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SOME ASPECTS OF MISCIBLE PHASE DISPLACEMENT AS APPLIED TO THE RECOVERY OF OIL RESERVOIR CRUDE

by

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A

THESIS

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ABSTRACT

Recent application of the miscible slug displacement process as a method to increase recovery from petroleum reservoirs has resulted in a great deal of laboratory investigation, none of which provided conclusive evidence as to the amount of mixing taking place between the displacing and displaced fluids. This investigation attempts to provide a possible insight into the rate and degree of mixing of two fluids with respect to flow path transversed and the rate of advance of the fluids. The laboratory investigation consisted of displacing a fluid from a packed core with another fluid under completely miscible conditions.

Experimental evidence indicates that mixing between two miscible fluids does not necessarily stabilize with respect to volume composition, although the length of the mixing zones might approach a constant value. Rate of flow has little effect on the volume of the mixing zone; however, it was noted that the volumetric concentration of the displacing fluid in the mixing zone decreased with slower rates of advance.

It would be possible as well as practical to conduct investigations using fluid samples from a given reservoir prior to the instigation of a flood of this type. Results determined from such investigations could be used to predict behavior in the reservoir.

INTRODUCTION

The problem of economically recovering, by natural or externally supplied energy, virtually all of the crude oil originally present in a reservoir, has been a matter of intense concern for many years. The most common method now in use to increase recovery is water flooding. In a flood of this type, water is injected into injection wells to push the reservoir oil and gas toward the production wells. Although this method will often double the amount of oil recovered by natural reservoir energies alone, about thirty percent of the oil originally in the portion of the reservoir swept by the water is left in place. The principle factors responsible for this inefficiency are surface tension and wettability.

One relatively new method being considered to increase efficiency of recovery is a miscible phase displacement process. In a process of this type, a quantity of solvent capable of mixing with the reservoir oil and gas is injected into the reservoir and forced through by injected gas which is soluble with the solvent. The advantage of this method, over immiscible floods, such as water floods, is the elimination of interfacial tension caused by surface tension between two fluids.

A fluid is said to wet a surface when the molecules of the fluid are more strongly adhesive to the surface than to each other. When two immiscible fluids, such as water and oil at ordinary reservoir temperature and pressure, are in contact in capillary openings in a reservoir, oil might preferentially adhere to the side of the capillary, in which case the reservoir rock would be classified as oil wet.

Molecules in the body of a fluid are attracted equally on all sides by surrounding molecules; however, molecules at the surface of the fluid are not completely surrounded by other molecules of the fluid, but are in contact with a different substance. If the liquid does not wet the adjacent substance, there is a resultant force which acts as a thin confining membrane across the surface of the fluid. It is this force which causes water to form spherical drops when in contact with air. In the event the fluid wets the surrounding substance, there will be a resultant force directed across the contact surface which will tend to hold the liquid to the substance. The forces described are defined as interfacial tension and are measured in units of force per unit area.

When two immiscible fluids are in contact with each other in a capillary, there is a pressure drop across the curved interface of the two fluids. This pressure drop, which is due to interfacial tension, is defined as capillary pressure. This pressure is great enough to force a fluid to a certain height in a capillary provided the surface of the capillary is wet by the fluid. In naturally occurring oil-gas-water-reservoir rock systems, the magnitude of capillary pressure is great enough to prevent much of the reservoir oil from being produced by immiscible floods. Flooding with a miscible fluid will eliminate the interfacial tension causing the capillary pressure and allow the oil to be produced from the reservoir pore space swept by the flood.

Although various types of miscible processes have been considered to improve recovery, the type considered here will be the liquefied petroleum gas (LPG) slug-dry gas process. In a flood of this type, LPG, consisting of propane or butane, or a combination of both, is injected into the reservoir. Since it would be uneconomical to completely fill a reservoir with expensive LPG, a dry gas consisting predominantly of methane is injected behind the LPG. The object is to inject a fluid (LPG) miscible with the reservoir oil and gas, then driving this fluid to the

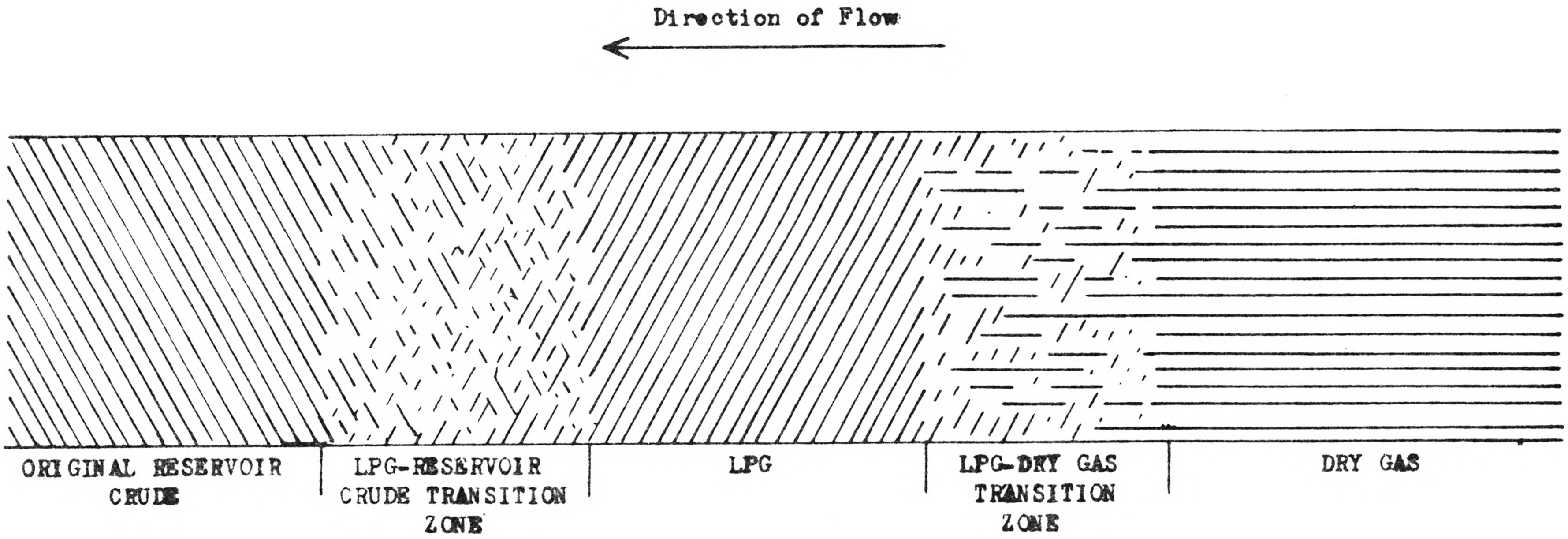

Figure 1. - Zones of fluids in the reservoir during miscible displacement process.

production well with another fluid which is also miscible with the LPG.

In a flood of the type under discussion, the fluids in the reservoir will be divided into zones as shown schematically in figure 1. The zone outermost from the injection well along the direction of flow represents an uninvaded portion of the reservoir and will consist of the fluids present in the reservoir prior to the flood, that is, oil, free gas and water. The injected LPG will blend into the reservoir oil and gas to form a transition zone of LPG and reservoir fluids. There will be little or no free gas present in this area as it will go into solution with the LPG and reservoir oil. A zone of undiluted LPG will follow the transition zone. This zone will become smaller as the flood transverses the reservoir until either the zone is completely diluted or mixing between the fluids ceases. A second transition zone resulting from mixing between the LPG and the injected dry gas will follow the undiluted LPG which will, in turn, be followed by dry gas. The water originally present in the reservoir rock will either be left in place or a portion of it will be carried along by the advancing hydrocarbons.

FACTORS INFLUENCING MISCIBLE PHASE PROCESS

A number of factors will influence miscible phase processes. The most important are:

1. Miscibility between reservoir fluids and injected fluids;
2. Fingering of injected fluids into reservoir fluids;
3. Amount of mixing at the interface of the displacing and displaced fluids in the reservoir.

These three factors will determine the economical feasibility of any miscible flood. Favorable conditions with respect to any two of the factors will not necessarily lead to a successful flood if the remaining factor is adverse.

