8c

ENHANCED OIL RECOVERY
USING
LIGNOSULFONATES

by

B.B. Bansal

A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirement for the
degree of

MASTER OF APPLIED SCIENCE
in the
Department of Chemical Engineering
University of Ottawa

Ottawa, Canada. July, 1978

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ACKNOWLEDGEMENT

The author would like to express his sincere thanks and gratitude to his Research Directors Dr. G.H. Neale and Dr. V. Hornof for their guidance and encouragement throughout the course of this work and in the preparation of this thesis.

Thanks are due to Mr. G. Gasperetti for the fabrication, installation and maintenance of the experimental set-up.

Finally, the author wishes to thank Imperial Oil Limited (ESSO) (Montreal), Stepan Chemical Company (Northfield, Illinois), American Can Company (New Jersey) and Shell Canada Limited (Montreal) for providing various oils and surfactants required for this work.

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The effect of lignosulfonates on the recovery of oil from porous media has been investigated using unconsolidated cores packed with Ottawa sand. Displacement tests were conducted using three different lignosulfonate concentrations for both secondary and tertiary stages. The effect of concentration of lignosulfonates on interfacial tension and viscosity was also studied.

The experiments showed that the reduction in interfacial tension between various oils and Marasperse solutions was small, and concentrations higher than 1% yielded no appreciable change in interfacial tension. Also, no significant increase in the viscosity of Marasperse solutions, which would yield more favorable mobilities, was found.

The results of displacement tests showed that the additional secondary oil recovery, using different concentrations of Marasperse, varied between approximately 1% and 7% at 1 pore volume (PV) injection. A drop in additional recovery, compared with waterflooding, was observed for injection of Marasperse solutions over 1 PV. The additional tertiary recovery for a waterflooded core was found to be approximately 3-4% at 2 PV injection of 1% Marasperse and showed no improvement with increasing concentration. The study showed that Marasperse solutions, when used alone in the tertiary stage, tend to follow the water channels which resulted from waterflooding.

CHAPTER 1

INTRODUCTION

INTRODUCTION

Enhanced Oil Recoverey (EOR) refers to retrieving the oil remaining in a petroleum reservoir after it has been pumped 'dry'. Whereas the first stage of the recovery, called Primary Recovery, takes place as a result of the release of internal energy associated with the oil/gas/brine system in the reservoir, any EOR method will require introduction of external energy into the oil well to release the remaining oil. The desire to tap this remaining oil is spurred by the existing oil-price structure and the vast amount of oil still unrecovered. In certain reservoirs this oil amounts to as much as 70% of the original oil in place. Table 1 shows the production and consumption of petroleum in Canada and the United States, and how EOR, if found economically feasible, could significantly reduce our dependence on foreign countries. These figures indicate that EOR could create one of the most important energy supplies between now and the year 2000.

Enhanced oil recovery includes both secondary and tertiary processes and involves the use of water and other chemicals. Figure 1 shows the secondary and tertiary recovery methods currently available. The application of any of the above methods to a reservoir depends on the characteristics of the reservoir and oil and on the experience of the production personnel. Whereas water is commonly used as the displacing

TABLE 1

POTENTIAL, PRODUCTION AND DEMAND OF PETROLEUM IN CANADA AND USA

	Oil Potential 10^9 Barrels	Oil Recoverable 10^9 Barrels	Oil Already Recovered 10^9 Barrels	Oil Remaining to be Recovered 10^9 Barrels	Oil left Unrecoverable 10^9 Barrels	Domestic Oil Production 10^6 BBL/Day	Oil Demand 10^6 BBL/Day	Production by EOR 10^6 BBL/Day	Production Expected by 1995 10^6 BBL/Day
Canada	43**	14	7	7	29	1.73	1.71	na	na
US	418*	137	109	28	281	7.9	15-16	0.24	22

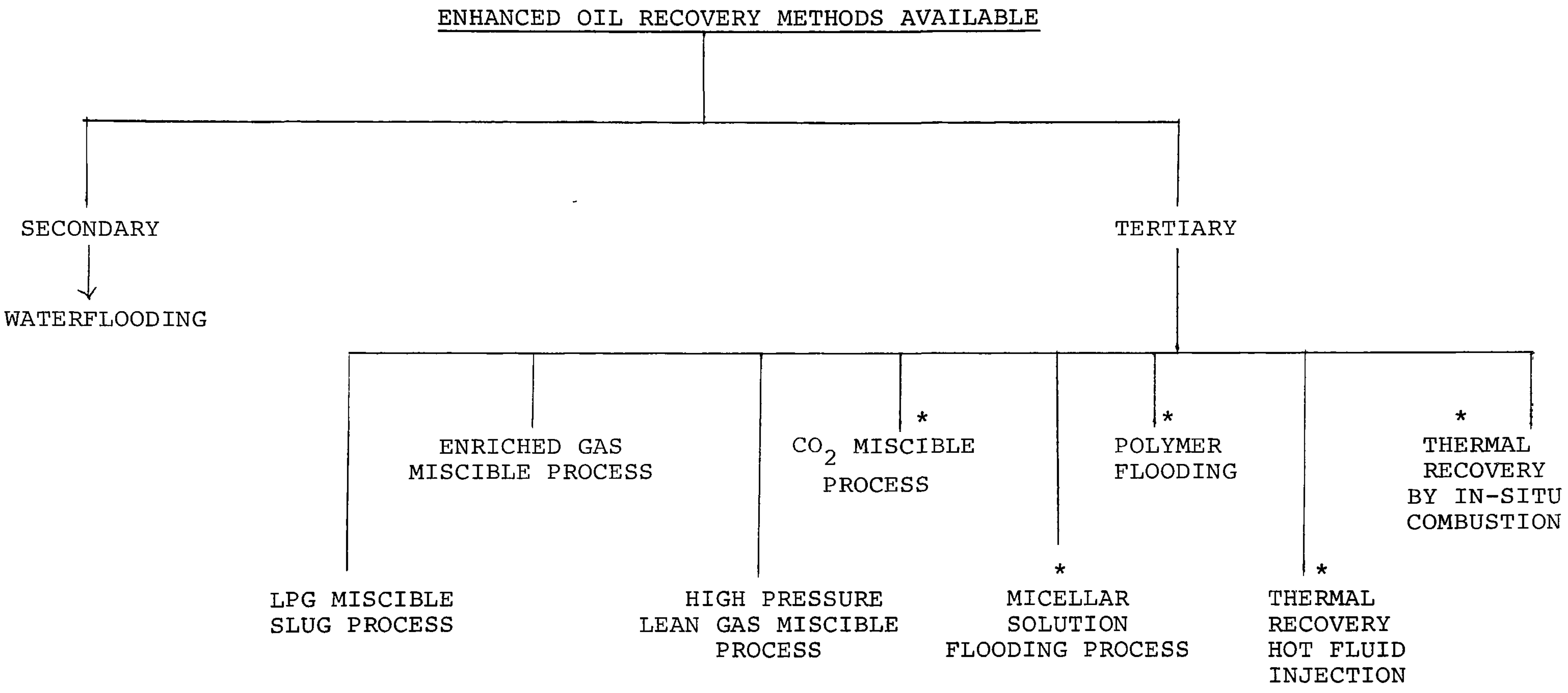
All figures to the end of 1975

* Excluding Alaska's North Slope

** Excluding Tar Sands

na: Data Not Available

Source: APl Report, EMR Report ER 78-2



* Under active testing

FIG. 1 ENHANCED OIL RECOVERY METHODS

fluid in secondary recovery operations, no such single tertiary method is available which is applicable to all reservoirs.

In secondary recovery operations, the reservoir is flooded with water from a series of wells resulting in the displacement of the oil to the producing wells. The waterflooding operation is, in fact, duplication of the natural water drive in Primary Recovery and releases about 15%-25% of additional oil. Waterflooding has advantages over other injection processes. Water is relatively inexpensive to obtain (from produced brine in the oil-fields) and it works well in the displacement to obtain additional oil. Artificial water flooding, however, is not found to be as efficient as the natural water drive operation because the structures associated with natural water drive reservoirs are more homogeneous and permeable. The flooding is discontinued whenever the cost of this operation (treatment, injection and production) becomes equal to the value of the produced crude oil. Since there is still residual oil (30-70%) trapped in the pores of the reservoir, a tertiary method of recovering this residual oil may be attractive if found economically feasible.

In tertiary recovery, external energy is introduced into a reservoir in some form depending on the type of forces holding the residual oil. Tertiary recovery operations are undertaken following waterflooding and employ the existing wells and equipment. In very few oil fields would new wells be drilled and any major alterations made in the equipment without rendering the operation unprofitable. Any tertiary recovery method involves high operating cost in terms of chemical requirements.

The principal forces responsible for trapping the residual oil in the pores of a petroleum reservoir are (1) capillary forces and (2) viscous forces. Depending on which forces predominate, various techniques are available as shown in Figure 1. Residual oil may be recovered by injecting a fluid miscible with the oil. The injected fluid mixes with the oil, reducing the capillary forces and releasing the oil. Hydrocarbons and carbon dioxide under favorable conditions of temperature and pressure are miscible with oil to a varying degree. LPG (Propane), enriched gas (C_2-C_6), high pressure lean gas (Methane) and carbon dioxide have been used in various fields as the displacing fluids. Each process has found wide application depending on the particular reservoir and oil characteristics. However, all hydrocarbons are expensive and in great demand and therefore recovery of the injected fluid becomes important and adds to the cost of the operations.

On the other hand, if the oil is immobile in the pores because of the viscous forces, reduction in viscosity would release this oil. This is called thermal recovery of oil and involves the use of either hot fluid injection or in-situ combustion of the oil. In hot fluid injection, heat is generated externally and is transported into the reservoir in the form of hot water or steam. High investment, high operating cost and lower oil price involved in this process tend to reduce the profit. Since the necessary energy is generated by burning fuel, a part of the oil is therefore lost. In-situ combustion involves the generation of heat within the reservoir using the oil therein and injection of air for combustion reaction.

Capillary forces can also be reduced by lowering the interfacial tension between oil and water. This method of recovering oil is called chemical or micellar solution flooding. It is one of the more promising tertiary recovery methods presently available and involves the use of surfactants. Surfactants have the ability to change the interfacial characteristics even when present in small amounts. This technique involves the injection of certain amount of a surfactant (micellar) solution into the reservoir. Since the surfactants are expensive, the injection is in the form a finite slug which moves slowly through the reservoir pushed by a polymer slug and large volumes of cheaper brine. The surfactant, because of its ability to reduce the interfacial tension, releases the oil at the front end, which then moves toward the producing wells. Fig. 2 illustrates the micellar flooding process[1-3]. Use of a co-surfactant (alcohol) and an electrolyte (sodium chloride) is common since these additives improve the quality

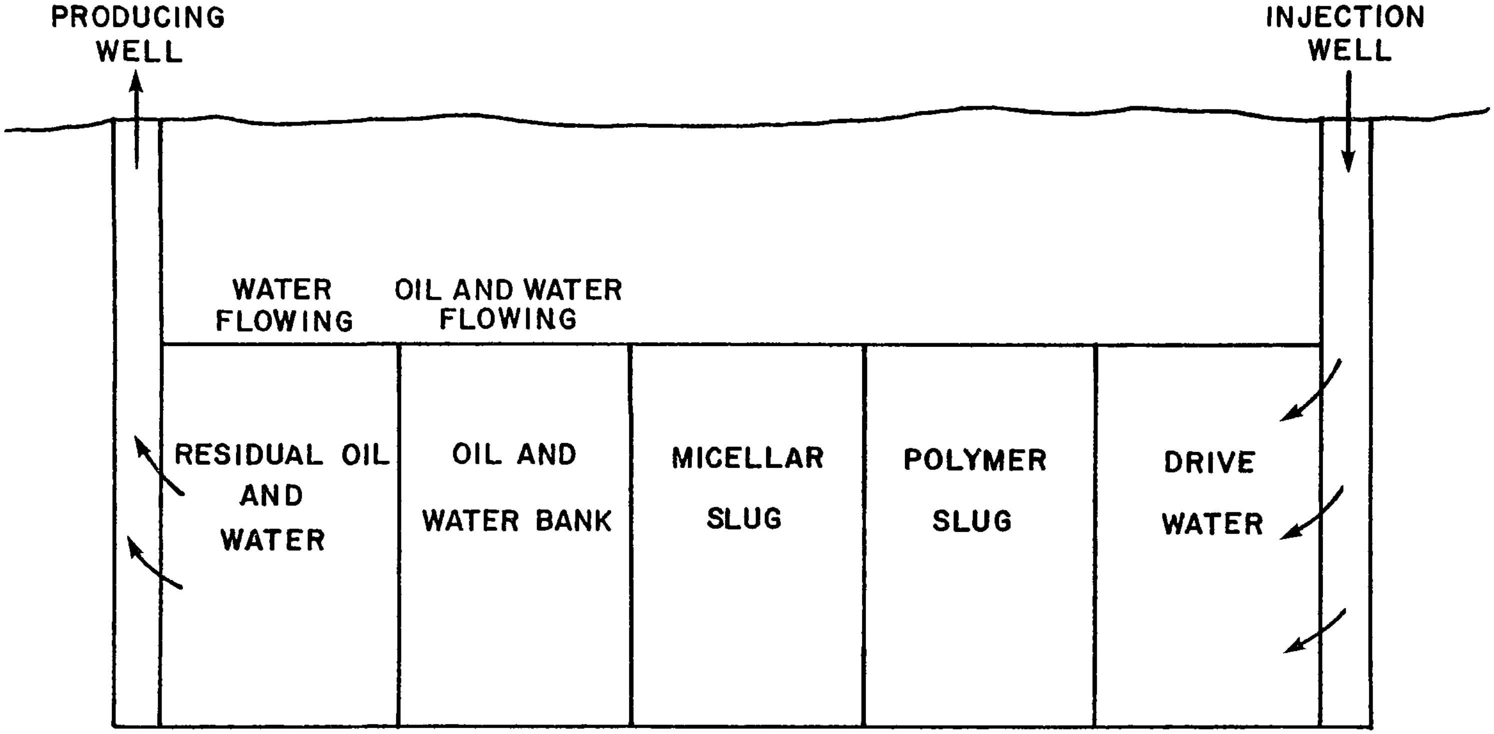


FIG. 2 MICELLAR FLOOD PROCESS

of the slug. The surfactants normally used are petroleum sulfonates and are required in large amounts. Since petroleum sulfonates and other required chemicals are expensive, subsequent recovery of the injected chemicals can make the operation more profitable.

Micellar flooding application to any oil field must be preceded by a detailed study and design. In any case, residual oil saturation has to be a minimum of 25-30% pore(40) volume for any possible tertiary method application.

In the present work, a widely different class of chemicals, known as lignosulfonates, have been investigated as possible alternatives to petroleum sulfonates in the tertiary recovery of oil. Lignosulfonates are wood based chemicals manufactured from the sulfite liquor effluents emanating from pulp and paper plants. These effluents contain a mixture of sulfonated lignin, polysaccharides and wood sugars dissolved in water. The sulfonated lignin upon purification and removal of undesirable material yields lignosulfonate products. Many lignosulfonates possess favorable surfactant and emulsification properties. If successful, their use in Tertiary Oil Recovery Operations would serve two purposes. Firstly, it would cut down the amount of expensive petroleum sulfonates needed in micellar flooding. Secondly, the pollution problem caused by the pulp mill effluents would be reduced, since lignosulfonates form a major non-biodegradable constituent in the effluent from pulp mills.

Other advantages of lignosulfonate stabilized emulsions include their stability to temperature variations, to mechanical stress and to electrolytic contamination.

Economic considerations and Impact of EOR on the Chemical Market

Laboratory and pilot studies are being carried out to determine the most economical micellar solution composition. Micellar solutions cost typically from \$8 to \$15/bbl and tend to follow the price of crude oil(27). Herbeck et al(27) report that for a 20-acre, 5-spot well-pattern micellar flood with 20% porosity and 30 ft. thickness, the micellar and polymer costs can vary from \$600,000 to \$1,900,000 depending on the surfactant and slug size.

As costs of energy go up, EOR becomes more attractive. Although the cost of chemicals involved is high, the existing oil price level permits profitability for a given set of residual oil saturation and percentage recovery. Since the chemicals used are made from petroleum itself, the price of oil would decide the cost of these chemicals also. Producers of surfactants, alcohols and polymers are waiting anxiously for the potentially huge market to develop in the oil fields of the US.(28) Between now and the year 2000, this market could add between \$22 billion and \$118 billion to their sales depending on the oil price.(28) Table 2 shows the potential of chemical market which could emerge as a result of micellar flooding.

TABLE 2

MICELLAR FLOODING: PROFILE OF EMERGING CHEMICAL MARKET(28)

	Oil	Price
	$15 per bbl	$25 per bbl
Oil recovery, 1976-2000, billions of barrels[a]	2.1	8.3
Chemical Requirements		
lb per bbl		
surfactant[b]	17.5	17.5
alcohol[c]	5.25	5.25
polymer[d]	1.0	1.0
Total Chemical requirements,		
billions of lb.		
surfactant[b]	36.8	145.3
alcohol[c]	11.0	43.6
polymer[d]	2.1	8.3
Total	49.9	197.2
Average price per lb		
surfactant[b]	0.43	0.59
alcohol[c]	0.20	0.27
polymer[d]	2.1	2.52
Chemical market,		
$ billions		
surfactant[b]	15.8	85.7
alcohol[c]	2.2	11.8
polymer[d]	4.4	20.9
Total	22.4	118.4

---

[a] Assumes 10% discounted cash flow rate of return. If the

rate is 20%, oil recovery drops to virtually nothing for $15 oil and only 0.8 billion bbl for $25 oil.

b 100% active

c Assumes isopropyl alcohol. Use of higher alcohols will change data.

d Assumes equal volumes of polyacrylamides and polysaccharides.

Source: National Petroleum Council, USA.

CHAPTER 2

LITERATURE SURVEY

LITERATURE SURVEY

Enhanced oil recovery techniques are being applied to many existing oil-fields and are rapidly gaining importance. The origin of these methods, however, is not recent. Waterflooding and other methods involving chemicals have long been used to displace oil from reservoirs. The recent developments, on the other hand, relate to the use of micellar methods involving surfactants (petroleum sulfonates) to attain ultra-low interfacial tensions and ways to minimize associated problems of adsorption, degradation and recovery of these surfactants. The emphasis is on developing a micellar slug process that is both effective and economical for a given oil field.

The following survey presents primarily the literature available on the use of various chemicals, including conventional surfactants and lignosulfonates.

Waterflooding, as a secondary method, was first used over a hundred years ago but it gained wide application in the 1950's. Since then the studies have centered on improvement of mobilities of the fluids in a well-pattern.

Aronofsky(1) reported the effect of mobility ratio on sweep efficiency. His results indicated efficiencies of 61.0 percent and 86.6 percent for mobility ratios of 10 and 0.1

respectively for idealized direct-line drive systems consisting of alternate rows of injection and producing wells. The recovery at breakthrough by waterflooding for this system was 42 percent greater with a mobility ratio of 0.1 as compared to a ratio of 10.

Dyes et al$^{(2)}$ established a close correspondence between water flooding and miscible flooding. They studied the rate of oil recovery after breakthrough over a wide range of mobility ratios and concluded that there could be as much as 50 percent of the ultimate oil recovery obtained after breakthrough. For floods with no saturation gradient in the mobility of fluids in either the swept or unswept regions, mobility ratio was characterized as:

$$M = \frac{\left(\frac{k_o}{\mu_o} + \frac{k_w}{\mu_w}\right)_{\text{unswept}}}{\left(\frac{k_o}{\mu_o} + \frac{k_w}{\mu_w}\right)_{\text{swept}}}$$

Based on the data collected, it was shown that low mobility ratios lead to early declines in the fraction of total flow from the <u>unswept</u> region and therefore result in less favorable rates of recovery.

The use of polymers for improvement in the sweep efficiency has been of considerable interest in recent years. Polyacrylamides or polysaccharides have been used as mobility buffers. Polyacrylamides achieve improved mobility ratios by permeability reduction (attributed to adsorption) of the reservoir whereas polysaccharides obtain the same effect through increased viscosity.

Pye(3) reported the use of high molecular weight synthetic polymers in very dilute solutions to decrease the mobility of water. The results indicated additional recoveries up to 20% at 84% water cut. It has been shown that another Newtonian solution of the same viscosity (1.55 cp glycerine) showed only minor improvement over water flooding. This behaviour, whereby the apparent viscosity of a polymer solution in the rock departs markedly from the viscometer values, and exhibited by a very few types of polymer solutions, was referred to as "resistance factor". Similar effects have been recorded more recently by Patton et al(4).

Lee and Claridge(5) investigated the effect of fluid velocity on the mobility ratio in a five-spot pattern. They established that due to the pseudoplastic behaviour of polymer solutions and the velocity distribution in the pattern, the displacement is governed by local mobility ratios which are time dependent. They also reported lower areal sweep at breakthrough for polymer solutions than that obtained with a Newtonian fluid of comparable average viscosity. This, however, improved at the later stages of the flood (at 1 PV throughput).

Other water-soluble chemicals have been suggested by various researchers to enhance oil recovery for the secondary and tertiary stages. These include such chemicals as salts of fatty or sulfonic acids, fatty acid soaps, polycyclic sulfonic salts, substituted aromatic sulfonic acids and conventional petroleum sulfonates.

De Groot(6) patented a process involving the use of substituted aromatic sulfonic compounds (comprising an aromatic nucleus (eg. Naphthalene), alcohol residues (propyl alcohol), sulfonic acid residue and ammonium, hydrogen or metallic ion) for recovering fixed oil adsorbed on the particles of sand. These chemicals, soluble in hard water or salty water, were used in a concentration range of 25-1000 ppm.

Holbrook(7) recommended the use of such chemicals as organic perfluoro compounds, fatty acid soaps and polyglycol ethers in a concentration range of 0.01 to 1.0 percent. Approximately 20 percent of additional oil was recovered when the surfactant slug was followed by another slug of oil (0.01 to 0.1 pore volume), followed by flooding with ordinary water. The second flood front at the oil/surfactant interface established the continuity of the oil phase.

