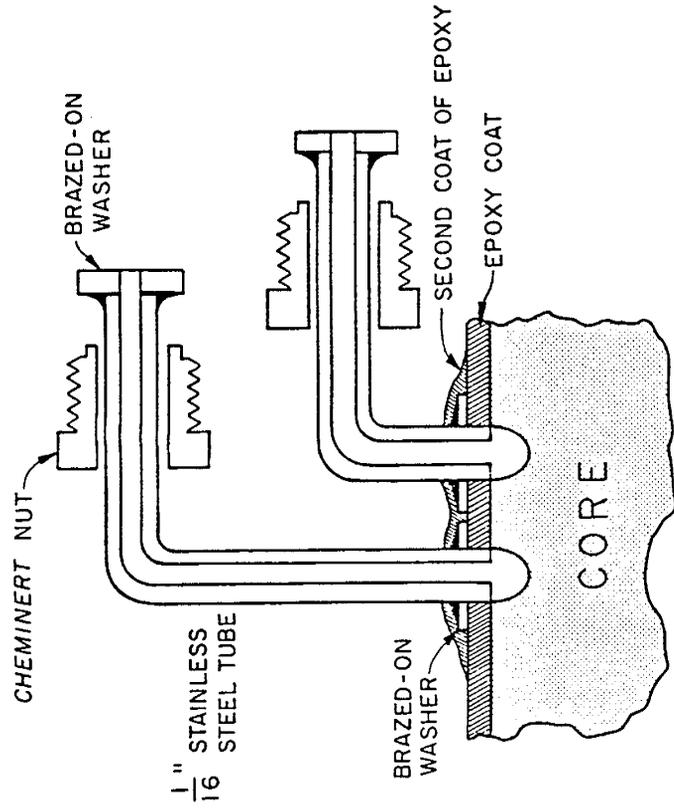
Unfortunately such an ideal technique is not available. Even a computer tomography Xray scanner (a "CAT-scanner," which is effectively ruled out by its cost and expense of operation) would be somewhat limited in time and space resolving power for the above measurements. Instead, a compromise plan was developed to collect data concerning only the longitudinal extent of the transition zone. To this end, two other measurement objectives were carried out in the design and operation of the instrumented core. Both of these are efforts to observe more closely the events which occur inside the core during the flood.

4. Measurement of Pressure Gradients

From the macroscopic point of view, the development of viscous fingers during a displacement with unfavorable mobility ratio is a consequence of the lower pressure gradient behind the front, than ahead of it. The measurement system described here was designed to provide estimates of the gradient at four places along the length of the core. The values of these pressure gradients during a flood can be used directly to calculate the mobility of the fluids contained in that section of the core. Their changing values, as the flood proceeds, are also a direct indication of the tendency toward frontal instability and the growth of fingers.

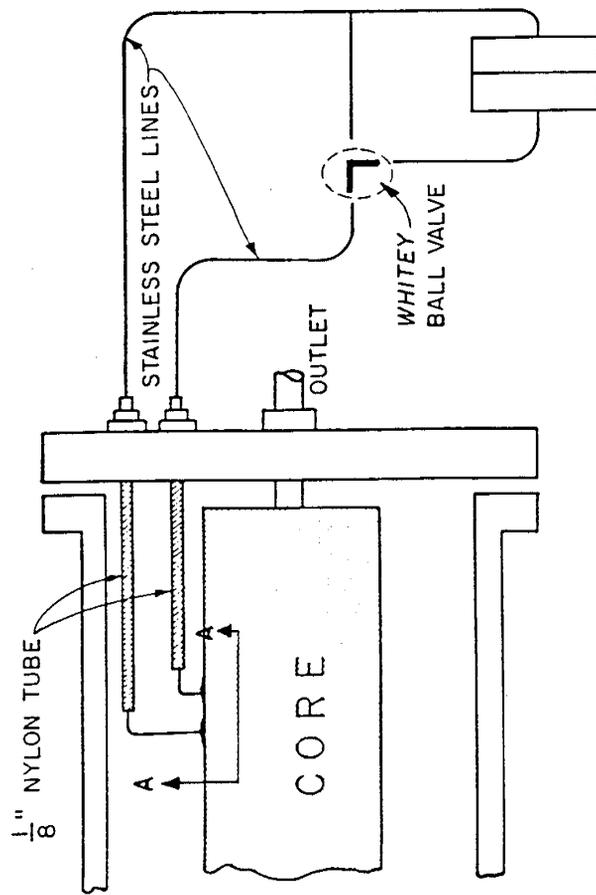
The measurements were accomplished by observing the pressure difference between pairs of pressure taps separated by one centimeter in the direction of flow. These pressure taps were 1/16 inch deep, 1/16 inch diameter holes into the side* of the core, epoxy-sealed to a length of 1/16 inch stainless steel tubing that terminated in a Cheminert-type fitting. Each pair of adjacent pressure taps were connected, through tubing that led through a large flange at one end of the high-pressure core container, to a Validyne differential pressure transducer. The manner of connecting tubing to the side of the core for the pressure taps is shown in Figure 1a. A schematic diagram is shown in Figure 1b of the tubing connection to the transducer. This latter figure also shows the way in which a 3-way ball valve (Whitey) is used across each transducer in order to re-zero it periodically, to enable corrections for its drift. In order to avoid severe interference with the electrical measurements that are described in the next sub-section, it was necessary to have an insulating portion in each of the tubes leading to the differential pressure transducers. For this purpose, the major part of each fluid conductor line internal to the pressure vessel was made of semi-rigid (1/8" OD, 1/16" ID) nylon tubing. Brine fills the pressure tap lines only from the core as far as a brine-oil interface located in the nylon tube section. From there on through the pressure bulkhead into the stainless steel high pressure tubing leading to the transducers themselves, the lines are filled with Soltrol. The feed-through connections by which the pressure transducer tubing is brought through the walls of the high-pressure container are also electrically insulating. They are constructed from standard High Pressure Equipment Co. (HIP) tubing fittings with some specially designed attachments. A detailed sketch of these electrically insulating feed-throughs is shown in Figure 2. The capillary pressure drop across a brine-oil interface in the nylon tube, calculated from $P = \sigma \cos \theta / R$, is about 0.01 psi for complete wetting of the nylon by Soltrol. Each differential pressure measurement contained two such interface pressure drops in opposition. Thus even if the two tube

*Although such pressure taps can measure the actual fluid pressure only near the side boundary, there is independent evidence⁴⁸ that this is only slightly influenced by even rather severe local permeability heterogeneities. Thus to a good approximation, the Darcy pressure gradient can be expected to be the same over any part of a cross section through a linear flow system.



SECTION A-A (Fig. 1a)

1b



VALIDYNE DIFFERENTIAL PRESSURE TRANSDUCER

1a

Fig. 1. Details of pressure taps.

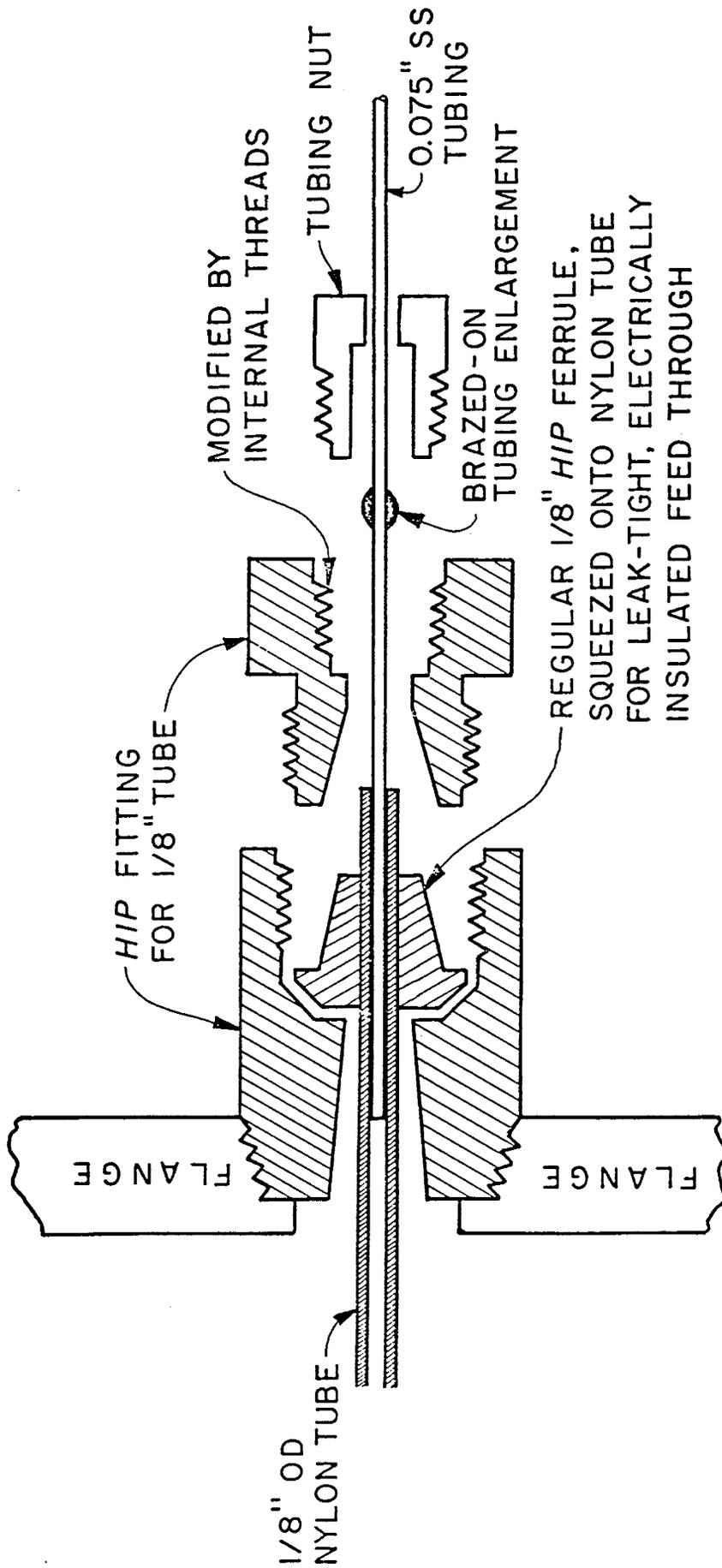


Fig. 2. Pressure tap feed-through.

diameters or wettabilities differed by as much as 10%, the resulting error would be no more than .001 psi. Flowing pressure drops varying upwards from 0.05 psi were thus expected to be measurable with acceptable precision. Such low values would occur for displacement velocities of about 1.2 feet per day for fully brine-saturated rock.

In operation, the differential pressure system has deviated from design standards in two important respects, both of which spring from the same unforeseen characteristic of the transducers. The deviations unfortunately have prevented full use of these measurements for their intended purpose. Analyses of the difficulties are presented in the following paragraphs, and certain corrective modifications of the design are also given. With these changes, proper operation of future models of the system seems assured.

The differential pressure transducers utilized for this work, like most other such instruments, operate by making an electrical measurement of the distortion of a diaphragm that separates small reservoirs of the two fluids. Two great advantages of Validyne's variable reluctance design accrue from the fact that the electrical elements on the two sides of the diaphragm are isolated from the fluids. Therefore any fluids may be used which are compatible with the stainless steel gauges. In addition, the diaphragm itself may be easily replaced by one of different thickness to give a different calibration constant.

The unfortunate characteristic of these transducers, not properly appreciated when the system was designed, is that a significant motion of the diaphragm is required for a reading. Such a motion corresponds, of course, to a measurable volume of fluid. It turns out that for any range (except for minor differences due to the details of the diaphragm's thickness distribution), a volume change of about 0.01 cc (or 10 microliters) is required for a full-scale reading. This volume change represents a 10 μ l increase in the fluid volume on the high side of the diaphragm, and a decrease of the same amount on the low side. Unfortunately this full-scale volume requirement, or its equivalent, the "hydraulic impedance" in $P/\Delta V$ psi/cc for a given pressure range, is not customarily listed among the transducer's advertised specification. (In fact, it is often difficult to obtain information about this characteristic from the manufacturer, even in answer to a direct request). This is because, in most applications for which these differential pressure transducers are used, the value of the mechanical impedance can be safely assumed to be quite high. Compared to the quantity available, only an insignificant amount of fluid is needed to be forced into the gauge in order to make the measurement. To continue the implied electrical analogy used above, the impedance is completely reactive--the transducer can be compared to a capacitance, so that in linear systems its effect is only on transient pressure changes. The less-than-instantaneous response of the system represents the first of the deviations from ideal behavior that were mentioned above.

The response of the pressure transducer in the above system to a change in flow rate through the core is quite analagous to the voltage

response across a capacitor connected through a resistance to a changing voltage. The reading does not change instantaneously after a step change in the source, but rather approaches the new value exponentially, with a time constant equal to the product $R^H C^H$. Here R^H is a "hydraulic resistance" (in atm-sec/cc) and C^H is the "hydraulic capacitance" (in cc/atm). For the manner of connection of the pressure taps which has been described,* the hydraulic resistance per tap is about 6.5 atm sec/cc if the rock is completely brine saturated in the neighborhood of the tap. It turns out that the hydraulic resistance of the tubing is negligible in comparison. The hydraulic capacitance of the transducer, when equipped with a 5 psi full-scale diaphragm,** is about .029 cc/atm. Thus, for this case, the time constant for the differential pressure measurement is about 3.8 seconds. Whereas this does not seem excessive, it does represent a minimum--the response is still slower when the brine saturation of the rock is less than 100%, and its relative permeability is further decreased. Furthermore, the saturation condition also induces much more serious effects as well.

The second way in which the differential pressure system deviates from ideal behavior is a consequence of the same transducer characteristic (its finite hydraulic impedance). It also interferes most with the measurements during times of low water saturation, when it unfortunately has an even more serious additional effect. The force on the transducer's diaphragm is modified by the capillary pressure changes in the rock around the pressure tap, as the fluid volume required for the measurement is moved through it. In fact, the position of the diaphragm--which is electrically translated into the instantaneous transducer reading--is at any time determined by a dynamic balance among several forces. The previous paragraphs on transient behavior dealt with a linear situation of the balance between the restoring force on the diaphragm and the Darcy pressure in the portion of the rock around the pressure tap. When the brine saturation near the tap is changed by the flow itself, a more complicated, non-linear situation arises. In the earlier case, the diaphragm moved gradually towards an equilibrium position determined unambiguously by the steady pressure drop longitudinal to the core. In this case, however, the final reading will be of a pressure that includes two capillary pressure terms that may not be the same. When the zeroing valve is switched on, there will be a flow of fluid into the high side and out of the low side of the transducer. Trouble clearly results if brine is not the only mobile phase in the core near the taps. At the low side, the flow out of the transducer will push brine into the rock, thus increasing the water saturation in the region surrounding the tap. Flow into the high side tubing, on the other hand, will be composed of both water and of the non-aqueous phase. If water remains continuous from the rock into the tubing, it will be at a pressure lower than that which would

*Considering flow outward from a half sphere with radius a to a larger one of radius b, Darcy's equation gives $P = Q / (2\mu R) (1/a - 1/b)$. The hydraulic resistance $R^H = \Delta P / Q$ is then $\mu / 2\pi k (1/a - 1/b)$. This is in atm sec/cc if μ is in cp, k in darcies and a and b are in cm

**The hydraulic capacitance, is the ratio of the 0.01 cc/FS given earlier, to the pressure required for a full-scale reading, 0.34 atmospheres.

otherwise be in equilibrium with the low side pressure, by the capillary pressure difference. This latter value is of course dictated by the different saturation states of rock at the two taps. The erroneously low (or even negative) pressure differential could be expected to correct itself slowly by means of a compensating flow. This flow would tend to drive the different saturations toward equality, but could not keep up with the frontal motions the system was designed to track.

A possibly worse situation would occur if the continuity of water were not preserved at the high side tap's rock interface. In this case the pressure in the high side tubing would be higher than in the previous situation and would increase as the saturations at the two taps approached each other. In this case a stable, erroneous value would be eventually achieved even if flow were halted. It would be given by the capillary pressure of the rock at the final saturation.

The magnitudes of these effects in a flowing situation, and the likelihood that brine continuity in the tubing will be destroyed at the high side tap depend on the hydraulic impedance of the transducer and on the area of the rock exposed at the pressure taps. In the system constructed, both of these were too low. Consequently, proper mobility measurements could only be made during flows in which no phases other than brine were mobile. After these troubles were discovered, the principal measure taken to protect the pressure tap system was to keep the zeroing valves "off" during those periods when the brine saturation was so low that oil or CO₂ could flow.

For improved design of such a pressure tap system, several changes can be specified, based on the lessons learned from the present system. These are as follows:

1. Expose more area of rock to the pressure taps. This area can be situated on the sides of grooves cut into the rock perpendicular to the average flow and protected with rigid covers rather than merely the sides of holes drilled into the core. By this means, substantial gain can be achieved, resulting in a much smaller flow into or out of the rock (at the rock-fluid interfaces of the pressure tap) for a given volume change demanded by the transducer.

2. Re-fit the transducers with thicker diaphragms so that less fluid is needed by them in response to pressure changes. Of course, this will decrease the sensitivity--i.e., with less diaphragm motion for a given pressure differential there will be a correspondingly lower electrical signal. This can be compensated for, to some extent, by increasing the gain of the amplifiers. Random signal variations (noise) can be kept from increasing proportionately by reducing the amplifiers' cut-off frequency. The relatively greater drift and temperature sensitivity of the transducers can be controlled by frequent re-zeroing of the valve, if the attempted gain has not been too much.

3. Install "mini-pump" fittings in each differential pressure line

by which a small amount of additional fluid can be forced into the tubing, so brine can be forced into the core at the tap. This is especially important at the high sides, but the capability would be useful also in the low side lines of each differential pressure system.

Despite the disappointment of not being able to use the differential pressure tap system in all phases of these experiments, the basic principles of its design has been verified, and this method of assessing the effectiveness of mobility control agents remains as attractive as before. In addition, the analysis of the experimental difficulties has produced recommendations for design changes that should be generally useful to other groups engaged in similar experiments. The use of taps to measure pressure along the sides of the core is superior to the usual method, in which only the input and output pressures are observed. Only changes in "average permeability" can be measured by such observations, and evidence obtained in this way for changes in flow distribution during a displacement is at best ambiguous. But the local mobilities calculated from direct measurements of differential pressure between closely spaced taps is more informative. These measurements and their change in time with the progress of the flood can distinguish much more subtle changes among floods run under different conditions. The technique should then be of great interest in more basic experiments than those attempted in this project, the object of which was simply to evaluate the relative worth of different mobility control agents.