Miscibility

The first engineering factor to be considered before undertaking a miscible phase displacement project is the degree of miscibility between the displacing and displaced fluids. The LPG should be miscible with the reservoir crude, while the gas should be miscible with the LPG. In a system in which the LPG is not miscible with the crude, interfacial tension will cause crude to be left in the reservoir resulting in decreased efficiency. Similarly, if the gas is not miscible with the LPG slug, expensive LPG will be left in the reservoir in place of less expensive crude.

Temperature, pressure, and composition of the displaced reservoir crude, as well as the composition of the LPG and dry gas will determine miscibility. Reservoir pressure can be controlled to a limited degree, but the temperature of the reservoir and the composition of reservoir hydrocarbons can not be effectively controlled.

Mixtures of a ternary system which will insure miscibility can be determined by plotting the composition of each of the three fluids along the axis of a triangular graph. As reservoir fluids consist of a large number of hydrocarbon components, an arbitrary grouping of reservoir components may be used to represent a pseudo-ternary system of the type shown in figure 2. In the illustrative figure, A represents the mole percent of methane; B the mole percent of ethane, propane, butane, pentanes, and hexanes; and C represents the mole percent of the remaining hydrocarbons.

Pseudo-ternary diagrams may be constructed for a given reservoir temperature, pressure, and crude composition, provided that appropriate equilibrium constants are available. The method of calculation would consist of finding the dew point and bubble point curves for all possible compositions of the groups of hydrocarbon components. The envelope shown in figure 2 represents a dew point and a bubble point curve which meet at the critical point of the system (denoted by p in the illustration).

Mixtures of hydrocarbons having compositions lying outside the envelope will form homogenous solutions, while mixtures with compositions such that they lie within the envelope will separate into two phases. All combinations of fluids A and B and fluids B and C are completely miscible with each other. However, fluids A and C are only partially miscible.

Referring to figure 2, a mixture of composition n will divide into two phases of composition a and b. The line connecting points a and b is known as a tie line; the lengths of the lines a-n and b-n are inversely proportional to the volume of the system in phase a and b respectively. Although the tie line has been arbitrarily constructed parallel to the

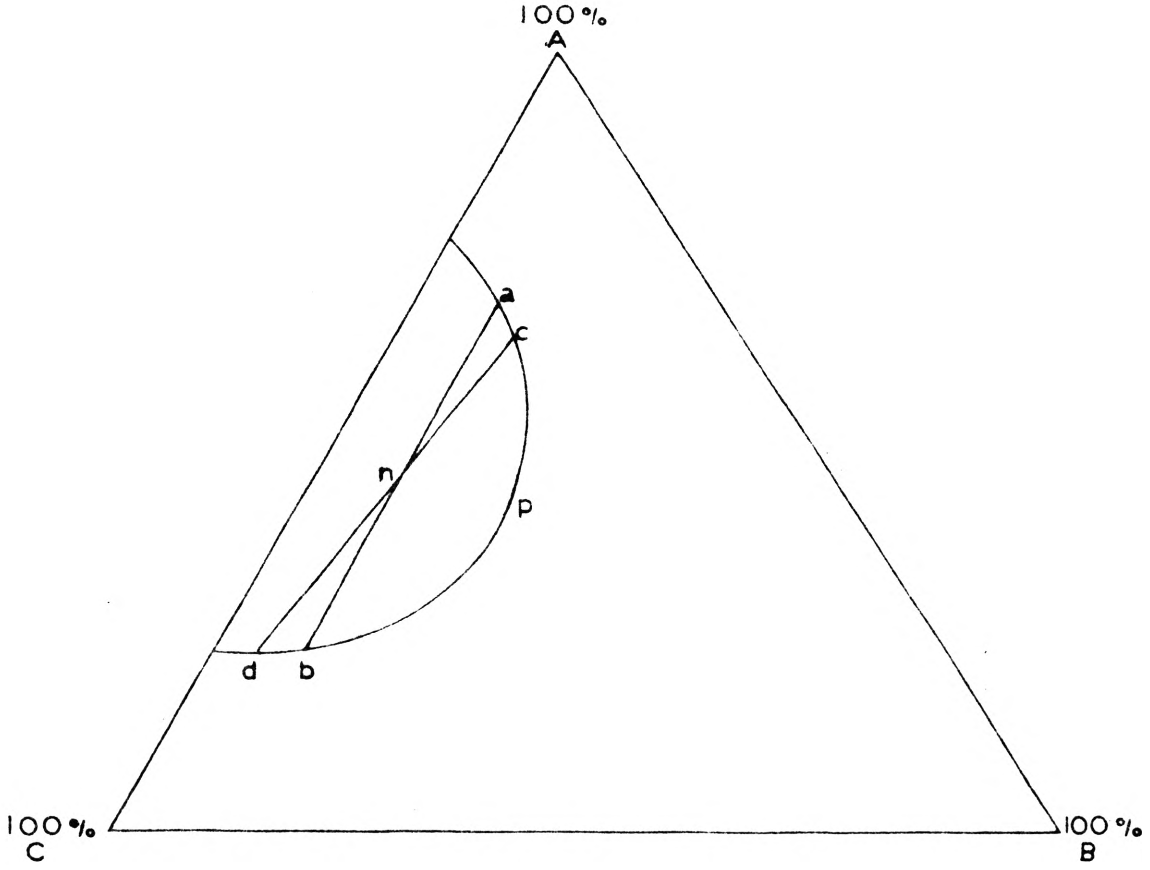

Figure 2 - Pseudo-ternary system representing volumetric composition for complete miscibility.

A-X axis, it could slope upward from the axis either to the right or left depending on the relative solubility of fluid B in A or C. The tie line c-d represents a mixture in which fluid B is more soluble in fluid A than in fluid C.

Fingering of Injected Fluids

For an ideal flooding process through a homogenous medium, the boundary between the displacing and displaced fluids would be represented by an advancing plane during a linear process, or a cylindrical boundary for radial flow. However, in actual practice, fingers of the displacing fluid are thrust into the fluid being displaced. These fingers are initiated by inhomogenous conditions in the reservoir. Once started, they will grow due to mobility difference between the two fluids in the reservoir rock.

The flow of each of the fluids will follow Darcy's law which states that the velocity of a fluid is governed by

$$\bar{v} = - \frac{k \nabla p}{u}$$

in consistent units where $\bar{v}$ is a vector representing velocity, k/u the ratio of effective permeability to viscosity (mobility), and ∇p is the pressure gradient causing the flow. A displacing fluid of high mobility would have a tendency to move at a greater rate then a less mobile displaced fluid under identical driving forces. Therefore, when a finger is formed, the displacing fluid in the finger will tend to flow at a greater rate then the surrounding fluid. During a miscible slug recovery process, the entire volume of the slug could enter fingers or channels of this type, and completely by-pass part of the reservoir oil.

One of the earlier papers (1)[1] on the subject of miscible displacement concludes that oil viscosity is the most important factor effecting efficient recovery. Later work (2,3,4,5) on the subject revealed that, as the ratio of the mobility of the displacing fluid to that of the displaced fluid (mobility ratio) increased, fingering of reservoir fluids increased and efficiency decreased.

The effects of mobility ratios on fingering have been studied with scaled models representing a quarter of a five-spot, consisting of a single injection well and a producing well. Using models of this type, investigators have displaced liquids with other liquids under conditions of miscibility in order to investigate the following:

1. The effect of mobility ratio on the dilution of the injected liquid and fingering;
2. The minimum size LPG slug that should be used for a miscible slug process in a rock system of given dimensions;
3. The effects of injection rate on fingering;
4. The sweep efficiency of the slug.

In general, it was found that permeability and rate of flow have little or no influence on breakthrough sweep efficiency. However, mobility ratios are the controlling factors in a miscible flood. Figure 3 shows the results obtained by Habermann (2) using a model of the type mentioned above. These results, which are in close agreement with other published data, indicate that mobility ratios less than one are desirable for an efficient flood.

During an immiscible flood, the advancing interface between the two

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[1] Numbers in parentheses refer to items in the bibliography at the end of the thesis.