Enhanced oil recovery by wettability reversal has been under active study in recent years. Bobek et al(8) reported oil recoveries from water-wet rock to be higher than those from oil-wet rock by 15% of the original oil in place during waterflooding.

Wagner and Leach(9) studied the effect of wettability on oil-displacement efficiency. They carried out flood tests using Ottawa-sand to show that preferential wettability reversal (from oil wet to water-wet) resulted in lower residual oil saturation. The core-wettability was changed by the advancing flood water using 0.025-1.0 N HCℓ. Their study suggested wettability reversal could be particularly attractive for reservoirs with high viscosity oils.

Mungan(10) investigated the effects of wettability-reversal on oil recovery using the cores and oil from the fields of Sinclair Oil Company and employing 0.5 N NaOH. The tests performed at reservoir temperature, showed rapid wettability reversal leading to an increase in recovery of 11-15 percent. At room temperature, the NaOH solution did not recover any additional oil.

Dranchuk et al(11) studied the effect of various chemicals on the recovery of viscous crude oil (Lloydminster) by waterflooding. They reported the use of such chemicals as sodium hydroxide, potassium hydroxide, sodium carbonate and sodium phosphate, which formed stable emulsions with Lloydminster crude oil as a result of low interfacial tension. This was attributed to the presence of constituents in the crude oil which change the preferential wettability of Ottawa sand from water-wet to oil-wet.

Ehrlich and Wygal(12) reported the use of caustic waterfloods for improved oil recovery. It is attributed to the presence of organic acids in the oil, which react with the caustic to produce surface-active materials. These surfactants enhance the oil recovery by mechanisms such as lowering of interfacial tension, wettability changes and changes at the oil-water and liquid-solid interfaces.

Literature Pertaining to the Use of Lignosulfonates

The use of water soluble chemicals such as polycyclic sulfonic salts and wood sulfite liquor was first patented in the early 1930's. De Groot and Monson (13) described a process involving the use of an aqueous solution containing wood sulfite liquor to release the oil in an abandoned well. It was suggested that this liquor could be obtained as a waste product in the manufacture of paper stock by the sulfite process. Another source of supply is the direct or principal product during cooking of inferior woods not suitable for quality paper stock. The liquor was neutralized and used in a concentration range of 25-1000 ppm in cold or preheated water. The following table 3 illustrates the composition of the wood sulfite liquor in one specific case:

TABLE 3

Specific gravity	30.2° Be
Ash	6.59%
Iron	0.034%
Lime (CaO)	1.32%
Magnesia (MgO)	1.54%
Solids	51.03%
Soluble solids	51.03%
Non-tannin	28.80%

TABLE 3 (continued)

Tannin	22.23%
Tannin purity	43.54%

De Groote and Monson indicated that the principal advantages of their process were that the liquor solution does not clog the oil sand and it will recover oil from abandoned sand beds that contain appreciable quantities of asphaltic or similar material at much lower costs.

Kalfoglou(14) patented the use of lignosulfonates as sacrificial agents in oil recovery by micellar dispersion. The results indicated that the presence of lignosulfonates in the rock as a result of a preflush or from within the dispersion slug reduced the adsorption of the expensive surfactant. The process employed injection of a slug of micellar dispersion containing 1.0 percent lignosulfonate (eg. Marasperse N-22), followed by a drive fluid such as thickened water to push the dispersion to the producing well. Additional oil of 16.5% was obtained compared to the case when no lignosulfonate was employed. It was established that the lignosulfonates, with strongly ionized sulfonate groups, cover the potential adsorption sites of the rock imparting negative charge to them. Since the surface would be inert toward anionic surfactant, adsorption would be minimized and the slug would retain its effectiveness. The adsorption of lignosulfonate has been explained as due to electrostatic attraction or by hydrogen bonding to active sites of the rock.

Other patents relate to using lignosulfonates as clay-coating materials. Parker(15) reported additional recovery of 16.5 percent when 0.3 pore volumes of aqueous slug containing 2 percent calcium lignosulfonate was injected ahead of 2 pore volumes of aqueous slug containing 0.06 wt. percent Igepal Co-530 and 0.01 wt. percent Philblack (carbon black, 0.001-1.0 micron). Carbon black acts as a surfactant carrier which, when in suspension, transports the surfactant deeper into the stratum.

Enhanced Oil Recovery Using Surfactants

Enhanced oil recovery methods using surfactants date back to 1927 when Atkinson(16) proposed the use of aqueous solutions of soap to decrease the interfacial tension between oil and the flooding medium. Ozeda et al(17) correlated residual oil saturation in cores (after a surfactant flood) with $\gamma/\Delta P$ and a pore geometry parameter, $(K\phi)^{1/2}$. These correlations indicated that residual oil saturation could tend to zero at values of $(\gamma/\Delta P)$ approaching zero. In the last two decades researchers have utilized various kinds of surfactants to improve the efficiency in oil recovery, to change the wettability and to reduce adsorption and retention of the surfactants.

Gogarty and Tosch(18) reported the use of a new process called micellar flooding. They used a micellar solution slug of 12 percent pore volume consisting of pentane, sulfonate, isopropyl alcohol and water to recover essentially all of the oil. Mobility control was achieved by judicious selection of the slug composition and a thickened water buffer. They also proposed the use of co-surfactants (alcohol) and electrolytes in small concentrations. The adsorption on the porous media was shown to be small.

Hill et al(19) obtained very low interfacial tensions between crude oil and aqueous solutions containing less than 1 weight percent petroleum sulfonates and showed that optimum NaCl concentration was important in any micellar slug composition. Recovery of residual oil varied from only 4 percent with zero NaCl concentration to 100 percent with 0.4 molar NaCl. Their study showed that sodium tripolyphosphate improves compatibility of the system with multivalent cations and reduces the adsorption of sulfonate.

Knaggs et al(20) conducted tests utilizing 0.2 pore volume of 3% active sulfonate slug in 1.5% NaCl and 0.4% hexanol to obtain oil recoveries of over 98 percent. Increased oil recoveries were obtained with increasing surfactant slug pore volumes. Their studies indicated that the petroleum sulfonates lead to ultra-low interfacial tensions, improved brine tolerance and satisfactory adsorption characteristics.

Gogarty(21) studied the effect of concentration of surfactant on oil recovery. For low concentrations and high pore volume injection, oil production lasted for a longer period of time with comparatively higher water-oil ratio (WOR) than for high-concentration, low-pore volume injection. Field results also indicated higher oil recoveries when using high-concentration surfactant, low-pore volume systems. They also concluded that proper formulation of the micellar solution results in improved recovery partly because of reduction in adsorption.

Healy and Reed(22) studied immiscible microemulsion flooding. Since oil recovery is largely affected by displacement efficiency in the immiscible regime, the cores were flooded with microemulsions immiscible with oil and/or water. Correlations were developed between oil recovery and interfacial tension, capillary number and solubilization parameters.

Jones and Dreher(23) investigated the effects of co-surfactants (alcohols) on micellar solutions. It was shown that the type and concentration of co-surfactant controls the amounts of oil and water that a microemulsion can solubilize. It was concluded that alcohols modify phase behaviour and that viscosity could be adjusted using a suitable co-surfactant.

Bae and Petrick(24) investigated the adsorption of petroleum sulfonates in 2 in x 2 ft Berea cores. Using blends of petroleum sulfonates, they showed that adsorption almost doubled when the injection rate was decreased from 13 to 2 ft/day for sulfonate concentration of 1 percent. At a higher concentration of 2%, adsorption at the lower rate was almost five times more than that with the higher rate. The adsorption isotherm goes through a maximum which depends upon the flow rate. A sacrificial chemical (Na_2CO_3) was tested to determine its effectiveness. Results showed that it reduced the adsorption of sulfonate when used in a pre-flush rather than in the sulfonate solution.

Lawson and Dilgren(25) also showed that equilibrium adsorption isotherms of commercial sulfonates contain maxima, but that pure surfactants do not exhibit such characteristics. Heterogeneity of surfactant structure and impurities possibly lead to such adsorption behaviour. Selective adsorption (essential for slug activity) was found to be absent.

Field Application Using Low-Tension Process

A 9-year project(26) involving a chemical flooding process to recover more than 700,000 bbl of additional oil is being launched in Big Muddy field, Wyoming. It will consist of nine 10-acre five spot patterns and five existing wells will be used for production and another eight for injection. A preflush from January 1979 until January 1980, followed by surfactant injection until August 1980, polymer injections until June 1983 and a postflush until June 1987 has been planned. This field has large potential reserves, good oil saturation and has yielded primary and secondary productions of 24.4 and 6.9 million bbl, leaving 60.1 million bbl of 35° APl crude in place.

CHAPTER 3

EXPERIMENTAL

EXPERIMENTAL

A. EXPERIMENTAL SET UP

The displacement runs were carried out in horizontal core-holders packed with Ottawa sand.Fig. 3 is the schematic diagram of the set-up used, which consists of reservoirs for oil, water and surfactant solution, feed and vacuum pumps, liquid separator and fraction collector. The experimental set-up consists of three parts.

(i) Deaeration and saturation section
(ii) Oil displacement section
(iii) Collection and analysis section

The details of the core-holder are given in Fig. 4 and the specifications in Table 4. The core-holder is a 5.2 cm (ID)x121.5 cm(L) stainless steel (Type ASTM A312) pipe flanged at both ends. The flanges can be removed to facilitate operations such as emptying, cleaning, drying and filling. The inlet and outlet connections for the core-holder are made using two stainless steel 1/4" fittings. There are two glass windows near the ends to observe saturation and displacement phenomena. The glass is held between two flanges, one welded to the core-holder and the other placed on the top of the glass. This assembly is held in place by bolting the top flange to the bottom one. Teflon gaskets are used to make the windows leak-proof. There are four manometer tappings on the core-holder, at 15 cm and 30 cm from the center on each side.

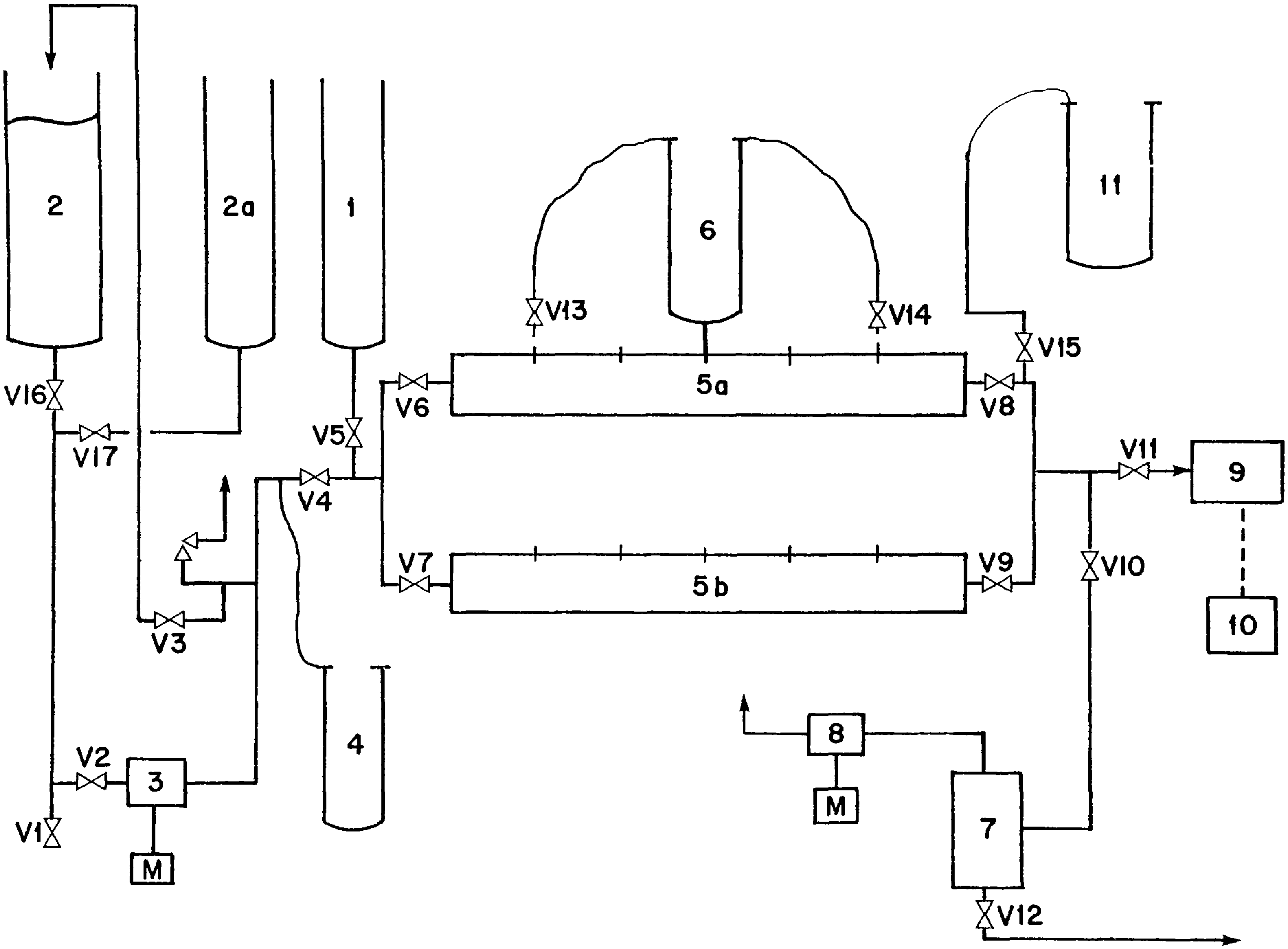


FIG. 3 EXPERIMENTAL SET-UP

LEGEND FOR FIG. 3

1: Oil holding vessel, V-1

2: Water holding vessel, V-2

2a: Surfactant solution holding vessel, V-3

3: Feed pump, P-1

4: Manometer (Pump Discharge), M-1

5a,5b: Core holders CH-1, CH-2

6: Manometer (across two points), M-2

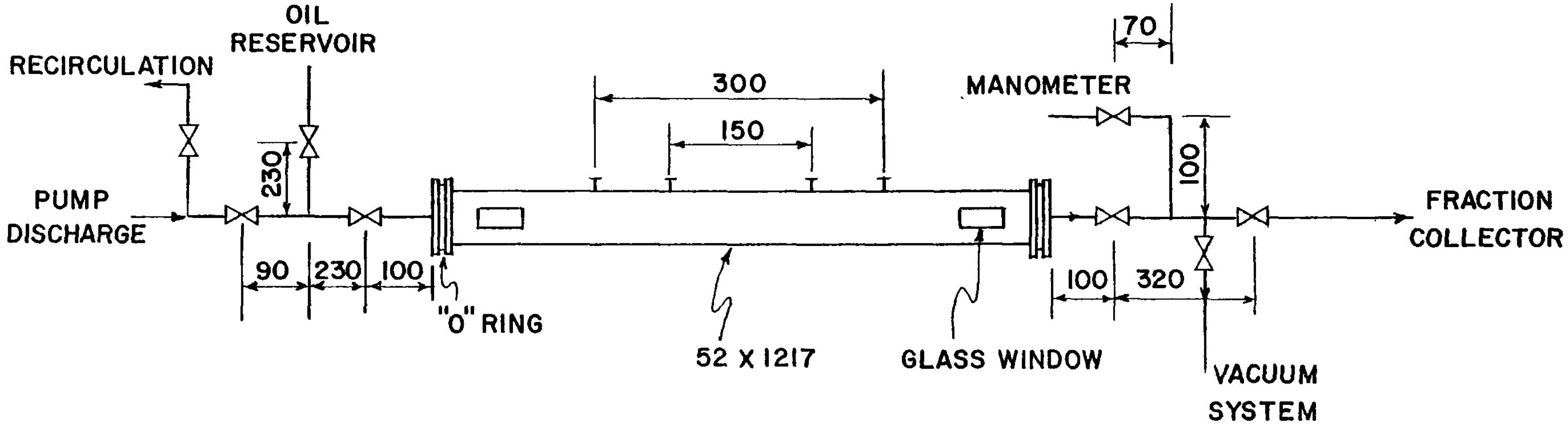
7: Liquid separator, V-4

8: Vacuum pump, P-2

9: Fraction collector

10: Analysis equipment

11: Manometer (vacuum), M-3



ALL DIMENSIONS IN MILLIMETERS

FIG. 4 CORE HOLDER AND PIPING DETAILS

TABLE 4

CORE-HOLDERS

The core-holders were fabricated from 2" ASA Schedule 40 ASTM A312 stainless steel pipe supplied by Drummond McCall & Co., Montreal.

	CH-1	CH-2
Inside diameter, cm	5.206	5.216
Length (flange to flange), cm	121.9	121.5
Cross-sectional area, cm^2	21.29	21.37
Volume empty, cm^3	2595.3	2596.2
Weight empty, Kg	11.57	9.68
Window dimensions cmxcmxcm	9.4x2.0x0.56	7.12x1.96x0.56
volume cm^3, app.	10	8
Average internal volume, cm^3	2595.8	

One pair of tappings is connected to the manometer M_2 (normally 30 cm tappings) and the other is closed off with nylon caps. To avoid any carry-over of sand in the effluent, the end connections are provided with a pelyethylene/stainless steel 70 micron pore filter. This pore size is smaller than the minimum particle size in the sand. The polyethylene filter was changed for every run on lighter oils, particularly Kerosene and Furnace oil.

Deaeration and Saturation Section

The deaeration and saturation set-up consists of an oil reservoir, a liquid separator and a vacuum pump connected to the core holder. The Oil Holding vessel is a 4.96 cm (ID) x38.5 cm (L) glass cylinderical vessel designed to minimize the loss of lighter oils. This vessel can be isolated from the rest of the set-up by means of a stainless steel isolation valve. The vessel is elevated above the core-holder to facilate saturation, particularly when the vacuum has been lowered to such an extent that saturation proceeds very slowly. The deaeration and saturation set-up is provided with a vacuum gage and a manometer which can be isolated during the displacement. Also, all other connections from the feed pump and the fraction collector can be closed. The Liquid Separator is a 15.6 cm(ID)x27 cm(L) vessel which prevents any liquid from going into the vacuum pump. The separator and the vacuum pump can also be isolated during saturation and displacement. The specifications of reservoirs, vessels and pumps are given in Tables 5 and 6.

Displacement Section

The displacement section consists of water and surfactant solution reservoirs and feed pump connected with the core-holder via associated piping and valves. Two manometers are provided for the feed pump discharge and across two points on the core-holder. The reservoirs are 19 cm(ID)x 54 cm(L) and 19 cm(ID)x28 cm(L) vessels having holding capacities of approximately 15 and 8 litres. The feed pump draws liquid from the vessel and transports it either to the core-holder or back to the vessel. This is achieved by two stainless steel valves in each of the lines. There is a manometer and a pressure gage on the main discharge line which permits measurement of the pressure upstream of the core-holder. The pressure drop across two points on the core-holder during a displacement run is measured by a manometer which can be connected to the tappings at the 15 cm and 30 cm positions. The progress of the displacement can be observed through the two glass window on the core-holder. The effluent from the displacement equipment goes to a calibrated collector.

Collection and Analysis Section

The fraction collector permits the collection of the effluent in 16x100 mm tubes (volume=10ml). If cummulative recovery is desired, the effluent goes to a 100-ml flask.

TABLE 5

RESERVOIRS AND VESSELS

	V-1	V-2	V-3
Fluid	oil	water	surfactant solution
Inside diameter, cm	4.96	19.0	19.0
Length, cm	38.5	54.0	28.0
Cross-sectional area based on I.D, cm^2	19.3	283.5	283.5
Volume, cm^3	743	15,311	7,940
Material of construction	Glass	Plexiglass	Plexiglass

TABLE 6

PUMPS

	P-1	P-2
Type	Positive Displacement	Vacuum
Model	DC-1-30R Milroyal Simplex Model D	1405
Supplier	Milton Roy Company	Welch Sci. Co.
Capacity	1230 mℓ/hr	35 lit/min. (free air)
Discharge Pressure	70.0 Kg/cm^2	$5x10^{-5}$Torr Hg
Temperature	Ambient	Ambient
Suction Pressure	Flooded	-
Suction/Discharge Connection	$\frac{1}{8}$" / $\frac{1}{8}$"	$\frac{1}{2}$" ID/-
Capacity Control	stroke adjustment by micrometer	-

In either case, volumes of oil and aqueous phases are known as a function of time. An International Centrifuge determines the volume of both the phases.

B. OILS, SURFACTANTS AND SAND

Typical specifications of the oils and the lignosulfonates which were employed in this study are given in Tables 7 to 9. The sieve-analysis of the Ottawa sand is shown in Table 10.

Viscosity measurements were carried out using Cannon-Fenske and Brookfield viscometers; density using a precision densitymeter DMA 02C. The surface/interfacial tensions were determined using a Fisher Autotensiomat (Model 215). The autotensiomat operates on the classical du Nouy ring method. The glassware and the ring for the Autotensiomat were cleaned as per ASTM designation D1331 and D971. These data were obtained for a temperature of 25°C and are shown in Table 13 and plotted in Figures 24-27. The real density of the sand was measured using a specific gravity bottle. The details of tensiometer, fraction collector, centrifuge and viscometer are given on pages 39-40. The specifications of chemicals are shown on page no. 41.