5. Electrical Measurements

A third method designed for the observation of displacement experiments in the instrumented core was also an attempt to "see into" the rock. By measuring the extent and development of the transition zone between displaced and displacing fluids, this method was also intended to allow evaluation of different mobility control agents. The observations are of rock conductivity at many locations along its length, and primarily reflect the ionic concentrations in the aqueous phase saturation at those places. The measurements of conductivity are averaged by the method itself over "slabs" spanning the entire cross section of the core, and of thickness, in the direction of flow, of 0.260 inches. (This distance is determined by the spacing of voltage electrodes along the side of the core.) The two current electrodes of gold-plated stainless steel mesh are located at the ends of the core and contact the entire fluid inlet and outlet faces. The voltage measurements are made using a high input impedance amplifier so that only negligible current flows into the rock from the voltage electrodes. There are two motivations for the use of independent voltage and current electrodes. The first of these is based on the fact that, with this method, the current drawn by the voltage measuring circuit is lower by a factor of 10,000 or more than the longitudinal current through the rock. Hence, neither a resistive coating on the voltage electrode surface or an atypical saturation condition of the rock itself near those electrodes would cause appreciable error in the readings. The second reason for this design is simply that the

multi-electrode method makes it possible to define the geometry more precisely.

Although the electrodes were all gold plated for corrosion resistance, polarization at both the current electrodes and the adjoining rock would occur if a direct current were to be passed through the system for an appreciable time. The measuring current was therefore applied in alternate pulses of opposite direction. The duration of each pulse, about 2 milliseconds, was only long enough to allow two voltage measurements to be made--one between a particular pair of adjacent voltage electrodes and one across a standard resistance in series with the core. As has been discussed in previous reports, the switching to accomplish these measurements and to move from one position to the next along the core is controlled by the TERA data acquisition micro-computer. The design and operation of that hardware/software system is unchanged from what was described and pictured in the 2nd Annual Report of this project³³ except for the development of additional software to record experimental data onto standard floppy disks as well as paper.

The original purpose of the instrumented core was the evaluation of various mobility control agents and the comparison of mobility-controlled with unprotected tertiary oil displacements. As noted above, no such evaluation experiments were performed. There is unfortunately no data yet available, therefore, on the progressive changes in conductivity profile during mobility-controlled displacements in the rock sample. One unprotected CO₂ flood was performed in the system, however. The set of conductivity measurements obtained is consistent with the volumetric results observed during the same run and discussed in section V.A.3. The majority of the changes in conductivity occurred during the time before CO₂ and oil breakthrough. Thereafter, only relatively small changes occurred as the continuing CO₂ flood displaced a small additional quantity of oil from the positions of the rock between the main fingers.

Although the electrical measurement system operated quite successfully on the instrumented core, there were lessons learned here too that can be incorporated into an improved version. A major improvement will be in the method of voltage electrode wiring. In the current model, the wires from the voltage electrodes are permanently connected (soldered) to the inner terminals of the radial printed circuit conductors forming the high-pressure feedthrough. This proved very unwieldy, and subjected the wires and their connections to excessive stress during handling. In a future model, it is planned to make permanent connections from the voltage electrodes to standard multi-pin sockets epoxied to the side of the core. This will allow the printed circuit card that carries the electronics to be kept separate from the sealing system by which the wires are passed through the high pressure wall. The latter can be accomplished by the use of commercially available flexible flat cable.

A second modification planned will enhance the measurement choices available. Subsequent to the original installation of the electrode system, it became apparent that the system can be used in an additional mode. It is also possible to use the voltage-measuring system at those

times when no current is flowing through the rock. The EMF's measured in this case are indicative of the differences in ion concentration and of electrode surface condition between adjoining electrodes. These measurements have been made with the present, gold plated voltage electrodes, and they do display some variation as a flood progresses, although it is not clear just what ion concentrations are responsible for the observed readings of EMF. In a future version of the instrumentation, the electrodes will be made of silver chloride coated silver wire. Such Ag/AgCl electrodes give a response proportional to the logarithm of the chloride ion concentration ratio at the surfaces of the two electrodes. The zero current EMF measurements will thus supplement the conductivity profiles obtained by the switched current technique, in providing information specifically concerning the distribution of chloride ion concentrations along the side of the core during floods.

B. Foam-Like Dispersions

The function of mobility control, as the phrase is used here, is to suppress or retard the formation of instability fingers in the frontal region between displacing and displaced fluids. This can be accomplished by thickening the displacing fluid--reducing its mobility to such a level that the finger growth rate is small enough that the instability-related displacement non-uniformities will not be a major problem. In this section we discuss the development and use of a "composite fluid" to accomplish the thickening of dense CO₂. The flow of this composite material must necessarily be different in microscopic detail (that is, in the pore space) from the flow of a molecularly homogeneous fluid. On a macroscopic scale, however, the flow of a foam-like dispersion through the rock is like that of a viscous Newtonian fluid. Because a greater pressure gradient is required for its flow, the larger scale effects on stability of the front are the same as those of a simple displacing fluid of low mobility or high viscosity.

1. Background

The flow of multiple fluid phases in rocks has of course been studied since the beginnings of the scientific consideration of oil production,^{34,35} and the use of relative permeabilities to describe the associated pressure gradient is well developed. In these "classical" situations, the interface, while necessarily adequate for separating the immiscible phases, is generally unable to delay the rapid coalescence of droplets or bubbles of a similar phase when they approach. Thus the immiscible phases establish multiple independent "channels" in which the flow of a phase is controlled by the viscosity of that phase alone. This situation does not prevail when one of the phases contains a suitable surfactant that sufficiently strengthens the double film between the bubbles so that their coalescence is significantly delayed. The presence of these longer-lasting double films seems to produce a marked alteration in the flow regime in porous media, such that the relationship between flow rates and pressure gradients is no longer predicted by the same

relative permeability curves. The difference is particularly great in the case of a "foam-like dispersion," in which the phase that is present at higher volumetric saturation is discontinuous, separated into cells or "packages" by relatively stable double films of the continuous phase. In this case the resistance to flow through the rock can be very large.

2. The Literature of Foam in Porous Media

There is much discussion and data in the literature concerned with this reduced mobility in porous media. Much of it is devoted particularly to the flow of foam^{36,31,37-40} using air or other gas at relatively low pressure, or to the use of such a dispersion as an injection fluid to displace oil either from reservoirs,^{4,41,42} or from laboratory cores.^{43,44} Under some circumstances, the pressure drop required for appreciable flow was so great that foams were considered as blocking or plugging agents. Their use was even suggested to prevent unwanted flow,^{45,46} the sealing of gas reservoirs.

With this extensive background, it is not surprising that the increased pressure drop required to move "foam" has been recognized as presenting the opportunity for mobility control in CO₂ floods. But even without consideration of the as yet unknown microscopic mechanism of the mobility reduction, there were some serious questions about the application of foam for this purpose. These questions are concerned with the separation of this thickening effect from other phenomena, and with its evaluation under reservoir conditions. Two major questions concerning the applicability of literature data to the needs of CO₂ flooding arise from the use in most of the experiments of air or nitrogen as the non-polar component of the foam. At the high pressures of a CO₂ flood, it would be misleading to consider CO₂'s behavior simply as that of a "gas," merely because the field temperature exceeds the critical point (88°F). On the contrary, it seems more reasonable even at higher temperatures to consider the CO₂ as more liquid-like in its behavior. This is because, in any flood performed above the so-called "Minimum Miscibility Pressure" (MMP), the CO₂'s density lies in the range 0.5 to 0.9 g/cm³. At these high densities, its compressibility is considerably less than that of a gas near atmospheric pressure. The question then arises whether part of the reduced mobility of foam that is observed in low pressure experiments might be a result of the compressibility of the non-aqueous fluid.

A second question about the applicability of air-foam experiments is concerned with the different chemical environments in which surfactant finds itself. In an air foam at low pressures, the surfactant molecules can only reside either in the aqueous bulk phase or in the air-water interfaces. In a foam-like dispersion of the type which occurs in high pressure CO₂ experiments or in the reservoir, dense CO₂ is the non-aqueous component. This is then an alternative bulk phase in which surfactant molecules can be distributed, and could strongly modify the interfacial activity. It could also be of particular importance dynamically, during flow of the "foam" through porous media. In particular, in the event of appreciable solubility in the non-polar phase, surfactant would become

less available for rapid replenishment of interfacial concentrations during the sudden changes of detailed geometry that necessarily occur during flow. (As described below under "Surfactant Screening and Selection," an attempt has been made to simulate this problem in the procedure developed for that purpose.) All this is in addition to the chemical modification that results from the appreciable solubility of CO₂ in the water, which lowers the water's pH to 3 or less.

A third problem about the applicability of air-foam experiments is displayed by the wide variations in the manner of reporting experimental results. The use of permeability and relative permeability for the calculation of pressure gradients is so well-established in the petroleum literature that the temptation exists to use these same concepts even when difficulties result from their use. The difficulty in this case is the unsatisfied--and, in fact, virtually unsatisfiable--need that is presented for an "effective viscosity" for the foam if the usual formulae are to be used. The trouble arises because in any viscosity measurement, the calculated result can only be expected to be independent of the size of the viscometer if the fluid's microscopic structure is small compared to that scale. No trouble at all results from the use in Darcy's equation of the viscosity (as measured in standard viscometers) of molecularly homogeneous fluids. This is because the molecular structure of such fluids is much smaller than the pore spaces and channels of reservoir rock.* In the case of a composite fluid such as the foam-like dispersion under consideration, the structure may not even be small compared to that of common viscometers. In addition, of course, the usual macroscopic core flow experiment does not allow examination of the "foam's" structure inside the flow paths of the porous media which may indeed be variable. It is the contention here and in a recent paper²⁸ that efforts recorded in the literature^{36,47} to measure and use an "effective viscosity" for foam have demonstrated this variability. The values calculated for the effective viscosity do indeed vary with the viscometer dimensions, and there is no assurance that a stable value is achieved that might be applicable to flow in the pores.

Of course, the above does not alter the fact that the flow through a sample can be measured as can be the pressure drop across it. In a steady flow, the simple ratio of these - normalized for the macroscopic sample size - can be reported as the mobility of the foam:

$$\lambda = (Q/A)/(\Delta P/L) \quad (1)$$

The value of the mobility might be expected to depend on the structures of both the rock and the "foam." Presumably it would be

*Although the Klinkenberg effect observed in the flow of low pressure gas through fine-grained porous media at densities low enough that the molecular mean free path is comparable to the pore size is an exception and could be considered as a related case to that discussed.

smaller if the double films separating the non-aqueous fluid "cells" were tougher or more numerous in the rock. Similarly a rock with larger pores--a higher permeability rock--might be expected to exhibit a larger value of mobility for a given mixture of non-polar fluid and surfactant solution. Following this latter expectation, it might be useful in giving the results of an experiment, to report also the value of relative mobility λ_r , obtained by dividing the mobility by rock permeability:

$$\lambda_r = \lambda/k \quad (\text{cp}^{-1}) \quad (2)$$

The rate of flow of a molecularly homogeneous fluid through a rigid porous rock, at all but the highest flow rates, is of course observed to be accurately proportional to the pressure gradient as well as to the inverse of the fluid viscosity. This linearity is the essence of Darcy's Law and can be shown to follow from the application in the pore space of the Navier-Stokes equations in the "creeping flow" approximation--at flow rates low enough to render insignificant the terms in the square of velocity.⁴⁸ In the absence of any detailed microscopic mechanism or theory of the flow of a foam-like dispersion, however, there seems to be no a priori reason to suppose that the rate of such flow should be proportional to the pressure gradient (that is, that the mobility λ should be constant at different flow rates) or that the relative mobility λ_r should be independent of the rock in which it is measured. Rather, these matters must be left to experiment to determine.

The questions above impose some special requirements on the design of experiments to answer them, or on the selection of past work from which to obtain information on this aspect of mobility control. These are:

- a) The experiments should, as far as possible, eliminate the influence of the compressibility of the non-aqueous phase. Thus, in experiments with air or gas foams, the ratio of the pressure drop across the core to the absolute pressure should be small.
- b) The experiments should provide data for the calculation of mobility. In most cases, this will mean that they should be steady-state rather than displacement experiments.

Of the experimental work reported in the literature, there are several from which mobilities can be calculated. Table III (which is adapted from SPE 11233,²⁸ as is much of the following section) summarizes such data, giving both the authors' results and our calculations from the selected literature studies.

Bernard and Holm⁴⁹ in an early experimental study, gave their results in terms of the "reduced permeability to gas" as a result of surfactant injection; the reported reductions ranged from factors of 3×10^{-5} to 6×10^{-3} . It is to be noted that these numbers considerably exceed the ratios of liquid-to-gas viscosities. Thus these experiments indicate that foam can be an effective agent in reducing gas mobility. Unfortunately not

Table III Selected Previous Foam Studies

| | Bernard & Holm (Ref. No.46) | Marsden & Khan (Ref. No.36) | Holm (Ref. No.38) | Raza (Ref. No.43) | Chiang et al. (Ref. No.39) | Bernard, Holm & Harvey (Ref. No.31) |
|---------------------------------|--------------------------------|--|--------------------------|----------------------------|-------------------------------|--|
| Porous Medium | Sandpack | a) (Sandpack 25-120 mesh) b) Berea core c) Alumdum | Sandpack 100-200 mesh | Sandpack | Sandpack 60 mesh | Carbonate Core |
| Length | 1-30 ft. | a) 6.5 cm b) 3.8, 4 cm c) 3.8 cm | 2 ft. | 18,12 in. | 45.5 in. | 3 ft, 32.5 in. |
| Diameter | 0.5 in. | a) 2.5 cm b) 1.9 cm c) 2.7 cm | 1.5 in. | 1.5 in. | 11.375 in. x 0.25 in. | 2 in. x 2 in. |
| K(d) | 3-150 | a) 5.3-5.8 b) 0.26-0.4d c) 4.41 | 5 | 3-15.7 | 32.7 | 0.086 0.114 0.052 |
| ΔP | 5psi 150psi | ----- ----- | 10psi 14psi | 1.63-5.72atm | 0.21atm | 50psi 100psi |
| $\frac{Pi}{Po}$ | 1.34 11.20 | ----- ----- ----- | 1.68 1.95 | ----- | 1.21 | 1.02 1.03 |
| Foamer | 1% solution un-named agent | 0.1 or 1% Aerosol MA | 0.1% O.K. (1.5% NaCl) | 2.0% O.K. (0.25 N NaCl) | 1% Suntech IV | 1% Alipal CD-128 |
| λ (d/cp) | ----- | a) 0.006-3.5 b) 0.013-0.1 c) 0.35-0.75 | 0.75-0.35 | 0.013-0.041 | 3.0-3.7 | 0.003-0.063 |
| λ_r (cp ⁻¹) | ----- | a) 0.01-0.06 b) 0.05-0.20 c) 0.08-0.17 | 0.015-0.069 | 0.001-0.007 | 0.09-0.11 | 0.056-0.636 |

enough original data were included to enable quantitative calculations of the mobility of foam in the "pseudo-steady state" phase of these experiments.

Marsden and Khan³⁶ reported flow experiments for foams in sandpacks in Berea cores and in an Alundum synthetic sample. Apparently, they directly calculated and reported their results as mobility and as relative mobility (although not by these names) and presented the numerical results graphically. The major trend shown in the graphs is a decrease in mobility with increasing foam volume fraction of gas. (In much of the foam literature this fraction is called the "quality.") The maximum extent of this decrease is about a factor of 2.5 over the range from 70% to 90%. Unfortunately, the authors do not show any original data--the flow rates and pressure drops at which the runs were performed are unknown. There is also some uncertainty in the results presented, owing to several apparent mislabellings of the graphs and ambiguity about the concentration of surfactant used in some runs. A very positive feature of this work, though, is that it reports relative mobility measurements which are in the range needed for mobility control of CO₂ floods.

In a 1968 contribution, Holm³⁸ returned to the subject of foam flow. Of four major experiments described in the paper, two have been selected for further analysis here. Holm reported calculated values of k_g and k_w in these two steady-state experiments. It appears that these values, from Holm's Table 3, were calculated with the aid of Darcy's equation, using the measured and reported pressure drops, the flow rates of liquid and gas, and the single fluid viscosity of each phase. Thus, it is possible to compute the flow rates in the experiments. The calculated mobilities of foam, as shown in our Table IV, are of the same order of magnitude as those reported by Marsden and Khan³⁶ but exhibit a reversed trend with the gas volume fraction, or foam quality--the mobility increases by more than a factor of four as quality increases from 72% to 90%. It is interesting to note that in Fig. 6 of Holm's paper,³⁸ which shows the pressure distribution along the length of the sandpack (as revealed by comparing the pressures measured at two intermediate taps on the pack with those measured at the inlet and outlet ends), some apparently contradictory evidence is seen. Except for the lowest ΔP experiment, all measured pressures are everywhere above the straight line connecting the inlet and outlet pressures, as is to be expected due to the compressibility of gas phase in foam. But the curvature is so great as to suggest that the foam mobility was less near the outlet end (where the foam quality was greater), rather than being larger. This would be in conflict with Holm's other result, but would agree with Marsden and Khan's conclusion about the direction of the foam mobility-quality trend.

Foam mobility values have also been calculated from Raza's 1970 work,⁴³ and are shown in Table V. Unfortunately, the magnitudes of pressures were not specified explicitly--to obtain the mobility values in our table, the pressure drops were first back-calculated from the reported relative permeability data. These ΔP values turn out to be in the order of 1.8 to 5.7 atm, which indicates that unless the outlet pressure had been regulated at much greater than atmospheric, the

Table IV Calculations from Holm (Ref. 38)

| Exp't. | K_w^a (md) | K_g^a (md) | Q_w (cc/sec) | Q_g (cc/sec) | Flowing Foam Quality | λ (d/cp) | λ (cp ⁻¹) | Saturation S_g^c |
|--------|--------------|--------------|-----------------------|-----------------------|-----------------------------|------------------|-------------------------------|-----------------------|
| 2 | 29.0 | 6.40 | 3.56×10^{-3} | 45.5×10^{-3} | 0.927 ^b 0.900 | 0.346 | 0.0692 | 0.673 |
| 3 | 20.2 | 1.02 | 3.08×10^{-3} | 8.42×10^{-3} | 0.732 ^b 0.718 | 0.0753 | 0.0151 | 0.731 |

a Average of K_{eff} reported

b Calculated from data reported

c Derived from average of S_1 reported

Table V Calculations from
Raza's Table 3 (Ref. 43)

| K(md) | Q_g (cc/hr) | Q_1 (cc/hr) | q = $\frac{Q_g}{Q_g + Q_1}$ | | K ₁ (md) | ΔP (atm) | λ (d ^d /cp) | λ_r (cp ⁻¹) | S _g |
|--------|---------------|---------------|-----------------------------|-------------|---------------------|----------|--------------------------------|---------------------------------|----------------|
| | | | Q_g | $Q_g + Q_1$ | | | | | |
| | 8.2 | 48.8 | 0.14 | 0.03 | 10.90 | 4.94 | 0.0127 | 0.00423 | 0.798 |
| | 17.2 | 48.8 | 0.26 | 0.07 | 11.53 | 4.72 | 0.0156 | 0.00520 | 0.795 |
| | 34.5 | 48.8 | 0.42 | 0.15 | 11.53 | 4.72 | 0.0197 | 0.00657 | 0.796 |
| 3,000 | 35.7 | 48.8 | 0.42 | 0.14 | 10.15 | 5.36 | 0.0176 | 0.00587 | 0.789 |
| | 34.3 | 48.8 | 0.41 | 0.12 | 9.48 | 5.73 | 0.0162 | 0.00540 | 0.790 |
| | 62.8 | 48.8 | 0.56 | 0.22 | 9.56 | 5.72 | 0.0217 | 0.00723 | 0.798 |
| | 30.2 | 12.2 | 0.71 | 0.23 | 5.40 | 1.68 | 0.0187 | 0.00119 | 0.886 |
| | 76.8 | 12.2 | 0.86 | 0.61 | 5.55 | 1.63 | 0.0406 | 0.00259 | 0.886 |
| 15,700 | 78.3 | 24.4 | 0.77 | 0.27 | 4.90 | 3.70 | 0.0206 | 0.00121 | 0.890 |
| | 22.0 | 48.8 | 0.31 | 0.10 | 11.85 | 3.06 | 0.0172 | 0.00109 | 0.890 |

compressibility effect would have been too large to meet the criteria given earlier. The quality of the foam would have increased substantially from inlet to outlet end of the porous medium and would add significant complication to the interpretation of the foam mobility. Nevertheless, it is possible to calculate the average mobilities and flowing foam qualities from the reported data. It is evident that the results from Raza's work agree with the conclusion reported by Holm--that the mobilities increase with increasing quality. The quality values themselves, though, are lower than those used by other investigators. Another interesting conclusion from Raza's work is that the gas saturation reached in the steady-state experiment, shown in Table V, was essentially independent of the flowing foam quality. The values of liquid saturation, $(1-S_g)$ are all in the range one would expect for the interstitial water saturation.