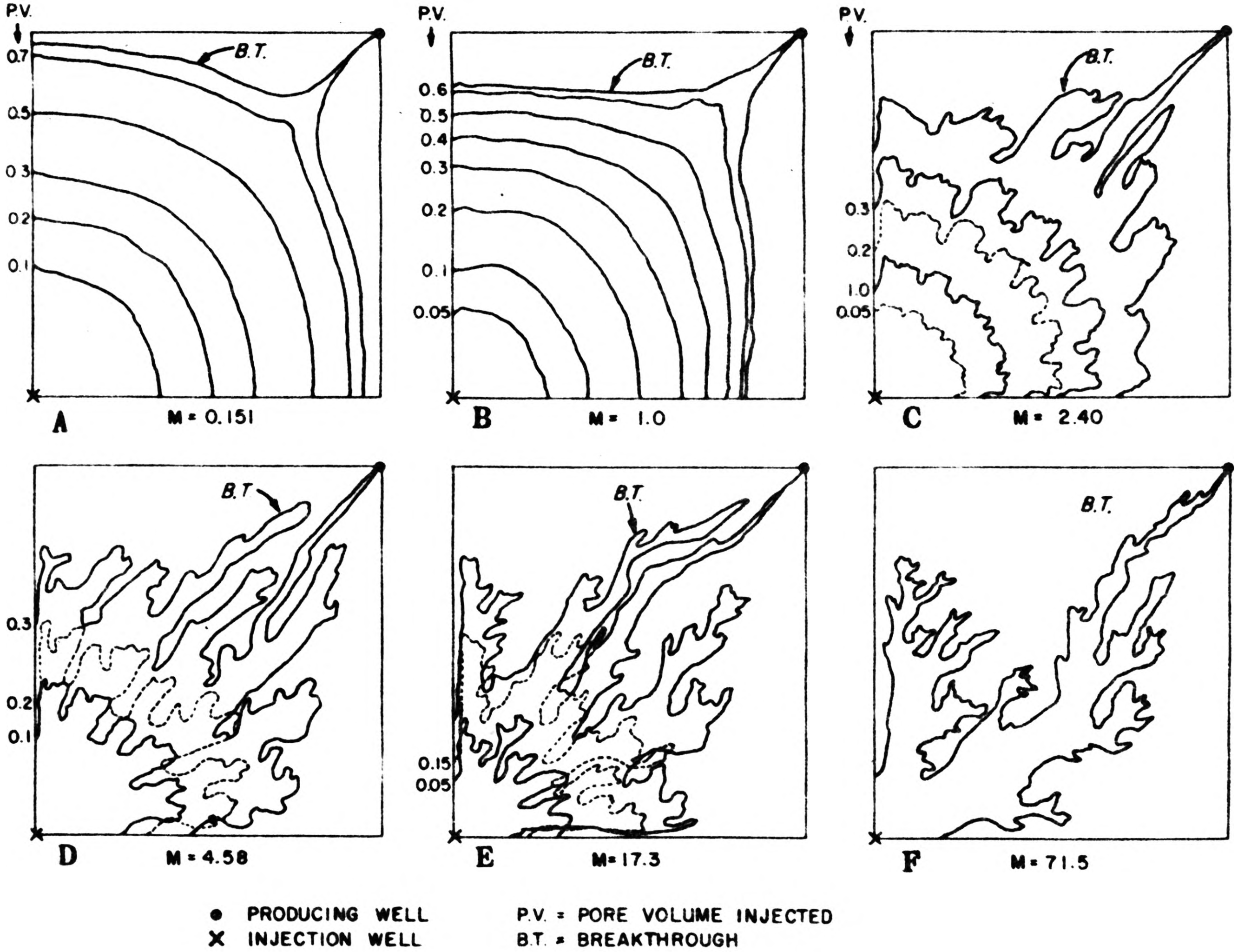

Figure 3 - Displacement fronts for different mobility ratios and injected pore volumes until breakthrough, quarter of a five-spot. - Reproduced from reference (2)

fluids forms fingers with fairly sharp points. This was not the case with the fingers observed by Habermann, who noted that the fingers formed with miscible liquids having high mobility ratios have a rather blunt front with small fingers developing laterally from their sides.

The unusual shape of the fingers noted by Habermann might be explained in terms of mobility and concentration gradient. At the foremost edge of the finger, there is mixing between the two fluids resulting in a zone of graded viscosity. The viscosity at the back of the mixing zone will be nearly the same as that of the displacing fluid. However, the viscosity will increase along the zone until it is the same as that of the fluid being displaced. As the length of the mixing zone increases, the mobility ratio of any two adjacent sections across the zone will approach one. This will result in a slower rate of growth of fingers in this area due to a more favorable mobility ratio. Therefore, the finger will not be as readily pushed ahead but will expand to either side where the viscosity grading is not as pronounced.

A concentration gradient produces a force which will drive fluids from a region of high concentration to one of lower concentration. This factor could influence the unusual shape of the fingers. The region of greater mixing at the tips of the fingers will result in a relatively low concentration gradient and consequently a lower mixing force while a higher gradient will be present at the sides of the fingers.

MIXING AT THE INTERFACE OF TWO MISCIBLE FLUIDS

While the degree of miscibility and fingering are important factors in a solvent flood and should warrant consideration, they are characteristic of a given system and can not be considered on a broad basis. The third important factor to be considered, that is, the rate and degree of mixing between the injected and displaced fluids, can be studied in more detail. Although highly theoretical relationships have been established for the rate and degree of mixing, they have never been completely verified by experimental work.

Experimental work on the subject has led to varied opinions. Some investigators (1,6,7,8) have reported that the rate of injection has little or no effect on the rate of mixing for fluid systems with mobility ratios near one. Others (9) have reported that velocity is an important factor to be considered. Another conflict of opinions has arisen over stabilization of the mixing zone. It has been reported (7) that mixing is accelerated in the early life of the flood, but soon reaches a state of equilibrium in which no additional mixing takes place. Other investigations (6,9) did not substantiate this fact.

It can reasonably be assumed that the mixing between the two fluids will be, to some extent, dependent upon diffusion. Fick's first law (11) states that the amount of substance dm passing through a given area A, in a short interval of time dt, is proportional to the area and to the concentration gradient $\partial C/\partial x$ or

$$dm = -\frac{DA\partial Cdt.}{\partial x} \qquad \text{equation 1}$$

The constant of proportionality, D, is the diffusion coefficient and is expressed in units of length squared per unit time. The negative sign indicates that diffusion takes place from a region of higher concentration to a region of lower concentration.

Fick's second law is derived from his first law and the relation between the amount of fluid in a given area or $m = CAx$ from which the change of the amount of fluid with respect to distance can be expressed as

$$\frac{dm}{dx} = CA \qquad \text{equation 2}$$

where C is the concentration of the substances under consideration. If D is assumed independent of concentration and equation 1 is differentiated with respect to x and equation 2 is differentiated with respect to t, the mathematical expression for Fick's second law

$$\frac{\partial^2 C}{\partial x^2} = \frac{1}{D}\frac{\partial C}{\partial t} \qquad \text{equation 3}$$

is obtained.

In addition to the diffusional mixing, a slug of LPG will be diluted by mechanical mixing. Koch and Slobod (1) flowed miscible fluids through a sand packed pipe and found that dilution of the slug varies with distance traveled according to the relationship,

$$S = Nx^{\frac{1}{2}}C \qquad \text{equation 4}$$

where S is the slug size (expressed as a percent of the pore volume) necessary to provide a given slug concentration C at the center of the slug after traveling a distance x. N is an experimentally determined constant depending on the grain characteristics of the porous medium traversed.

Diffusional mixing will, no doubt, play an important role in mixing between the reservoir crude and the injected fluid. However, the amount of mixing between the fluids in a flowing system is too great to be attributed entirely to diffusion. This additional mixing is the major factor to be studied in this investigation.

Aronofsky and Heller (5) presented a mathematical analysis of mixing at an interface. They did not specify an exact mechanism for the mixing process, but applied a "modified" version of Fick's second law which included a mass transport term. The equation applied was

$$E \frac{\partial^2 C}{\partial x^2} - \frac{v \partial C}{\partial x} = \frac{\emptyset \partial C}{\partial t} \qquad \text{equation 5}$$

where E is a dispersion coefficient dependent on mechanical and diffusional factors, v represents the macroscopic velocity of flow and $\emptyset$ the porosity of the medium. It is no simple matter to write boundary conditions for this equation, and a rigorous treatment is very difficult. Paceman and Rachford (10) have presented a solution to the equation by solving a number of difference equations.