TABLE 7

TYPICAL OIL SPECIFICATIONS

Oil Specifications	Kerosene	Furnace Oil	Fuel Oil No.4
Gravity, °API	46.5	34.5	27.0
Specific Gravity 15°C/4°C	0.796	0.85	0.89
Flash (PMCC), °C	-	52	85
Colour	-	Dyed Blue	-
Pour point °C	-	-1	-4
Sulfur, wt %	-	0.3	1.0
Viscosity Cp @ 25 °C	1.6	2.2	16
CCR-10% BTMS,%	-	0.02	-
Kcal/kg	-	10,930	10,750
Distillation °C			-
IBP	186	160	
10%	-	188	
50%	-	266	
90%	-	332	
FBP	212	366	

TABLE 8

LIGNOSULFONATES

PHYSICAL CHARACTERISTICS

Lignosulfonate / Specifications	Marasperse C-21	Marasperse N-22
Usual form	powder	powder
Bulk density kg/M^3	560-640	560-640
Moisture content (Max. % H_2O)	7.5	7.0
Color	Brown	Brown
Solubility in Water (%)	100	100
Solubility in oils and most organic solvent (%)	0	0
Surface tension, 1% Solu. (dynes/cm)	49.4	52.8

TABLE 9

LIGNOSULFONATES

TYPICAL ANALYSIS*

Lignosulfonate / Specification	Marasperse C-21	Marasperse N-22
pH - 3% solution	7.0-8.2	7.5-8.5
Total sulfur as (s), %	6.8	7.3
Sulfate sulfur as (s), %	0.3	1.0
Sulfite sulfur as (s), %	0.09	0.12
CaO, %	5.2	0.55
MgO, %	0.3	0.30
Na_2O, %	6.1	13.2
Reducing sugars, %	1.5	0.8
OCH_3, %	7.9	7.7

* Moisture free basis

SAND

Standard, graded Ottawa sand supplied by Canlab Supplies Ltd. ASTM Designation C-190

TABLE 10

SIEVE ANALYSIS*

Mesh size (US)	Tyler Designation	Wt. %
20^+	20^+	zero
30^+	28^+	2.1
40^+	35^+	25.8
50^+	48^+	50.5
60^+	60^+	12.1
80^+	80^+	8.6
100^+	100^+	0.8
120^+	115^+	0.1
120^-	115^-	0

---

* Using a protable sieve shaker (Model RX-24) W.S. Tyler Co. of Canada Ltd.

TENSIOMETER

Fisher Model 215 Autotensiomat$^{(R)}$ supplied by Fisher Scientific Company, Ottawa.

Range	0 to 100 dynes/cm
Sensitivity	0.02 dynes/cm
Readout	Analog Panel Meter and Potentiometric Recorder
Recorder	0.02 dynes/cm on 0-5 dynes/cm range
Precision	0.25% Std. deviation
Relative Accuracy	± 2%

FRACTION COLLECTOR

Buchler Fractomette Alpha 200 supplied by Canadian Laboratory Supplies Ltd., Ottawa.

Capacity	20 test tube racks each holding 10 tubes (13-18 mm D-D)
Collection System	Time, drop, volume

CENTRIFUGE

International Centrifuge, Model HN-S supplied by International Equipment Company, USA.

VISCOMETER

Brookfield Synchro-lectric Viscometer, Model LVF with the Brookfield VL Adapter supplied by Brookfield Engineering Laboratories Inc., USA.

SPECIFICATIONS OF CHEMICALS

OILS

1. Toluene

Certified ACS, Fisher Scientific Co.

2. Kerosene

Shell 140 Kerosene, untreated, containing aromatics. The kerosene was filtered before use to remove suspended particles.

3. Oil No. 2 and oil No. 4

Esso Furnace Oil (Fuel oil No. 2) and fuel oil No. 4 meet the specifications of Canadian Government 3-GP-2d Type 2 (ASTM D-396 Type 2) and 3-GP-2d for type 4 (ASTM D-396). Representative specifications are shown in Table 7. The actual density and viscosity are given in Table 13.

4. Sodium Chloride

Crystal, 'Baker Analysed' Reagent.

5. Hexadecyl Trimethyl Ammonium Bromide

'Baker Analysed' Reagent. Actual Lot Analysis:

Assay ($CH_3 (CH_2)_{15} N (CH_3)_3 Br$)	99.8%
Insoluble matter	0.008%
Residue after ignition	0.03%

C. EXPERIMENTAL PROCEDURE

The experimental procedure for a typical run involved the following three steps:

1. Preparation: This included dismantling and cleaning of the core-holder, reservoirs, associated piping and valves followed by remounting of the equipment in the flow system.
2. Displacement: This included deaeration and saturation of the sand followed by displacement of the oil using an aqueous solution.
3. Collection: This included the collection of effluent from the core-holder and analysis of the incoming and outgoing streams.

These steps are described in more detail below.

Preparation

The core-holder from the previous run was dismantled, removed to the cleaning area and the flanges were opened to permit removal of the sand. Since the sand always contained some residual oil, the cleaning was performed in a cleaning drum (capacity 45 gallon) provided with a drain near the bottom and a water-hose connection. This sand was thoroughly washed so that it was nearly stripped off its oil content. The core-holder and the flanges were cleaned with a detergent using a brush followed by repeated washings with cold and warm water. The core-holder was kept under running warm water hose for about half an hour followed by rinsing with distilled water. The core-holder was held on a stand and air was passed through it to allow it to dry. The sand was disposed of after it was dry.

The clean and dry core-holder and flanges were assembled and the core-holder was weighed empty. The core-holder was then filled with sand starting from one open end with repeated tapping of the holder so that the packing was uniform throughout the length of the core-holder. The core-holder was then weighed to check the amount of sand packed. The core-holder was ready for hook-up after replacing the flange on the filling end.

The water reservoir was cleaned and connected to the feed pump. The piping on the upstream and downstream ends of the core-holder were cleaned with toluene, then with hot water, for about half an hour and finally with distilled water. It was subsequently dried with air. The core-holder was hooked up to the rest of the equipment with isolation valves V7 and V9 closed (Fig. 3).

2. Displacement

This step involved deaeration, testing for leakage, saturation and introduction of the displacing fluid, water or surfactant solution.

Deaeration

The vacuum pump was started 2-3 hours prior to the starting of deaeration with valves V15 and V10 open and V9 and V11 closed. The barometric pressure and the room temperature were recorded. The core-holder was connected to the vacuum system by opening V7 & V9 and keeping all other valves (V4, V5, V6, V13 & V14) closed. The vacuum pump was allowed to run for several hours so that it would stabilize and draw nearly all the air out from the pores of the sand. Complete deaeration was verified by the manometer reading M3 and the barometric pressure.

Leakage Test

To ensure that leakage of air, on isolation of the core-holder from the vacuum pump, may be within the acceptable limit, a leakage test was performed before each run. This involved closing valve V10, keeping V9 open and reading manometer M3 every minute. A typical leakage test is shown by the vacuum vs time data as given in Table 21. If leakage was observed, the column would be pressurised and tested for leakage to locate the cause. This was generally located at the end flanges and was due to a loose or distorted 'O'-ring.

Saturation

To saturate the core-holder with the oil, valve V7 was opened while V4, V10, V11 remained closed. The saturation was completed in about fifteen to forty minutes and the progress of saturation was observed through the sight-glasses near each end of the core-holder. The completion of the saturation was also ensured by letting in a known oil volume, equal to the pore volume plus that of the associated piping. A steep fall in the rate of saturation (approaching zero) indicated complete saturation of the bed.

Displacement

The feed pump was set at 25% stroke length and put on recirculation to achieve a steady flow rate. Valves V5, V15,V10 were closed and the feed pump was switched on to the core-holder from recirculation by opening valve V4. The effluent was collected in the fraction collector or in a 100-ml flask. The manometer readings M1(and M2)were noted every half an hour and the times for water breakthrough and the first appearance of oil were recorded. The displacing fluid equivalent of 2-3 pore volumes was injected for each displacement run. Thereafter the flow from the feed pump was diverted to the Reservoir in line and the core-holder was isolated, ready either for a tertiary run or for dismantling and cleaning for the next run.

3. Collection and Analysis

The effluent from the core-holder was collected in 10 ml-tubes or 100 ml-volumetric flasks. If the effluent after breakthrough was an emulsion, the volumes of oil and aqueous phase were measured separately after breaking the emulsion. For system of fuel oil No. 4 and Marasperse, the oil from 100 ml effluent was separated using 0.03M hexadecyl trimethyl bromide. The amount of demulsifier varied depending on the concentration of the lignosulfonate.

CHAPTER 4

THEORY

THEORY

The displacement of oil from a porous medium by water, or by a surfactant solution, plays an important role in the production of petroleum by secondary or tertiary schemes. In the natural-water drive, too, where the water from large adjoining aquifers expands and thereby fills the pores of the stratum, displacement is a fundamental process. Efficient recovery of oil demands knowledge of this displacement mechanism as well as the physical characteristics of the reservoir. This knowledge can then be applied to choose the most suitable process which would yield maximum possible ultimate recovery. The following factors may influence the recovery of oil:

- the characteristics of the production formation such as porosity, permeability, uniformity, wettability and structural configuration;
- the properties of the reservoir oil including its viscosity, density and type;
- residual oil saturation;
- the well conditions and structural location;
- experience of and controls exercised by the reservoir engineer and production personnel in the development and operation of the field.

The rate at which oil is recovered in its initial stages of production from a reservoir has a significant influence on whether enhanced recovery methods will yield efficient rates of production. The production rate during early stages of recovery should not exceed the maximum efficient rate (MER) which is the highest rate than can be sustained for an appreciable length of time and which, if exceeded, would lead to uneconomical secondary or tertiary processes.

The performance of secondary recovery processes is governed by many factors including those which can be externally controlled. These include injection rate and the addition of chemicals to achieve uniform flooding. High rates of injection of the fluid may not necessarily yield economical maximum ultimate-recovery even when coupled with a tertiary run. The economics of each of the injection processes will show the most desirable enhanced oil recovery program. The study of the displacement mechanisms in the injection processes are important and are discussed below for secondary and tertiary stages of recovery.

Secondary Recovery

The amount of oil-recovered during water-flooding is a function of the following efficiency factors[27]

1) Areal sweep efficiency
2) Contact factor
3) Displacement efficiency.

These factors, based on homogeneous pore structure, explain why there remains some residual oil after a water-flooding operation. Attempts are made to improve these factors in order to increase the recovery of the remaining oil.

Areal Sweep Efficiency, E_a

Areal sweep efficiency is the fractional area of a pattern that is swept by water. Fig. 5(a) shows a 5-spot pattern where water has swept an area A_{SB} and breakthrough occurs at the production well. E_a is then defined as $\frac{A_{SB}}{A}$. In real situations areal sweep efficiency of a waterflood depends on the following factors:

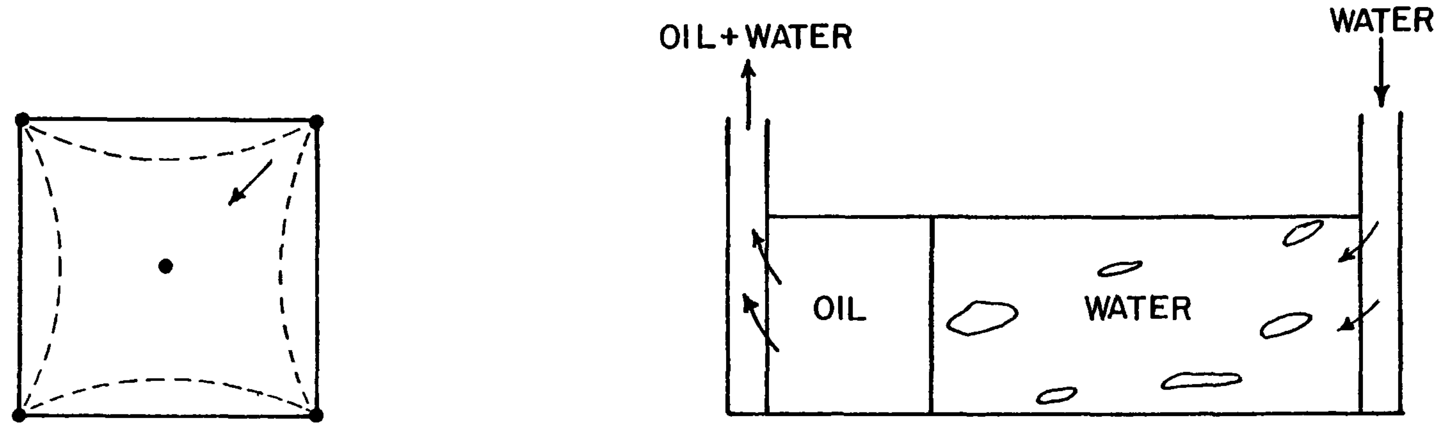
- Mobility ratio
- Distribution of porosity and permeability
- Relative permeabilities and capillary-pressure
- Geometry of the well-pattern and the reservoir
- Injection and production rates.

Mobility Ratio

Mobility ratio, M, is defined as (mobility of injected fluid)/(mobility of displaced fluid) or

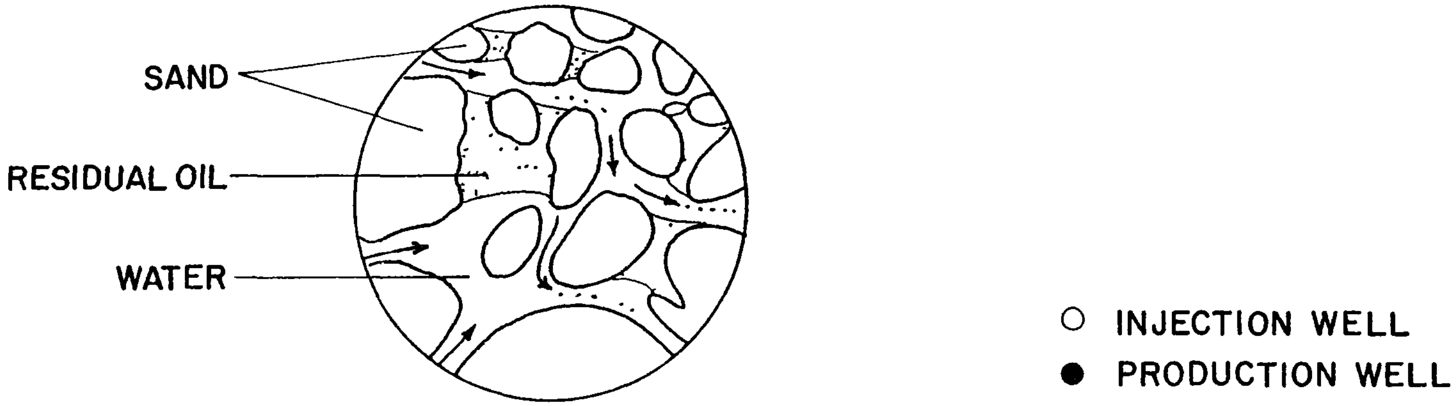
$$M = \frac{k_w/\mu_w}{ko/\mu o}$$

A value of one for M means that injected water and produced oil have the same ability to flow through the reservoir. With higher values of M, the ability of water to flow becomes greater than that of oil. Fig. 9 shows the effect of mobility ratios on areal sweep efficiency for a 5-spot injection pattern.(27) The fraction of the area swept



(a) AREAL SWEEP EFFICIENCY

(b) CONTACT FACTOR



(c) DISPLACEMENT EFFICIENCY

FIG. 5 WATERFLOODING EFFICIENCY

for a given mobility ratio is shown at breakthrough and at increasing water-cuts of the produced fluid. Table 11 shows the effect of mobility ratio on sweep efficiency for the case of water-breakthrough and 95% watercut.(27)

TABLE 11

EFFECT OF MOBILITY RATIO ON AREAL SWEEP EFFICIENCY

Mobility ratio	Sweep area at water breakthrough	Sweep area at 95% water-cut
10	0.35	0.830
2	0.58	0.970
1	0.69	0.980
0.5	0.79	0.995
0.25	0.90	0.998

At higher mobility ratios, the injected fluid (water or surfactant solution) tends to move through the oil instead of pushing it through the pores of the medium resulting in frontal instability which gives rise to the formation of "viscous fingers". In any oil-recovery process involving displacement by a fluid, therefore, low mobility ratios are desirable. Mobility ratios close to one are considered favorable and values of ten or greater are considered unfavorable. For homogeneous strata, increase in areal sweep efficiency results in higher recoveries and the mobility ratio can be improved either by increasing the viscosity of the injected fluid (polymer flooding) or by decreasing the viscosity of the reservoir oil (thermal methods).

Contact Factor

Contact factor(27) is the fraction of the swept volume that has been contacted by the injected fluid.

$$\text{Contact factor} = \frac{\text{Reservoir volume contacted by water}}{\text{Total reservoir volume swept}}$$

Fig. 5(b) shows the cross section of the reservoir with advancing oil bank followed by the injected fluid. The reservoir volume, although swept by the fluid, has not been completely contacted. Islands of oil are left intact due to heterogeneities in the reservoir including permeability variations, faulty structure and shale barriers. Most reservoirs have contact factors in the range of 75-90%. A sand reservoir will have a contact factor approaching 100%. Improvement in the contact factor, in cases where variation in permeability is the cause of low values, can be achieved by lowering the mobility ratio during the tertiary stage of the recovery process. The oil trapped in regions where the injected fluid does not penetrate is obviously not recoverable. The performance of the reservoir during waterflooding provides insight into the reservoir heterogeneities and, therefore, the contact factor. On the basis of this information, the feasibility of tertiary recovery operation can thus be evaluated.

Displacement Efficiency

Displacement efficiency (E_d) is the fraction of initial oil saturation (i.e., before waterflooding) that is displaced from the reservoir during waterflooding.

$$\text{Displacement efficiency } E_d = \frac{\text{Initial oil saturation-Residual oil saturation}}{\text{Initial oil saturation}}$$

Figure 5(c) shows a part of the reservoir which has been swept and contacted but not all of the oil has been displaced. This unrecovered oil is left in the pores as microscopic droplets and/or macroscopic "ganglia".

Displacement efficiency can be determined from laboratory results of water-flood experiments on core samples and gives the average residual oil saturation. Since there are large portions of the reservoir that have not been contacted, recoverable oil volume will depend on both areal sweep efficiency and displacement efficiency. The factors which affect the displacement efficiency are

- Initial saturation conditions;
- Fluid viscosity ratio;
- Relative permeability ratios;
- Capillary pressure;
- Reservoir pressure and fluid properties.

At extremely low rates of displacement, where frictional factors are negligible, the displacement efficiency is controlled to a large extent by the balance between capillary and gravitational forces. Capillary forces, which lead to displacement of oil by water, can also cause oil to be retained. Fig. 6 shows an idealised capillary model that explains why residual oil is left in the pores.(29) The oil in two pores of different radii is displaced with salt water. The walls of the pores are coated with salt water originally present in the pores. As the displacement proceeds, the oil in the larger pore is the first to be displaced and the pores become filled with water. Two cases arise: either the oil and water have equal viscosities or the oil is the more viscous. In the first case, the progress of displacement is such that much oil is produced before water breakthrough occurs in the larger pore. A small amount of oil is recovered even after breakthrough. In the second case of oil being less mobile, the oil in the larger pore moves even faster than before because the resistance decreases as water penetrates the larger pore. A larger amount of water is produced before all the oil is recovered. Fig. 7(a)(29) shows another model where the constrictions of three capillaries at the main capillary are important since the capillary pressure which holds the oil and prevents it from getting displaced is higher than the pressure gradient available. This oil is "punched" off in the small constriction and represents the residual oil recoverable in the tertiary stage.

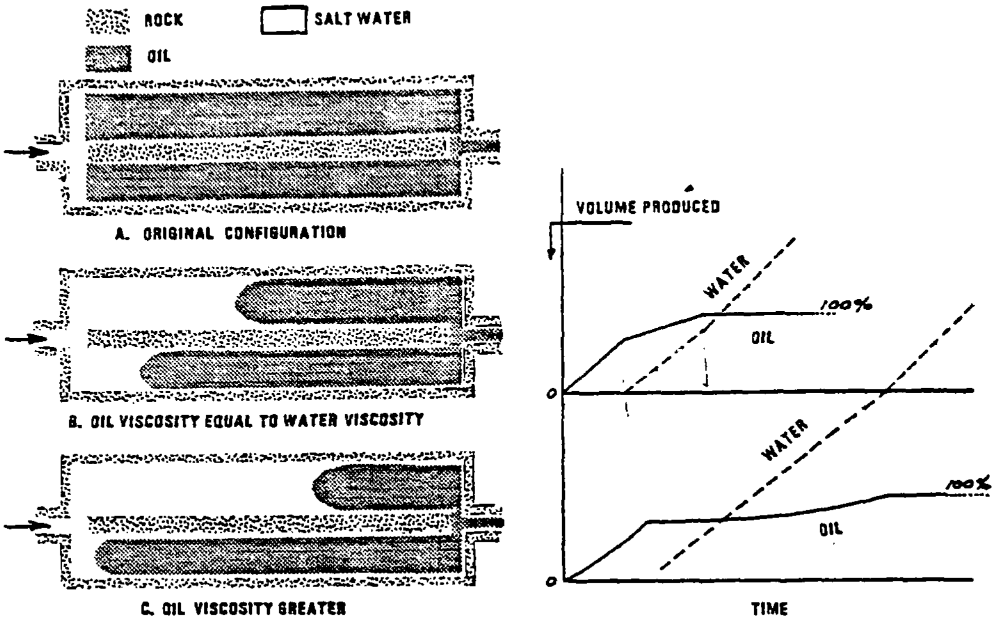


Fig. 6 Water Displacement of Oil in an Ideal Pore Model of Parallel Capillaries (29)

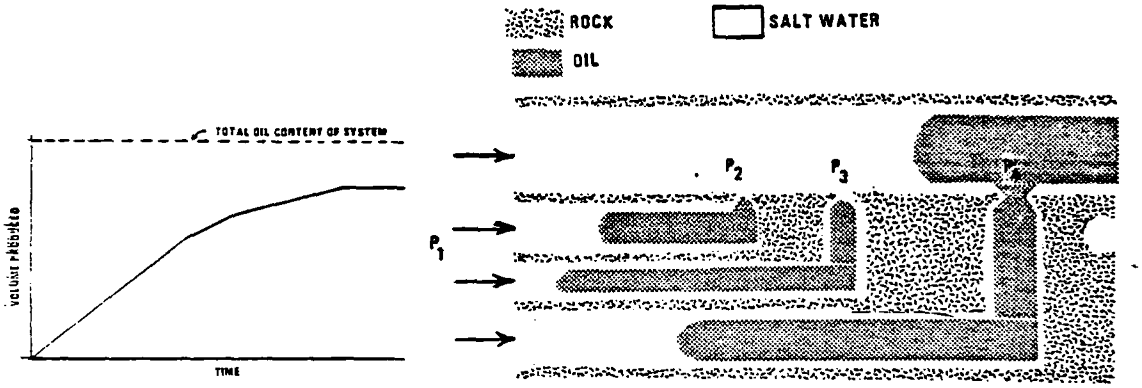


Fig. 7a Water Displacement of Oil in Capillaries in Parallel, Two of Which are Constricted and Therefore Bypassed (29)