In recent years foam has been studied as a potential mobility control agent in displacing oil by steam, as well as in CO_2 flooding. Chiang et al.³⁹ investigated the reduction of gravity override of injected N_2 with foam generated in situ. Although these experiments were not steady-state, but rather displacements of surfactant solutions by gas, it was again possible to compute foam mobilities from data obtained after breakthrough. Values calculated from Chiang et al.'s run performed with 1% Suntech IV are shown in the first part of our Table VI. These values indicate that the mobility increases with increasing foam quality after breakthrough. The total effluent flow rate changes during the run, though the experiment was conducted under a constant ΔP . Since only gas was being injected, as in many other "displacement-type" foam experiments, the runs could not attain a steady state.

A final experiment to be noted here was performed not with air in the neighborhood of atmospheric pressure, but rather with dense CO_2 . This work was first reported by Bernard, Holm and Harvey³¹ in 1979. It consisted of several displacements by CO_2 at 135°F at either 1000 or 2500 psi of brine or of surfactant in brine solution, from Berea or carbonate cores of about 3 feet in length. These experiments showed for the first time that dense CO_2 can form the expected type of emulsions or "foam-like dispersions" with water and surfactant, and demonstrated again how effectively such a fluid can displace water or waterflooded oil from porous media. The experimental approach was similar to that reported earlier by Bernard and Holm.⁴⁹ Although no flow rates were given in their steady-state experiment, the authors reported the mobility of CO_2 , and the CO_2 liquid production ratio as functions of CO_2 saturation. From their graphs, the mobility and quality of foam can be calculated, as shown in the second part of our Table VI, and the results agree with the numerical results obtained by Marsden and Khan.³⁶

Except for the major disagreement on the dependence of foam mobility on quality, the six experiments examined here show remarkably similar results. If we look only at the values of relative mobility--thus attempting to place the different porous media used on a common footing--we find that the largest variation of λ_r (see Table III) is from .001 to 0.6, a range of only a factor of 600. Much of this observed variation may be due to the type and concentration of surfactant used.

Table VI Calculated Mobilities
from Chiang et al. (Ref. 39)^a

| Exp't. | K(d) | Q_1 (cc/sec) | Q_g (cc/sec) | $q = \frac{Q_g}{Q_1 + Q_g}$ "Flowing quality" | ΔP (atm) | λ (d/cp) | λ_r (cp ⁻¹) |
|---|------|-----------------------|----------------|---|------------------|------------------|---------------------------------|
| Displacement of 1% Suntech IV by N ₂ | 32.7 | 0.013 | 0.104 | 0.889 | 0.21 | 3.32 | 0.102 |
| | | 5.07x10 ⁻³ | 0.128 | 0.962 | | 3.74 | 0.114 |
| | | 5.56x10 ⁻³ | 0.122 | 0.956 | | 3.61 | 0.110 |
| | | 3.17x10 ⁻³ | 0.104 | 0.970 | | 3.02 | 0.092 |

from Bernard Holm and Harvey (Ref.)

| | | | | | | | |
|--------|--------------------|-----------------------|------------------------|-------|------|--------|-------|
| Core A | 0.086 ^b | 0.32x10 ⁻³ | 9.99x10 ⁻³ | 0.969 | 3.40 | 0.0547 | 0.636 |
| Core C | 0.114 ^b | 2.22x10 ⁻³ | 58.07x10 ⁻³ | 0.963 | 3.40 | 0.0628 | 0.551 |
| Core D | 0.052 ^b | 0.90x10 ⁻³ | 5.42x10 ⁻³ | 0.858 | 3.40 | 0.0059 | 0.113 |
| Core D | 0.052 ^b | 1.50x10 ⁻³ | 4.13x10 ⁻³ | 0.734 | 6.80 | 0.0029 | 0.056 |

* Calculated from reported data

a Data taken from Table 12 in DOE/ET/12056-T1 report, Aug. 1980, by Chiang et al. (experiment described in Ref.).

b Calculated from brine mobility data in B,H,H (Ref.).

These range from 2% of "OK Liquid" (a modified ammonium lauryl sulfate) for the lowest relative mobility found in Raza's⁴³ results, down to 0.1% Aerosol MA reported by Marsden and Khan.³⁶ The overall relationship of foam mobility to surfactant concentration is certainly unresolved by these experiments, however. Similarly, the effect of foam quality on steady-state mobility is also not ascertained, and there is no clear-cut evidence in the works reported regarding the questions of whether mobility depends at all on flow rate, on rock permeability in other than in simple direct proportionality, or on other rock properties.

3. Surfactant Selection and Screening

A surfactant, or foamant, is needed to stabilize the aqueous films which surround the cells or bubbles of a foam-like dispersion. Although a considerable amount of experience has been accumulated about which kinds of surfactants are most useful for such service, there does not seem to exist a general quantitative theory to enable reliable and detailed predictions of foam properties. Empirical standards and test procedures have therefore played a large role in surfactant selection for use as foam producers--both in and out of the oil field. For instance, although it is apparent that protection from bubble coalescence or from rapid foam drainage is conferred by a surfactant which impedes flow in the films, the effectiveness of a particular chemical structure is not always evident prior to testing. This is particularly true in the situation of concern here where the desired properties can only be specified with precision at the application level.

Thus, of the thousands of surfactants listed in McCutcheon's⁵⁰ catalog, a small fraction are described as "good foamers." The water solutions of these surfactants can be shaken or beaten with air to produce long-lasting high gas volume fraction (GVF, or quality) foams. Most of the surfactants which have been selected and used in laboratory studies of the flow-resistant properties of foams in porous media have been of this type. Although the foams produced with these agents have shown very low mobilities in flow through sandpacks, it is not clear that the selection criteria--ease of foaming with air and high foam persistence in bulk testing geometries--are related to the properties actually needed for mobility control in CO₂ floods.

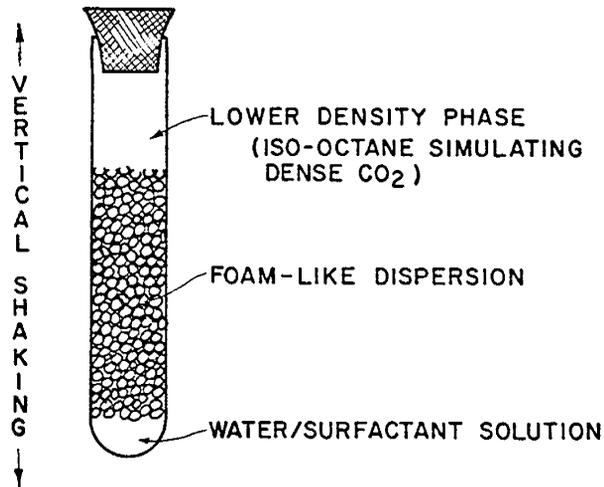
The requirements for a useful surfactant for this application may be different from those for a good foamer in air. At the reservoir conditions under which CO₂ exhibits high microscopic displacement efficiency against crude oils in slim tube experiments, its density is greater than 0.6 gm/cc.^{51,5,52} From other considerations (involving our search for direct thickeners), it appears that CO₂ at this density is comparable^{53,33} in solvent properties to a light hydrocarbon. It therefore seems appropriate, in searching for a surfactant to stabilize a foam-like dispersion of dense CO₂ in water, to also explore those which are classified as emulsifiers. For such surfactants, the properties of the non-polar fluid would affect the distribution and activity of surfactant molecules at the interface. This much larger class of surfactants is itself loosely classified by the so-called HLB number, a

"hydrophile-lipophile balance." The scale is somewhat arbitrary, but represents the ratio of molecular contributions of the polar hydrophilic "head" to the non-polar, lipophilic "tail." Although the surfactants needed to make a foam-like emulsion of CO₂ in water should be water-soluble and thus, have a substantial polar portion of the molecule, they can be expected to be generally lower in HLB than the foamers which can emulsify air.

A first screening procedure was therefore used to evaluate, for possible mobility control agents for CO₂ floods, those surfactants which are classified as "emulsifiers" with HLB numbers in the range⁵⁴ 8 to 13. It is also required that they be soluble in mixed NaCl/CaCl₂ brine and they not be strongly cationic. The purpose of the latter requirement is to lessen the chance that the surfactant will be strongly adsorbed on reservoir rock. The screening procedure was designed to measure in a semi-quantitative way the ability of the surfactant to stabilize a "foam-like dispersion" in which dense CO₂ is simulated by isooctane. A few milliliters (20% of the tube volume) of surfactant solution in the mixed brine is introduced into a test tube which is then filled to overflowing with isooctane. A cork is carefully inserted to exclude air, and the tube is shaken violently enough to throw the liquids up and down in the tube. Ease of formation of the "foam-like dispersion" of isooctane in the surfactant solution is observed. In addition, its persistence and the absence of inverse emulsion are recorded.

A further important observation is whether the same fluids will "re-foam" when shaken again a few days later. If this mixture does not "re-foam," it can be assumed either that the surfactant has been degraded chemically or else that enough of it has gone into solution in the non-polar phase to reduce drastically the amount available for use in forming films. This would be an important factor in reducing the utility of the surfactant for this application. The reduction of mobility observed during flow of a "foam-like dispersion" through the pores of a rock must depend on the dynamics of the film-formation process. As flow in the complex geometry proceeds, films of the surfactant-containing aqueous phase are continually created and broken. Among other factors, the rate at which surfactant molecules can diffuse to these films will be of great importance in determining the films persistence. These films will be effective in lowering the mobility of macroscopic flow if they can keep the low-viscosity, non-polar phase "packaged" in small enough volumes that it is prevented from moving at a rate determined by its low viscosity. Most surfactant molecules that are dissolved in the non-polar phase will be unable to migrate rapidly enough to the films to be of any use in stabilizing them. A surfactant that is soluble in isooctane may also dissolve appreciably in dense CO₂--this is the rationale behind the "re-foaming" criterion used in the surfactant screening test. A schematic of the test is shown in Figure 3, and results for those surfactants tested to date are given in Table VII.

SURFACTANT SCREENING (LOW-PRESSURE)
FOR FOAM-LIKE DISPERSIONS



SHAKING AT A FREQUENCY f (≈ 2 Hz) WITH AN
AMPLITUDE A (≈ 20 cm) PRODUCES ACCELERATION

$$-\frac{d^2y}{dt^2} = (2\pi f)^2 A \sin(2\pi ft)$$

SO

$$F_{\text{TOTAL}} = (e_{\text{H}_2\text{O}} - e_{\text{iso8}}) V (g + (2\pi f)^2) A \sin(2\pi ft)$$

$$F/V \approx 0.31 (980 \pm 3000) \text{ dynes/cc}$$

THE FORCE IS PERIODICALLY NEGATIVE, AND
THROWS THE FLUIDS BACK AND FORTH IN THE
TUBE.

NOTE

$$(e_{\text{iso8}} = 0.692)$$

Fig. 3. Low pressure "foam" screening test.

Table VII

"Foaming" Results of .05% (active) Surfactants
in Mixed Brine* with Isooctane

| | <u>Surfactant</u> | <u>HLB</u> | <u>Ionic Type**</u> | <u>Mfr.***</u> | |
|--|---------------------------|------------|---------------------|----------------|---|
| "foamed" in <1 min. to full height of tube | Emsorb 6915 | | N | e | "Refoamed" easily after aging "several days" |
| | Emulphogene BC-720 | | N | f | |
| | Neodol 25-3A | | A | j | |
| "foamed" in <3 min. to full height of tube | Alipal CD-128 | | A | f | |
| | Arfoam 2213 | | A | b | |
| | Arnox 930-70 | | N | b | |
| | Bio Soft EA-10**** | 15.0 | N | k | |
| | Cordova Chem. Co. XA-1017 | | C | d | |
| | Emulphogene BC-840 | | N | f | |
| | Foaming Agent 1275 | | A | k | |
| | Igepal CO-630 | 13.0 | N | f | |
| | Igepal CO-710 | 13.6 | N | f | |
| | Makon 12 | | N | k | |
| | Makon 14 | 15.0 | N | k | |
| | Monateric ADFA | | Z | i | |
| | Neodol 23-6.5 | 14.4 | N | j | |
| | Neodol 25-12 | 12.0 | N | j | |
| | Neodol 45-13 | 14.4 | N | j | |
| | Stepanflo 1315 | | A | k | |
| | Sulfotex PAI | | A | h | |
| Sulfotex RIF | | A | h | | |
| Trycol TD-A8 | 12.5 | N | e | | |
| Witcolate 1259 | | A | n | | |
| Witcolate 1276 | | A | n | | |

Table VII (Continued)

| | <u>Surfactant</u> | <u>HLB</u> | <u>Ionic Type**</u> | <u>Mfr.***</u> | |
|---|-----------------------------|------------|-----------------------|---|--|
| "foamed" in <1 min. to full height of tube | Polyfon O**** | | A | m k k o l | |
| | Stepan Foaming Agent 1279** | | A | | |
| | Stepanflo 1344 | | A | | |
| | Thermophoam A | | ? | | |
| | Tretolite BL-4288 | | ? | | |
| "foamed" in <3 min. to full height of tube | Aerosol 30 | | Z | a f k h h e o j c c m k k h h l n | Did not "Refoam" easily after aging "several days" |
| | Alipal CO-436 | | A | | |
| | Amphosol CG**** | | Z | | |
| | Bio Soft EA-8 | 14.5 | N | | |
| | Deriphath 160-C | | Z | | |
| | Deriphath BAW | | Z | | |
| | Emsorb 6900 | 15.0 | N | | |
| | Morasperse C21**** | | A | | |
| | Neodol 91-8 | 14.1 | N | | |
| | Plurafac C-17 | 16.0 | N | | |
| | Pluronic L64 | | N | | |
| | Polyfon H**** | | A | | |
| | Stepanflo 1313 | | N | | |
| | Stepanflo 1314**** | | A | | |
| | Sulfotex AOS**** | | A | | |
| Sulfotex AOS-W**** | | A | | | |
| Tretolite BL-4287**** | | ? | | | |
| Witcolate 1247-H | | A | | | |
| "foamed" in <3 min. to less than full height of tube | Emersal 6462 | | A | e | |
| | | | | | |
| shaken >3 min; very little "foam" produced | Bio Soft EA-4 | | N | k e i m m k | |
| | Emsorb 6903 | | N | | |
| | Monamid 716 | | N | | |
| | Polyfon T | | A | | |
| | Reax 88B | | A | | |
| Reax 100m | | A | | | |
| Stepanflo 1343 | | A | | | |
| Aerosol 22 | | A | a a a e o | Did Not Test (precipitate formed) | |
| Aerosol 18 | | A | | | |
| Aerosol C-61 | | C | | | |
| Emsorb 6905 | | N | | | |
| Sodium Laurel Sulfate | | A | | | |

Table VII (Conclusion)

- * Mixed Brine : 0.5% CaCl₂, 0.5% NaCl by wt.
in distilled water

- ** Ionic Type : A = anionic, N = nonionic,
C = cationic, Z = zwitterionic

- *** Manufacturer: a = American Cyanamid
b = Arjay
c = BASF
d = Cordova Chemical Company
e = Emery Industries
f = GAF
g = Gulf Chemical Company
h = Henkel Chemicals
i = Mona Industries
j = Shell Chemical Company
k = Stepan
l = Tretolite
m = Westvaco
n = Witco Chemical Company
O = Unknown

**** Required surfactant concentration >.05%.

4. Adsorption Screening Measurement

It is expected that adsorption will be a major cause of difficulty with any oilfield process involving the injection of a surfactant solution. There is a wealth of information in the literature in this connection^{55,56} concerning the surfactants used in micellar and low tension waterflooding. Problems with the surfactants used in the application considered here, the making of "foam" with CO₂ for mobility control, are similar but not the same. The surfactants are of a different type, and the concentrations required are lower. For the purpose of this work, the adsorption loss of surfactant is divided into two categories that can be considered separately. The first of these is the "reversible adsorption" onto the rock minerals, from which the surfactant is released as soon as the surfactant concentration in the solution filling the pore space is decreased. The principal effect of this component of adsorption is the chromatographic delay of a concentration pulse moving through the reservoir. The velocity of such a concentration change is equal to a fraction f_v of the velocity of a concentration peak of a non-adsorbing tracer, where

$$f_v = \phi / (\phi + M') \quad (3)$$

in which ϕ is the rock porosity, and M' is the (dimensionless) slope of the adsorption isotherm.

The second component can be called the "permanent" or "irreversible" adsorption. This corresponds to the amount of surfactant which is not desorbed from the rock (at least, not so quickly) when the concentration in the saturating liquid is decreased. This portion of the adsorbed surfactant will be lost to the process and becomes unavailable to stabilize the "foam" films.

The two components of adsorption can be distinguished in a laboratory experiment in which the surfactant is introduced only as a short slug during the flow of brine through a core sample. The apparatus, which utilizes several liquid chromatography instruments, is shown in Fig. 4. An ISCO pump displaces brine (in the experiments conducted so far, this has contained 0.5% NaCl and 0.5% CaCl₂ by weight) through the system which consists of a filter, a Valco LC valve, a 5 1/2 inch long core sample in a flow cell, another filter, a Tracor variable wavelength LC detector, and a 50 psi back pressure regulator. (The purpose of the latter is to prevent air dissolution and the formation of bubbles in the UV absorbance cell of the detector.) The 0.1cc sample loop of the Valco valve is loaded with the surfactant solution to be tested, dissolved in the same brine.