EXPERIMENTAL PROCEDURE AND APPARATUS

The rate of growth of the mixing zone at the interface of two miscible fluids was studied with respect to rate of flow and path length for two different fluid systems. During the investigation, fluids were pumped through a horizontal sand packed pipe and samples obtained at the outflow end of the core. The specific gravity of the samples, and consequently their composition, was determined to obtain the volume of the mixing zone as it flowed through the outlet of the core. The investigation was carried out by displacing isobutane with propane at 80° Fahrenheit and 2000 psia; and by displacing water with a fifty percent glycerol solution at about 75° Fahrenheit and a pressure of at least 20 psig. Fairly rapid flow rates were used to mask diffusional mixing, thereby allowing a clearer study of velocity effects.

Selection of Flow System

A number of flow systems of this general type has been described in the literature. The systems used by different investigators varied in length from only a few inches up to 100 feet. Most of the investigators have reported certain "end effects" due to capillarity at the discontinuity which gave faulty readings for short systems.

The method of analyzing samples also differed from system to system. Investigators experimenting with electrolytic solutions determined the composition of the mixing zone by resistivity methods. In general these determinations were made as the fluids flowed past a given reference point, or were conducted on samples obtained at the outflow end of the core. In systems containing non-electrolytes, the samples were either obtained at the end of the core or withdrawn at outlets along the core and analyzed to obtain their composition by various appropriate methods.

Both of the above mentioned methods of obtaining samples have disadvantages. Analysis conducted at a given reference point would give a faulty mixing zone length as there would be additional mixing or growth of the mixing zone, between the time of measurement at the front and back of the zone. Removal of displaced fluid from the system would have a certain influence on the mixing rate near the outlet of the core. As the fluids were removed after breakthrough, there would be no additional, undiluted, displaced fluid to mix with the displacing fluid. However, the displacing fluid could be expected to move on into the mixing zone, thereby giving rise to a faulty concentration gradient.

In this investigation, samples were obtained at the outlet of the core and their composition determined by specific gravity measurements. A calibrated chainomatic specific gravity balance was used to determine the composition of the liquid samples. The specific gravity of the propane-isobutane mixtures was determined by the effusion method. The accuracy of the effusion method was checked periodically with the Edwards balance.

The volume per pound mole occupied by isobutane and propane at 2000 psia and 80 degrees Fahrenheit was determined by standard pressure volume procedure with a pressure volume temperature cell.[2/] Then by applying the relationship

$$X_3Sg_3 + X_4Sg_4 = Sgm_1$$

where Sg represents specific gravity, the mole fraction of the propane, X_3, was calculated. The volume fraction of propane at 2000 psia and

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2/ A more detailed explaination of the procedure appears in the Appendix.

80° F was determined from

$$V_3 = \frac{X_3 V_{3L}}{X_3 V_{3L} + X_4 V_{4L}}$$

where V_3 represents the volume fraction of propane, V_{3L} and V_{4L} represent the volume occupied per pound mole of propane and isobutane respectively at 2000 psia and 80° F.

Specific gravity and flow rate measurements of the gas presented a problem due to the cooling of the gas while expanding from 2000 psia to atmospheric pressure. As the rate of efflux of the gas was measured with a wet test meter, it was necessary to allow the gas to reach room temperature before taking meter readings. This problem was eliminated by allowing the gas to flow from the system through a twelve foot rubber tube into a glass container, then through a second rubber tube into the meter inlet. Temperature readings from a thermometer in the meter indicated the success of this method. Samples of gas to be analyzed were taken in air free rubber bags at the outlet of the core. These samples, which were about 100 cc in size, were allowed to remain at room temperature for a period of time of not less than twenty minutes before being analyzed. It was assumed that this allowed the small volume samples ample time to reach room temperature.

Throughout this experiment, it was impossible to determine the precise end points of the mixing zone. Therefore, an apparent breakthrough time, or the time where the last measurement indicated that no displacing fluid was being evolved from the core outlet was determined. This apparent breakthrough time was taken as a zero point and samples were taken and analyzed at regular timed intervals after the apparent breakthrough time. The volume percent of displacing fluid removed at the outlet of the core was plotted against the total volume of fluid removed from the flow system after apparent breakthrough. The area under the resulting curve was measured between five and ninety-five percent volumetric composition of the displacing fluid in the mixing zone. Using this area as the volume of the displacing fluid in the mixing zone, and reading the total volume of fluid in the same zone from the graph, it was possible to relate the data from different runs with respect to average composition of the mixing zone and the time involved in mixing. The total time involved for the mixing, including the time after breakthrough, was calculated using the total volume of fluid displaced and the flow rate.

The flow system (figure 4) consisted of one and one-half inch seamless high pressure pipe packed with sand. This gave an unconsolidated sandstone core with a porosity of 48.7 percent and an effective permeability of approximately 19.3 darcys[3] to liquids. A small consolidated sandstone core of high permeability was placed at the inlet and outlet of the system. The core at the outlet was to prevent the flowing fluids from carrying the unconsolidated sand out of the pipe, thereby causing channels in the core. The consolidated core at the inlet of the system was to dampen any surges caused by the pulsating motion of the pump.

Two needle valves were placed in series at the outlet of the core. The valve nearest the core was used to regulate the flow of fluids from the system. The second valve allowed the system to be closed off with no loss of fluids. Once the pump was adjusted to deliver at a certain rate, the entire operation could be shut down for a period of time, then

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[3] Porosity and permeability determinations are shown in the Appendices.

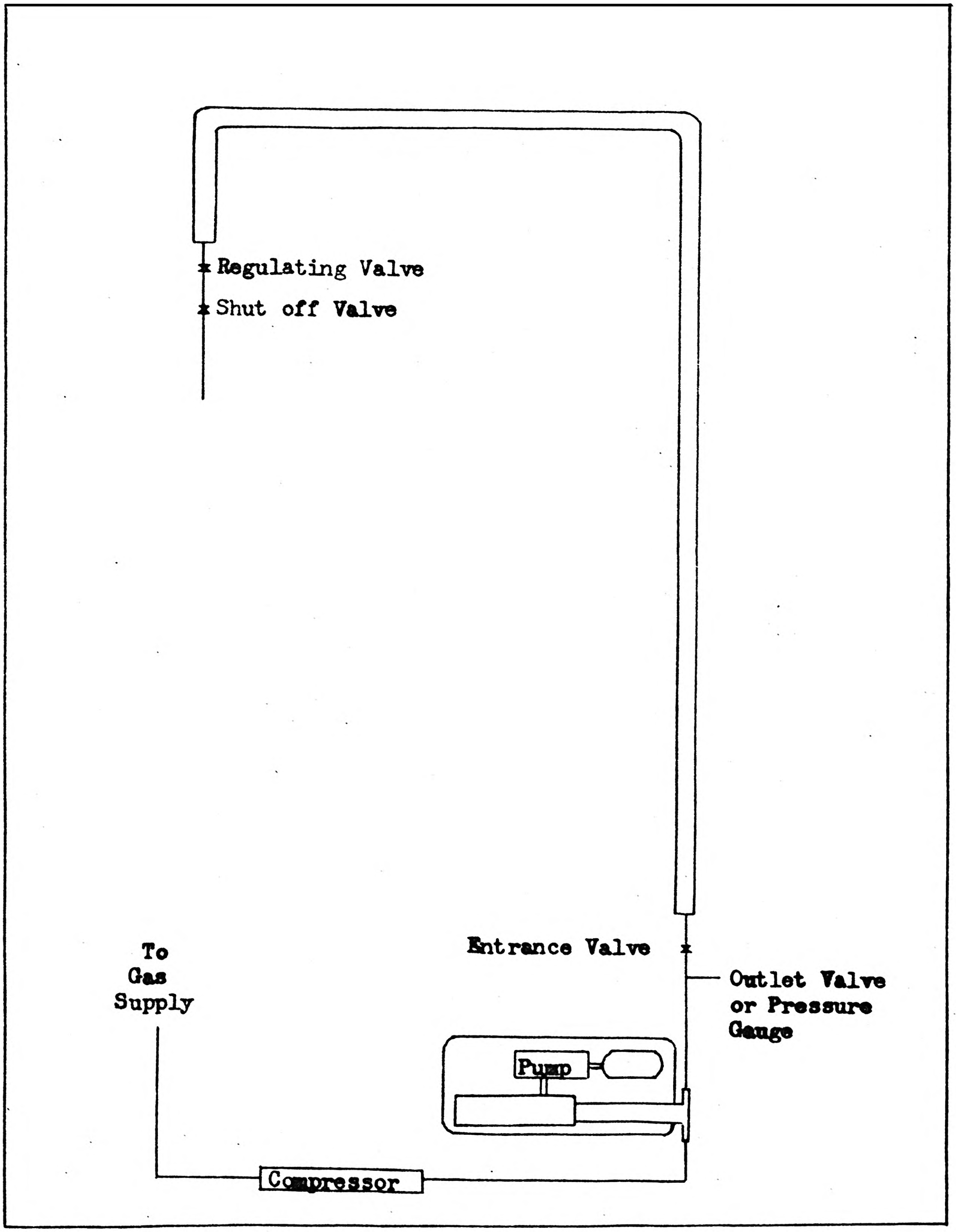

Figure 4—Schematic Diagram of Flow System

started again at the same rate. Any pressure regulation necessary to keep a constant flow rate after the beginning of a run was done with the regulating valve, not the pump.