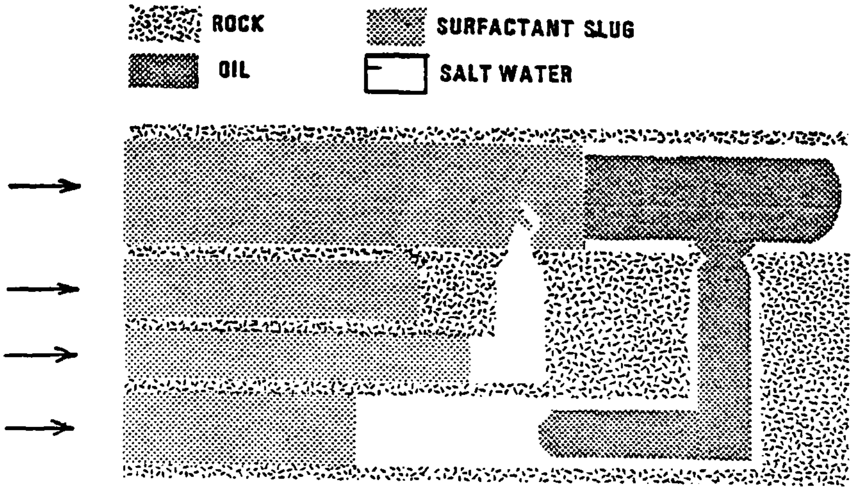


Fig. 7b Tertiary Recovery Using a Surfactant (29)

Tertiary Recovery

Tertiary recovery methods are designed to recover the residual oil which remains after waterflooding of a reservoir is discontinued. These methods are designed to improve areal sweep efficiency, contact factor and displacement efficiency. The performance of waterflooding and the recovery therefrom indicate which of the above factors is responsible for low recovery and, therefore, which of tertiary recovery methods should be applied. The mobility ratio provides some information about the sweep efficiency while rock characteristics provide information about the extent of heterogeneties. Most important of all, however, is to determine the displacement efficiency, during waterflooding that is the residual oil saturation after the water flood. One way to estimate the residual oil saturation is to drill a core from the stratum as a representative sample and conduct an analysis thereon. This is coupled with tracer surveys and logging methods to determine accurately the residual oil saturation.(34)

The areal sweep efficiency for a well-pattern can be improved by the judicious choice of displacing fluid (one which produces a favorable mobility ratio). In some reservoirs, this leads to an improved contact factor but, usually, the contact factor is assumed to be the same during a tertiary recovery operation as during the preceding secondary recovery. Since the residual oil after waterflooding is held in pores by capillary forces, any tertiary method aimed at recovering this oil should attempt to reduce these capillary forces between the oil and water and thereby release the oil. The capillary force is a function of interfacial tension, and the use of surfactant to reduce the interfacial tension between the oil and water increases the recovery. Fig. 7(b) shows how the surfactant solution displaces the oil from the constrictions under available field pressure. Micellar solution flooding gives good displacement efficiency and sweep efficiency. It therefore displaces most of the contacted reservoir oil. Favorable mobility ratios using the proper composition in the surfactant slug and drive water lead to high sweep efficiencies. Since the micellar solution is itself displaced by another displacing fluid, the mobility ratio between the two becomes an important factor too. If water is the displacing fluid, it may lead to reduced sweep efficiency and water fingering through the advancing micellar solution slug ahead of it. The slug then becomes diluted and hence loses its recovery effectiveness.

Micellar Solution Flooding Process

In this flooding process a volume of micellar solution is injected to form a slug in the reservoir. This slug, because of its ability to release the oil, moves through the reservoir with an oil/water bank ahead of it. The micellar slug is followed by a bank of polymer-thickened water to inhibit fingering. The concentration of polymer is then reduced until, at its end, only drive water is injected.

The micellar slug composition for any tertiary operation depends upon the following factors

1. Composition, type and characteristics of crude oil.
2. Composition of connate water associated with oil.
3. Type of porous media.
4. Adsorption of the chemicals in the porous medium.
5. Thermal degradation of the chemicals at the reservoir temperature.
6. Recovery of the surfactant, co-surfactant in the presence of metal ions.

Apart from the surfactant, the other components of a micellar slug are co-surfactant and electrolyte. A co-surfactant, normally an alcohol, helps in adjustment of viscosity, solubilises more oil and water, stabilises the solution and reduces the adsorption of the surfactant on the rock. Electrolyte helps in adjusting the viscosity. Sodium chloride or ammonium sulfate are normally used in low concentrations. The overall composition varies widely depending on the above factors. The range of composition of a micellar solution is typically:(27)

Surfactant	4-10%
Hydrocarbon	4-80%
Co-surfactant	about 4%

Electrolyte	about 1%
Water	10-92%

The characteristics and type of oil determine the success of any micellar flooding process. For a low-gravity, high-viscosity crude, the operation may not be ecnomical since the viscosity adjustment of the micellar and drive-water slugs would lead to high costs. For each crude oil and brine system in a reservoir, the selection of surfactant, co-surfactant and electrolyte has to be such that the oil/aqueous phase interfacial tensions are ultra-low, generally between 10^{-2} and 10^{-4} dynes/cm or less.

The composition of the connate water affects the recovery since the interfacial tension of oil and water is affected by the presence of sodium chloride. For example, it is reported(20) that in the absence of co-surfactant, lower interfacial tension is obtained at 2% than at 1% NaCl. The action of the surfactant is also affected by the presence of calcium and magnesium cations in the connate water. The selection of the most effective slug, therefore, depends upon the tolerance which each of the components in the slug possesses towards the metallic cations present in the connate water.

The micellar flooding technique is particularly applicable to sandstone reservoirs since such reservoirs are not associated with water containing excessive calcium or magnesium ions. Its use in carbonate reservoirs is limited since adsorption of the surfactant is usually high whence the slug loses its effectiveness.

Since the cost of the chemicals involved in a micellar slug is high, the recovery of these chemicals becomes very important. Any attempt leading to a reduced loss of surfactant would make micellar process economically more attractive.

Wettability

Another factor which affects the recovery of oil is the wettability of the reservoir rock. Wettability of the rock with respect to water or oil has a profound influence on residual oil saturation, capillary pressure, relative permeability etc. The reservoir rock may be completely water-wet, completely oil-wet, or may exhibit mixed or intermediate wettability. Wettability is defined in terms of the contact angle between the fluid and the solid surface which it wets. The knowledge of reservoir wettability plays an important role in the choice of improved recovery processes. The microscopic continuity of oil is governed by the wetting properties of the reservoir rock acquired during the geological formation of the oil reservoir. Wettability measurements have been performed in laboratories using original rock samples and core fluids under simulated reservoir conditions.(30) Laboratory waterflood results(30) have shown that in mixed-wettability cores, the oil saturation continued to decline as long as water was injected. The water-wet core for the same oil showed that the oil saturation quickly reached a constant value. An early breakthrough of water occurs followed by continuous production of oil in the case of strongly oil-wet reservoirs. In this case, considerable residual oil saturation remains after extended flooding and much of this residual oil (wetting phase) is retained by capillary forces in the smaller pores and at grain contacts. Treiber et al(31) have reported the wetting characteristics of oil producing reservoirs. The results obtained by contact angle measurement indicate that the majority of the reservoirs tested are moderately oil-wet. Different types of wettability can result in wide variations in the residual oil saturations after waterflooding and knowledge of this helps in evaluating a tertiary recovery process. In some mixed wettability systems the residual oil saturations will be higher(30) than those measured for either a uniformly water-wet or uniformly oil-wet system. Studies on wettability characteristics have indicated that the preferential wetting of a reservoir rock is largely controlled by compounds adsorbed at the rock surface. This explains(30) the mixed wettability condition existing in some reservoirs. As oil accumulates in the reservoir, it displaces the water present initially from the larger pores while the smaller pores retain water because of capillary forces. The mixed wettability condition could develop over long periods of exposure if some organic material from the oil were deposited onto the rock surfaces. This is supported by evidence since most crude oils have been found to contain surface active materials.

For high oil-recovery, strongly oil-wet paths along pore surfaces are necessary(30) for oil to drain. If the points of contact between particles contain connate water rather than oil, the displacement will lead to early water breakthrough. The mineral composition of the rock has been reported(30) to affect the drainage of oil from mixed wettability laboratory cores.

Adsorption and Retention of Sulfonates

Adsorption and retention of sulfonates on the reservoir rock are two of the major problems in micellar flooding processes. Both of these problems lead to reduced concentration of the surfactant and hence to a reduced ability to recover the oil. This affects the profitability of its application to a reservoir. The cost of micellar solutions tends to follow the price of crude oil and any loss of surfactant would alter the profitability. The factors(20) affecting the adsorption are the equivalent weight of the surfactant, the nature of the micellar slug-oil system, composition of reservoir fluids, mineralogy of rock structure, flooding rate and reservoir temperature.

Use of Lignosulfonates

Lignosulfonates are wood-based chemicals made from the sulfite liquor generated during the sulfite process of wood pulping. Sulfite liquor contains a mixture of sulfonated lignin, polysaccharides and wood sugars. Lignosulfonates are water soluble, anionic surface active derivatives of lignin.

The properties of commercial lignosulfonates can be adjusted with respect to sulfonate content, molecular weight, kind and amount of cation and surface activity, etc.

Marasperse(R) products, used in the present study, are the purest lignosulfonates available and are made by the American Can Company. The basic functional constituent of the Marasperse products is lignosulfonate which is an anionic polyelectrolyte having a molecular weight between 1,000-20,000. The organic structure of lignosulfonate has not been completely determined but the basic lignin monomer unit is a substituted phenyl propane. Fig. 8 shows the structure of a section of lignosulfonate.(32) The complex structure of lignosulfonates makes them completely insoluble in oils. The molecular weight and degree of sulfonation governs the extent of electrical change of the system under consideration. The type of metallic ions in the Marasperse affects the properties of the Marasperse as shown in Tables 8 and 9.

Marasperses as Emulsifiers

Marasperse-stabilised emulsions(33) remain stable under extreme pH variations although some coarsening of the emulsion may take place. The presence of electrolytes such as sodium chloride, sodium sulfate and sodium phosphate does not appreciably affect the stability of these emulsions. On the other hand, a small amount of sodium hydroxide enhances the activity of Marasperse solutions. The electrolyte and sodium hydroxide tend to lower the interfacial tension in the emulsion, rendering it more stable. Some alcohols have

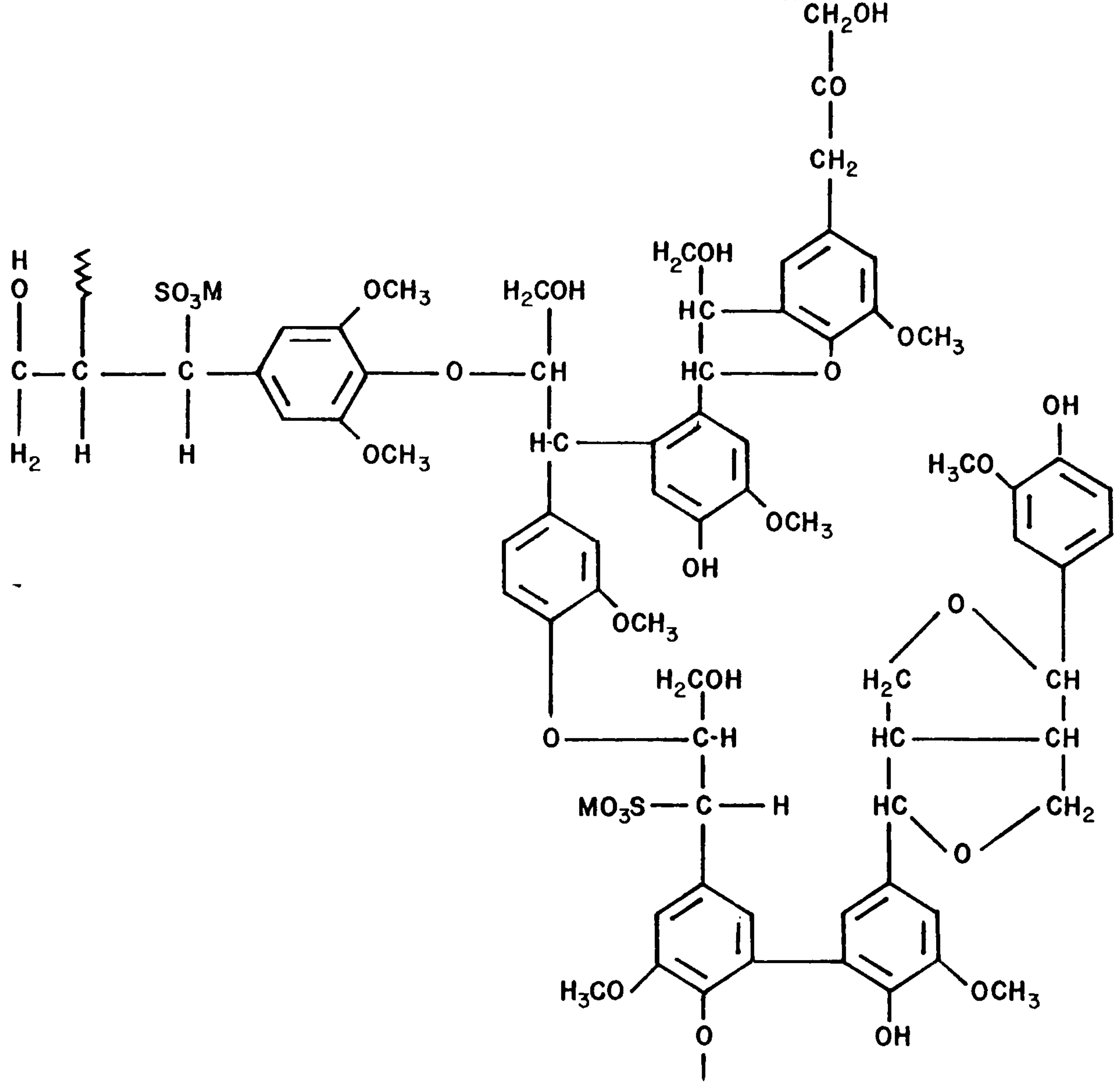


FIG. 8 STRUCTURE OF A SECTION OF LIGNOSULFONATE

been found to assist in the preparation of emulsions by lowering interfacial tension. Since Marasperses are insoluble in oil, addition of alcohol in small amounts to the marasperse solution helps in emulsification. Marasperse-stabilised emulsions are not adversely affected by mechanical handling during operations such as pumping. Since they tend to be rather more stable after such operations, the handling should, in fact, be minimised so that the resulting emulsion can be broken easily. Marasperse-stabilised emulsions are resistant to temperature variations and will remain stable in pressurised systems at 110°C or higher.(33)

Since Marasperse do not sufficiently lower interfacial tensions in oil-water systems, the addition of some other chemicals is necessary to achieve high recovery rates comparable with conventional petroleum sulfonates. However, the addition of conventional surfactants is not recommended(33) for this purpose. Instead, addition of sodium hydroxide and inorganic electrolytes has been suggested. The degree of lowering of interfacial tension desired will depend on the particular oil-water system.

Demulsification of Marasperse-stabilised Emulsions

Since the Marasperse-stabilised emulsions are quite stable, the conventional methods of breaking emulsions are not entirely effective. The most effective way to nullify the action of Marasperse is by addition of a cationic surface active agent. Small amounts of quarternary amonium compounds have been found effective in breaking the emulsion and, in the present work, hexadecyl trimethyl ammonium bromide was chosen for this purpose.

Mechanism of Stabilisation of Emulsions by Marasperse

Marasperse solutions may be regarded as sub-colloidal, high molecular weight polyelectrolytes. Unlike other colloidal electrolytes, they do not exhibit micelle formation tendency and do not possess a hydrophobic-hydrophillic molecular structture. The emulsification and stabilisation mechanisms, therefore, are different from those of conventional surfactants. Since the oil is present in the form of a subdivided phase in the pores of the reservoir, the emulsification takes place when the oil is displaced from these pores by the injected Marasperse solution. The stabilization of the emulsion is the result of adsorption of Marasperse at the oil-water interface. This establishes the following:

- an electrokinetic charge
- a semi-rigid film

The Marasperse molecules in the solution are highly charged and cover the entire surface at the oil-water interface

The charge associated with these Marasperse molecules is considerably stronger than that observed in the usual double layer effect. Also, the zeta-potential associated with the oil-water interface of the emulsion droplet is greater than with the soluble surface-active agents. The surface of the emulsion droplets, having adsorbed sufficient Marasperse, assume a double layer structure and consequently the electrical properties are exhibited by the Marasperse molecule in the solution. This separation of high charge leads to stabilisation of the emulsion of oil in the aqueous phase. For a given pore volume, the smaller the pore size, as in oil reservoirs, the higher would be the area of contact between the oil and water phases and hence more stable would be the emulsions.

When the concentration of Marasperse is increased, the Marasperse molecules are packed closer together and are forced into the interface. This explains why reduction in interfacial tension is observed at increased concentrations until, at a certain value ($\sim$10%), it becomes constant. If the concentration becomes such that the Marasperse is salted out, the electrokinetic effects vanish. These electrostatically inert Marasperse particles also stabilise the emulsion.

The action of sodium hydroxide is two-fold.(10) Firstly, it increases the zeta-potential and, therefore, the dispersing tendency of the Marasperses. Secondly, it enhances the surface activity of the Marasperses by increasing their amphipathic properties.

Flow of Fluids Through Porous Medium

The flow of a fluid in a porous material for creeping flow conditions is defined by Darcy's law. If horizontal linear flow of an incompressible fluid is established through a sample of porous material, of length L in the direction of flow, and of cross-sectional area A_c, under an applied pressure differential ΔP, then

$$\frac{q}{A_c} = \frac{K}{\mu}\left(\frac{\Delta P}{L}\right) \tag{4.1}$$

This is Darcy's law and it relates the flow of the fluid to the applied pressure gradient by 'K', the fluid conductivity of the porous material, which is called the permeability. It is the property which characterizes the ease with which a fluid can flow through the pores of the medium. It is roughly a measure of the mean square pore diameter and is determined by the structure of the porous material. A material having a permeability of unit darcy would require a pressure differential of 1 atmosphere for a fluid of viscosity 1 centipoise to flow through a cube having sides 1 centimeter in length at the rate of 1 cubic centimeter per second. Permeability (k) of a medium can be determined by establishing creeping flow of a known fluid in the medium (of known length and area) and then measuring the pressure drops for given flow rates. Darcy's law is not valid for inertial or turbulent flow. The range for creeping fow is defined in terms of the Reynolds number. In sands and sandstones, the transition from creeping to non-creeping flow occurs for Reynolds number between 1 and 10, where:

$$Re = \frac{q\rho\delta}{\mu A_c \phi} \qquad (4\text{-}2)$$

The grain diameter, δ, is employed as a measure of pore diameter since it is generally difficult to define the channel diameter of a porous material.

The application of Darcy's Law has been extended to the displacement of oil from petroleum reservoirs using water or aqueous solutions. Mathematical descriptions of secondary(35) (waterflooding) and tertiary(38) (surfactant system) processes have been formulated based on a one-dimensional, homogeneous rock system with uniform properties.

The displacement of oil by a fluid (immiscible with oil) as in natural-water drive and secondary-water flooding is mathematically described by the Buckley-Leverett equation. This assumes low interfacial tension, so that effects of capillary-pressure can be neglected. Gravity effects are also neglected. For oil and water, from Darcy's Law, we have

$$q_w = - \frac{K_w A_c}{\mu_w} \left(\frac{\partial p_w}{\partial x} \right) \tag{4.3}$$

and

$$q_o = - \frac{K_o A_c}{\mu_o} \left(\frac{\partial p_o}{\partial x} \right) \tag{4.4}$$

where the capillary pressure is defined by:

$$p_c = p_o - p_w \tag{4.5}$$

For simultaneous flow of oil and water through the porous medium, the continuity equation for each phase yields

$$\frac{\partial q_w}{\partial x} = - \phi A_c \cdot \frac{\partial S_w}{\partial t} \tag{4.6}$$

and

$$\frac{\partial q_o}{\partial x} = -\phi A_c \cdot \frac{\partial S_o}{\partial t} \tag{4.7}$$

Also

$$S_w + S_o = 1 \tag{4.8}$$

Equations 4.6, 4.7 and 4.8 yield

$$\frac{\partial}{\partial x} (q_w + q_o) = o \tag{4.9}$$

so that the total flow rate

$$q = q_w + q_o \quad \text{is constant}$$

Defining the fraction, f_w, of the flowing stream which is water, by

$$f_w = \frac{q_w}{q} \tag{4.10}$$

and for oil

$$f_o = \frac{q_o}{q} = 1 - f_w \tag{4.11}$$

Equations 4.6 and 4.7 yield on combining with 4.10 and 4.11

$$\frac{q}{\phi A_c} \left(\frac{\partial f_w}{\partial x} \right) = - \frac{\partial S_w}{\partial t} \tag{4.12}$$

and

$$\frac{q}{\phi A_c} \left(\frac{\partial f_o}{\partial x} \right) = \frac{-\partial S_o}{\partial t} \tag{4.13}$$

Combining equations 4.3, 4.4 and 4.5,

$$q_o = \frac{-k_o}{\mu_o} A_c \left[\frac{-\mu_w q_w}{k_w A_c} + \frac{\partial p_c}{\partial x} \right] \tag{4.14}$$

Substituting

$$q_w = f_w \, q$$

and $$q_o = (1-f_w) q$$

yields

$$f_{w}= \frac{1 + \frac{k_oA_c}{\mu_o q}\left(\frac{\partial p_c}{\partial x}\right)}{1 + \frac{k_o\mu_w}{k_w\mu_o}} \tag{4.15}$$

For high total flow rates and/or low interfacial tensions,

$$f_w \simeq \left(1 + \frac{k_o\mu_w}{k_w\mu_o}\right)^{-1} \tag{4.16}$$

$$\text{i.e. } f_w = f\ (S_w, \frac{\mu_w}{\mu_o}) \tag{4.17}$$

Since viscosity ratio is constant, f_w is a function of S_w only. Therefore,

$$\frac{\partial f_w}{\partial x} = \frac{df_w}{dS_w} \cdot \frac{\partial S_w}{\partial x} \tag{4.18}$$

Equation 4.12 becomes,

$$\frac{q}{\phi A_c}\left(\frac{df_w}{dS_w} \cdot \frac{\partial S_w}{\partial x}\right) = -\frac{\partial S_w}{\partial t} \tag{4.19}$$

Since this equation is non-linear in S_w, the saturation distribution can be determined by numerical methods, i.e.

$$\frac{dS_w}{dt} = \frac{\partial S_w}{\partial x} \cdot \frac{dx}{dt} + \frac{\partial S_w}{\partial t} \tag{4.20}$$

For a fixed S_w at x=x(t),

$$\frac{dS_w}{dt} = o \tag{4.21}$$

and

$$\left(\frac{dx}{dt}\right)_{S_w} = -\frac{\partial S_w}{\partial t}\left(\frac{\partial S_w}{\partial x}\right)^{-1} \tag{4.22}$$

Equation 4.22 gives the advance of the saturation S_w.