In operation, the signal from the Tracor variable wavelength detector is proportional to the concentration of surfactant in the sample passing through it. When the surfactant slug that has been introduced by the sample valve reaches the detector, a peak is observed in its signal. From the record of this signal, two parameters that are related to the two adsorption components described above can easily be determined. The ratio of the delay prior to the appearance of the peak to the corresponding

SURFACTANT ADSORPTION MEASUREMENT

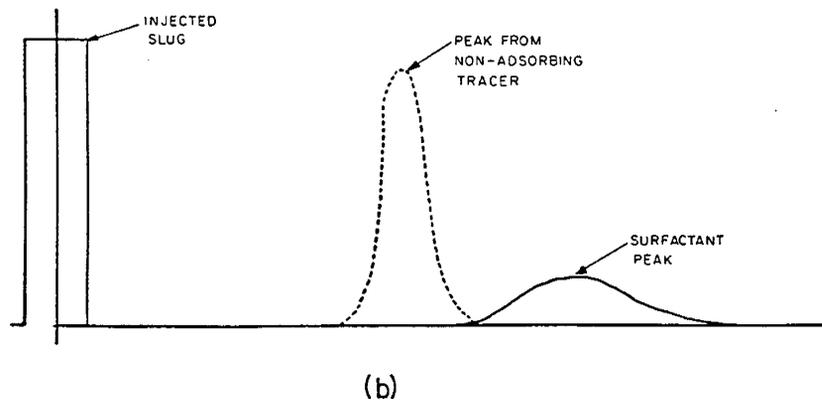
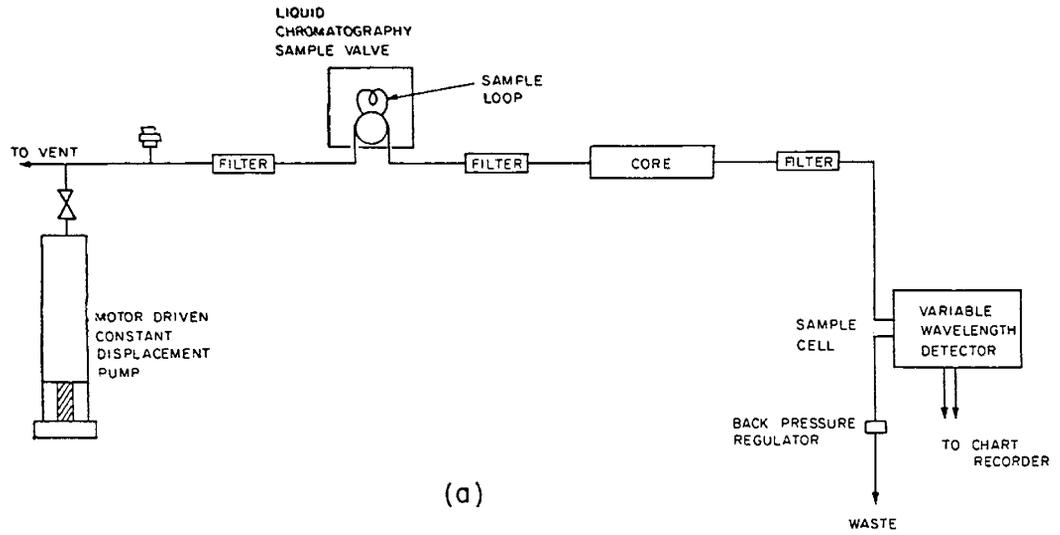


Fig. 4. Surfactant adsorption test.

travel time of a non-adsorbing tracer gives directly the velocity fraction f_v defined above. The second parameter is the ratio of the area of the emergent peak to the area of a surfactant peak measured without the core sample. From this second ratio can be calculated the specific permanent adsorption per unit volume of rock. This is

$$M = C_{in} V_s (A_{in} - A_{out}) / (A_{in} V_b) \quad (4)$$

where V_s is the volume of surfactant slug injected,
 C_{in} is its concentration
 V_b is the bulk volume of the core sample,
 A_{in} , A_{out} are the peak areas measured on the record.

With V_s and V_b in the same units, and C_{in} in grams per cc, then M would be in grams of surfactant adsorbed per bulk cc of rock.

The results of tests with three surfactants, (with M translated into field units) are given below:

TABLE VIII

Surfactant Adsorption Parameters

| <u>Surfactant</u> | <u>Velocity Ratio f_v</u> | <u>M, lb. surfactant/bulk cu.ft. of rock</u> |
|-------------------|--|--|
| Alipal CD 128 | 0.91 | 5.6×10^{-4} |
| Monateric ADFA | 0.91 | 8.7×10^{-4} |
| Neodol 25-3A | 0.95 | 9.8×10^{-4} |

With these results it is possible to estimate the surfactant requirements needed to counter its adsorption in a CO_2 flood using a foam-like dispersion for mobility control. The operational procedure could be to inject a "pad" of surfactant solution prior to the CO_2 -foam injection, in order to satisfy the adsorption requirements of the formation and to anticipate the amount of chromatographic delay before surfactant reaches the furthest extent of the volume to be swept. Before more discussion of this calculation, however, another topic of laboratory experiments needs to be discussed.

5. Mobility Measurements

The two screening tests described above have the virtue of relative ease in application, but they do not give an unequivocal answer to the question: Which surfactants are best suited to make a foam-like dispersion with CO_2 for mobility control? To provide more information on this, a test has been designed which is targeted more directly towards the application.

The purpose of this test is to measure mobility and relative mobility during the flow of foam-like dispersions through reservoir rock. The tests are steady-state flow experiments, in which dense CO₂ can be used under reservoir conditions to test particular surfactants. Two important criteria in the design were speed and ease of testing--it was desired to be able to achieve steady-state flow conditions, to take measurements quickly, and also to change fluids and rock samples easily. For this purpose, the core plugs used were cut to 1/2 inch diameter and 1 inch long. After mild cleaning and extraction, they were epoxy-coated and fitted with aluminum rings at each end. A high-pressure core holder, shown in Fig. 5, enabled a hydraulic oil to be pumped into the annular region surrounding the core in order to apply overburden pressure on the epoxy coating around it. One version of the laboratory flow system is shown schematically in Fig. 6. It utilizes two high-pressure positive displacement pumps--one for the surfactant solutions and one for the CO₂. (The former has a low-corrosivity, zero-dead-volume cylinder that can be directly loaded with the brine/surfactant solution being tested.) In an early means used for foam generation, the two fluids were pumped simultaneously at a common high pressure into a high pressure container in which revolved a magnetic stirring bar. This bar rested on a horizontal wire screen separating the two chambers into which the aqueous phase and the CO₂ are pumped. The resulting "foam" then flowed via a parallel-window visual cell into the core holder described above. In later versions of this apparatus, different means have also been utilized to generate "foam." These have included both a commercial mixer (made for liquid chromatographers) that also uses a magnetic stirring bar, and also a short section of porous rock. The results obtained have been quite similar in these different cases. Our tentative conclusion is that an appropriate bubble-size distribution for the "foam" is quickly established inside the porous medium. This occurs within a very short distance from the entry face, as long as it is exposed to both the aqueous and the non-aqueous phases. The effluent from the core is led through an identical visual cell to an electronic back pressure regulator (BPR) set to maintain a pressure higher than the vapor pressure of CO₂ at ambient temperature. To compensate for the cooling caused by the expansion of CO₂ to atmospheric pressure, and to maintain it at room temperature, the valve of the BPR is heated as required. Pressure drop across the core is measured by means of a Validyne Model DP-15 variable reluctance differential pressure transducer and recorded. A high-pressure, 3-way ball valve is connected in such a way that the gauge can be zeroed at any time. Fritted stainless steel filters, of nominal pore size 7 micrometers, are included in the system to keep particle contamination from plugging the core or interfering with the operation of the BPR.

Prior to each foam flow experiment, the core was saturated with brine. Permeability was measured with brine alone, and then with brine/surfactant solution, by use of the surfactant pump and the differential pressure transducer. Following this, sets of measurements were made to calculate foam mobility. Each set was made with the same flowing fraction (flowing foam quality), surfactant type and concentration and consisted of a series of steady-state measurements of pressure drop across the core for a descending series of values of total flow rate. The

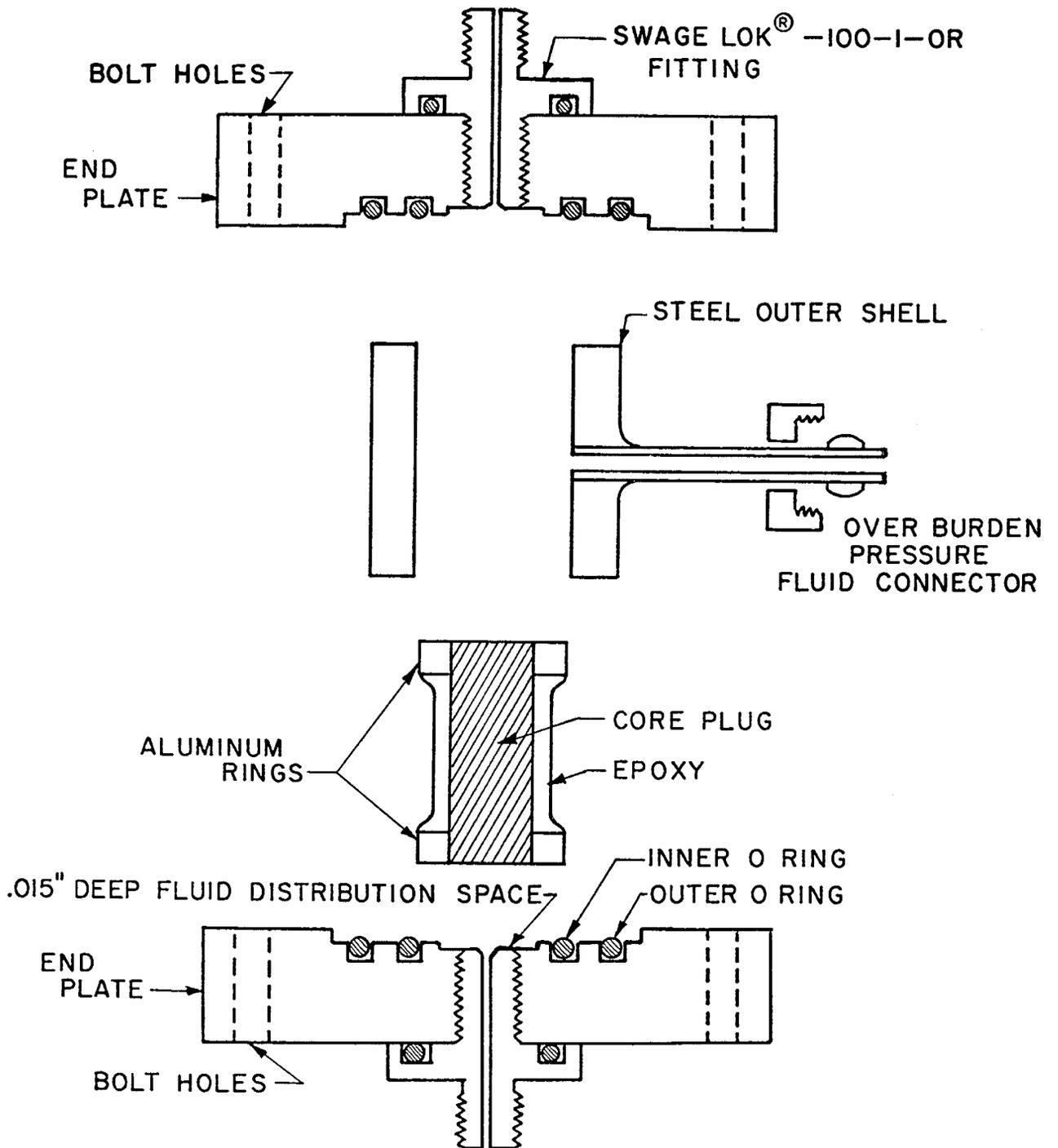


Fig. 5. High pressure core holder.

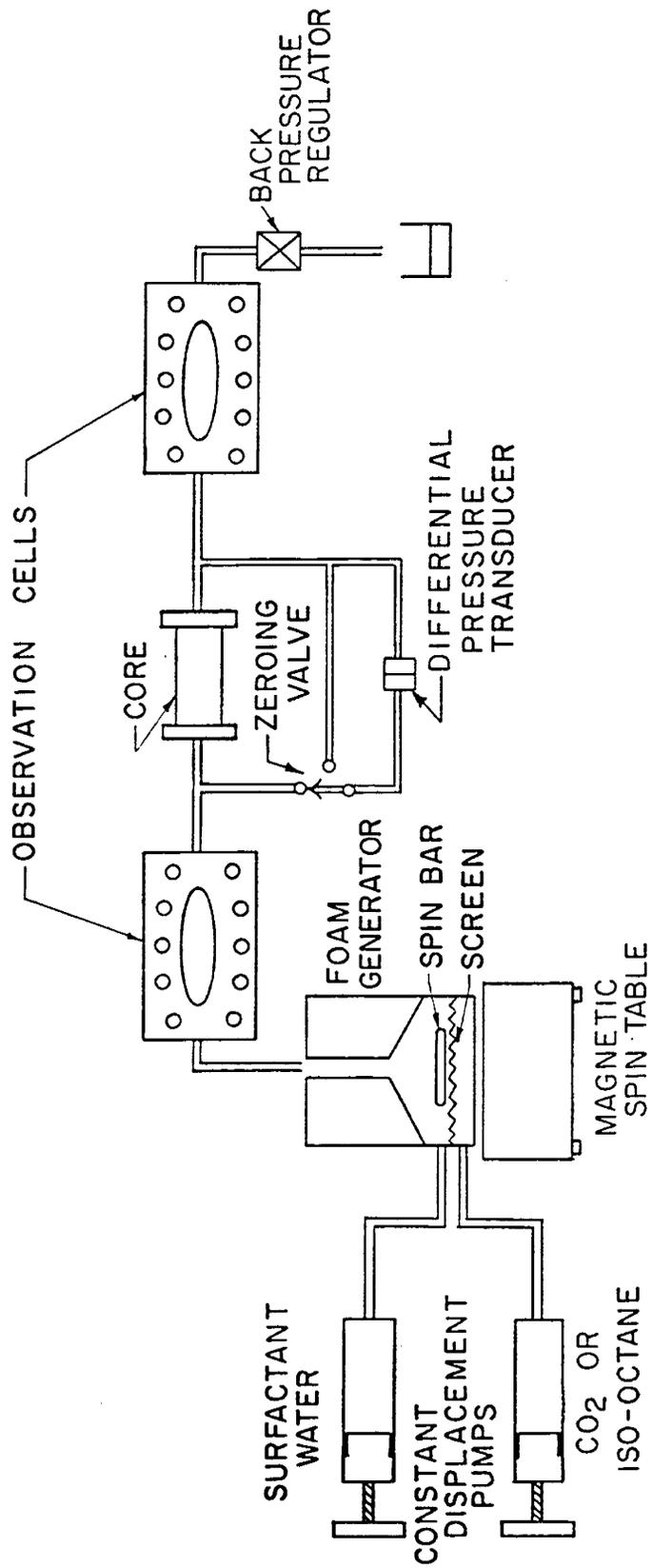


Fig 6. High pressure foam mobility measurements.

system response to the changes in total flow rate (keeping constant the ratio of pump rates) is much more rapid than is its response to change in quality (i.e., to changes in the ratio of CO₂ pump rate to the total rate).

In the graphs of results shown in Figs. 7 - 10, each set of measurements, as described above, is distinguished by its own plotting symbol, and the points of the set are connected by straight lines. Different sets of measurement made with different flowing foam quality are shown on the same plot. In each of these graphs, the Y axis represents relative mobility--that is, the mobilities calculated from Eqn. 1 were divided by the permeabilities measured in the same rocks when they were fully saturated with the surfactant/brine solution in question. Because these single phase permeabilities differed for the different samples (the values are listed on the graphs), comparisons between graphs of the magnitudes of relative mobility must be made with caution. It is not yet clear how dependent relative mobility is on the permeability of the sample. It is possible, however, to evaluate from each graph the observed change of foam mobility with total flow rate and also to observe the dependence of foam mobility on quality.

As of May 1983, these experiments have been performed with only two surfactants--Emulphogene BC-720 and Alipal CD-128. Preliminary mobility experiments were also done with the Emulphogene, in which iso-octane was used to simulate dense CO₂. The iso-octane tests were done before completion of the back pressure regulator needed for use of the system with CO₂. They serve to illustrate the similar flow behavior of foam-like dispersions made with different non-aqueous, but dense components in porous media.

6. Discussion of Mobility Measurements

The results of these experiments can be summed up as follows:

- a. The mobility of a foam-like dispersion in reservoir rock is not constant with flow rate, but increases at higher darcy velocities. It is not yet known whether this trend continues to very low total flow rates, but it is apparent that the flow of foam, in the velocity range studied, is not linear. It is thus important that experiments to assess the mobility should be made at flow rates near those at which field use is to take place. A greater mobility at higher flow rates is of the "shear-thinning" type of variation and would seem (if relative mobility is independent of rock permeability) to be in the opposite direction to that which might be preferred to control the flow rate in highly stratified reservoirs. However, there is also an advantageous feature of this type of non-linearity. Because the darcy velocity is necessarily much greater in the vicinity of the injection wells than it is further out in the reservoir, the observed non-linearity

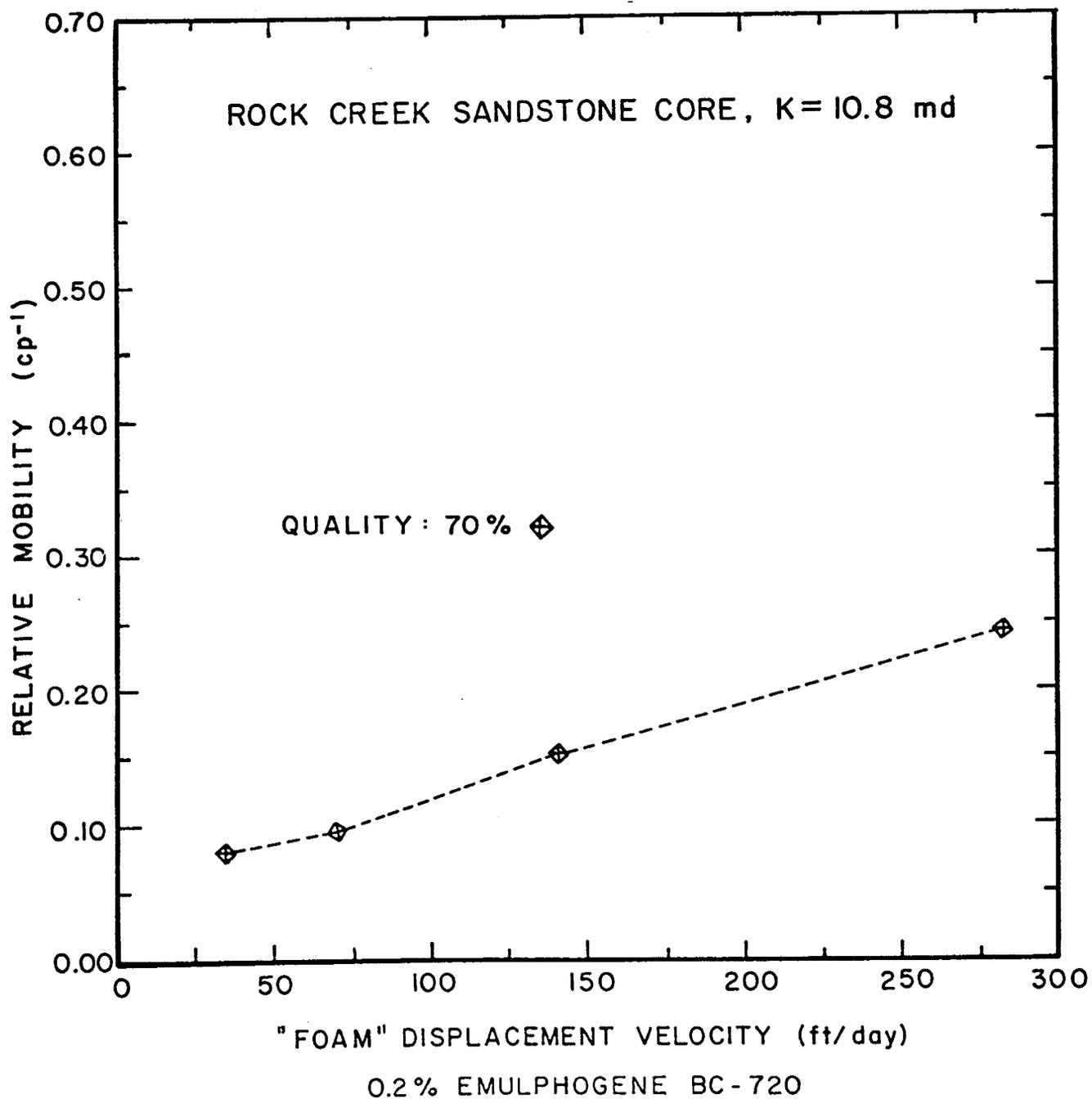


Fig. 7. Relative mobility of isooctane foam.