Method Used to Fill the Flow System With Fluids

The sand packed system was evacuated with an electric driven vaccum pump to remove entrained air, prior to filling with isobutane. A quantity of isobutane in the gaseous phase was then flowed through the system to remove any remaining air, and the flow system was pressured up to the desired pressure of 2000 psia.

A valve on the outlet shown in figure 4 was then opened to allow the isobutane present in the one-eighth inch pipe connecting the core and the motor to escape. This also resulted in the removal of isobutane from other connections leading from the compressor to the outlet as the pressure on the fluid still in the compressor was of sufficient magnitude to force gas on through the pump. This portion of the system was then throughly flushed with propane.

The outlet valve was replaced with a pressure gauge and the system up to the core was pressured up to approximately 2050 psia with propane. This additional pressure was to insure that no isobutane would move back into the propane and to avoid a slight pressure drop at the end of the core when the entrance valve was opened.

As the pressure between the shut off valve and the core was the same as that in the core, it was possible to open the valve slightly, immediately prior to starting the pump with no appreciable pressure drop on the flow system as the fluid in the system had to first diffuse through the regulating valve, then through the shut-off valve. After the pump was in operation, the shut-off valve was slowly opened to allow removal of the gas between it and the regulating valve.

The same core used for the hydrocarbon tests, was used for other tests with a fifty percent glycerol solution displacing water. Water was induced into the core in a manner similiar to that employed with the LPGs except the vacuum pump was left running during the entire filling time. The outlet of the core was slightly elevated during the filling process to derive any benefits available from gravity segregation between the induced liquid and any gas which might be in the core. An instaneous pressure build up in the system assured the absence of gas.

DISCUSSION OF RESULTS

Mixing trends presented in figures 5 and 6 describe the effects of path length and injection rate in controlling the mixing at the interface of the glycerol solution and water. Results shown in figure 5 indicate that the amount of displacing fluid in the mixing zone will stabilize with path length. However, the length or volume, of the mixing zone did not reach a definite state of stabilization over the path length studied. Table 1 shows that 363 and 360 cc of the displacing glycerol solution were present in the zone at 4.15 and 8.13 meters respectively, while the volume of the respective mixing zones were 743 and 693 cc. Similarly, the volume of displacing propane in the propane-isobutane flood seemed to approach a constant value at the 2.91 and 4.15 meter path lengths.

The results shown in figure 6 indicate that velocity had some influence on the amount of mixing during the glycerol-water displacement. As the injection rate was decreased, the volume of the mixing zone increased fairly rapidly, with only a slight increase in the volume of the displacing glycerol solution. This resulted in a decrease in volumetric composition of the glycerol solution in the mixing zone as shown in Table 2. In the case of the more mobile propane-isobutane flood, there was an increase in the volume of the mixing zone with velocity; however, the volume percent of displacing fluid again decreased with increasing flow rates.

It seems evident from these results, that the length or volume of the mixing zone is no exact measure of the amount of displacing fluid in the mixing zone, but simply defines a system. Although the volume of the

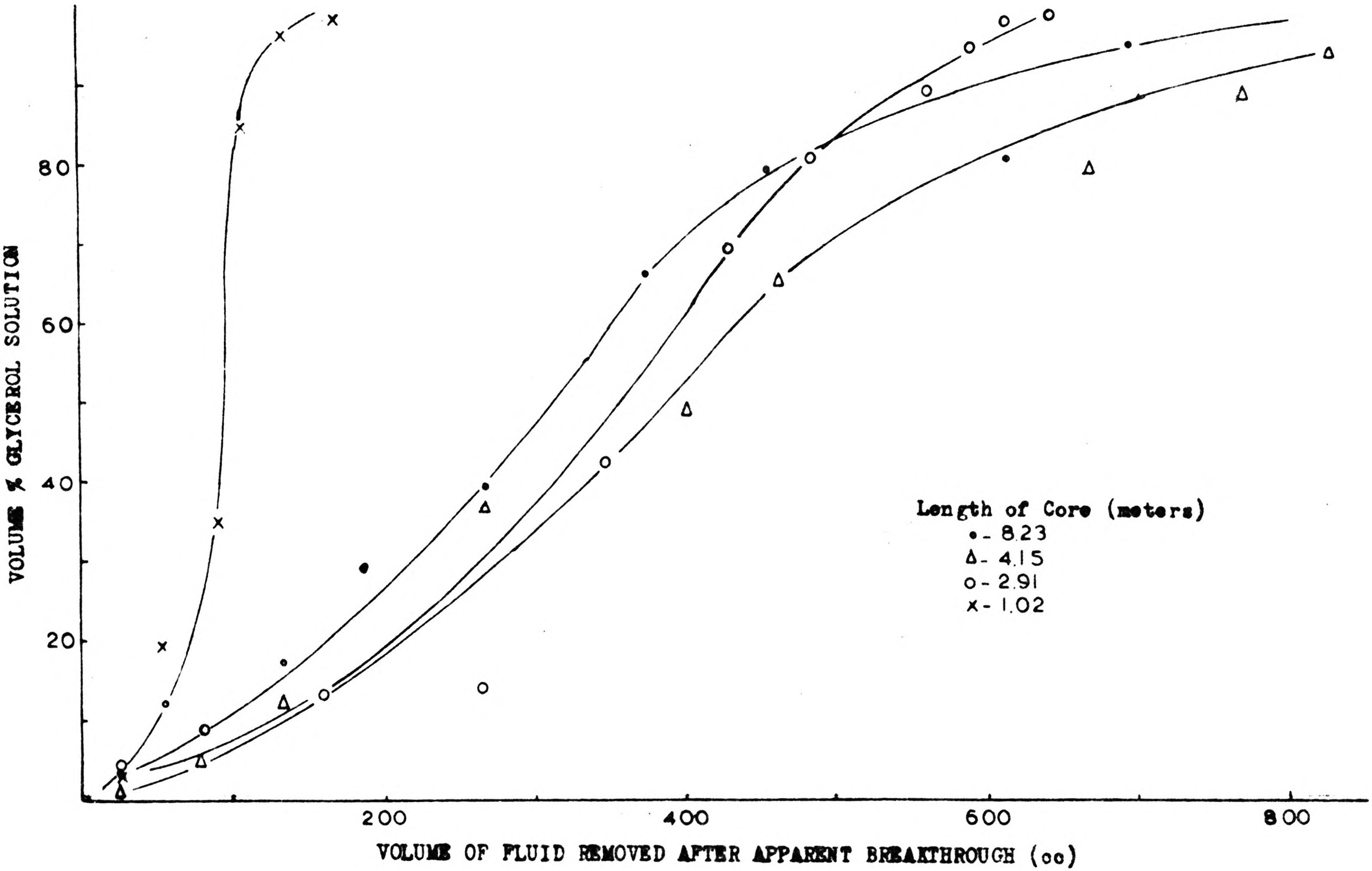

Figure 5.- Concentration profiles for different length flow paths (glycerol solution displacing water).