Combining 4.19 and 4.22,

$$\left(\frac{dx}{dt}\right)_{S_w} = \frac{q}{\phi A_c} \frac{df_w(S_w)}{dS_w} \tag{4.23}$$

This is called the Buckley-Leverett equation. On integrating with respect to t,

$$x_{S_w}(t) - x_{S_w}(o) = \frac{Q(t)-Q(o)}{\phi A_c} \cdot \frac{df_w(S_w)}{dS_w} \tag{4.24}$$

$x_{S_w}(t)$ and $x_{S_w}(o)$ are the co-ordinates of the plane at which S_w exists at time t and zero respectively, and Q(t) and Q(o) are the cumulative total volumes passed through the system at times t and zero respectively. If K_o/K_w is known as a function of saturation S_w, $\frac{df_w(S_w)}{dS_w}$ can be evaluated for every saturation and hence the saturation distribution at any time t>o can be computed.

Definitions

The following terms have been used in this report and are defined in detail below.

Fluid Saturations

The saturation of a porous medium with respect to a particular fluid is defined as the fraction of the medium filled by the fluid in question. Thus, S_w, the saturation with respect to fluid w, is given by

$$S_w = \frac{\text{volume of fluid in the medium}}{\text{total volume of voids in the medium}}$$

For two fluids, w (wetting) and nw (non-wetting),

$$S_w + S_{nw} = 1$$

Saturation is a bulk property and does not take into account the relative distributions of the fluids within the porous structure of the material.

Capillary Pressure

Capillary pressure between two immiscible fluids is the discontinuity in pressure at the point of contact. It depends upon the curvature of the interface separating the fluids. This is given by

$$P_C = \gamma_{12}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Permeability/Relative Permeability

Permeability is the property of a porous material which characterizes the ease with which a fluid may be made to flow through the material by an applied pressure gradient. Permeability is the fluid conductivity of the porous material. Darcy's Law, Eqn. (4.1), defines permeability in mathematical form.

When two immiscible fluids, oil and water, flow simultaneously through a porous medium, the permeability for each fluid is independent of flow rate and fluid properties. These permeabilities depend only on the fluid saturation within the porous sample. Darcy's Law then relates the flow rate of each fluid and the pressure differential by those permeabilities $K_w(S_w)$ and $K_o(S_w)$.

K_w and K_o can be expressed as fractions of the single phase permeability, K, of the porous medium, i.e.

k_w, relative permeability of water = $\frac{K_w}{K}$

k_o, relative permeability of oil = $\frac{K_o}{k}$

These relative permeabilities are each less than unity and (K_w+K_o) is also less than unity for all saturations except zero and one. Typical relative permeability curves are shown in Fig.10.

Residual Oil Saturation

When two immiscible fluids flow through a porous medium, each establishes its own channels of flow through the medium. As the saturation of non-wetting fluid (oil) is reduced as in the displacement of oil, these channels tend to break down until isolated islands of non-wetting fluid (oil) remain. These islands are stationary for all reasonable pressure gradients. The saturation corresponding to this immobile state is called the residual oil saturation.

Connate Water Saturation

When the saturation of wetting fluid (water) is reduced, the channels of flow for this fluid tend to break down and become discontinuous, and the wetting fluid (water) ceases to flow. The saturation corresponding to this case is called connate water saturation.

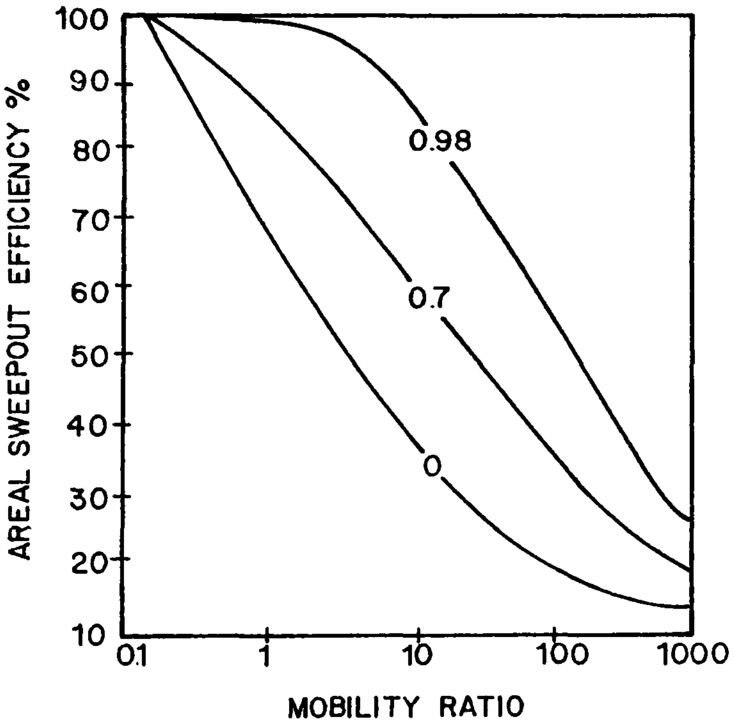


FIG. 9 AREAL SWEEPOUT EFFICIENCY AS A FUNCTION OF MOBILITY RATIO FOR A FIVE-SPOT WELL PATTERN

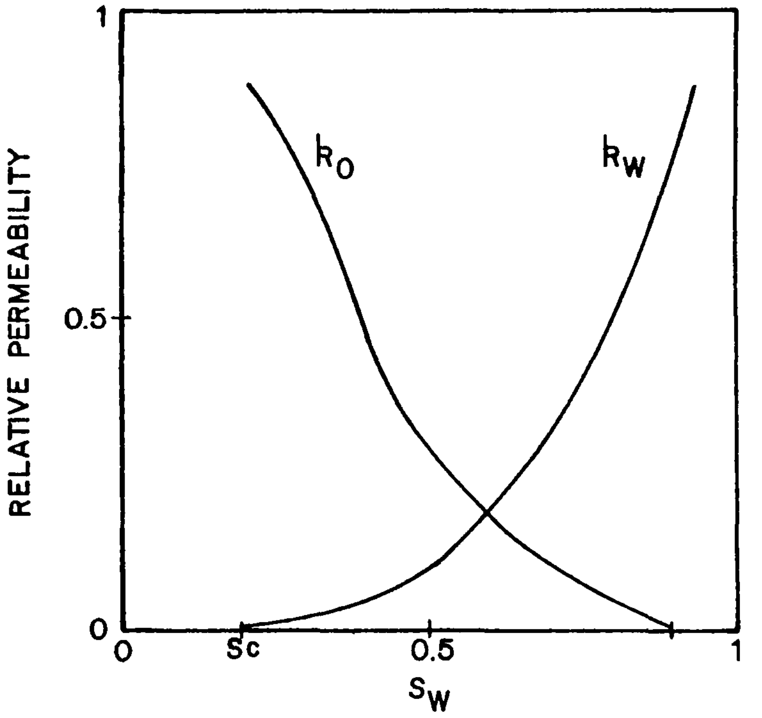


FIG. 10 TYPICAL RELATIVE PERMEABILITY CURVES

Breakthrough

Breakthrough is defined as the first appearance of the displacing fluid in the produced effluent. Both the displaced and displacing fluids are present in the effluent thereafter, until the displacement phenomena takes place in such a way that no more original fluid is displaced. Breakthrough time, indicative of the movement of the displacing fluid against the other fluid,is a measure of "fingering" effects, which were discussed earlier. The shorter the breakthrough time, the higher is the degree of fingering.

CHAPTER 5

RESULTS

RESULTS

The experimental work was carried out with an unconsolidated sand core having porosity and permeability of approximately 33.7% and 53.1 darcy respectively. The characteristics are shown in Table 12. It was assumed that Ottawa sand, having the particle size distribution shown in Table 10, does not swell as a result of saturation with oil or water and that its permeability, therefore, remained constant. The absence of any change in pressure drop across the core during extended displacement tests showed this assumption to be valid.

The displacement tests consisted of secondary and/or tertiary runs. After saturation with the oil, the core was flooded with deaerated distilled water, or brine containing 1.5 percent sodium chloride. Water was used as the displacing fluid for light oils like toluene, kerosene and fuel oil No.2. For displacement runs involving lignosulfonates, the core was flooded with brine. After injection of approximately 2-3 pore volumes of water or brine (thus reducing the core to a certain residual oil saturation) the core was subjected to a tertiary run using an aqueous solution of the surfactant. The surfactant solution was injected for 2-3 PV after which the displacement was stopped and the core was inspected. All recovery data were obtained using a displacement rate of 385-390 ml/hr.

The effects of the following variables on the recovery of oil were studied

(i) Viscosity of Oil

(ii) Addition of lignosulfonates to the displacing fluid in the secondary and tertiary stages

(iii) Concentration of lignosulfonates

Recovery has been defined as the fraction of the original oil in place which is recovered. Oil recovery at two stages of the displacement run has been included in presenting the results of this study - one at breakthrough and the other at the end of the injection of the fluid under consideration. These are called "Recovery at Breakthrough" and "Ultimate Recovery" respectively. The additional secondary and tertiary oil recoveries with Marasperse solutions relate to additional oil recovered if the core was flooded for an equal additional injection of water (or extended waterflooding). The breakthrough time for each set of oil and displacing fluid has been taken as the time for the displacing fluid to first appear in the effluent at the downstream end of the core. This indicated the presence of any unfavorable mobility ratios during the displacement phenomena. The pressure drop profile recorded during the displacement run substantiated any conclusions based upon the breakthrough time and the mobility ratio.

The breakthrough time and recovery were corrected so that the results pertain to the core only and excluded the effect of piping at the entrance and exit of the core.

The viscosity of Marasperse solutions was measured at various shear rates using a Brookfield viscometer with U/L adapter. The operating viscosity of lignosulfonate solution for any displacement test was based upon the pressure drop and, consequently, the shear stress measured during the run.

Figures 12-15 show the recovery of oils when the core was flooded with water. The breakthrough and utlimate recoveries have been shown in Table 16. Figs. 19-21 show the progress of recovery of oil no. 4 using water initially (waterflooding), followed by injection of 1%, 3% and 10% solutions of Marasperse N-22. The secondary recovery of the oil using respectively 1%, 3% and 10% solutions of Marasperse N-22 is shown in Figs. 16-18. The extended waterflooding of the core is shown in Fig. 22 and is the basis of comparison for additional secondary and tertiary recoveries using Marasperse N-22. Fig. 23 shows the pressure drop profile across the column indicative of unfavorable mobility ratios and viscous fingering. The surface and interfacial tensions of oil and Marasperse solutions are shown in Figs. 24-25. The viscosity of Marasperse solutions is shown in Figs. 26-27.

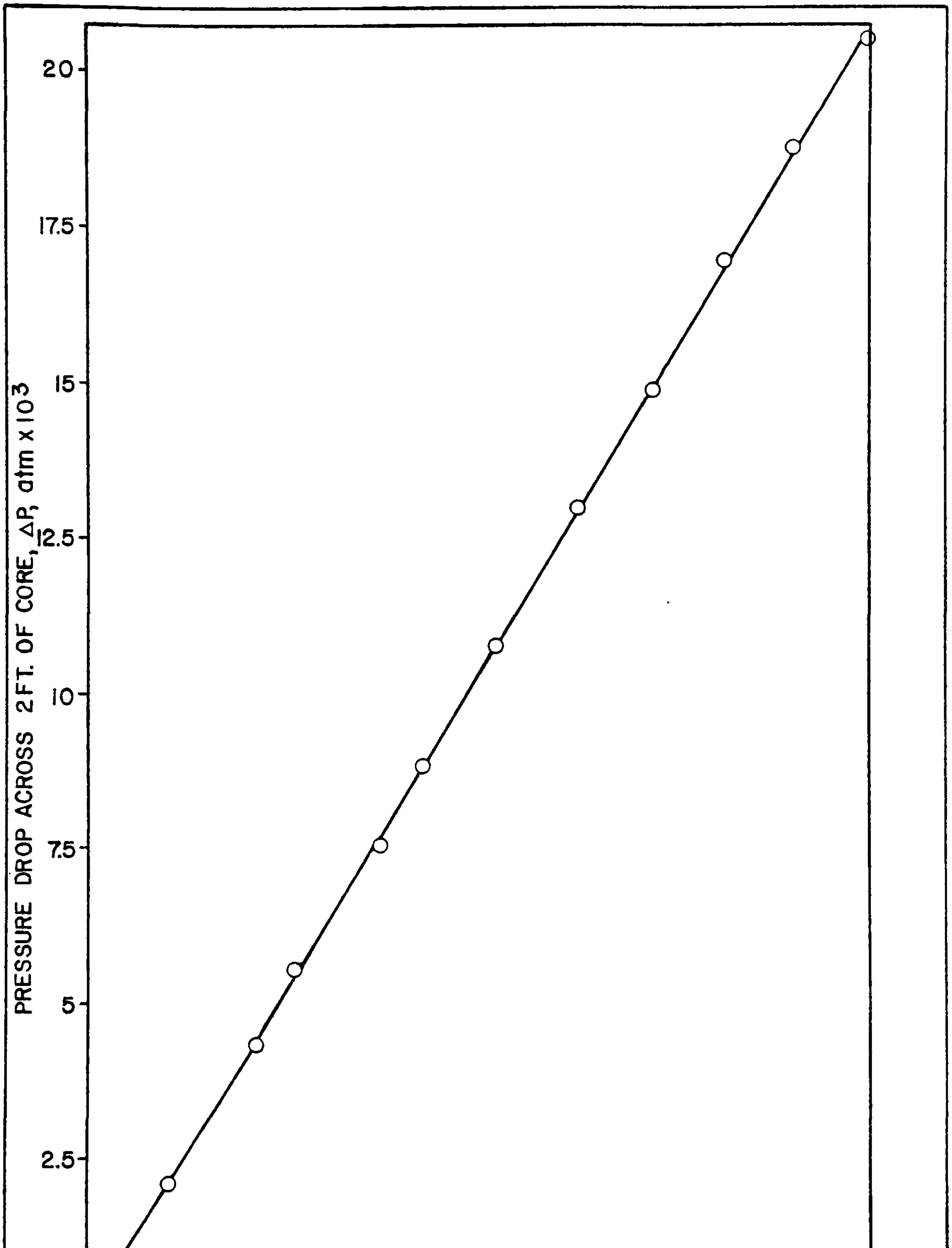


FIG. 11 PERMEABILITY OF UNCONSOLIDATED SAND-CORE

TABLE 12

CHARACTERISTICS OF THE UNCONSOLIDATED SAND CORE

Dimensions		
I. Diameter	cm	5.21
Length	cm	121.7
Permeability and Porosity		
Permeability, darcies		53.10
Porosity (percent)		33.6-33.9
Pore volume, cc		874-878
Grain density gm/cc		2.6501
Mean Avg. particle diameter, cm		0.03512

TABLE 13

PROPERTIES OF OILS USED

Oil	Density, 25°C gm/cc	Viscosity, 25°C cp.	Surface Tension, 25°C Dynes/cm
Toluene	0.8624	0.66	27.8
Kerosene	0.7913	1.60	24.1
Oil No. 2	0.8349	2.87	26.0
Oil No. 4	0.8818	19.6	28.2

TABLE 14

DENSITY OF MARASPERSE SOLUTIONS

(gm/cc, @ 25°C)

Concentration	Density of Marasperse Solution		
	N-22	C-21	1.5% NaCl, N-22
1%	1.0021	1.0022	1.0113
3%	1.0115	1.0114	1.0201
6%	1.0227	1.0254	1.0307
10%	1.0442	1.0435	1.0494