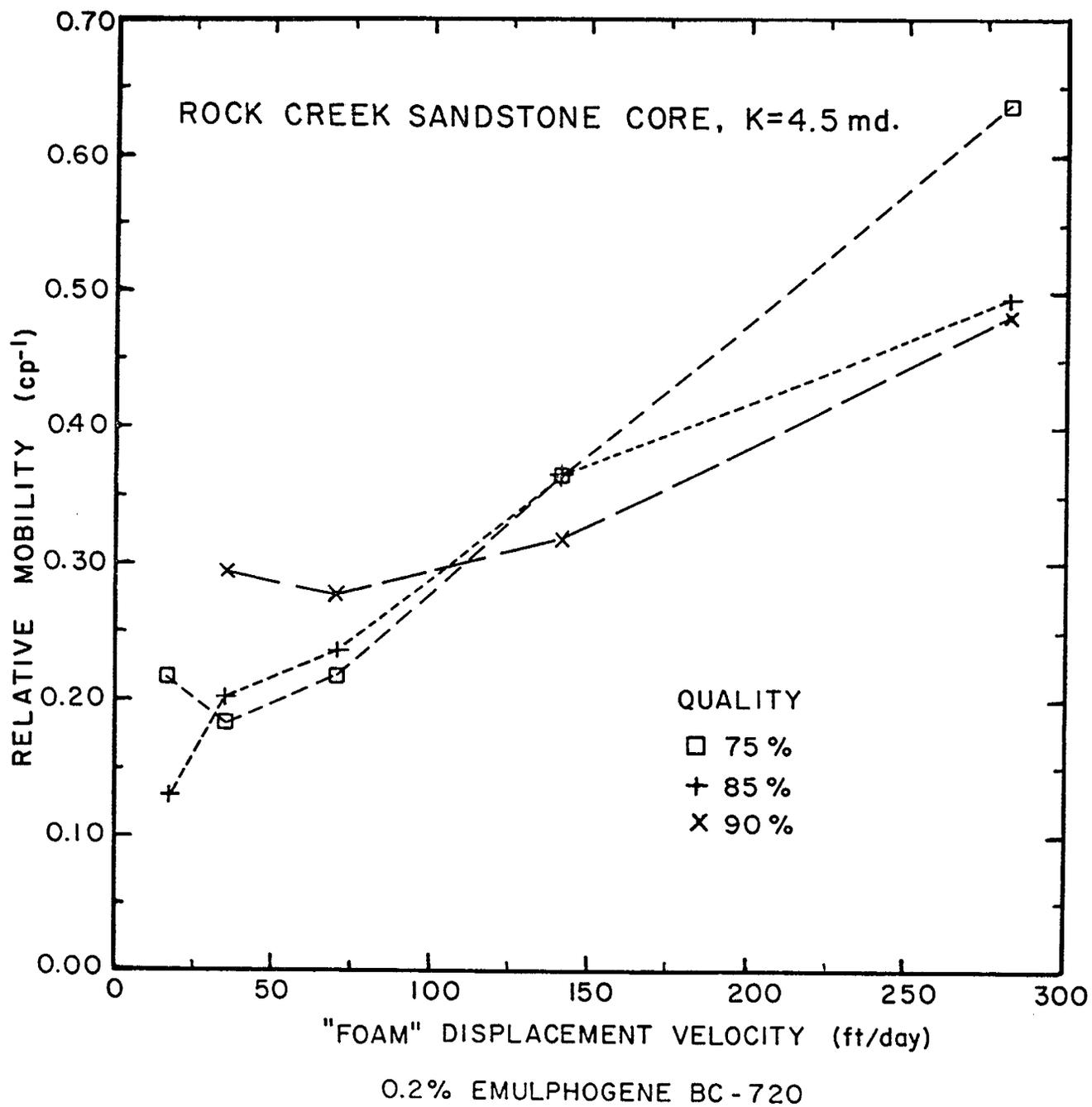


Fig. 8. Relative mobility of dense CO₂ foam - 0.2% EMULPHOGENE.

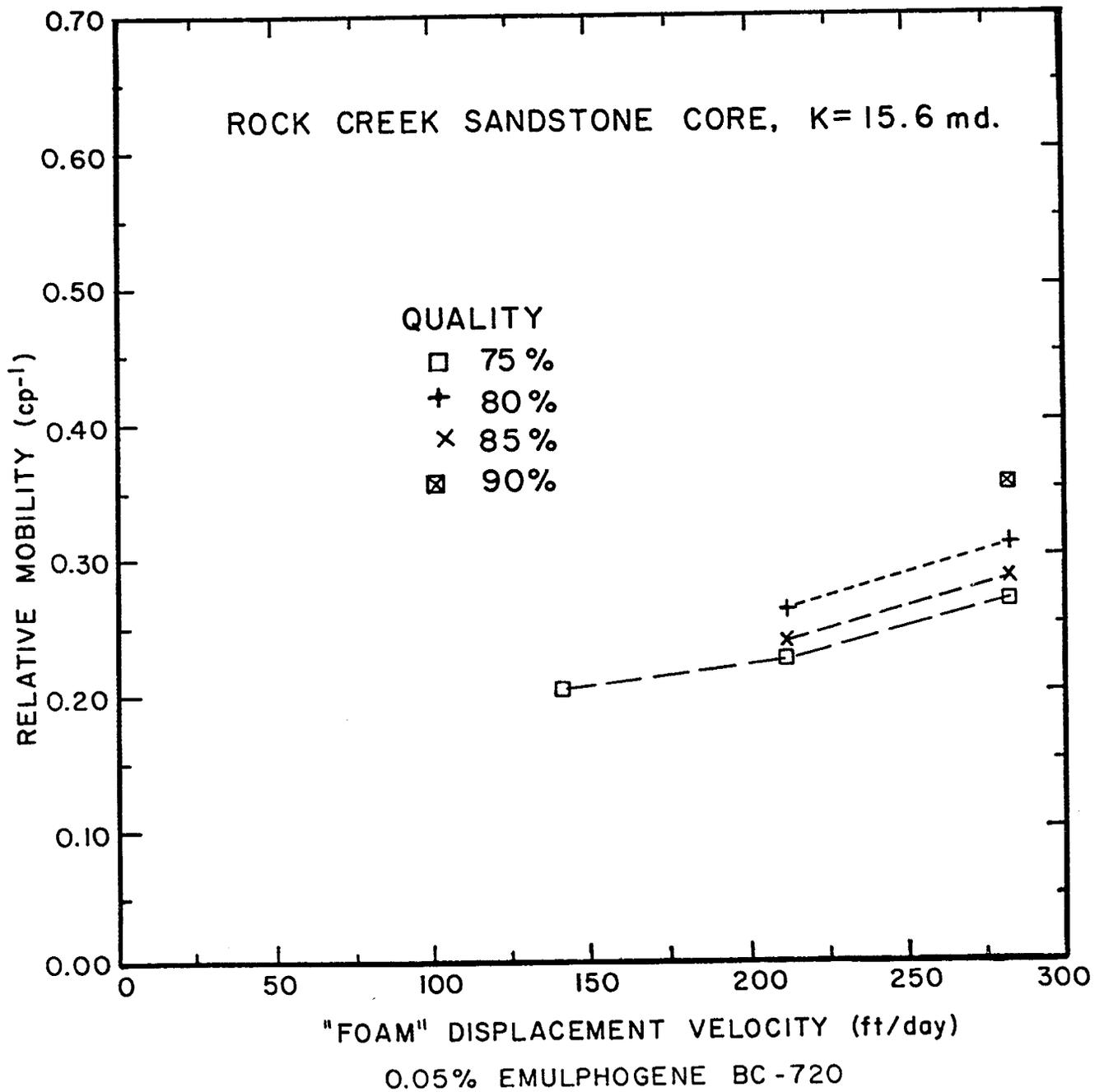


Fig. 9. Relative mobility of dense CO_2 foam - 0.05% EMULPHOGENE.

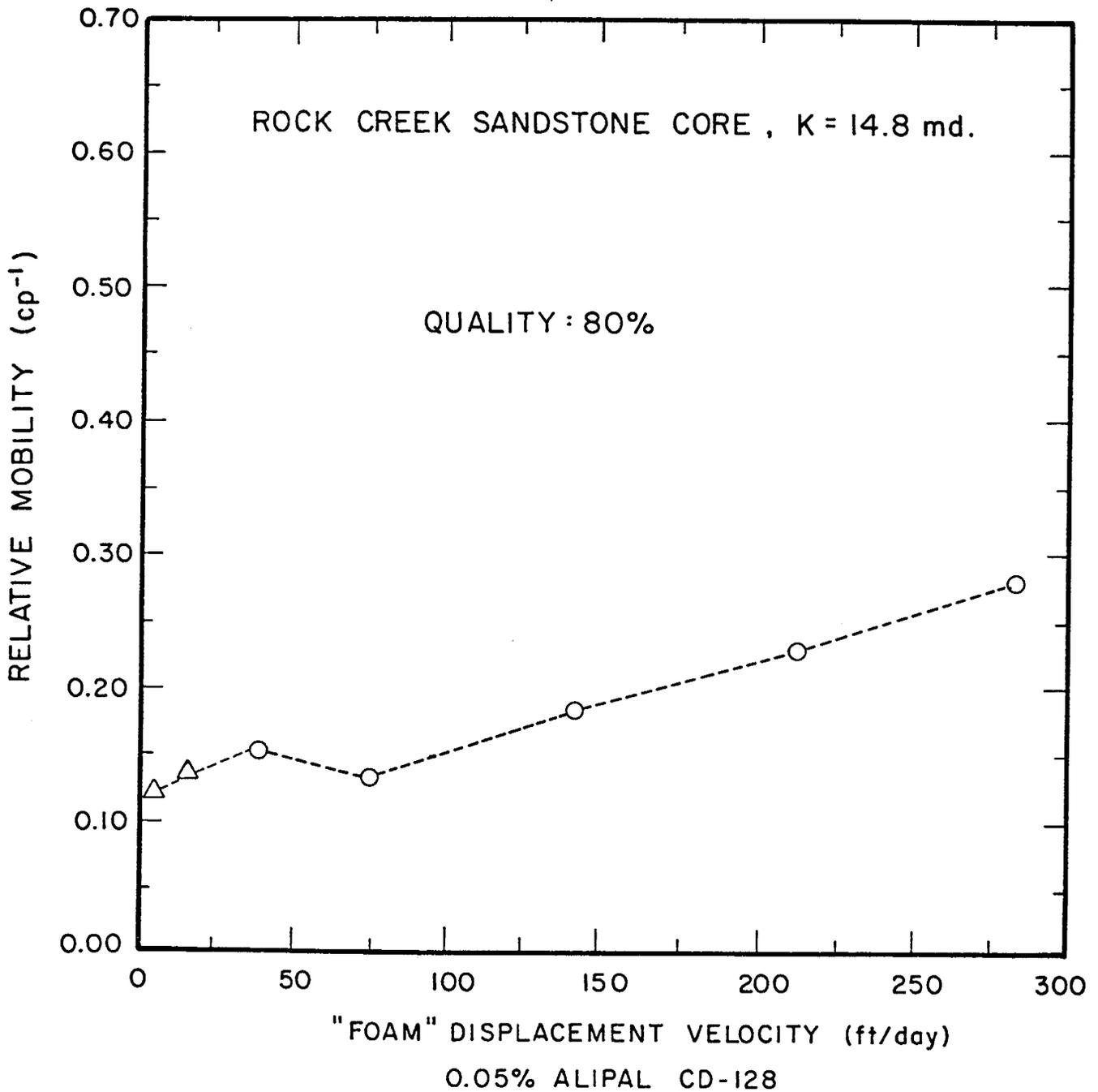


Fig. 10. Relative mobility of dense CO₂ foam - 0.05% Alipal CD-128.

would mean that the near-well pressure drop would not be so great. Therefore, the overall level of mobility control could be raised without violating the pressure constraints which limit injection rate at most injection wells.

- b. Foam mobility generally decreases with increasing surfactant concentrations. Although we have not yet fully explored this relationship, it appears that at concentrations of a fraction of a percent or less, the rate of change of mobility with concentration is low. At much higher levels of surfactant concentration in the aqueous phase, however, the mobility, itself, becomes quite low. Under these circumstances, the CO₂ and iso-octane dispersions we have studied are quite comparable to the foams which have been recommended by several previous authors^{45,46} for use as diverting agents or as blocking agents to plug high permeability thief zones.

For the purpose of our work, however, such extremely low mobilities are not desired. For mobility control of CO₂ floods, it is sufficient to reduce the relative mobility (λ_r) to the range expected for that of water or oil--that is, from around 20 cp⁻¹ for "unfoamed" dense CO₂ to the range from 0.1 to 0.5 cp⁻¹. Reduction of relative mobility to values less than this would be counterproductive. Because injection pressures are limited, such low values of injection fluid mobility would cause the overall injection and production rates to sink to uneconomic levels. Mobility control differs, in this view, from flow diversion. The goal of mobility control, as the term is used here, is to decrease the displacing fluid's mobility only to the order of that of the displaced fluid. In this way the extremely rapid growth of frontal instability patterns, which occur when the mobility ratio exceeds two or three, will be eliminated. Some further gain--especially when the formation is quite stratified--would be obtained by decreasing the mobility ratio to values less than one. But such additional increases in flow uniformity would be more dearly bought, at the expense of decreased rate of exploitation of the field.

- c. Mobility of the foam-like dispersions examined here changes only moderately with foam quality. For the "foams" studied, a small decrease of mobility is observed with increasing quality, up to 90%, the maximum value used in these experiments. Tentative conclusions from this observation are that the first requisite of CO₂ mobility control "foams" can be fulfilled. It will be possible to use foams which introduce only a

minimum quantity of water into the formations. Thus, the fraction of residual oil which can be contacted by the dense CO₂ carried within the foam-like dispersions will be maximized.

- d. Although comparisons of relative mobility for different samples are somewhat questionable because of the unknown dependence on rock permeability, the approximate equality of the numbers obtained with isooctane "foams" to those obtained with CO₂ "foams" indicates an approximate independence of relative mobility on the viscosity of the discontinuous phase.

7. Reservoir Considerations for Use of Foam-Like Dispersions

Whereas important general questions still remain about the use of a "foam-like dispersion" for mobility control in a CO₂ flood, the method seems viable at this time in situations where the compatibilities of materials have been verified. Necessary tests to assure this would include measurements of the chemical stability of the surfactant at reservoir temperature and in contact with the ions and hydrocarbon fractions present in the reservoir fluids. In addition, the mobility of the foam-like dispersion that is formed by CO₂ and the surfactant solution in reservoir rock must be determined by experiment at rates similar to those of interest in the reservoir.

In addition to such tests to ascertain the surfactant's suitability, there are design questions to be answered concerning the use of this form of mobility control in the reservoir as a whole. It has already been suggested that adsorption of surfactant by the reservoir rock is to be counteracted by the injection of a "pad" of higher concentration surfactant solution prior to the "foam" slug. Because of adsorption, the surfactant concentration front moves more slowly, by the factor f_v , than would plain water. The volume of the pad is calculated to be sufficient so that it will not be dissipated until the "target volume" of the reservoir has just been swept. Similarly, the extra concentration of surfactant in the pad is calculated to be just that quantity which will be "irreversibly" adsorbed on the amount of reservoir rock contained in the "target volume." Here again, the calculation utilizes the measured value of this parameter obtained from laboratory experiments.

A further reservoir question concerns the design of the "slug" of foam-like dispersion itself. To calculate the quantity needed, a knowledge of the mechanisms of slug degradation is important. The front end of the "foam" slug, which does the important work of forming and displacing the "oil bank," decays and becomes indistinct by two processes. The first of these is growth of instability fingers, and the second is the process of dispersion as modified by the presence of immiscible phase (water) and by the nature of the partial miscibility between crude oil and CO₂. With the decreased mobility of the "foam," there will presumably be no fingers formed at this front. As to the second process, although the

influence of the complicating factors mentioned are not fully understood, it is probable that the growth of the dispersion zone will be at a rate less than linear with the distance travelled, and can therefore be considered of minor importance over reservoir distances.

On the other hand, the rate of slug degradation at its rearward boundary, where the "foam" is driven by the chase water, is appreciable. Here, in fact, the loss of material in the slug is directly proportional to the distance travelled. The proportionality occurs because the chase water is unable to displace all of the CO₂ in the slug, but leaves a residual. This then offers a convenient way of calculating the slug volume required to maintain the displacement front until a "target volume" in the reservoir has been swept. On the assumption that the CO₂ residual is of the same magnitude as residual oil fraction, it is apparent that at least this much CO₂ must be injected in the slug of "foam." The "target volume" itself can be calculated from the gross geometry of the reservoir, as that portion of it in which the absolute pressure of CO₂ can be kept above the MMP.

The need to operate the flood at optimum conditions from the point of view of economics will modify the above considerations, of course. Thus the target volume may be adjusted to include areas near the production well where, at practical well rates, CO₂ will not be at sufficient density for most efficient displacement. By this means, a loss in total recovery could be traded off for a gain in production rate. Similarly the gain that could be achieved in total production by operating with a mobility ratio slightly less than one (to suppress fingers entirely) may not be quite so useful economically as a higher exploitation rate achieved at the expense of a greater-than-unity mobility ratio which would allow slow finger growth rate. The influence of such economic factors has been investigated in the M.S. thesis of P.K. Pande,⁵⁷ although their full exploration must await further work that will define more precisely the technical influence of the various factors on recovery and recovery rate.