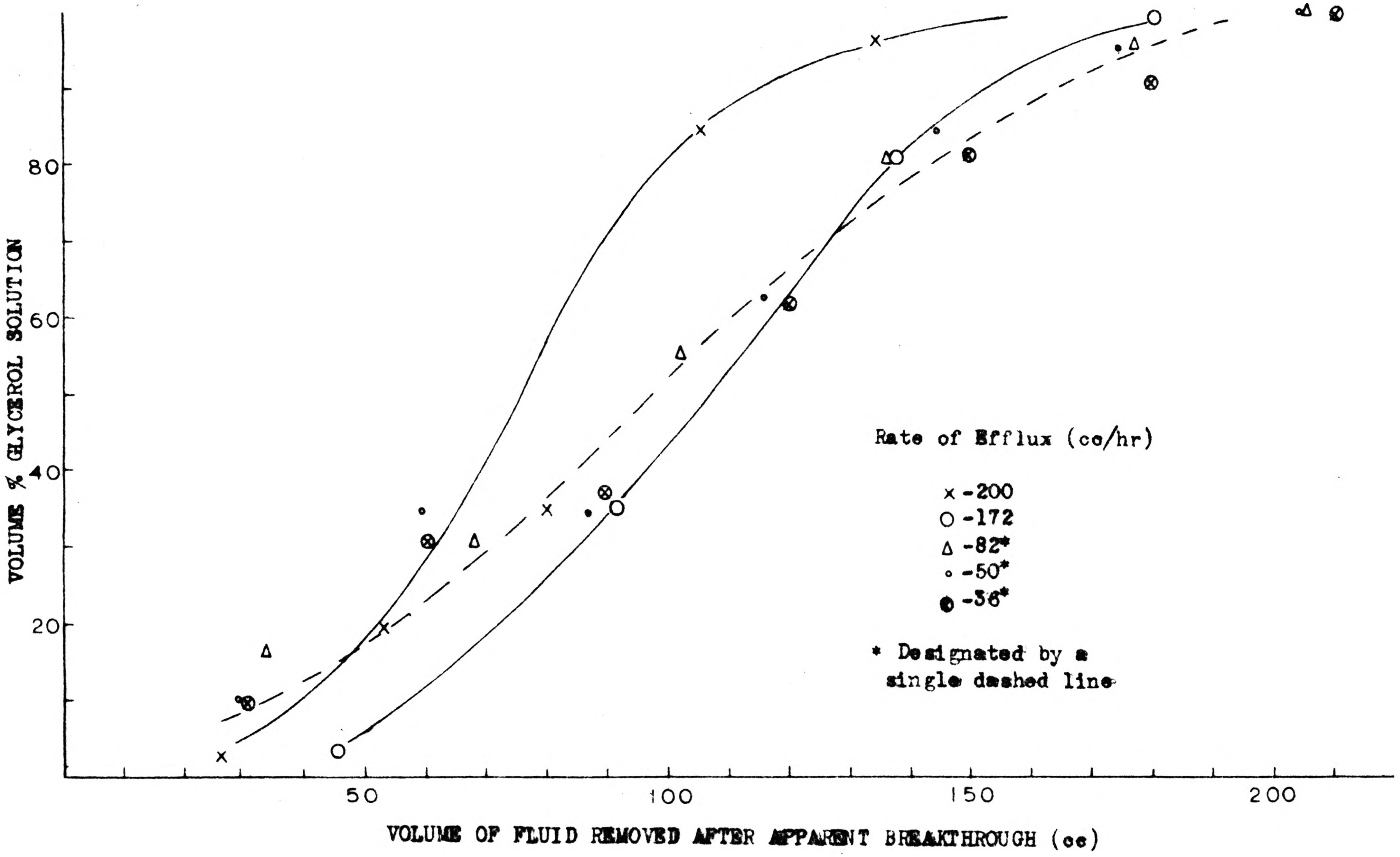

Figure 6-Volume percent of displacing glycerol solution in the mixing zone after apparent breakthrough as a function of the rate of efflux.

TABLE 1. SUMMARY OF DISPLACEMENT DATA

Run No.	Displaced Fluid	Displacing Fluid	Injection Rate cc/hr.	Length of Core (m)	Total Time of Flow Until 95% Displacing Fluid Efflux (min)	Volume of Mixing Zone 5-95% comp. (cc)	Volume of Displacing Fluid in Mixing zone 5-95% comp. (cc)
1	Isobutane	Propane	115	1.02	230	214	119
2	Isobutane	Propane	115	2.91	573	479	253
3	Isobutane	Propane	115	4.15	689	525	264
4	Isobutane	Propane	34	1.02	589	71.6	34.8
5	Isobutane	Propane	46	1.02	682	84.0	45.0
6	Glycerol Solution	Water	200	1.02	105	100	53.9
7	Glycerol Solution	Water	200	2.91	343	598	250
8	Glycerol Solution	Water	200	4.51	480	743	263
9	Glycerol Solution	Water	200	8.23	816	693	360
10	Glycerol Solution	Water	36	1.02	600	151.9	66.5
11	Glycerol Solution	Water	50	1.02	449	158.9	69.9
12	Glycerol Solution	Water	82	1.02	278	147.0	71.2
13	Glycerol Solution	Water	172	1.02	130	116.2	60.0

TABLE 2. EFFECTS OF INJECTION RATES ON VOLUMETRIC COMPOSITION OF MIXING ZONE

Propane Displacing Isobutane

Rate of Efflux (cc/hr.)	Volume % Displacing Fluid[4]
115	55.6
46	53.6
34	48.6

Glycerol Solution Displacing Water

Rate of Efflux (cc/hr.)	Volume % Displacing Fluid[4]
200	53.9
172	52.2
82	48.4
50	44.0
36	43.8

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[4] The volume percent of the displacing fluid in the mixing zone was determined from samples removed at the outlet of the core.

mixing zone might tend to stabilize with path length as reported in the literature, this does not represent true equilibrium with respect to the concentration of the fluids in the mixing zone.

There was more mixing between the more mobile propane and isobutane than between the glycerol solution and water in the early life of the floods. However, the rate of mixing between the less mobile fluids leveled off between the 2.91 and 4.15 meter path lengths while the glycerol solution and water did not appear to level off until a longer path length had been transversed. This indicates that stabilization, if reached, is a function of the physical properties of the fluids under observation; and that mobility ratios can not be used as an absolute criterion to determine the amount of mixing which will take place.

In conclusion, it appears that the degree or amount of mixing between two fluids is a function of the mobilities, but not necessarily the mobility ratios, of the flowing fluids. While no rigorous determination of the rate and amount of mixing is available; correlations could be obtained from laboratory investigations with reservoir fluids under reservoir conditions to determine the size of LPG necessary for a specific flood.

APPENDICES

APPENDIX A

GLOSSARY OF TERMS

Breakthrough sweep efficiency: The percent of the reservoir pore volume invaded by the injected fluid at the time the injected fluid first reaches the production well.

Bubble point: The state of a system characterized by the co-existence of a liquid phase with an infinitesimal quantity of gas phase in equilibrium.

Concentration gradient: The change in concentration of the miscible displacing fluid with distance. The concentration gradient will tend to move fluid molecules from a region of high concentration to a region of low concentration.

Critical point: The point where the dew point and bubble point of a system is the same. There is no distinction between vapor and liquid phases at the critical point as they have the same properties.

Dew point: The state of a system characterized by the co-existence of a gas phase with an infinitesimal quantity of liquid phase in equilibrium.

Dry gas: A mixture of gases composed principally of methane with small amounts of ethane, propane, and butane. It might contain minute amounts of heavier components but will remain in the gaseous phase both at surface and reservoir conditions.

Five-spot: A regular array of wells consisting of four injection wells at each corner of a square shaped area with a producing well in the center.

LPG (Liquified Petroleum Gas): A term usually applied to propane and/or butane in liquid phase.

Mobility: Ratio of the effective permeability to a fluid to its viscosity.

Mobility ratio: Ratio of the mobility of the displacing fluid to that of the displaced fluid. For miscible, single phase systems, the effective permeabilities to each fluid are the same and the mobility ratio reduces to the ratio of the viscosity of the displaced fluid to the viscosity of the displacing fluid.

Vapor liquid equilibrium constants: The equilibrium ratio of the mole fraction of a component in the vapor phase to the mole fraction of the component in the liquid phase.