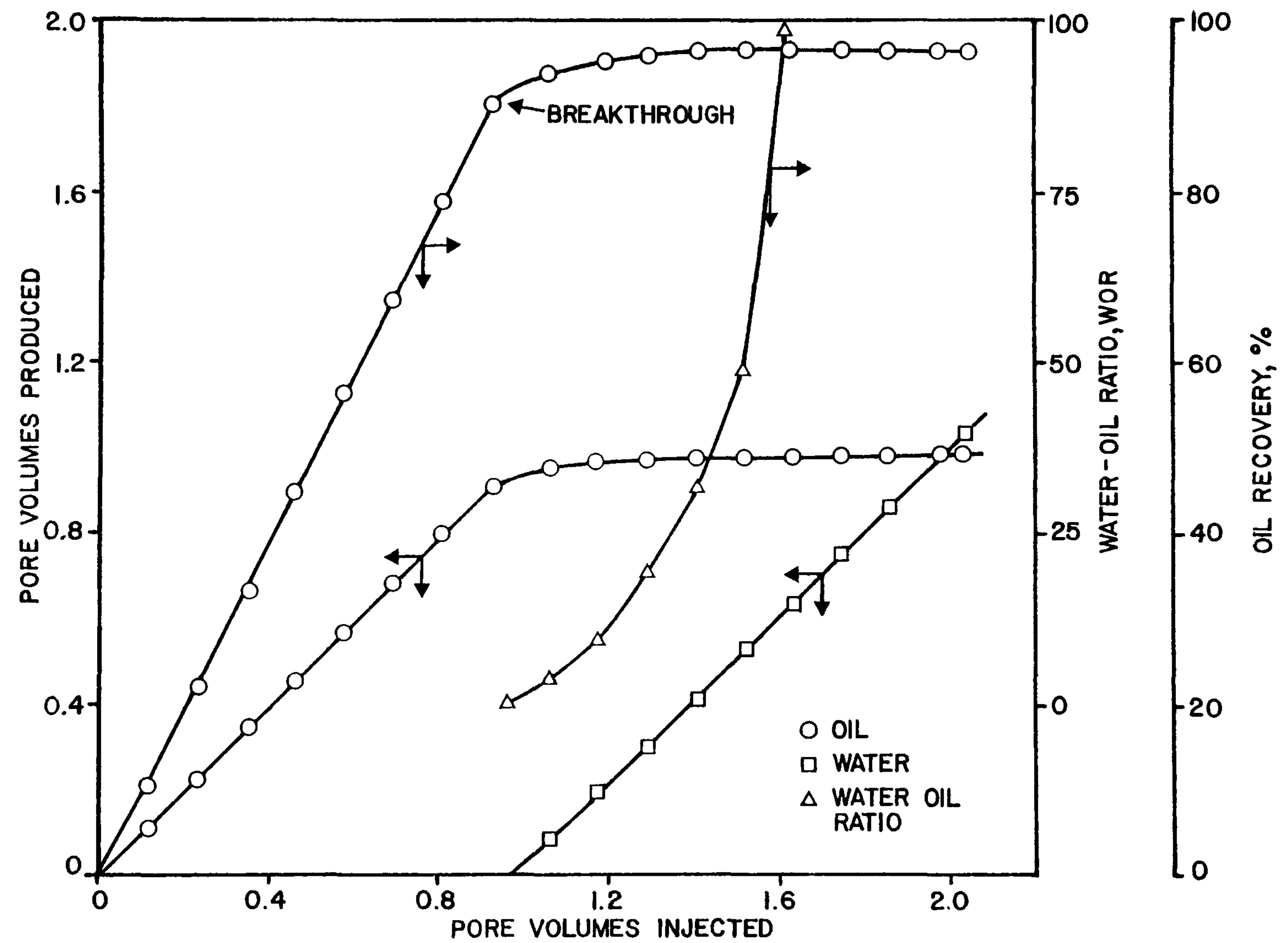


FIG. 12 PRODUCTION HISTORY FOR DISPLACEMENT OF TOLUENE BY WATER

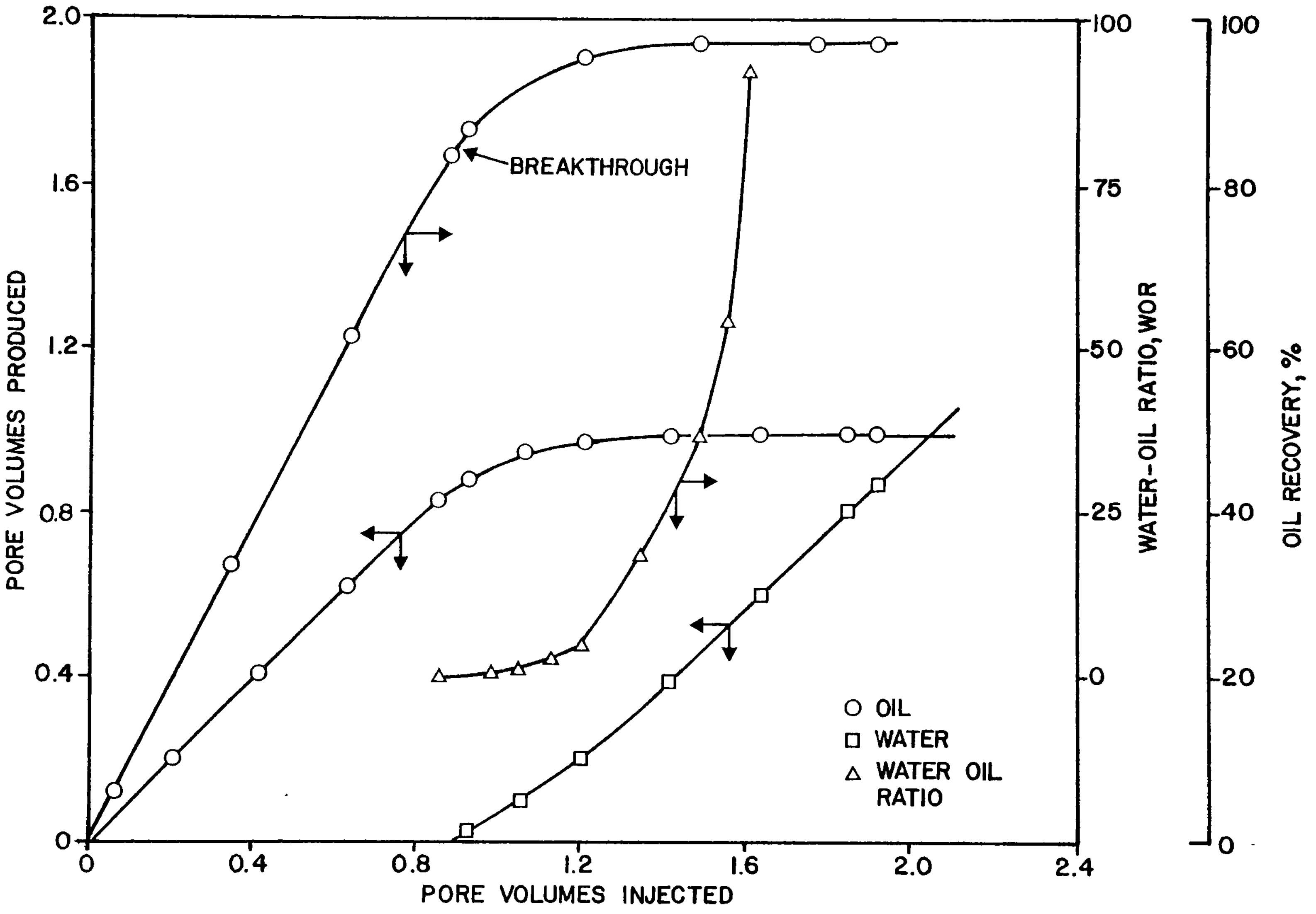


FIG. 13 PRODUCTION HISTORY FOR DISPLACEMENT OF KEROSENE BY WATER

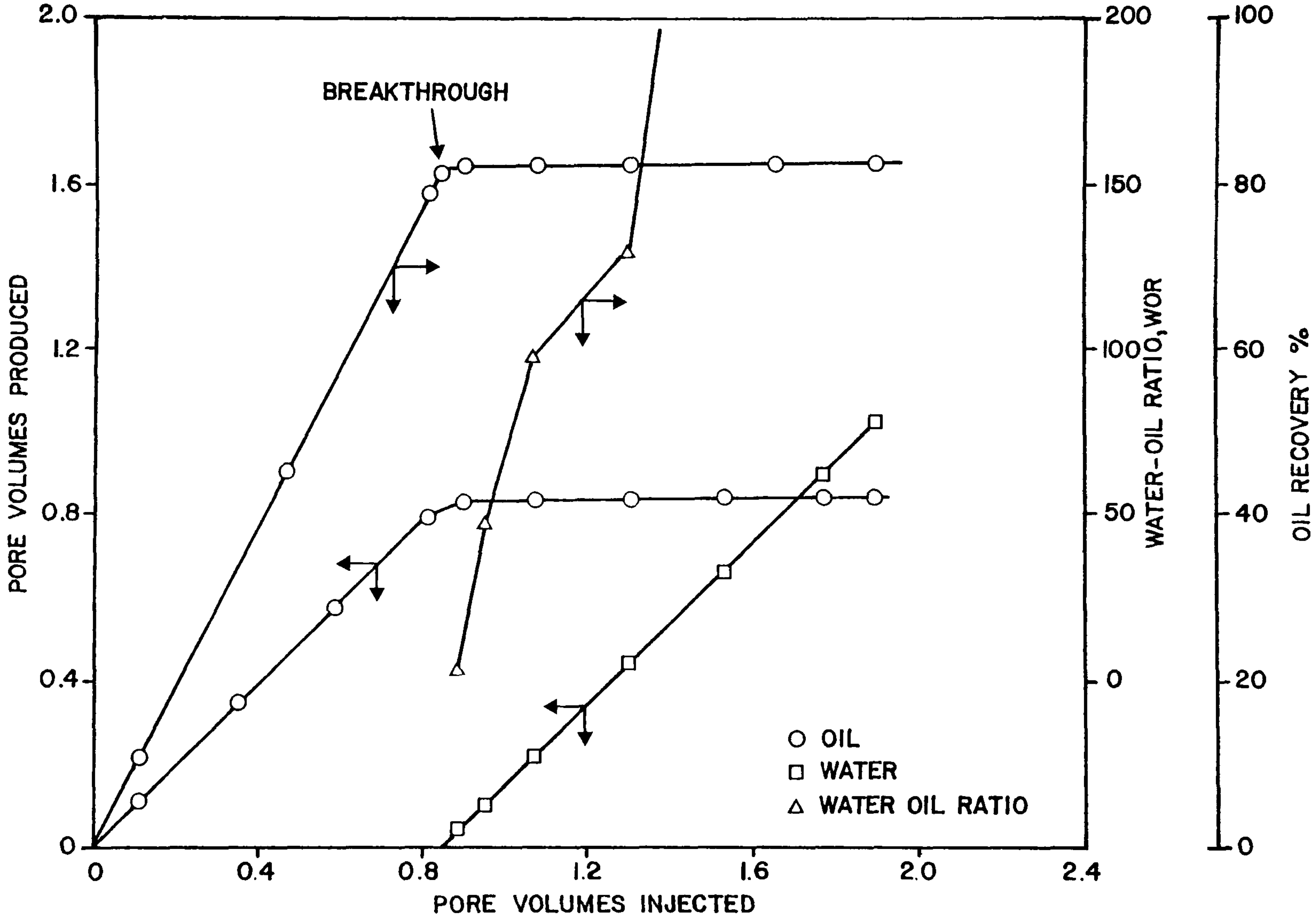


FIG. 14 PRODUCTION HISTORY FOR DISPLACEMENT OF OIL NO. 2 WITH WATER

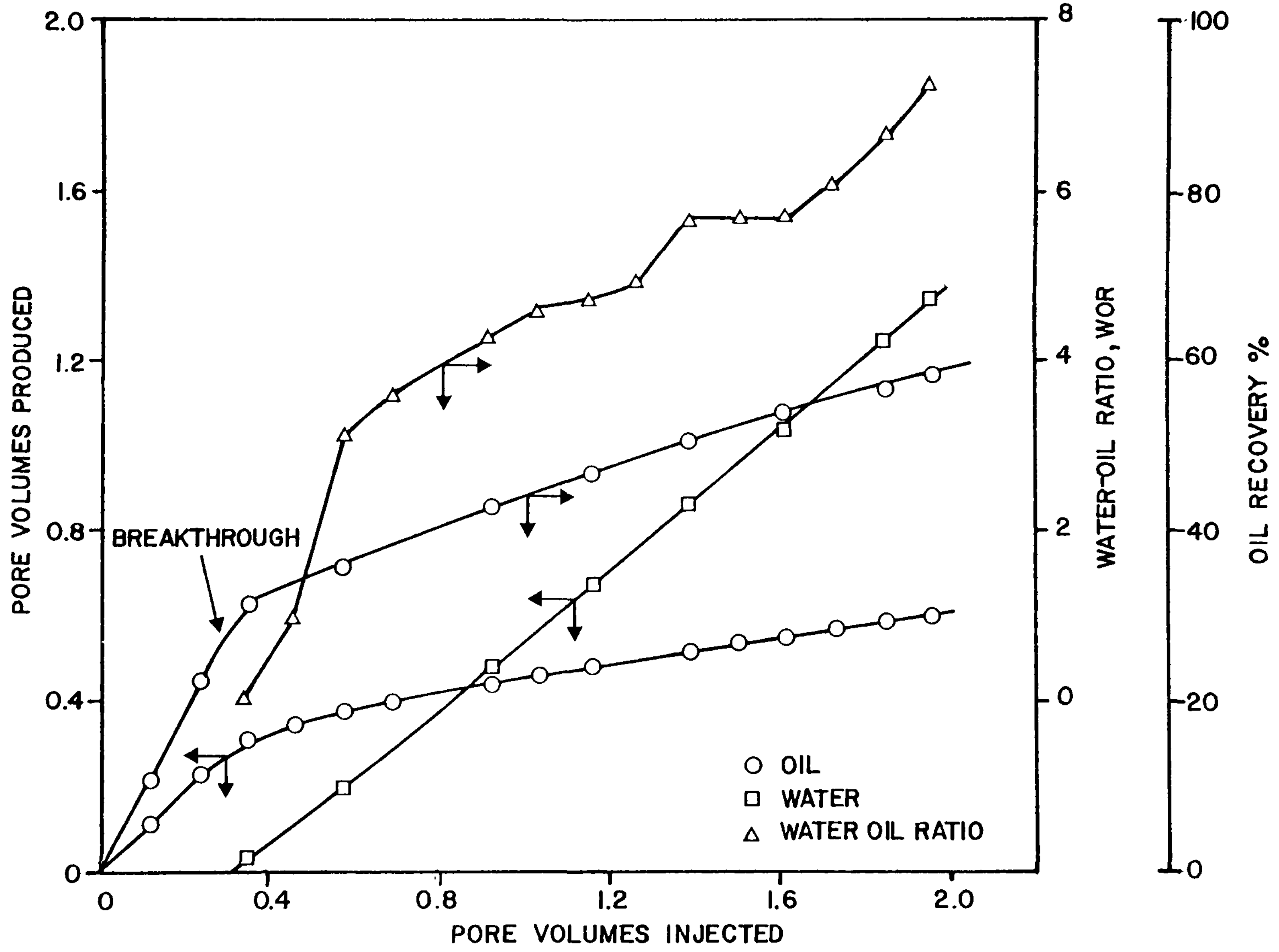


FIG. 15 PRODUCTION HISTORY FOR DISPLACEMENT OF OIL #4 WITH WATER

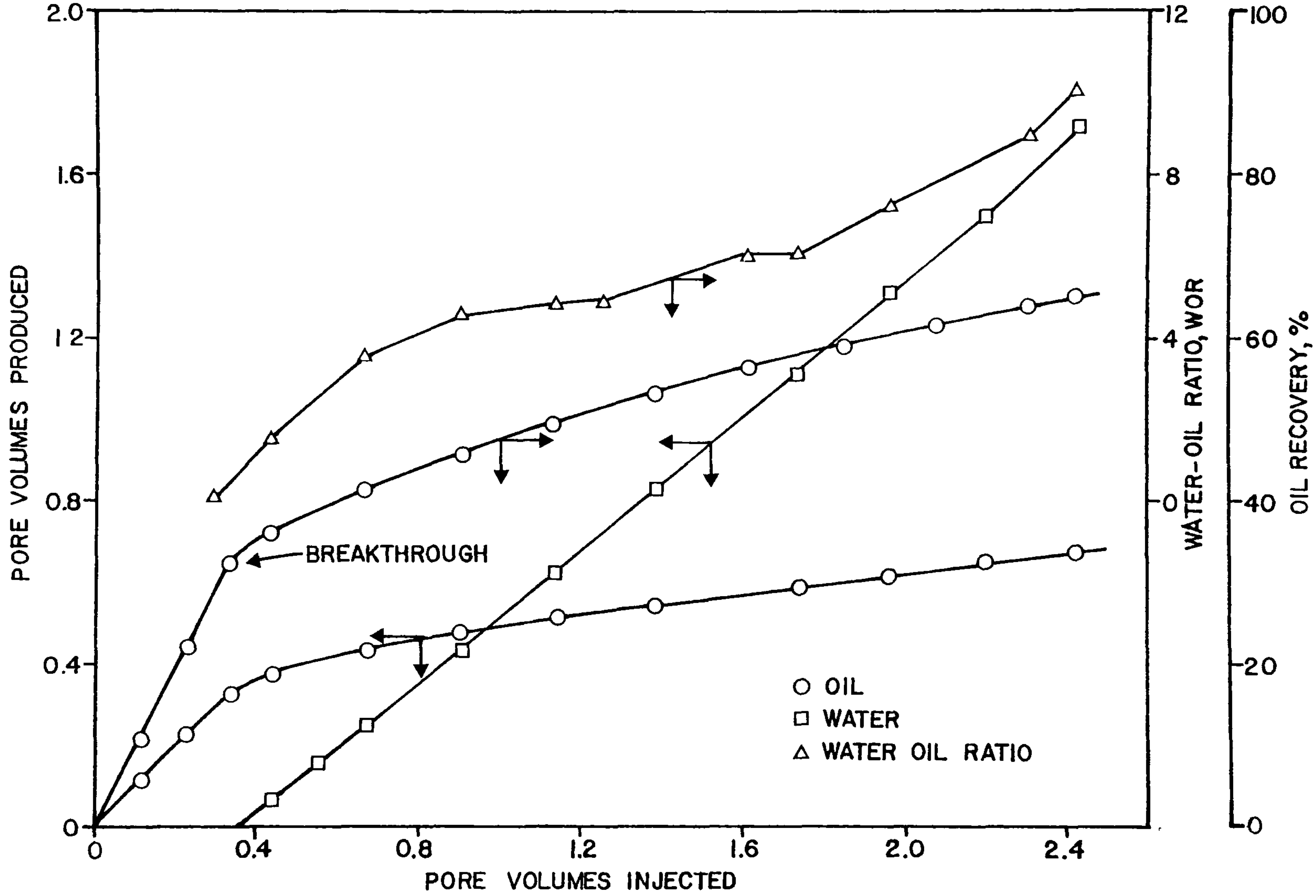


FIG. 16 SECONDARY FLOODING (1% N-22, 1.5% NaCl) FOR OIL #4

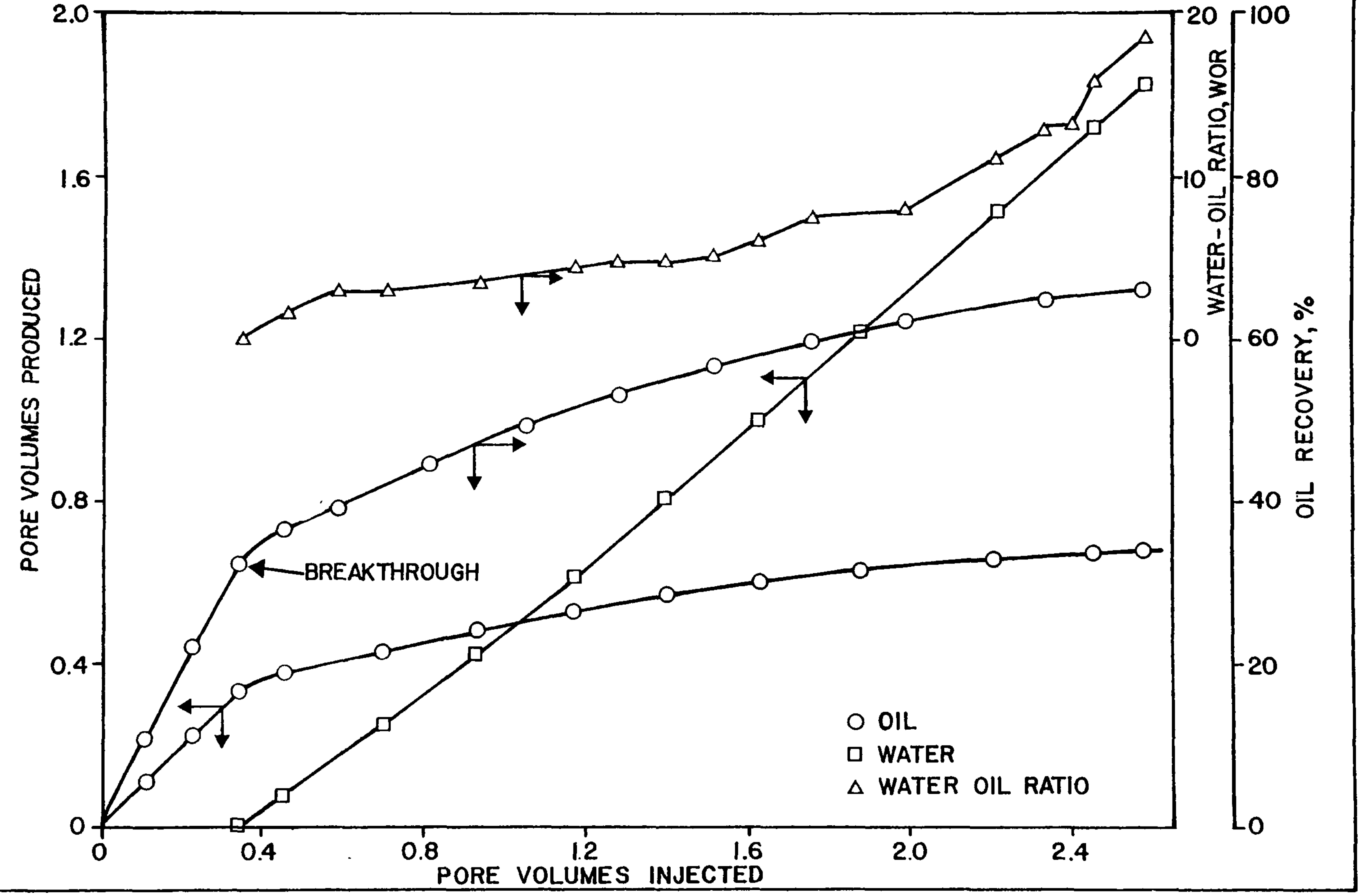


FIG. 17 SECONDARY FLOODING (3%N-22, 1.5% NaCl) FOR OIL #4

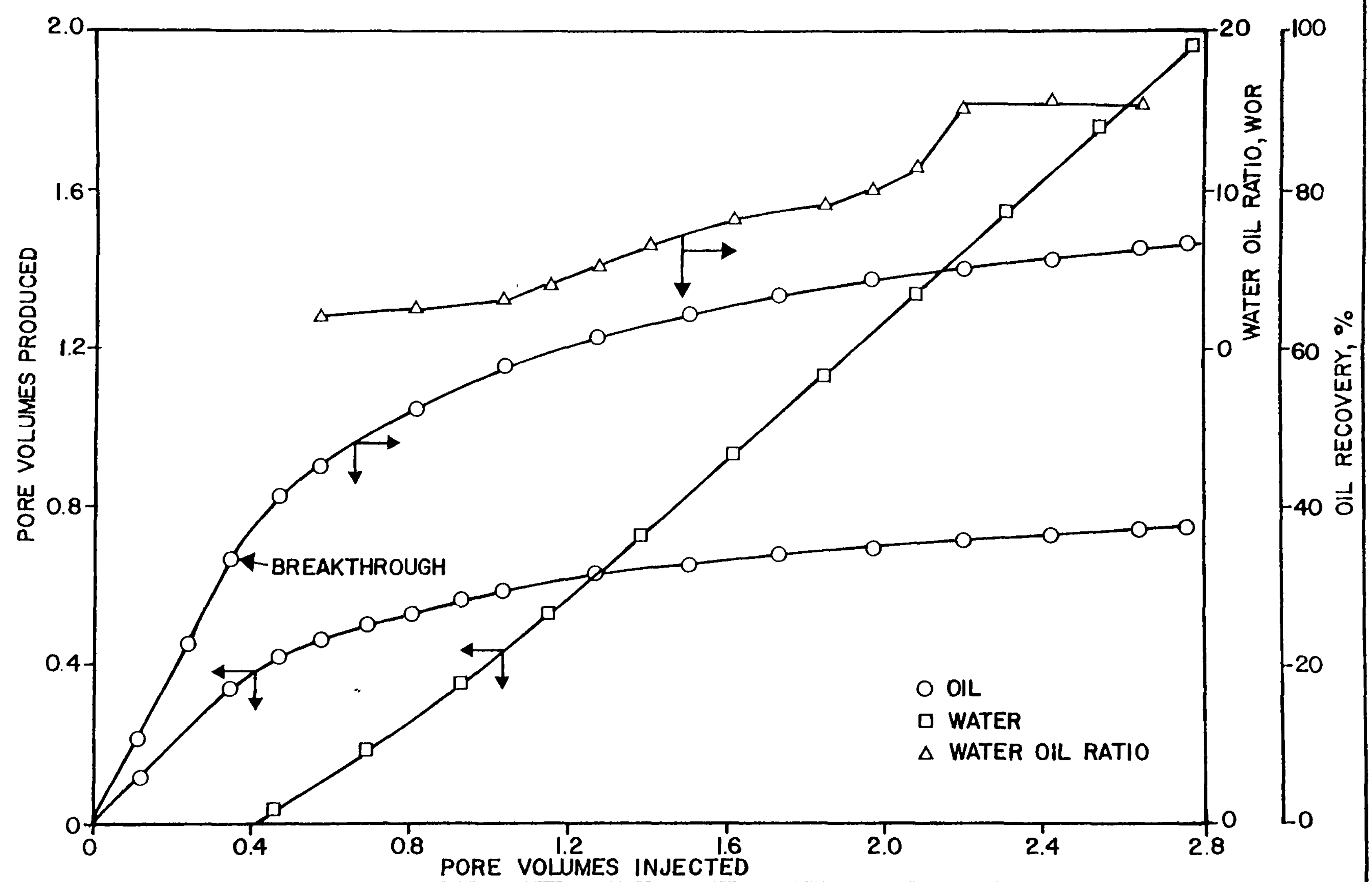


FIG. 18 SECONDARY FLOODING (10% N-22, 1.5% NaCl) FOR OIL #4

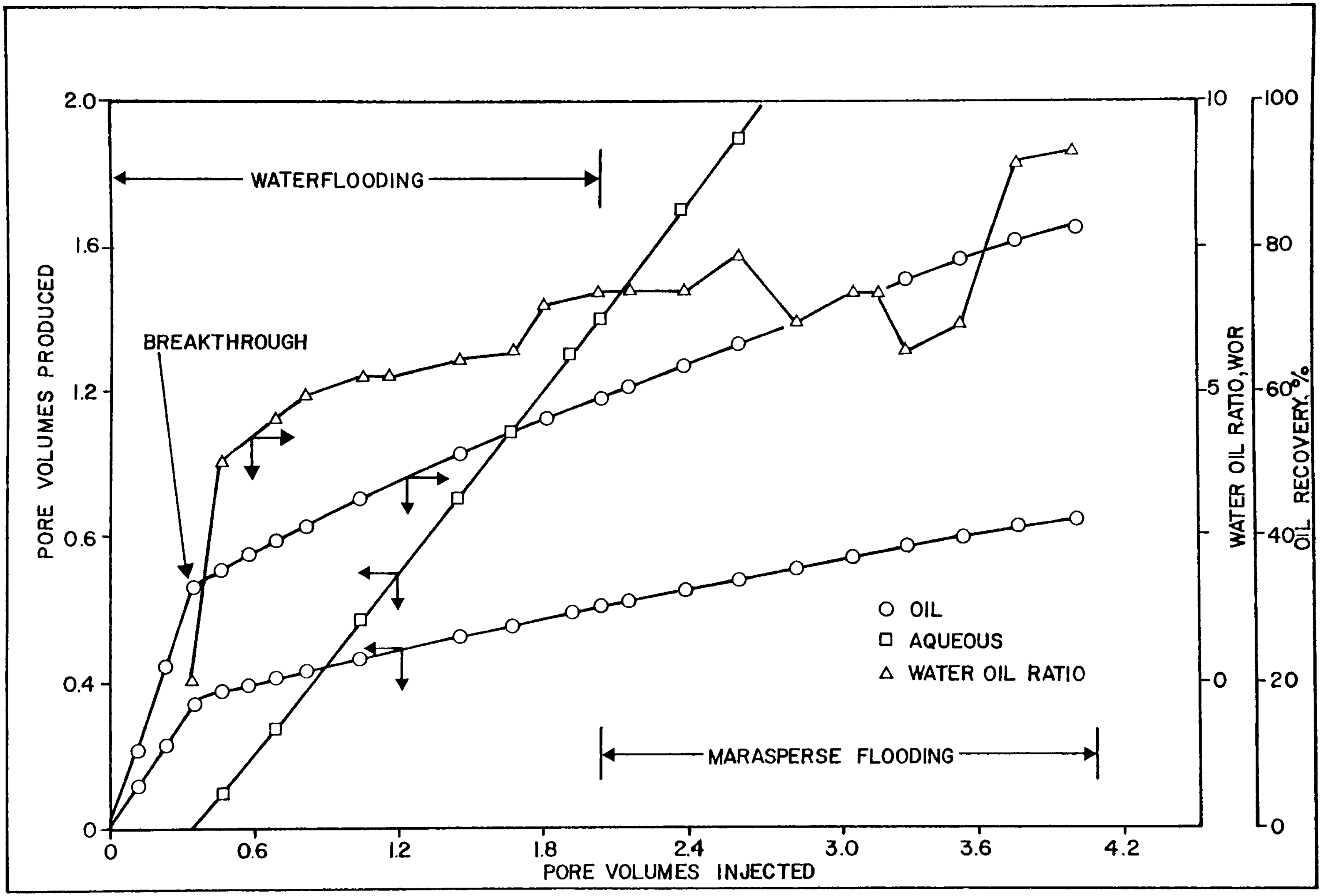


FIG. 19 WATERFLOODING AND MARASPERSE FLOODING (1% N-22) FOR OIL #4

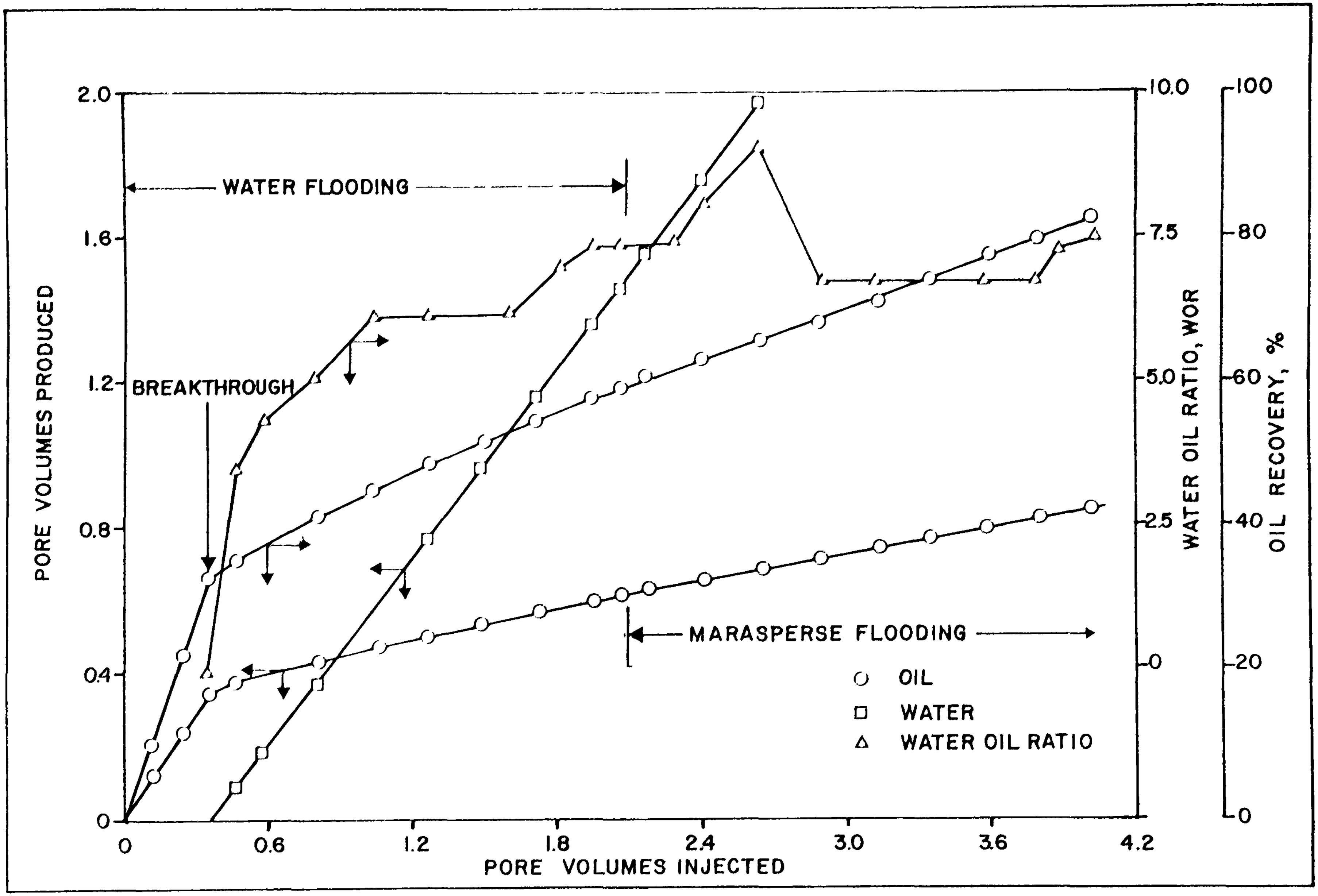


FIG. 20 WATERFLOODING AND MARASPERSE FLOODING (3% N-22) FOR OIL #4

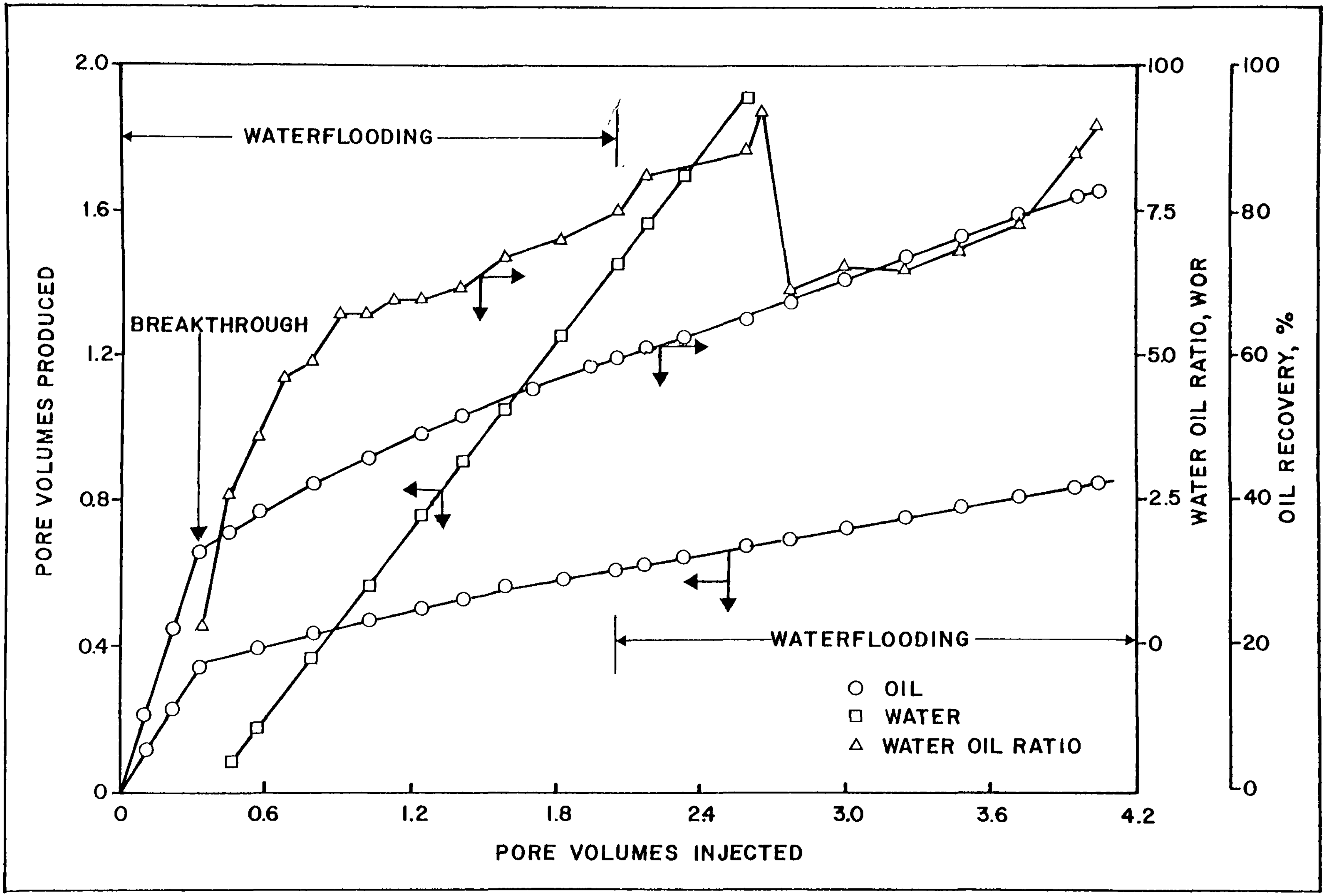


FIG. 21 WATERFLOODING AND MARASPERSE FLOODING (10% N-22) FOR OIL #4