C. Direct Thickeners

1. Background

To achieve maximum effectiveness as a displacement fluid, CO₂ must be compressed enough to be capable of extracting some of the lighter ends from the crude oil. This same ability of the CO₂ to dissolve some components of the oil raises the possibility that polymers might be found which are soluble to a sufficient extent in the dense CO₂ (whether above or below its critical point) to raise its viscosity enough for mobility control. Such a "directly thickened" CO₂ would be especially advantageous, in several ways, because no added water would be involved in its use. On a microscopic scale, this absence of added water would decrease the amount of oil which is bypassed or "shielded" from the CO₂, both in the currently used WAG process, and also during use of foam-like dispersions. A second benefit that would be obtained by not using any water in the injected fluid is a greatly reduced corrosion problem.

Of course, weighed against the advantages in the use of a direct thickener for mobility control are the possible difficulties. Only a low concentration of direct thickener level could be tolerated, because the dissolved polymer would necessarily come out of solution and be deposited in the lower pressure regions of the reservoir, when these regions are reached by the thickened CO₂. A second possible difficulty would be the expense--a direct thickener would need to be relatively inexpensive for its use to be justified.

Most of all, however, a useable direct thickener needs to be obtainable, preferably in quantity, and off-the-shelf, from a chemical supplier experienced in oilfield products. Unfortunately this condition is currently far from being satisfied. The work reported here has been unsuccessful in finding a ready-to-use direct thickener among the current products of any manufacturer. On the other hand, however, significant progress has been made in defining the types of polymers most likely to be useful for the purpose. There is a good possibility that further research - either at PRRC or elsewhere - can succeed in synthesizing such polymers. The next sections discuss the significant literature, the experimental apparatus developed for the search, the results obtained with it and the general conclusions which can be drawn.

2. The Literature on Solubility in CO₂

The solubility of a large number of organic materials in liquid CO₂ was studied extensively by A.W. Francis, who reported his results in two early papers.^{58,59} The compounds studied were mostly organic, with emphasis on hydrocarbons. The solubility of such compounds is directly involved in the ability of CO₂ to extract crude oil components and generate a miscible displacement front in flow geometries where viscous fingering is suppressed. The relationship that exists between the solubility of these components and the CO₂ density is being investigated actively in a continuous-operation cell by Orr et al.^{60,5}

There have also been other research groups, with very different motivations, who are concerned with the solvent properties of dense CO₂ and other highly compressed gases. Among these are the chromatographers such as Stahl et al.⁶¹ McManigill and co-workers⁶² at Hewlett Packard, Giddings⁵³ and Peaden⁶³ who are interested in the use of dense gases for the separation of materials, utilizing also their very rapidly increasing change of dissolving power with density. There have also been recent reports of the use of supercritical CO₂ in the extraction of soybean oils, and of caffeine from coffee.⁶⁴

All of this work has contributed to the possibility that direct thickeners for CO₂ might be found. Although dense CO₂ is non-polar, and not a particularly strong solvent, there seems to be a wide variety of lower molecular weight organic compounds which are soluble in it. An economic direct thickening polymer would have to be insoluble in water, so that it would not be leached out by the mobile and immobile water with which it would come in contact in the reservoir. A major obstacle to the

search for direct thickeners was the lack of information on the solubility in CO_2 of any polymers, or on the increase in CO_2 's viscosity which they might cause. Thus, even before all of the above cited information had been collected and digested, it was apparent that a search for direct thickeners would involve apparatus development and experimental measurements of solubility and viscosity.

3. Apparatus-Solubility Measurements

Fig. 11 shows a schematic of the apparatus that has three major functions in the measurement of solubilities. First, a saturated solution of the polymer in dense CO_2 is prepared, at predetermined pressure and temperature, in an air-free mixing chamber. For transparency, and to be able to use thin-walled tubing, the mixing chamber is a length of single crystal sapphire. The strength of this tube is more than adequate to contain pressures that have been used. Fig. 12 shows a detailed schematic of the mixing chamber. For mixing purposes, an axially placed, teflon coated magnetic stirring bar (b in Fig. 1) is supplemented in the sapphire tube by a short tubular extension (a in Fig. 11) constructed of a magnetic stainless steel. As these are moved up and down inside the sapphire tube by means of a strong magnet that is moved along the tube externally, the mixing action is assisted by vanes shaped onto the lower end of the steel extension. The mixing chamber is supported vertically in a thermostated water bath by fittings at both ends. The fluid path through the lower fitting is extended upward into the sapphire tube as a thin-walled metal tube (c in Figs. 11 and 12) that protrudes into the mixing chamber. The vanes on the magnetic mixing device extend down into the annular space surrounding this metal tube, when the assemblage rests at the lower end of the sapphire tube. Undissolved polymer can settle into this annulus after the stirring operation when the magnets are lifted to the upper portion of the mixing chamber. If a sample is in the form of highly viscous liquid, undissolved polymer sometimes can remain stuck to the wall of the sapphire tube.

The second function of the apparatus is to transfer a known quantity of the resulting saturated solution to a chamber in which the amount of dissolved polymer can be assayed. Fig. 13 shows details of the assay chamber that consists of a weighed test tube, three quarters full of glass beads, and contained within a large-bore stainless steel pressure vessel. The polymer solution is conducted to the test tube through a transfer tube entering the assay chamber, with a needle-tube extension to the bottom of the test tube as shown in Fig. 13. Before the transfer, the assay chamber is filled with nitrogen to the same pressure as that of CO_2 in the mixing chamber. This is followed by opening valve 5 (Fig. 11) to permit polymer-containing liquid or supercritical CO_2 to be displaced by a positive displacement pump into the assay tube without any appreciable change in the solution pressure which is monitored by sensitive transducers with electronic displays. A measured volume (about 3 ml.) of the solution displaces the nitrogen gas in the pore space of the glass beads in the lower portion of the test tube.

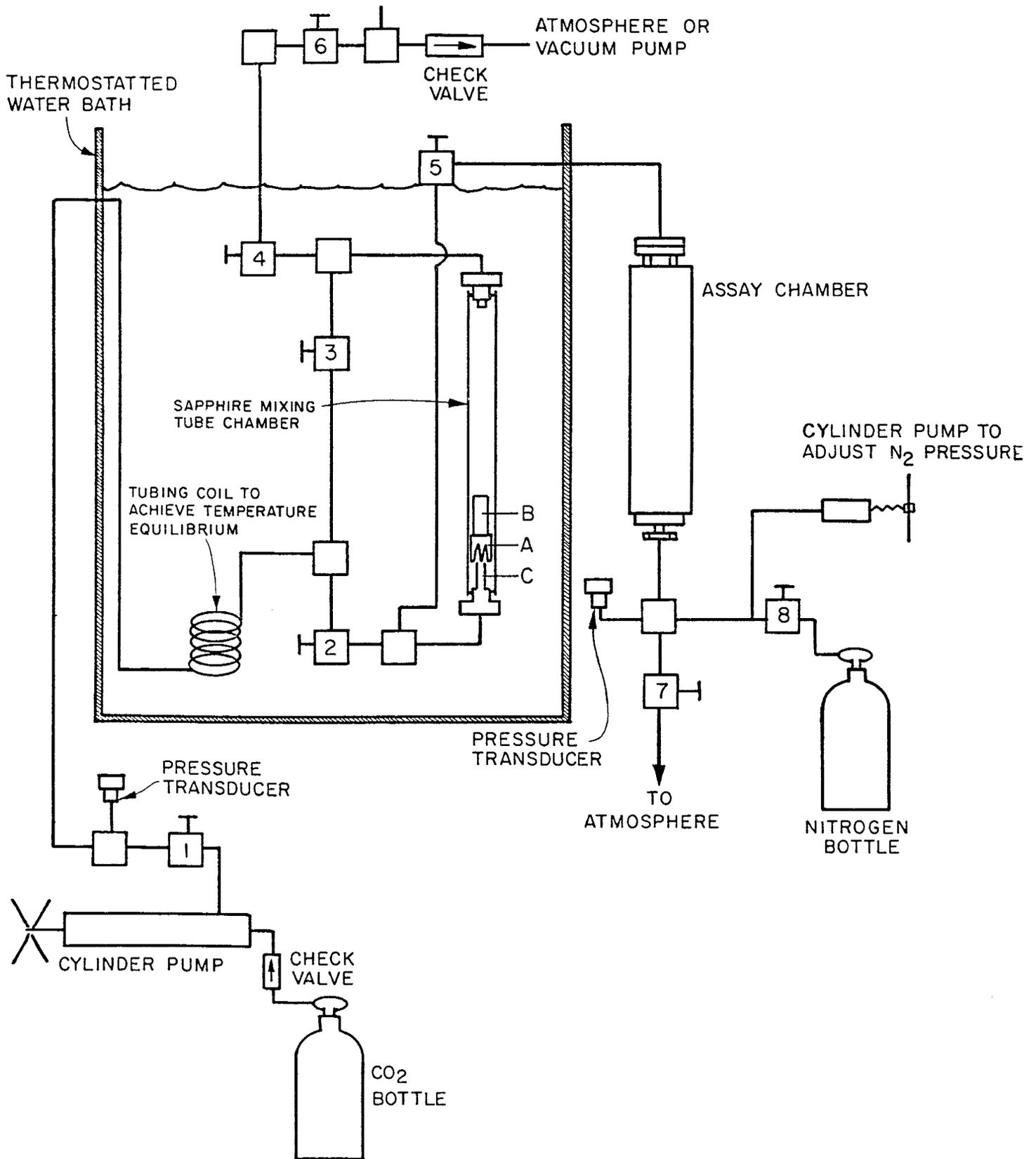


Fig. II. Apparatus to measure solubility in dense CO₂.

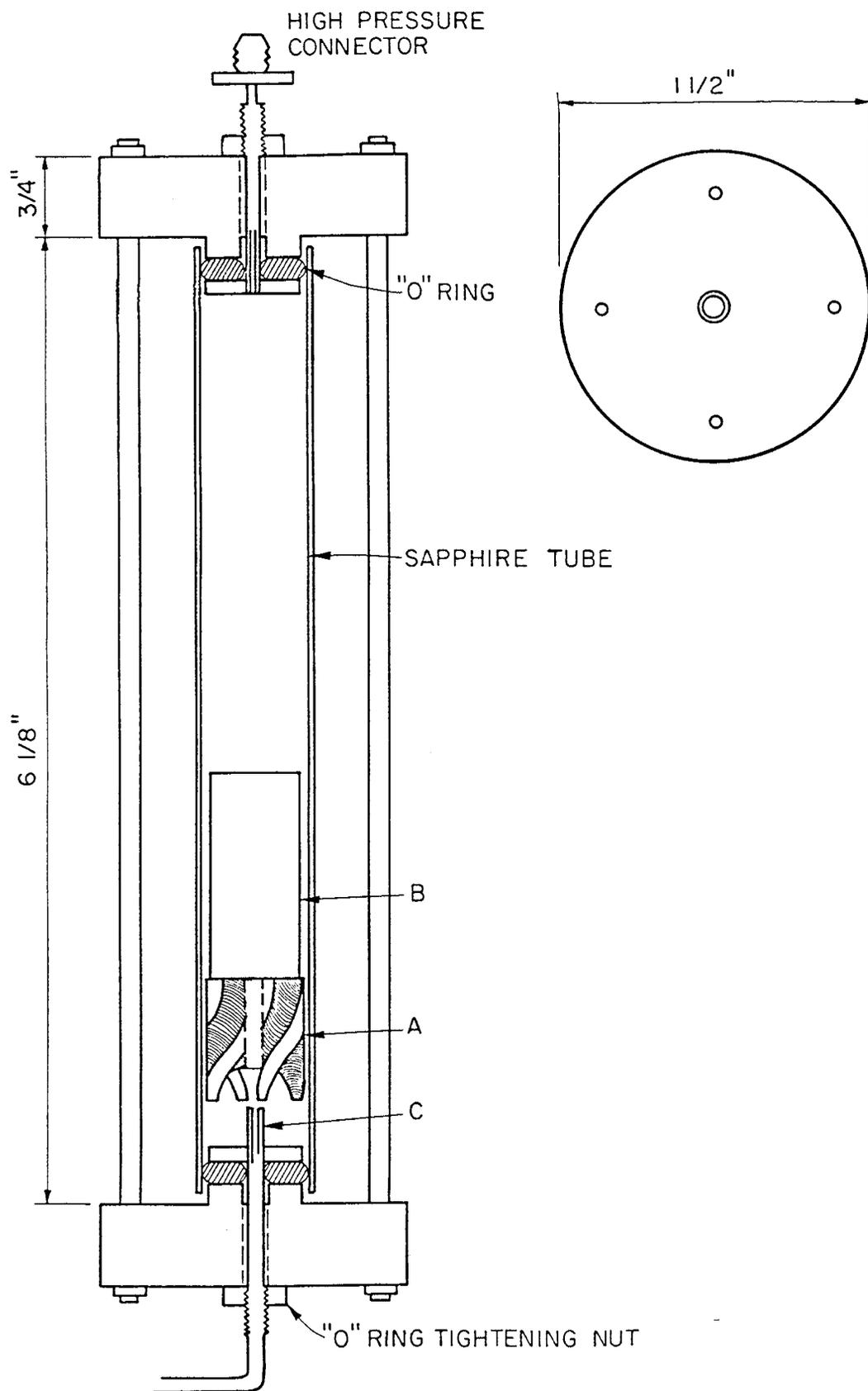


Fig. 12. Detail of sapphire mixing cell.

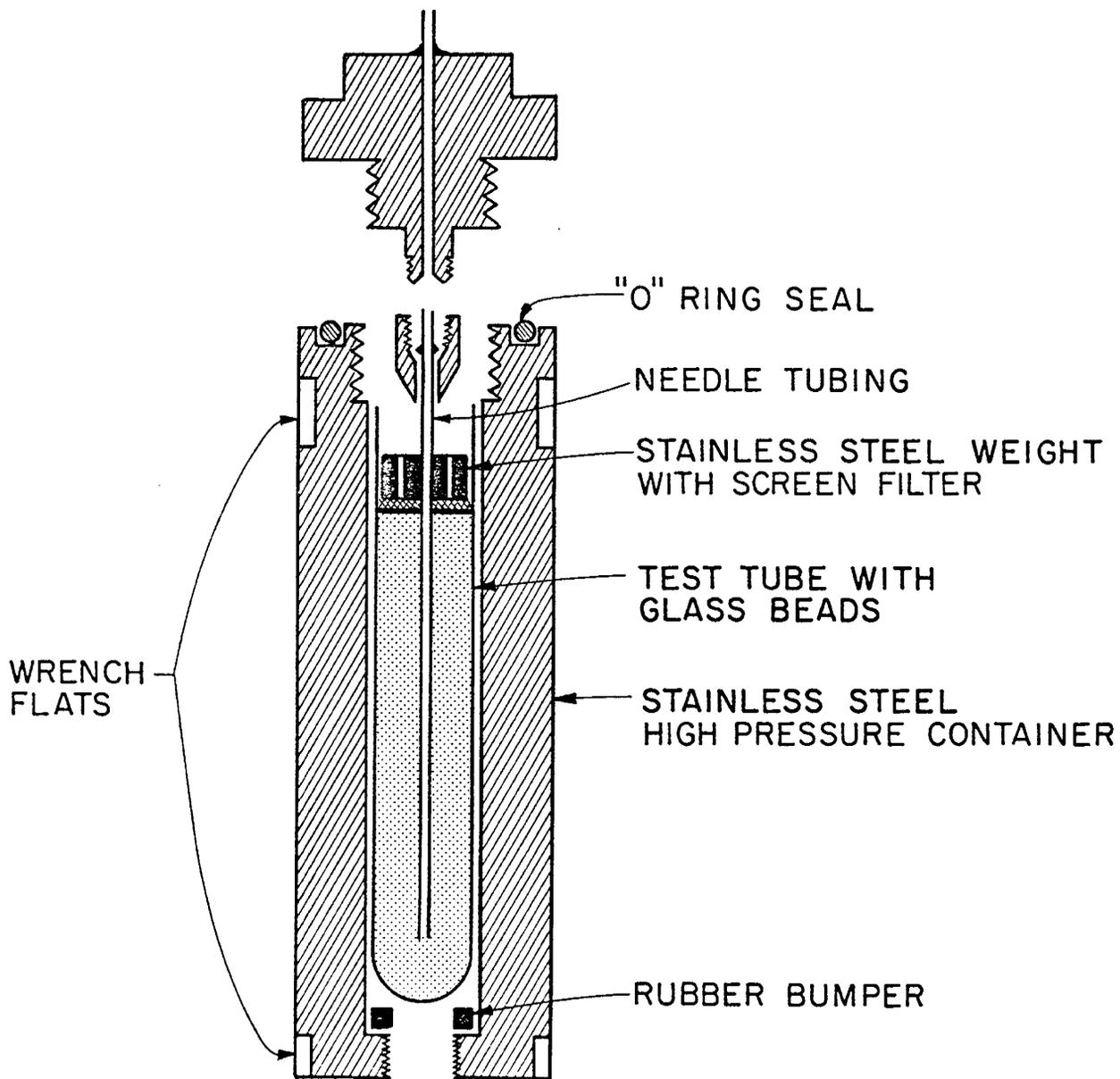


Fig. 13. Detail of assay chamber.

When this is accomplished, transfer valve 5 is closed and the third function of the apparatus is begun. Valve 7 is slowly opened to allow the pressurizing nitrogen gas and the CO₂ to depart the assay chamber gradually while leaving on the glass beads the polymer that had been carried over in solution in the CO₂. The difference in weight of the test tube before and after the experiment gives the amount of polymer dissolved in the previously measured volume of liquid or supercritical CO₂. In order to avoid gross movement of glass beads during release of pressure in the assay chamber, a weighted stainless steel screen (Fig. 13) pierced by a central hole for the needle tubing, rests on top of the beads in the test tube.

In an ordinary drying situation, most of the dissolved material is left at the surface of the bead pack, and a smaller fraction is deposited rather uniformly within the lower parts of the pack after liquid saturation has been reduced to less than that which can support liquid mobility.⁶⁵ The design of the assay tube in this apparatus encourages all of the dissolved material to be deposited in the lower part of the bead pack. Preliminary experiments which were performed with lower vapor pressure solvents showed the dissolved material to be retained quantitatively in the glass bead pack of the assay chamber.

4. Apparatus-Viscosity Measurement

There are no commercially available viscometers by which the influence of the dissolved polymers on CO₂ might be measured. The necessity to maintain the solutions at high pressures imposes difficult constraints on the operation of the usual viscometric devices. Thus, an apparatus based on the Couette or cone-and-plate geometries would pose severe problems in construction of rotating seals and the measurement of low values of torque through a pressure wall. Also, because a useful device should be operable above the critical temperature, no air or vapor interface is generally available, such as is used in the ordinary Ostwald viscometer to track fluid motion through a capillary tube.