APPENDIX B

DISPLACEMENT DATA

Run Number 1

Length of core: 1.02 meters.
Fluids in core: Propane displacing isobutane.
Pressure of system: 2000 psia.
Room temperature: 80° F.
Rate of efflux: 1.0 scf isobutane/hr.
Equivalent liquid efflux at 2000 psia and 80° F: 115.0 cc/hr.
Pore volume of core: 303.2 cc.
Time for apparent breakthrough: 100 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Specific Gravity	Mole Percent Propane	Volume Percent Propane
10	19.2	2.070	6.5	4.8
20	38.3	2.037	18.9	16.7
30	57.5	1.974	29.0	26.0
40	76.7	1.921	39.8	36.3
50	95.7	1.865	48.9	45.2
60	115.0	1.818	60.3	56.7
70	134.2	1.759	70.0	66.7
80	153.5	1.709	78.2	75.6
90	172.4	1.666	81.5	79.1
100	191.7	1.650	86.3	84.4
110	211.0	1.625	94.6	93.8
120	230.0	1.582	96.5	96.0
130	249.2	1.572	97.0	96.5

DISPLACEMENT DATA (CONT.)

Run Number 2

Length of core: 2.91 meters.
Fluids in core: Propane displacing isobutane.
Pressure of system: 2000 psia.
Room temperature: 80° F.
Rate of efflux: 1.0 scf isobutane/hr.
Equivalent liquid efflux at 2000 psia and 80° F: 115 cc/hr.
Pore volume of core: 868 cc.
Time for apparent breakthrough: 320 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Specific Gravity	Mole Percent Propane	Volume Percent Propane
10	19.2	2.037	6.6	4.9
20	38.3	2.001	13.5	11.8
30	57.5	1.982	17.2	15.2
40	76.7	1.971	19.3	17.1
50	95.7	1.944	24.6	21.9
60	115.0	1.930	27.3	24.4
70	134.2	1.903	32.5	29.3
80	153.5	1.878	37.3	33.8
90	172.4	1.815	49.5	45.7
100	191.7	1.830	46.6	42.9
110	211.0	1.806	51.3	47.5
120	230.0	1.780	56.3	52.6
130	249.2	1.766	59.0	55.3
140	268.4	1.749	62.3	58.7
150	298.7	1.736	69.8	61.3
160	306.7	1.720	67.9	64.5
170	326.0	1.694	72.9	69.8
180	345.2	1.677	76.2	72.3
190	364.2	1.665	77.8	75.1
200	383.4	1.651	81.2	78.8
210	402.7	1.636	84.1	82.0
220	421.6	1.623	86.7	84.8
230	440.9	1.611	89.0	87.4
240	460.1	1.580	95.0	94.2
250	479.1	1.582	94.6	93.8
260	498.4	1.575	95.9	95.3
270	517.6	1.570	96.9	96.4

DISPLACEMENT DATA (CONT.)

Run Number 3

Length of core: 4.15 meters.
Fluids in core: Propane displacing isobutane.
Pressure of system: 2000 psia.
Room temperature: 80° F.
Rate of efflux: 1.0 scf isobutane/hr.
Equivalent liquid efflux at 2000 psia and 80° F: 115.0 cc/hr.
Pore volume of core: 1238.4 cc.
Time for apparent breakthrough: 540 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Specific Gravity	Mole Percent Propane	Volume Percent Propane
10	19.2	2.031	7.7	6.7
20	38.3	2.014	11.3	9.8
30	57.5	1.980	17.6	15.5
50	95.7	1.939	25.5	22.8
80	153.5	1.886	35.8	32.4
100	191.7	1.847	43.3	39.7
120	230.0	1.828	47.0	43.3
140	268.4	1.777	56.9	53.1
160	306.7	1.742	63.6	60.1
180	345.2	1.721	67.7	64.3
200	383.4	1.676	76.4	73.6
210	402.7	1.669	77.8	77.4
220	421.6	1.658	79.9	75.0
230	400.9	1.669	77.8	77.4
240	460.1	1.622	86.8	85.1
250	479.1	1.611	89.0	87.4
260	498.4	1.609	89.4	87.8
270	517.6	1.581	94.8	94.0
280	536.9	1.571	96.7	96.2
290	555.9	1.568	97.3	96.9

DISPLACEMENT DATA (CONT.)

Run Number 4

Length of core: 1.02 meters.

Fluids in core: Propane displacing isobutane.

Pressure of system: 2000 psia.

Room temperature: 80° F.

Rate of efflux: 0.3 scf isobutane/hr.

Equivalent liquid efflux at 2000 psia and 80° F: 34 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 440 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Specific Gravity	Mole Percent Propane	Volume Percent Propane
20	11.4	2.058	2.5	2.2
40	22.7	1.997	14.3	12.3
70	39.6	1.822	49.2	45.5
90	51.0	1.800	52.4	48.7
110	62.3	1.743	63.4	59.8
120	68.0	1.672	77.2	74.4
140	79.3	1.600	91.1	89.8
160	90.6	1.555	99.8	99.8

DISPLACEMENT DATA (CONT.)

Run Number 5

Length of core: 1.02 meters.

Fluids in core: Propane displacing isobutane.

Pressure of system: 2000 psia.

Room temperature: 80° F.

Rate of efflux: 0.3 scf isobutane/hr.

Equivalent liquid efflux at 2000 psia and 80° F: 46 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 430 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Specific Gravity	Mole Percent Propane	Volume Percent Propane
20	15.3	2.061	1.9	1.6
40	30.6	2.014	11.0	9.6
60	46.2	1.923	28.6	25.6
90	69.1	1.982	17.2	15.2
100	76.7	1.775	57.2	53.5
120	92.0	1.693	73.1	70.0
140	107.3	1.611	89.0	87.4
160	122.9	1.554	100.0	100.0

DISPLACEMENT DATA (CONT.)

Run Number 6

Length of core: 1.02 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 200 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 56 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
8	26.7	0.9997	3.0
16	53.3	1.0176	19.5
24	80.0	1.0382	35.0
32	106.7	1.1051	85.0
40	133.3	1.1259	96.2
48	160.0	1.1313	----
56	186.7	1.1269	98.2

DISPLACEMENT DATA (CONT.)

Run Number 7

Length of core: 2.91 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 200 cc/hr.

Pore volume of core: 868.3 cc.

Time for apparent breakthrough: 168 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
8	26.7	1.0018	5.0
24	80.0	1.0063	9.0
48	160.0	1.0120	13.5
80	266.7	1.0124	14.0
104	346.7	1.0474	42.4
128	426.7	1.0856	70.2
144	480.0	1.1002	81.4
168	560.0	1.1125	89.6
176	586.7	1.1207	94.8
184	613.3	1.1264	98.6
192	640.0	1.1265	99.0

DISPLACEMENT DATA (CONT.)

Run Number 8

Length of core: 4.15 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 200 cc/hr.

Pore volume of core: 1238.4 cc.

Time for apparent breakthrough: 230 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
8	26.7	0.9980	1.5
24	80.0	1.0026	5.4
40	133.3	1.0104	12.4
80	266.7	1.0401	36.2
120	400.0	1.0535	49.0
168	560.0	1.0772	65.9
200	666.7	1.0980	79.8
232	773.3	1.1129	90.0
248	826.7	1.1201	94.8
256	853.3	1.1249	98.0
264	880.0	1.1253	98.4

DISPLACEMENT DATA (CONT.)

Run Number 9

Length of core: 8.23 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 200 cc/hr.

Pore volume of core: 2455.8 cc.

Time for apparent breakthrough: 608 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
8	26.7	1.0010	4.0
16	53.3	1.0103	12.4
24	80.0	1.0076	9.6
40	133.3	1.0169	17.8
56	186.7	1.0312	29.5
80	266.7	1.0443	39.6
112	373.3	1.0792	66.4
136	453.3	1.0980	79.8
184	613.3	1.0988	80.5
208	693.3	1.1201	95.0
248	826.7	1.1238	87.4
264	880.0	1.1255	98.6
272	906.7	1.1280	----

DISPLACEMENT DATA (CONT.)

Run Number 10

Length of core: 1.02 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 36 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 310 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
50	30	1.0069	9.8
100	60	1.0325	30.4
150	90	1.0416	37.6
200	120	1.0737	62.4
250	150	1.0995	81.0
300	180	1.1129	90.4
350	210	1.1278	100.0

DISPLACEMENT DATA (CONT.)

Run Number 11

Length of core: 1.02 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 50 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 240 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
35	29.2	1.0071	10.0
70	58.3	1.0387	35.0
105	87.5	1.0387	35.0
140	116.7	1.0750	63.5
175	145.8	1.1069	85.8
210	175.0	1.1218	96.0
245	204.2	1.1279	100.0

DISPLACEMENT DATA (CONT.)