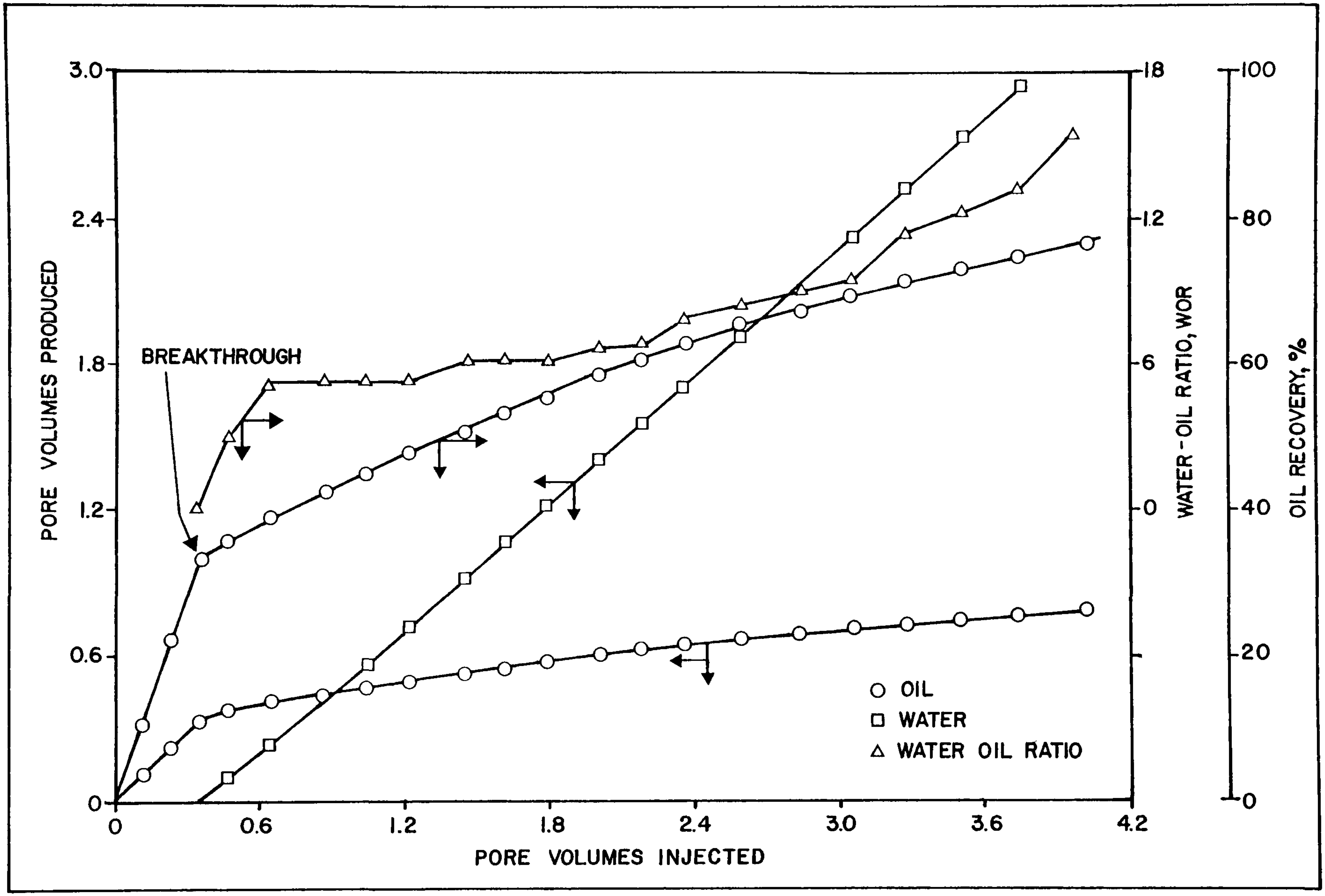


FIG. 22 PRODUCTION HISTORY FOR DISPLACEMENT OF OIL #4 BY WATER FOR EXTENDED INJECTION

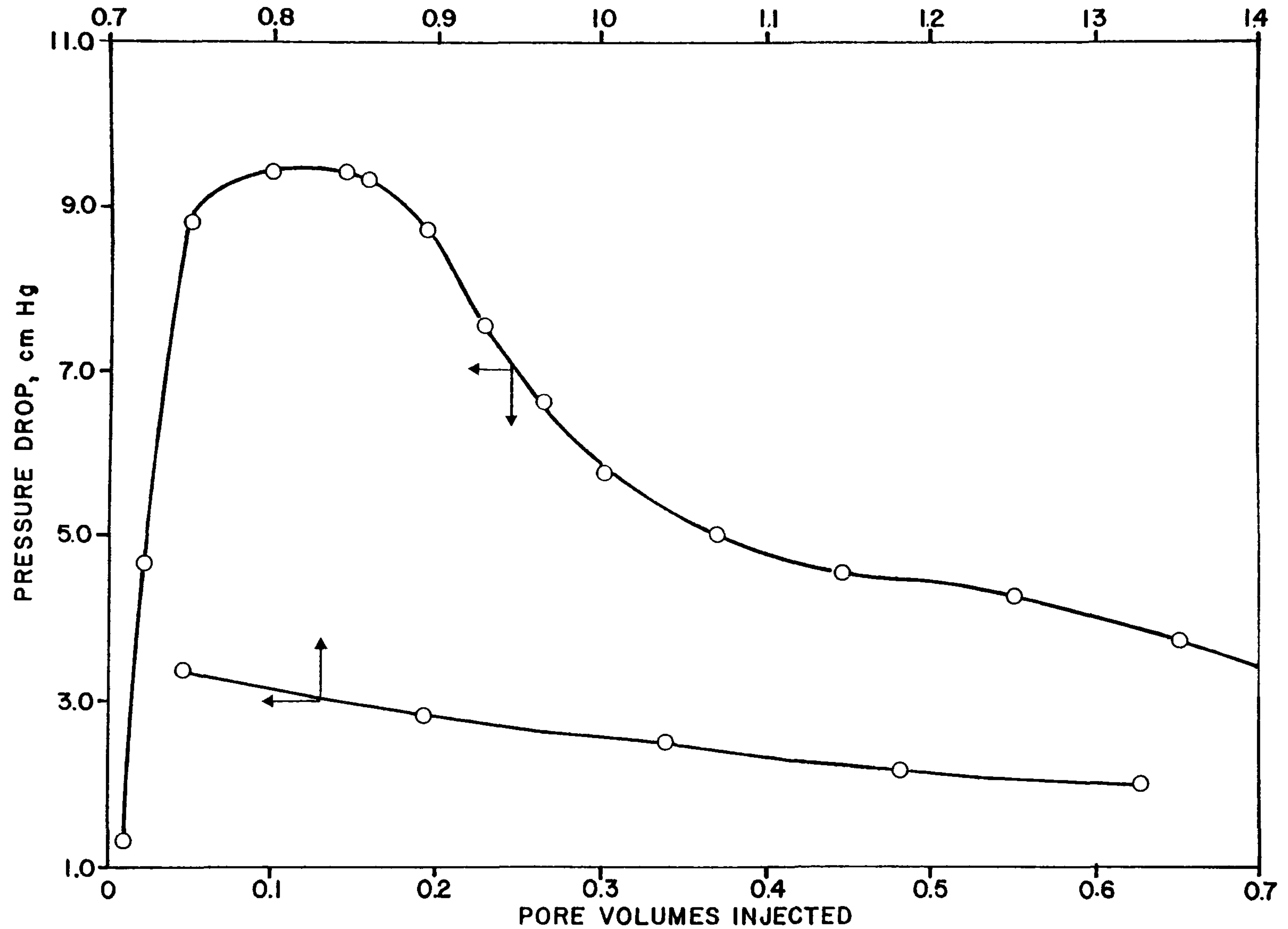


FIG. 23 PRESSURE DROP PROFILE ACROSS 2 FT. OF CORE HOLDER DURING SECONDARY FLOODING WITH 10% N-22

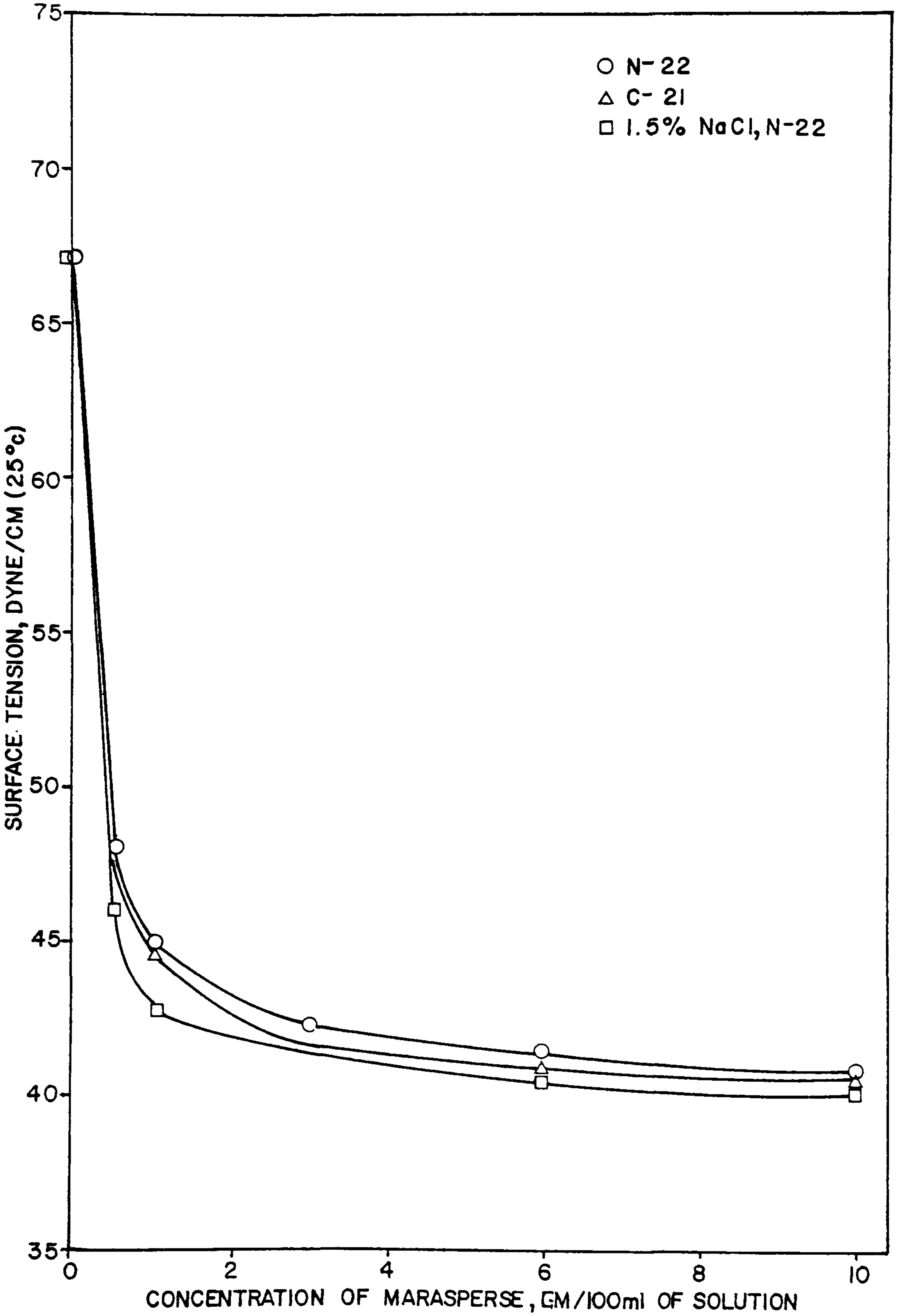


FIG. 24 SURFACE TENSION OF MARASPERSE SOLUTIONS

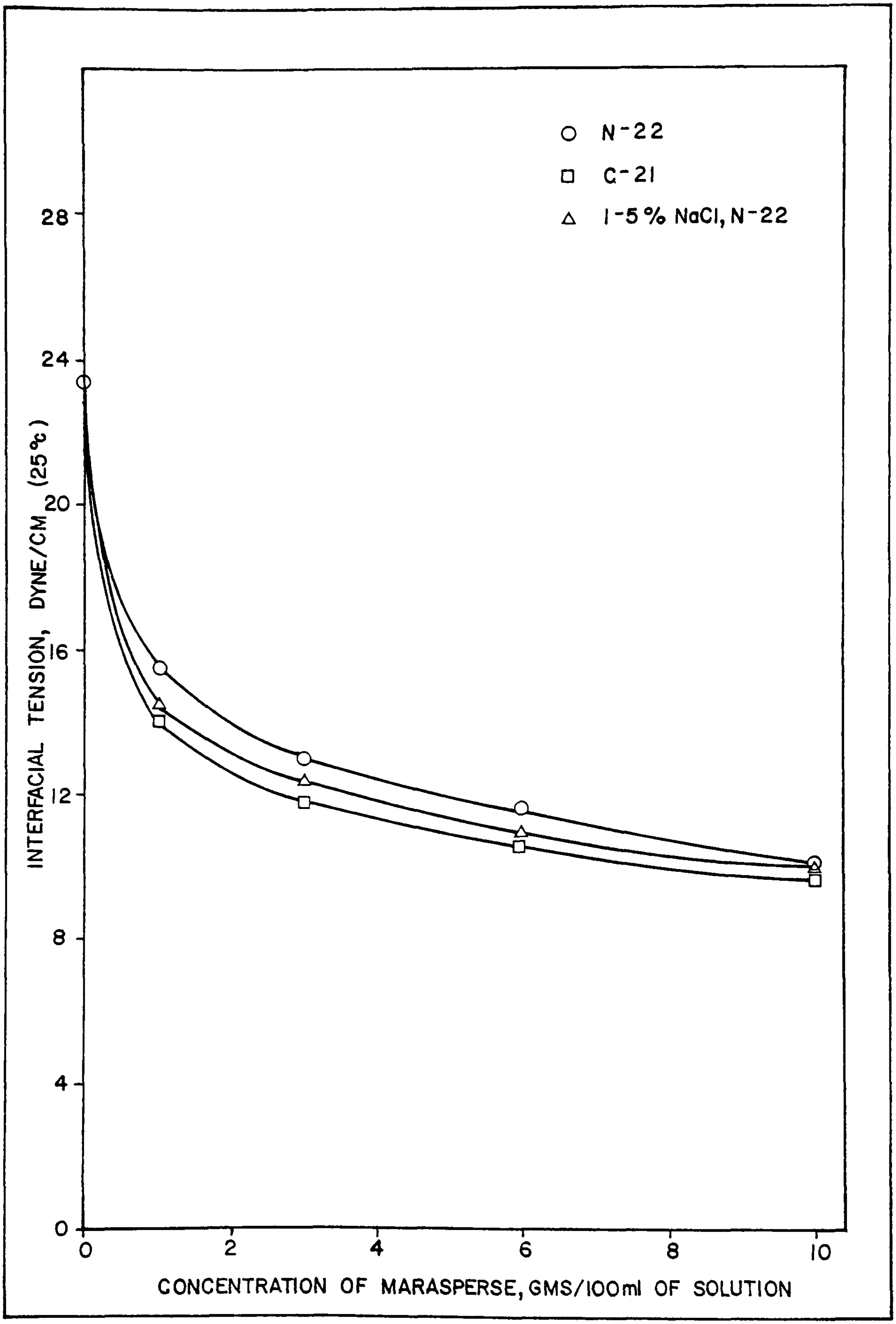


FIG. 25 INTERFACIAL TENSION OF OIL #4 AND MARASPERSE SOLUTIONS

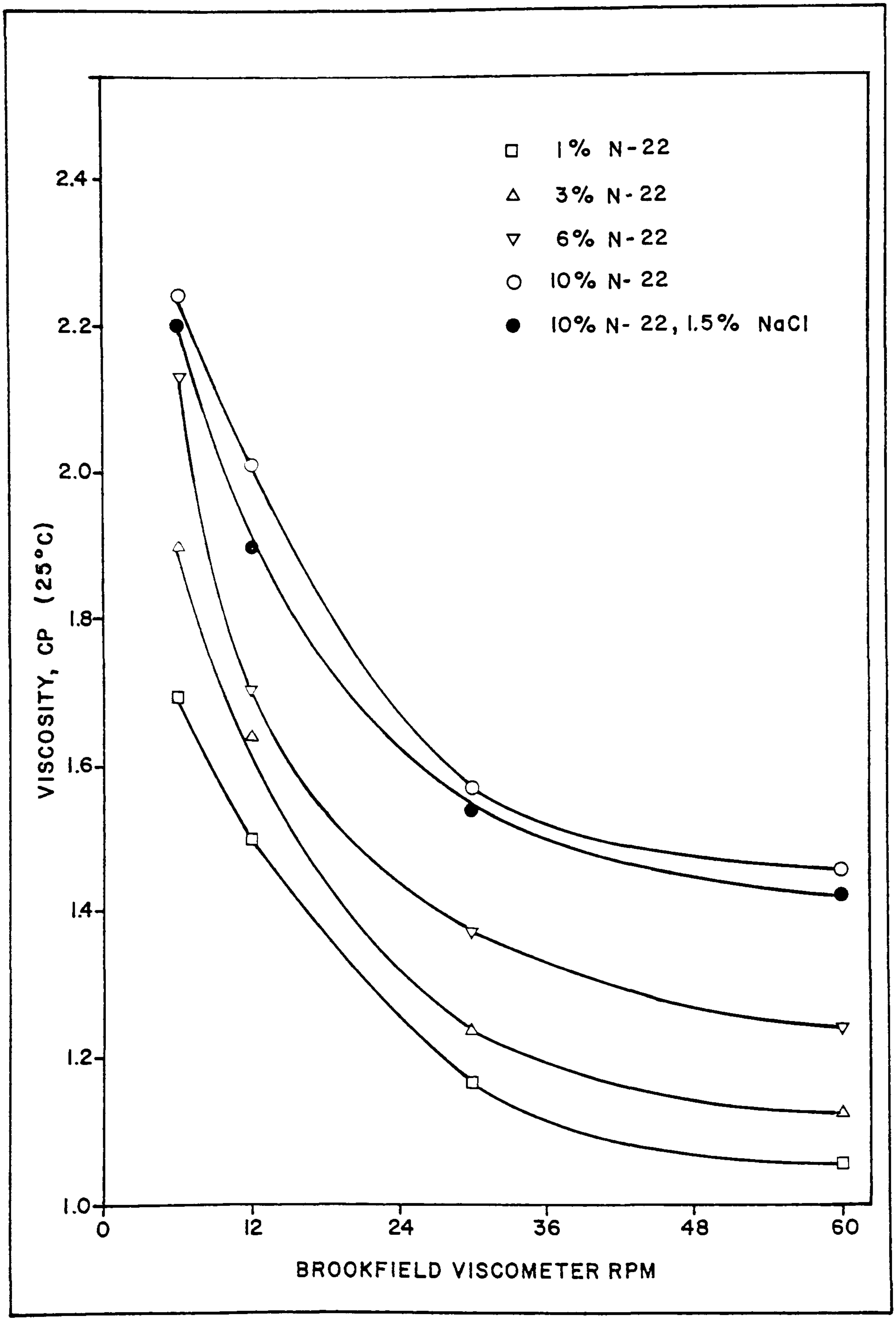


FIG. 26 VISCOSITY OF MARASPERSE SOLUTIONS

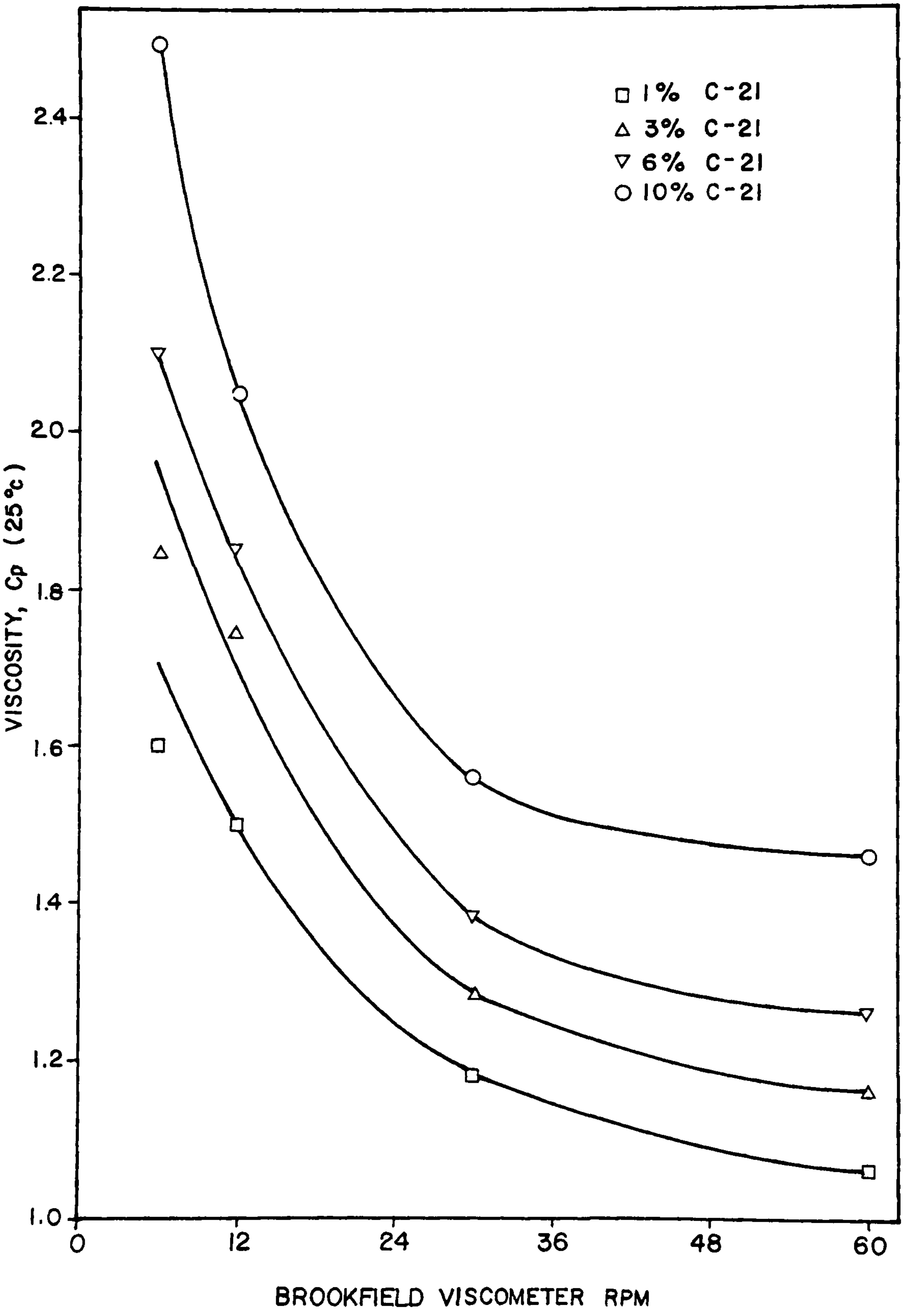


FIG. 27 VISCOSITY OF MARASPERSE SOLUTIONS

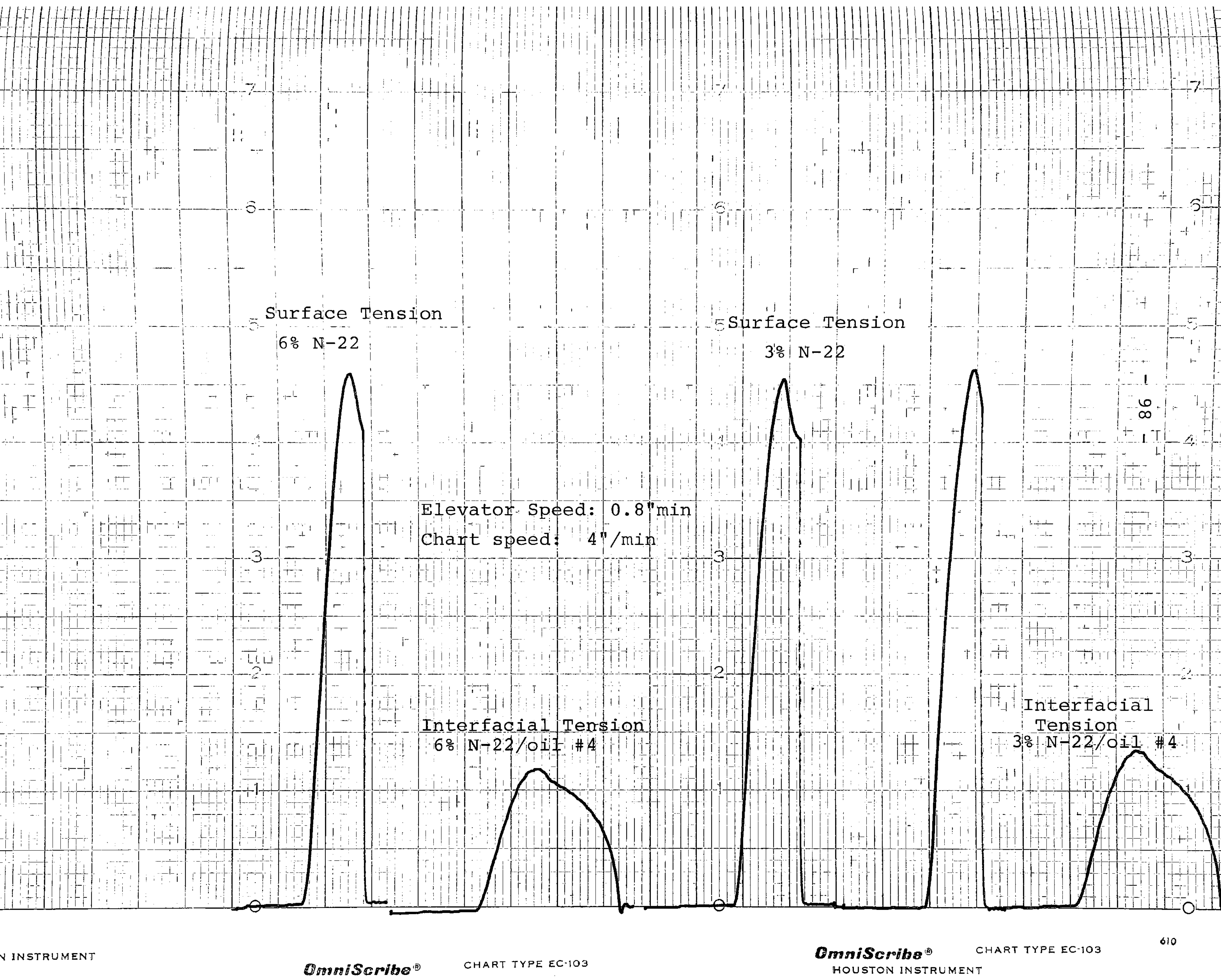


Fig. 28 Surface and Interfacial Tension Curves for 6% and 3% N-22 Solutions and Oil No. 4 at 25°C

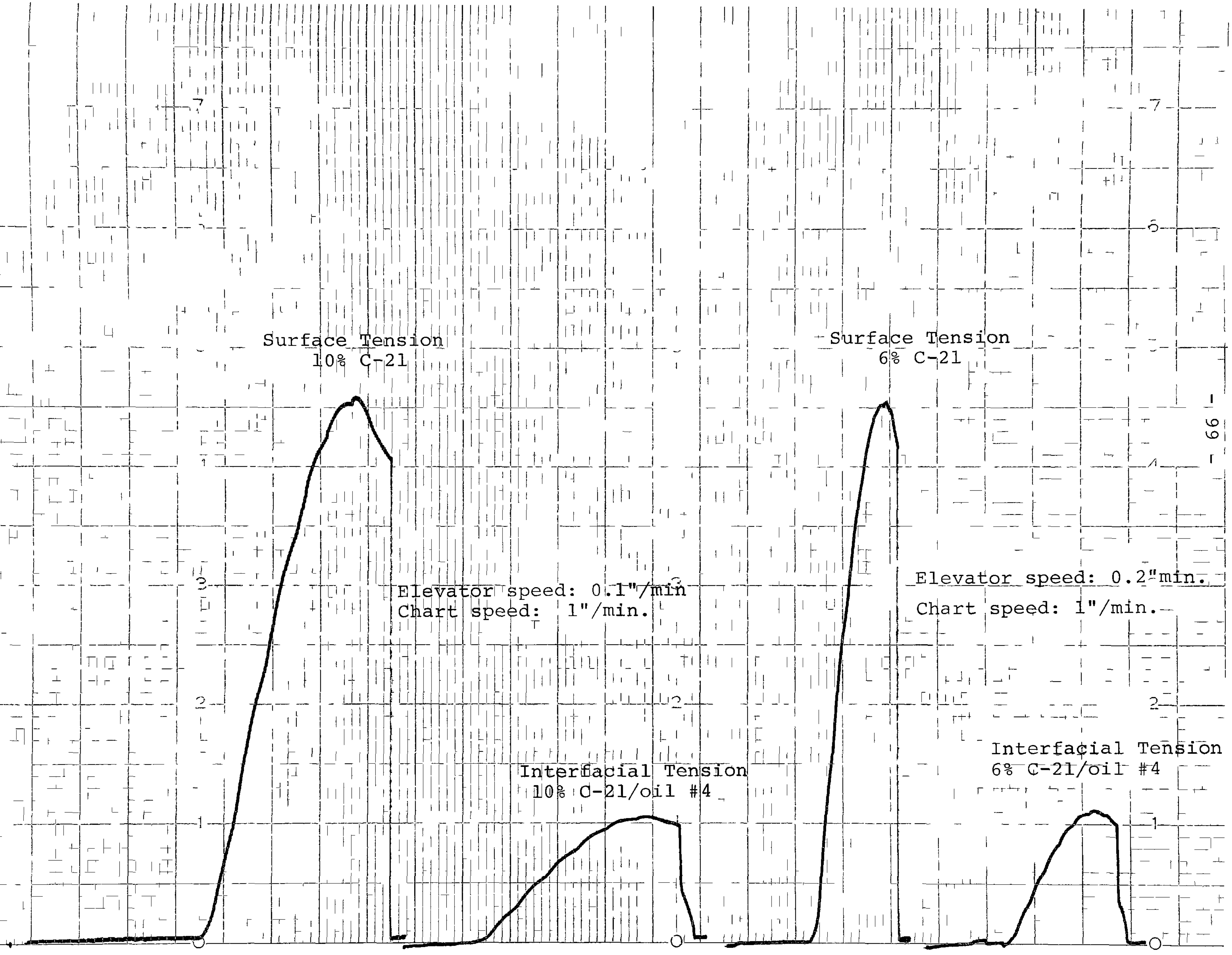


Fig. 29 Surface and Interfacial Tension Curves for 10% and 6% C-21 Solutions and Oil No. 4 at 25°C

TABLE 15

INTERFACIAL TENSION DATA FOR OILS

AQUEOUS PHASE: WATER, 25°C

OIL	INTERFACIAL TENSION, Dyne/cm
Toluene	35.0
Kerosene	16.2
Oil #2	19.6
Oil #4	23.4

TABLE 16