The apparatus utilized in this work to evaluate the viscosity of polymer solution in dense CO₂ is a falling cylinder-in-tube viscometer. This device is a modification of some of the same equipment used in the solubility measurements. For the viscometric mode, the sapphire mixing chamber is used as the tube for time-of-fall measurements. The magnet and its mixing extension shown in Fig. 12 are replaced by a smooth steel cylinder, with diameter only slightly smaller than the inner diameter of the sapphire tube. (Because the sapphire tube is not perfectly circular in cross section, the annulus is not regular. Its average dimension is about .015 cm) The tube is crossed by two horizontally oriented photoelectric lines-of-sight that are interrupted by the cylinder as it falls. Whereas the lower of these is placed just above the bottom of the tube, the placement of the upper photocell and light source represents a compromise. If they are too low, precision is lost in the measurement, due to the shortness of the time interval. If the upper line-of-sight is too high, then the cylinder will still be accelerating when the clock is started. In that case, the non-linearity in the relation between

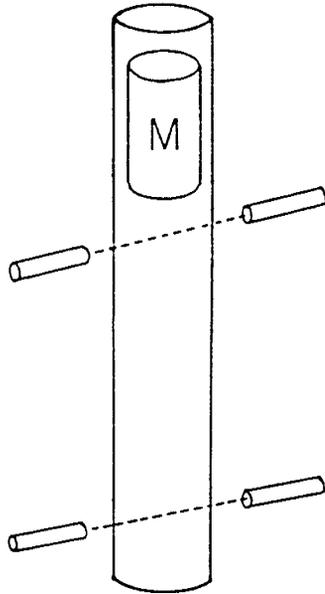
viscosity and time interval would be significant. The locations of these lines-of-sight are shown in Fig. 14. In the device constructed, the cylinder falls a distance of 1.24 cm before interrupting the first light beam and starting the timer. With the lower line-of-sight at 10.66 cm from the release point, the shortest times of fall (for pure CO₂ at the lower density range) are about 1.5 sec. In this case the non-linearity due to the fact that critical velocity has not been attained by the cylinder as it passes the upper station, is less than 1%; and insignificant in comparison with other errors, such as uncertainty in the CO₂ density.

In this type of viscometer, as in one based on flow through a capillary tube, a wide range of shear rate is encountered, which makes the method unsuitable for use with significantly non-Newtonian liquids. Practically all of shear occurs in the moving annulus between the tube walls and cylinder, with the liquid above and below it essentially static. The no-slip condition specifies that the fluid at the cylinder surface moves downward with the velocity of the cylinder, while that fluid at the tube walls is stationary. At the same time, the fluid velocity in most of the annulus is upward, since the result of the motion is to transfer the fluid which is initially below the cylinder to the space above it. A complete mathematical analysis of the flow is given in a DOE Report.³³

Although this viscometer has served well for its designed purpose, there are certain disadvantages in its use. The first of these has been mentioned--it is that the kinematics of flow renders the device unsuitable for unambiguous measurements of shear-rate dependence. It is presumed that this deficiency has not yet been felt in the work, because only relatively low molecular weight, CO₂-soluble polymer samples have so far been available. In addition to this potential trouble, however, there are also some immediate practical difficulties. One of these is that erroneously long travel time can be measured in the case of contamination. This can occur if a small amount of undissolved polymer is present and adheres to the tube wall, or if, because of a decrease in pressure, some polymer comes out of solution and is deposited on the walls on the cylinder. These troubles can be minimized by using the viscometer only for less-than-saturated polymer solutions.

A more serious trouble is that the tube, although strong enough to contain the CO₂ at pressures in most of the range that interests us, is noticeably elastic. Thus, there is a significant pressure dependence of the viscometer constant. Because the tube (being single crystal produced by an "edge defined" pulling-from-the-melt) is not exactly circular in cross section, and because sapphire is not isotropic, the geometry of the tube's distortion in response to internal pressure is complex. The pressure dependence must be determined experimentally, which makes the use in this application very dependent on independent viscosity vs pressure measurements of the solvent. Fortunately, Michels, Botzen and Schuurman⁶⁶ have published such data on the viscosity of dense CO₂.

FALLING CYLINDER VISCOMETER



Fluid fills tube; no flow out top or bottom. Velocity of fall $V_{(t)}$

$$V_{(t)} = V_L (1 - \exp\{-t/T_C\})$$

V_L is a limiting velocity:

$$= \frac{\rho_C - \rho_f}{\mu} C (g, r_C, r_f) \text{ cm/sec.}$$

T_C is a time constant

$$= \frac{1}{\mu} K (\rho_C, \rho_f, r_C, r_f) \text{ sec.}$$

$$\lim_{t \gg T_C} V_{(t)} = V_L = \frac{(\rho_C - \rho_f) C}{\mu}$$

$$\text{then fall time } F = \frac{\Delta X}{V_L} = \frac{\mu}{(\rho_C - \rho_f) C}$$

$$\text{so } \mu = (\rho_C - \rho_f) C F$$

ρ_C, ρ_f are densities of cylinder and fluid

r_C, r_f are radii of cylinder and tube

Fig. 14. Falling cylinder viscometer.

5. Soluble Polymers—Results and Discussion

a. Solubilities

The solubilities of several polymers in both liquid and supercritical CO₂ were measured following the procedure described in the previous section. Most of the polymers tested were obtained from commercial sources, and the molecular weight data for these polymers were not generally provided. Additionally, therefore, viscosity measurements at multiple dilutions were carried out at atmospheric pressure in suitable solvents to assess the approximate molecular weights. The intrinsic viscosity values for the polymers tested in this way are given in Table IX. This table also gives viscosity average molecular weights of those polymers for which K and a values in the Mark-Houwink equation were available in the literature.⁶⁷

In order to obtain fairly comparative data, most of the CO₂-solubility experiments were carried out at 25°C and pressures such that the density of liquid CO₂ was maintained in the range of 0.82 to 0.92 gm/cc. Table XI gives the list of polymers that are soluble at least in parts-per-thousand range in CO₂, and also the test conditions for individual experiments. Table XI shows polymers that are insoluble in CO₂ under given experimental conditions.

It is apparent from Tables X and XI that tacticity of a polymer plays an important role in determining its solubility in CO₂. Atactic poly(butene) and polypropylene oxide were soluble in CO₂ while isotactic polymers did not dissolve. This appears consistent with the fact that crystalline, isotactic polymers, in general, are either difficult to dissolve in common organic solvents, or require severe conditions for solution. Syndiotactic polymers of 1-butene and propylene oxide were not available.

Poly(propylene), poly(butene), poly(1-decene) and polyisobutylene were soluble while poly(styrene), poly(1-vinyltoluene), poly(4-vinylbiphenyl) were insoluble. This indicates that aliphatic side chains on the hydrocarbon polymer backbone indeed help in dissolving polymers in CO₂. On the other hand, the presence of aromaticity in some of these hydrocarbon polymers seems to reduce their solubility. Apparent exceptions to the latter are poly(1-vinylnaphthalene) and poly(acenaphthalene) which showed solubility in CO₂. Poly(vinyl ethyl ether), poly(n-decylacrylate) and poly(n-lauryl methacrylate) were soluble in liquid CO₂. This suggests that the presence of ether and ester groups on the side chains is not detrimental to the solubility of polymers in liquid CO₂, especially when these groups are located between the polymer backbone and long aliphatic chains. Another example of the CO₂ solubility of a non-polar polymer is polydimethylpolysiloxane.

It is evident from the list of polymers insoluble in CO₂ that the presence of amide, ester, carbonate, and hydroxyl groups in the polymer backbone imparts insolubility to the polymer. Similarly halogens, aldehydes, ring systems with unsaturation in the chain backbone and

Table IX
Polymer Solubility in Conventional Solvents

| <u>Polymer</u> | <u>Solvent</u> | <u>Temp</u> | <u>Intr. Visc.</u> | <u>Viscosity Average Mol. Wt.^{a,b}</u> |
|--|----------------|-------------|--------------------|---|
| Poly(ace naphthalene) | Toluene | 25 | .2242 | 216000 |
| Poly(vinyl ethyl ether) | Toluene | 25 | .06336 | ND |
| Poly(vinyl chloride) | Cyclohexanone | 25 | .9657 | 40950 |
| Poly(butadiene) | Toluene | 30 | .1486 | 5095 |
| Poly(isobutylene) | Dilsobutylene | 25 | .04556 | 1228 |
| Poly(isobutylene) | Benzene | 25 | .02239 | 501 |
| Poly(styrene) | Cyclohexane | 34.5 | .09955 | 10940 |
| Poly(butene) | Benzene | 30 | .01775 | 434.1 |
| Poly(benzyl methacrylate) | Benzene | 30 | 1.508 | 1993000 |
| Poly(n-butyl methacrylate- isobutyl methacrylate,50/50) | Benzene | 30 | .6659 | ND |
| Poly(vinyl isobutyl ether) | Toluene | 25 | 3.030 | ND |
| Terpene resin | Toluene | 25 | .06968 | ND |
| Poly(cis-isoprene) | Benzene | 25 | 3.174 | ND |
| Poly(propylene) | Benzene | 25 | .1287 | 5916 |
| Poly(acrylonitrile) | DMF | 25 | 1.934 | 158900 |
| Poly(ethylthiirane) | Toluene | 25 | 1.165 | ND |
| Poly(propylene oxide) | Benzene | 20 | .7138 | 66162 |
| Poly(methyl oxirane) | Benzene | 20 | .01284 | 408.9 |
| Poly(butene) | Benzene | 30 | .03913 | 1300.9 |
| Poly(alpha-decene) OS60832 | Benzene | 30 | .03196 | ND |
| Poly(2-vinyl pyridine) | Benzene | 25 | .09697 | ND |
| Poly(4-vinyl biphenyl) | Benzene | 25 | .3530 | ND |
| Poly(vinylidene fluoride) | DMF | 25 | .8638 | ND |
| Poly(n-decyl acrylate) | Toluene | 25 | .06285 | ND |
| Poly(hexadecyl acrylate) | Toluene | 25 | .05609 | ND |
| Poly(vinyl neodecanoate) | Toluene | 25 | .07877 | ND |
| Poly(n-lauryl methacrylate) | Toluene | 25 | .4229 | ND |

a) ND-No Data Available

b) k and a-Values taken from ref.

Table X

Polymers Soluble in Carbon Dioxide

| <u>Polymer</u> | <u>Solubilitya Parameter (cal/cc)^{1/2}</u> | <u>Mol. Wt. b</u> | <u>Temp. °C</u> | <u>Pressure PSI</u> | <u>Approx. Density of CO₂ g./cc</u> | <u>Solubility of Polymer in CO₂ g./lit.</u> |
|--------------------------------|---|--------------------|---------------------|-------------------------|--|--|
| Poly(propylene) atactic | * 9.2 | 5916 Mv | 1)•25 2)•32 | 1960 1960 | 0.865 0.82 | 2.2 1.2 |
| Poly(butene) atactic | * 7-8.5 | 434 Mv | 33 | 2600 | 0.855 | 8 |
| Poly(butene) atactic | * 7-8.5 | 1300 Mv | 30 | 3400 | 0.91 | 5.6 |
| Poly(α -decene) | | V | 25 | 2900 | 0.912 | 10.3 |
| Poly(isobutylene) | *7.8-8.1 | 501 Mv | 25 | 2950 | 0.913 | 4.0 |
| Poly(butadiene) | *7.2-8.6 | 5095 Mv | 25 | 2800 | 0.910 | 2.5 |
| Poly(1-vinylnaphthalene) | | | 25 | 3160 | 0.925 | 2.2 |
| Poly(acenaphthalene) | | 216,000 Mv | 20 | 1500 | 0.86 | 0.25 |
| Poly(benzyl methacrylate) | | V | 1)•25 2)•58 | 2000 2500 | 0.87 0.69 | 1.2 <1.2 |
| Poly(ethyl thiirane) atactic | | V | 25 | 3160 | 0.925 | 1.4 |
| Poly(vinyl ethyl ether) | * 7-11.1 | V | 25 | 2480 | 0.898 | 5.5 |
| Poly(dimethyl siloxane) | * 7-9.5 | 135,000 Mw | 1)•25 2)•52 | 2750 2850 | 0.907 0.71 | 0.3 1.0 |
| Poly(methyl oxirane) atactic | | 408 Mv | 25 | 2150 | 0.878 | 2.73 |
| Poly(2-methyl oxacyclo butane) | | 4200 Mn 9000 Mw | 25 | 2060 | 0.872 | 1.75 |
| Terpene resin | | V | 25 | 1700 | 0.835 | 4.0 |
| Poly(n-decyl acrylate) | | V | 25 | 2400 | 0.89 | 2.38 |

Table X (cont.)

Polymers Soluble in Carbon Dioxide

| Polymer | Solubility ^a Parameter (cal/cc) ^{1/2} | Mol. Wt. b | Temp. °C | Pressure PSI | Approx. Density of CO ₂ g./cc | Solubility of Polymer in CO ₂ g./lit. |
|--|---|------------|-------------|-----------------|---|--|
| Poly(n-butyl methacrylate isobutyl methacrylate 50:50) | *7.4-11.1 | V | 20 | 2200 | 0.905 | 0.6 |
| Poly(n-lauryl methacrylate) | | V | 25 | 2230 | 0.88 | 2.45 |

a) * For Polymer
+ For Monomer

b) Mv-Viscosity Average Molecular Weight
V -Refer to Intrinsic Viscosity Data in Table IX.

Table XI

Polymers Insoluble in Carbon Dioxide

| <u>Polymer</u> | <u>Solubility^a Parameter (cal/cc)^{1/2}</u> | <u>Mol. Wt.^b</u> | <u>Temp. °C</u> | <u>Pressure PSI</u> | <u>Approx. Density of CO₂ g./cc</u> |
|-----------------------------------|--|-----------------------------|---------------------|-------------------------|--|
| Poly(butene) isotactic | * 7-8.5 | Not Known | 25 | 3000 | 0.915 |
| Poly(isoprene) cis | * 7.4-10 | V | 25 | 2200 | 0.880 |
| Poly(norbornene) | + 8.7 | 2,000,000 | 1) 25 2) 50 | 2800 2800 | 0.910 0.77 |
| Poly(2-vinyl pyridine) | + 9.7 | V | 25 | 1700 | 0.825 |
| Poly(octadecene-maleic anhydride) | | 50,000 | 1) 30 2) 40 | 2500 2500 | 0.87 0.805 |
| Poly(styrene-maleic anhydride) | * 9.5-11.9 | 10,000 | 1) 25 2) 50 | 2800 2800 | 0.910 0.77 |
| Poly(vinylidene fluoride) | *12.0-12.3 | V | 1) 28 2) 38 | 2600 2600 | 0.885 0.83 |
| Poly(caprolactone) | | 10,000 | 1) 25 2) 40 | 2900 2900 | 0.912 0.845 |
| Poly(vinyl formal) | * 9.9-13.3 | 10,000 | 25 | 2800 | 0.910 |
| Poly(vinyl chloride) | * 8.5-11.1 | 80,000 | 25 | 2800 | 0.910 |
| Poly(vinyl pyrrolidone) | * 14.7 | 10,000 | 35 | 2500 | 0.84 |
| Poly(ethylene oxide) | * 8.9-12.7 | 600,000 | 25 | 3300 | 0.930 |
| Poly(propylene oxide) isotactic | + 8.8 | 66,162 Mv | 25 | 3500 | 0.935 |
| Poly(acrylonitrile) | *12.3-12.8 | 158,900 Mv | 25 | 2600 | 0.905 |

Table XI (cont.)

Polymers Insoluble in Carbon Dioxide

| <u>Polymer</u> | <u>Solubility^a Parameter (cal/cc)^{1/2}</u> | <u>Mol. Wt. b</u> | <u>Temp. °C</u> | <u>Pressure PSI</u> | <u>Approx. Density of CO₂ g./cc</u> |
|------------------------------|--|-------------------------|---------------------|-------------------------|--|
| Poly(methyl thiirane) | | 500,000 | 25 | 2600 | 0.905 |
| Nylon II | * >8.5 | | 25 | 1800 | 0.855 |
| Poly(styrene) | * 8.5-10.6 | 10,940 Mv | 25 | 2200 | 0.880 |
| Poly(carbonate) | * 9.5-11 | 36,000 | 1) 25 2) 40 | 2800 | 0.910 |
| Poly(4-vinyl biphenyl) | | V | 1) 25 2) 31 | 2800 2100 | 0.835 0.875 |
| Poly(octadecyl acrylate) | | 23,300 Mw 13,000 Mn | 25 | 2140 | 0.87 |
| Poly(octadecyl methacrylate) | | 671,000 Mw 97,200 Mn | 25 | 2420 | 0.89 |
| Poly(vinyl toluene) | | | 25 | 2500 | 0.91 |
| Poly(tetrafluoro ethylene) | * 6.2 | | 25 | | |

a) * For Polymer
+ For Monomer

b) Mv - Viscosity Average Molecular Weight

V - Refer to Intrinsic Viscosity Data in Table IX.

aromaticity in general are not desirable in a polymer to be soluble in CO₂.

Comparisons among the solubilities of different polymers in CO₂ would have been more informative if the molecular weights of all polymers had been in the same range. However, such a variety of polymers in a given molecular weight range were almost impossible to obtain from commercial sources. One sequence was available, however--four polybutenes from Chevron--and these were studied to understand the effect of molecular weight on their solubility in liquid CO₂. The results are summarized in Fig 15. The observed decrease in solubility with increase in molecular weight is consistent with the behavior of polymers in common organic solvents. The upper limits on molecular weight for solubility in CO₂ may, however, vary with polymer structure.

The concept of solubility parameter⁶⁸ (cohesive energy density) has been shown to be useful in the determination of the solubility of a solute in a given solvent. As a rule of thumb, a clear solution results when the solubility parameters of solute and solvents are matched. The solubility parameter of liquid CO₂⁶⁹ in the density range of 0.8 to 0.9 is between 5.5 and 6 Hildebrand (cal/cc)^{1/2}. Tables X and XI also list solubility parameter values for several polymers. In cases where such values were not available for polymers in the literature, the values for respective monomers have been given. It is apparent that most of the polymers have solubility parameters greater than 7. Polytetrafluoroethylene with solubility parameter of 6.2 was the closest commercially available candidate, and it was not soluble in CO₂. This suggests that polymer solubility is a too complex phenomenon to be described only with the solubility parameter.

b. Viscosities

As stated previously, the results of the viscosity measurements can be summed up rather briefly--none of the soluble polymers we have tested come close to rendering dense CO₂ viscous enough for our purposes. It has consequently been concluded that no commercially available polymers currently exist that could be used as "direct thickeners" in CO₂ floods. This does not mean that the search for such polymers is hopeless. It may well be possible to tailor-make polymers that will both dissolve in and viscosify CO₂ to a sufficient degree. This is a possible subject for future research and development. The remainder of this section is devoted to certain aspects of the viscosity measurements of CO₂ solutions of existing polymers, which may be of interest in such work.