Run Number 12

Length of core: 1.02 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 82 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 150 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
25	34.2	1.0148	16.0
50	68.3	1.0205	21.0
75	102.5	1.0642	55.0
100	136.7	1.1032	81.5
125	170.8	1.1230	97.0
150	205.0	1.1280	100.0

DISPLACEMENT DATA (CONT.)

Run Number 13

Length of core: 1.02 meters.

Fluids in core: 50% glycerol solution displacing water.

Rate of efflux: 172 cc/hr.

Pore volume of core: 303.2 cc.

Time for apparent breakthrough: 82 min.

Time After Apparent Breakthrough (min)	Volume of Fluid Removed After Apparent Breakthrough (cc)	Measured Specific Gravity	Volume % Displacing Glycerol Solution
16	45.9	0.9999	3.2
32	91.7	1.0387	35.0
48	137.6	1.1032	81.5
64	183.5	1.1262	99.0
80	229.3	1.1277	100.0

APPENDIX C

PRESSURE VOLUME RELATIONSHIP OF PROPANE AND ISOBUTANE

The pressure-volume relationship of propane and isobutane was determined using a volumetric calibrated mercury pump and a pressure-volume-temperature cell of known volume. The cell was filled with mercury to remove all air prior to filling with the hydrocarbon to be studied. The cell containing the hydrocarbon was pressured up to the desired pressure by forcing mercury into the cell with the mercury pump and a corresponding pump reading was taken.[5/] The pressure on the cell was reduced and gas bled off through a surge bottle and a wet test meter. A second pump reading was taken at 2000 psia to determine the amount of hydrocarbon bled off.

The pound moles of gas removed from the cell was calculated from the wet test meter readings and the corresponding volume per pound mole computed at the cell pressure. Data and sample calculations for this procedure are given below.

Pressure Volume Calculations for Propane

Initial pump reading at 2000 psia and 80° F: 78.630.

Volume of gas liberated: 0.02785 $(ft.)^3$ at standard conditions of 60° F 14.7 psia.

Pound moles of gas liberated: $0.02785/379 \doteq 7.348 \times 10^{-5}$.

Pump reading after bleeding off gas: 81.389.

[5/] All pump readings were taken at a pump pressure of 5,000 psia as a pump calibration constant was available at that pressure. This was possible as the cell could be closed off from the pump at one pressure, and the pump pressured up to 5,000 psia without changing the cell pressure.

Volume change of propane in the cell due to the removal of the gas:

$(81.389 - 78.630)\ (0.9996)/2.832 \times 10^4 = 9.740 \times 10^{-5}\ (ft)^3$.

Cubic feet of propane at 2000 psia per pound mole:

$9.740 \times 10^{-5}/7.348 \times 10^{-5} = 1.325$.

Initial pump reading at 1250 psia and 80° F: 81.191.

Pump reading after bleeding off gas: 78.250.

Volume change of propane in the cell due to the removal of the gas:

$(81.191 - 78.250)\ (0.9996)/2.832 \times 10^4 = 1.038 \times 10^{-4}\ (ft)^3$.

Cubic feet of propane at 1250 psia per pound mole:

$1.038 \times 10^{-4}/7.348 \times 10^{-5} = 1.413$.

Pressure Volume Calculations for Isobutane

Initial pump reading at 200 psia and 80° F: 68.731.

Volume of gas liberated: $0.0318\ (ft.)^3$ at standard conditions of 60° F and 14.7 psia.

Pound moles of gas liberated: $0.0318/379 = 8.39 \times 10^{-5}$.

Pump reading after bleeding off gas: 72.392.

Volume change of isobutane in the cell due to the removal of the gas:

$(72.392 - 68.731)\ (0.9996)/2.8317 \times 10^4 = 1.292 \times 10^{-4}\ (ft)^3$.

Cubic feet of isobutane at 2000 psia per pound mole:

$1.292 \times 10^{-4}/8.39 \times 10^{-5} = 1.540$.

APPENDIX D

POROSITY DETERMINATION

The porosity of the core was determined by lowering the pressure on the propane filled core from 2000 psia to 1250 psia and measuring the gas liberated during the pressure drop. This was done for cores of two different lengths and an average value was taken. The data and calculations for these determinations are as follows.

Core No. 1

Length of core: 40 inches.

Volume of pipe containing the core: 0.02199 $(ft)^3$.

Moles of propane in 0.02199 $(ft)^3$ at 80° F and 2000 psia:

$$0.02199/1.325 = 0.01659.$$

Moles of propane in 0.02199 $(ft)^3$ at 80° F and 1250 psia:

$$0.2199/1.413 = 0.01556.$$

Standard cubic feet of gas which would be liberated, assuming 100 % porosity:

$$(0.01659 - 0.01556)(379) = 0.3904 \text{ scf.}$$

Volume of gas actually liberated: 0.1901 scf.

Porosity of core: 0.1901/0.3904 (100%) = 48.69%.

Core No. 2

Length of core: 13.6 feet.

Volume of pipe containing the core: 0.08970 $(ft)^3$.

Moles of propane in 0.0897 $(ft)^3$ at 80° F and 2000 psia:

$$0.08970/1.325 = 0.06770.$$

Moles of propane in 0.08970 $(ft)^3$ at 80° F and 1250 psia:

$$0.08970/1.413 = 0.06348.$$

Standard cubic feet of gas which would be liberated, assuming 100 % porosity:

$$(0.06770 - 0.6348)(379) = 1.5994 \text{ scf.}$$

Volume of gas actually liberated: 0.7789 scf.

Porosity of core: 0.7789/1.5994 (100%) = 48.70%.

<u>Average Porosity</u>: $\frac{1}{2}(48.70 + 48.69) = 48.7\ \%$

APPENDIX E

PERMEABILITY CALCULATIONS

The permeability of the sand packed flow system was calculated using a modified form of Darcy's law. For gaseous flow a pressure correction factor of $(p_1 + p_2)/2p_b$ is applied to Darcy's law to correct for the pressure on the flowing gas. Darcy's law, with the pressure correction can be expressed as

$$Q_b = \frac{AK}{2uL} \frac{p_1{}^2 - p_2{}^2}{p_b}$$

where; Q_b is the volume rate of flow measured at the temperature of flow and the base pressure (taken as one atm.), in cc/sec.

A is the cross-sectional area of the core in $(cm)^2$.

k is the cores permeability to gas in darcys.

p_1 is the upstream pressure in atm.

p_2 is the downstream pressure in atm.

u is the viscosity of the gas in cps. at flow conditions.

L is the length of the core between the points where the pressure measurements are taken.

p_b is the base pressure (one atm.) to which the flow rate is calculated.

Gaseous propane was flowed through the core at varying rates of flow and values of A $(p_1{}^2 - p_2{}^2)/2uLp_b$ were determined for different values of Q. The permeability to gas was determined by the method of averages. Values of Q were then calculated for each flow rate using the value determined for permeability and compared with the measured values to determine if the relationship was linear (a necessary condition for viscous, non-turbulent flow and validity of Darcy's law).

Data and Calculations

Area of core: 6.127 $(\text{cm})^2$.

Length of core between points of pressure measurements: 66.04 cm.

Barometric pressure: 29.05 in. Hg.

Viscosity of propane: 0.0076 cp.

Volume of gas flowing during each set of measurements: 26,499 cc.

Room temperature: 80° F.

Upstream Pressure in. Hg.	Downstream Pressure in. Hg.	Q (cc/sec) at 1 atm. and 80° F.	$\frac{A\,(p_1^2 - p_2^2}{2\,uL}$	Q (calculated with determined permeability)
48.69	36.40	141.8	7.123	137.2
46.80	35.95	114.4	6.116	117.8
44.65	34.85	101.3	5.304	102.1
38.95	32.05	64.0	3.345	64.4
33.88	29.18	38.8	2.014	38.8
		460.3	23.902	

$$k = \frac{460.3}{23.902} = 19.3 \text{ darcys.}$$

It is common practice to extrapolate a plot of gas permeability versus $2/p_1 + p_2$ to infinite pressure to obtain the effective permeability to liquid flow. In the example given above, the permeability to gas at the low pressures used is nearly constant for each mean pressure, indicating that the cores permeability to gas approaches its permeability to liquid flow.

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