Two different aspects of these measurements are considered here. The first displays the dependence of the viscosity of poly(butene) solutions on molecular weight. The polymers examined are members of the same sequence whose solubilities are shown in Fig. 15. To investigate thoroughly the effectiveness of the polymers in raising the viscosity of the solutions would have required many more well-characterized polymer samples than were available, and many more individual experimental determinations than were performed. An indication of the directions of

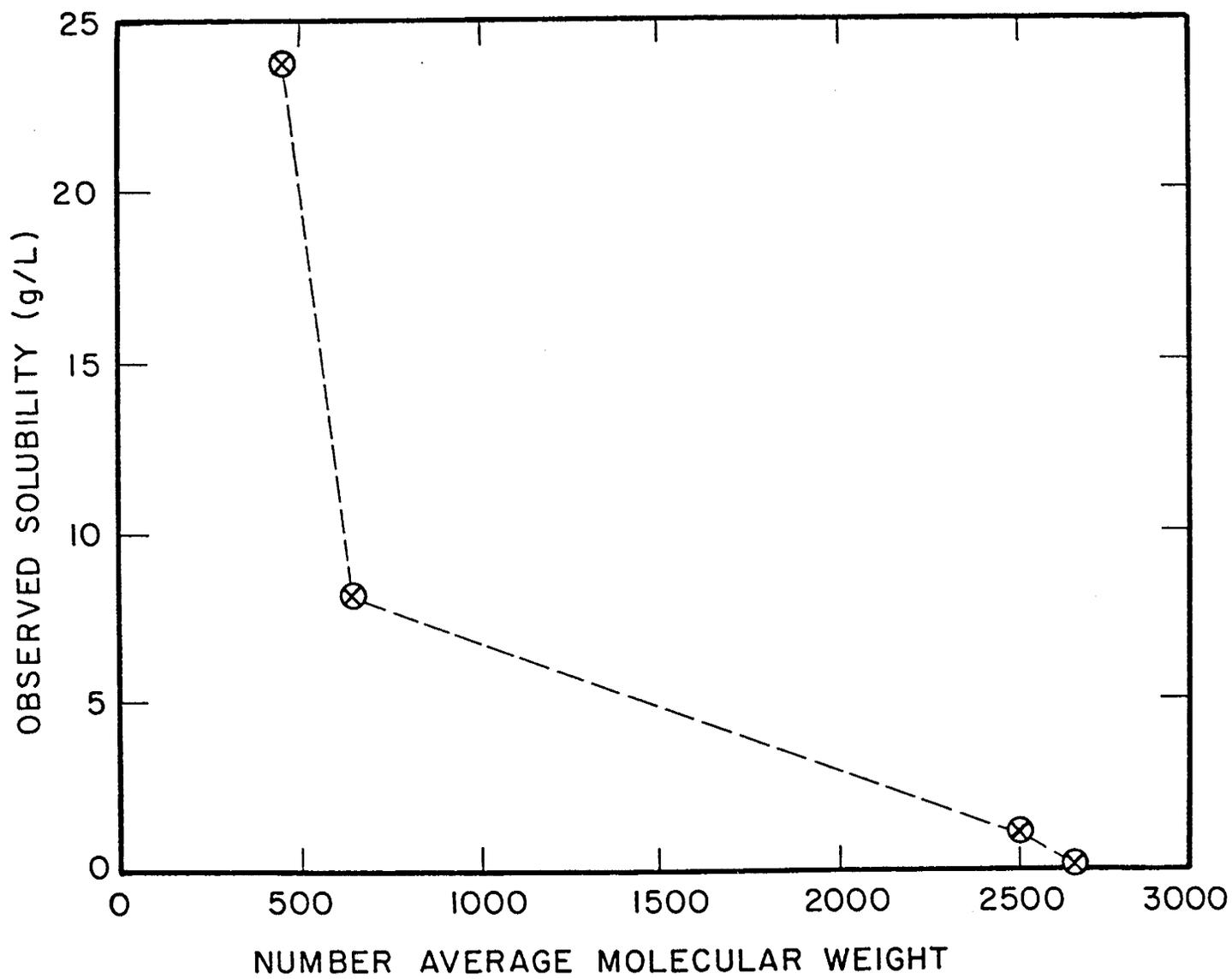


Fig. 15. Effect of molecular weight on poly(butene) solubility in dense CO_2 .

change are shown, however, in Table XII. which give the viscosities of polymer solutions and their ratios to that of pure CO₂ at the same pressures. Several interesting features may be observed from these results. The first feature, of course, is very striking. Even for these nearly saturated solutions, the values of the ratios, (the relative viscosities) are disappointingly small. Secondly, there is a barely significant trend by which the relative viscosities decrease still further as the pressure is raised. It is certainly apparent that these particular poly(butenes) could not be considered for use as direct thickeners. A further interesting feature can also be noted from the data in Table XII which shows that the higher molecular weight polymers are much more effective on a weight concentration basis in viscosifying CO₂. This is the behavior expected, of course, from studies of polymer solution viscosities in more conventional solvents.

A second interesting aspect of the viscosity measurements is given in Table XIII which shows the effect of temperature on the viscosity of a poly(methyl oxirane) solution in CO₂. For these measurements, the volume was held constant as the solution was heated through the critical temperature of CO₂, 31.04°C. For this polymer, of molecular weight 409 and at a concentration of slightly less than one weight percent, the relative viscosity increases significantly with temperature. This feature may eventually have some interest in reservoir applications--perhaps indicating that a given polymer may be more effective in deeper, hotter reservoirs.

6. Discussion of Direct Thickeners

This section has reported the project's search for polymeric "direct thickeners" for use in CO₂ floods for mobility control. Although the search has been unsuccessful in this purpose by a wide margin (whereas viscosity increase ratios of 20 or 30 are required, the best polymers found showed values of this parameter of less than 1.3), there are some interesting and encouraging results. These include:

- a) The design and construction of experimental apparatus by which the solubility of materials in liquid and in supercritical CO₂ can be measured. By slight modification, the same apparatus can be used for measuring the viscosity of the resulting solutions. This equipment can be used to test the effectiveness, as direct thickeners, of small samples, of the order of one gram or less, of prospective materials.
- b) A number of polymers have been tested with the apparatus. This experience makes possible certain generalizations about the solubility of polymers in CO₂:
 - i) No water-soluble polymers were found to be soluble in CO₂.
 - ii) The class of CO₂-soluble polymers includes only a few with molecular weights higher than 6000. They generally have low solubility parameters (less than 8) and are atactic and amorphous.

Table XII

Viscosities of Poly(butene)s in Liquid CO₂ at 25°C

| <u>Molecular</u> <u>Weight</u> | <u>Concentration</u> | <u>Pressure</u> | <u>Viscosity</u> <u>cp</u> | <u>Viscosity</u> <u>Ratio</u> |
|-----------------------------------|----------------------|-----------------|-------------------------------|----------------------------------|
| 440 | >20g/L | 1700 psig | .0824 cp | 1.070 |
| | | 2150 | .0921 | 1.064 |
| 640 | 8.5g/L | 1700 | .0841 | 1.092 |
| | | 2150 | .0932 | 1.077 |
| 2500 | 1.5g/L | 1700 | .0835 | 1.084 |
| | | 2500 | .0973 | 1.063 |

Table XIII

Viscosity of Poly(methyl oxirane)

at constant volume, constant
concentration = 9.57g/L, CO₂ density 0.853g/cc

| <u>Temperature</u> | <u>Pressure</u> | <u>Viscosity</u> | <u>Viscosity Ratio</u> |
|--------------------|-----------------|------------------|----------------------------|
| 28°C | 1986 psig | .0983 cp | 1.214 |
| 30 | 2364 | .1017 | 1.256 |
| 33 | 2570 | .1034 | 1.277 |

- iii) The class of those polymers insoluble in CO₂ includes those which have higher molecular weights, higher solubility parameters and are isotactic.
- iv) Several generalizations on the relation between polymer structure and solubility in CO₂ have been given above.
- v) The viscosity-concentration-molecular weight relationships do not seem anomalous for solutions of polymers in liquid and supercritical CO₂. It is, therefore, to be expected that larger viscosity increases for smaller concentrations of additive can be attained with high molecular weight polymers--if soluble ones can be synthesized.

VI. General Conclusions

A. Summary of Project Accomplishments

During the 3 1/2 years of this project, significant progress has been made in the field of "CO₂ Mobility Control." This has been reported in DOE and NMERDI Reports, and in various publications and technical presentations made both in Socorro and elsewhere. Efforts have been made to contribute to the general level of understanding within the industry regarding the reasons for non-uniform and inefficient oil displacement from reservoirs, and the need for mobility control in CO₂ floods. The Literature Survey,¹ which was an early product of this work, addressed these questions as well as those relating to measures which have been taken to deal with the problem.

Both in the writing of the Literature Survey, and in subsequent work, an unfavorable mobility ratio has been recognized as the basic cause of frontal instability or viscous fingering in CO₂ floods as in other predominately horizontal displacement programs. The extent of the deleterious effect on displacement efficiency depends on the ratio of the mobilities of displacing to displaced fluid. Its effect becomes increasingly serious at larger values and is already noticeably harmful when this ratio exceeds three or so. In the typical CO₂ flood, performed at a pressure greater than the MMP the viscosity of the dense CO₂ is only about .07 cp so that the mobility ratio in most reservoirs will be at least 15. It is thus very important to "thicken" the CO₂ in some way to increase the pressure drop associated with its flow through the rock, in order to increase the uniformity and efficiency of oil displacement.

At the same time it would not be economically practical to go too far in decreasing the CO₂ mobility. A strong point has therefore been made in this project that the most useful mobility control agents will be those that can be closely controlled. Even though lack of detailed reservoir data may prevent us from detailed calculation of the exact economic optimum, it is apparent that too much mobility control, by lowering the possible injection and production rates, will decrease the profitability of an oil field. At the same time, insufficient "thickening" of the CO₂

will still allow the formation of extensive viscous fingers and will not improve the reservoir sweep efficiency to the extent possible. Thus a sharp distinction is drawn between two alternative usages of the term "mobility control." According to the view presented here, the term does not mean the uncontrolled reduction of CO₂ mobility to whatever extent may be possible. On the contrary, the phrase is used here to imply the opposite--a useful mobility control agent must be capable of a more modest and adjustable degree of thickening when used with CO₂ so that an optimum recovery can be achieved or at least approached.

The laboratory work of this project has been directed towards the development of such controllable or adjustable mobility control additives, and towards their assessment in practical laboratory experiments. The accomplishments resulting from these efforts are summarized below:

1. The first kinds of additive investigated in this project for mobility control in CO₂ floods are members of the class of water-soluble surfactants that can be used to stabilize a coarse mixture or dispersion of dense CO₂ in water. The surfactant's function in this composite fluid is to extend the lifetime of aqueous films that separate "cells" or "bubbles" of the CO₂. Thus "packaged" between such films, the CO₂ is unable to move through the rock without also displacing the films. Consequently a larger pressure gradient is required to support a given flow rate than would be the case if the dense, but low-viscosity CO₂ were a continuous phase. Several specific accomplishments can be pointed out in this aspect of the project's work:

a. It has been shown, by high pressure flow tests utilizing dense CO₂ in steady-state flow through reservoir core samples, that sufficiently low mobility can be achieved in the flow of such "foam-like dispersions" even though the non-aqueous fluid has a high density and a relatively low compressibility. In other words, the non-aqueous fluid does not need to be a gas to achieve mobility control in this way.

b. An atmospheric-pressure "screening" test has been developed, by which two different properties of a prospective surfactant can be assessed in the presence of reservoir brine. These properties are:

i. The ability to form a "foam-like dispersion" between the surfactant solution and a light hydrocarbon in a low-energy shake test, with air excluded. This test is designed to indicate whether films can be formed under the similarly low energy conditions prevalent in the parts of the reservoir far from the injection wells, where flow rate of the displacing fluid is slow.

ii. The ability of the surfactant to diffuse quickly back to new interfaces in order to re-form bubble films and foam in a repeat of the above test after an original foam-like dispersion has decayed. This test is designed to indicate whether the surfactant remains dissolved in the aqueous phase from where it can be used to re-create new bubble-films as flow proceeds, even though it has been exposed for a long time to the non-polar fluid which is the major constituent of the dispersion.

(Although in the atmospheric-pressure screening test this non-polar fluid is isooctane, the non-polar phase is dense CO₂ in the reservoir situation. Independent evidence from the Direct Thickening part of the project indicates that while most organic compounds that are soluble in liquid or supercritical CO₂ are also soluble in isooctane, the opposite is not necessarily true. Thus this aspect of our screening test may be overly harsh, causing us to discard some surfactants that would actually be satisfactory from this viewpoint.)

c. The high degree of adsorption of surfactants onto the solid mineral constituents of reservoir rock is a well known difficulty encountered in "surfactant waterflooding." Although the function of the surfactant is different in CO₂ mobility control (extremely low interfacial tension and solubilization of the crude itself are not sought), and much lower surfactant concentrations are envisaged in this project, adsorption onto the rock would still be a severe problem for some surfactants. Not all aspects of the adsorption process have been studied in this project--rather the investigation was restricted to those features which directly influence the injection schedule and the amount of surfactant needed to maintain mobility control. For this purpose an "adsorption screening" test has been developed, from which can be derived two parameters describing field requirements for a particular surfactant.

2. The second kind of additive studied in this project is called a "direct thickener." Such substances are polymers that are soluble in dense CO₂, whether liquid or supercritical gas, and which increase the viscosity sufficiently when dissolved even at relatively low concentration. Unfortunately no such polymers have been found, and it is concluded that no commercial product exists which could be used today as such a "direct thickener." However, a number of polymers have been found which are soluble in CO₂, although the viscosity increases they produce are insufficient by a wide margin. Nevertheless, this aspect of the work has been marked by several notable accomplishments:

a. Apparatus has been developed by which high pressure measurements can be made of the solubility of materials in condensed gases both above and below the critical temperature. A modification of this apparatus permits it to be used for viscosity measurements of the resulting solutions.

b. About forty different polymers have been tested for their solubility in dense CO₂. Of these, more than a dozen have been found to be soluble at levels in the parts-per-thousand range or above. Through study and classification of these results, several hypotheses have been formulated which may enable the prediction of other polymer's solubility in CO₂.

c. As noted above, the polymers tested have in general done much too little towards increasing the viscosity of the dense CO₂. There are indications, however, that as with more conventional solvents, the higher molecular weight polymers are much more effective in increasing the

solution viscosity than are smaller polymer molecules. Unfortunately, in the one sequence of varying molecular weight polymers available, the solubility decreased rapidly with increasing molecular weight, as well.

3. Assessment of the utility of mobility control agents must be done in a porous flow system that simulates the reservoir in some ways. The accomplishments of the project in this area have been in the design, construction and operation of an experimental flow system of large enough dimensions so that viscous fingers are able to grow in response to an unfavorable mobility ratio. The system thus permits comparison between "mobility-controlled" and "unprotected" CO₂ displacements. In addition to the usual output fluid measurement facilities that enable gross flooding efficiency measurements to be made, two other instrumentation means were built into the apparatus to enable more detailed measurements of flooding profile. These were:

a. A pressure gradient measuring facility. Four pairs of pressure taps along the side of the rock enabled the collection of data for calculation of mobility at these four places during displacements.

b. An electrical conductivity measuring system. The data from this system enabled calculation of a "conductivity profile" along the length of the core.

Unfortunately the full usage of the instrumented core system was not achieved, due both to the late development of suitable mobility control procedures and to difficulties experienced with the first design of the side sealing and pressure tap systems. A redesigned version is planned.

B. Status of CO₂ Flooding in the Industry

CO₂ flooding has been recognized as an effective method of EOR--generally, in fact, it is the method of choice for any sufficiently homogeneous light oil reservoir that is deep enough to withstand the required pressure. In consequence, a growing level of investment has been observed in CO₂ sources and delivery systems. These include extensive production facilities and pipelines from several rich natural CO₂-saturated formations, as well as some plants for recovery of by-product CO₂, and are reaching into the billion dollar range. Even these investments do not guarantee the availability of sufficient CO₂ for all of the fields which could use this method of EOR.

The efficiency of CO₂ projects is thus becoming an increasingly important question both for operators who need to obtain the highest return possible on their investments, and for the Nation as a whole, so that the minimum of waste occurs in the non-renewable CO₂ as well as hydrocarbon reserves.

The traditional and, in most areas, the currently planned means by which high efficiency in CO₂ floods is sought depends on the use of the

WAG procedure. Although this procedure is widely practiced and does appear to postpone CO₂ breakthrough, serious questions have been raised about its effectiveness in permitting all of the oil to be contacted. The major objective of this project has been the development of more effective means for mobility control. The desirable feature of the methods developed is the adjustable thickening of the predominately CO₂ displacement fluid. Whereas the effective use of "foam-like dispersions" for this purpose has been demonstrated in the laboratory, further evidence of their widespread utility is needed. It is also suggested that a good possibility exists for the development of a directly soluble-in-CO₂, polymeric "direct thickener." The effectiveness of thickening agents in CO₂ floods has yet to be proved in the oil field, and their economic viability for the purpose has not yet been demonstrated to the industry.

Thus, the major point concerning the current status of CO₂ flooding practice is that it is in an expanding state and in growing need of ways to predict and improve its performance.

C. Remaining High Priority Research Questions

In concluding assessment of this project, and of the entire subject of mobility control for CO₂ floods, it is suggested that fruitful areas of research would be:

1. Further Development of Mobility Control Agents.

a. Foam-Like Dispersions

i. Examine additional surfactants, rocks, brines and crudes by methods similar to those developed in this project, particularly studying those which might be useful at higher reservoir temperatures.

ii. Investigate the fundamental, microscopic mechanism(s) of lowered mobility of "foams." With the knowledge to be gained, it could be expected that fewer empirical testing methods might be needed, and also that new insights might lead to new directions towards the formulation and application of these composite fluids.

b. Direct Thickeners

i. Synthesize novel polymers along the lines suggested by this work to obtain higher molecular weight CO₂-soluble polymers which could raise solution viscosity by the required factor of 20-30.

ii. Investigate other mechanisms by which the viscosity of polymer solutions is increased, especially in non-polar liquids. There are in the literature, for instance, references to enhanced viscosity resulting from interactions of polymer-polymer and polymer-solvent molecules.

c. Continue development of laboratory flow systems, like the instrumented core of this project, by which to assess the usefulness of mobility control agents in reservoir-like environments.

2. Development of Reservoir Calculation Methods for Mobility

Control in CO₂ Floods

There are a number of needs in this area, all of which would have as their primary goal the prediction of reservoir and economic performance, and the evaluation of the improvement in oil recovery and in profitability of mobility controlled over unprotected CO₂ floods. All of them would involve the development of algorithms and routines for computer simulation of particular reservoirs.

a. Extension of the MS thesis work of P.K. Pande at New Mexico Tech (Dec. 1982) on "Economic Predictions of Mobility Control Results in CO₂ Flooding."⁵⁷ The extension would incorporate more recent results on expected production history.

b. Extension of the post-doctoral research of Dr. Jim Yeh at New Mexico Tech (April 1983) involving the calculation of the growth of instability fingers in the symmetry section of a reservoir developed on a five-spot pattern.

c. Further development of calculation methods to estimate the gain in oil production resulting from the use of mobility control agents.

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