RESULTS OF WATERFLOODING VARIOUS OILS

Run No.	Oil	Displacing Fluid	Recovery (Percent PV)		Final WOR
			At Breakthrough	Ultimate	
1	Toluene	Water	92	97	>100
2	Kerosene	Water	84	97	>100
3	Oil No. 2	Water	81	83	>100
4	Oil No. 4	Water	29	58	7.3

TABLE 17

RESULTS OF SECONDARY RECOVERY USING MARASPERSE SOLUTIONS

FOR OIL NO. 4

(Displacing Fluid contains 1.5 Wt. % NaCl) Basis: 2.4PV

Run No.	Displacing Fluid	Recovery (percent PV)		Final WOR
		At Breakthrough	Ultimate	
5	1% N-22	32.5	64-65	10.0
6	3% N-22	32.7	65-66	13.0
7	10% N-22	34.6	70-72	15.0
8	0% N-22	32.7	64	8.5

TABLE 18

RESULTS OF TERTIARY RECOVERY USING MARASPERSE SOLUTIONS

FOR OIL NO. 4

Basis: Secondary Recovery at 2.02 PV, Breakthrough: 32.6%
Ultimate: 59.3%
WOR: 7.0-7.5
Tertiary Recovery 2.0PV

Run No.	Displacing Fluid	Tertiary Recovery (Percent PV)		Final WOR
		At Breakthrough	Ultimate	
9	1% N-22	6.0	22.6-23.2	∿9
10	3% N-22	5.9	22.6-23.5	∿8
11	10% N-22	6.05	22.5-23.6	∿9
8	0% N-22	-	18.2	∿16

TABLE 19

RESULTS OF SECONDARY AND TERTIARY RUNS USING MARASPERSE SOLUTIONS

For Tertiary Recovery, Basis: Waterflooding completed at
∿2.0PV
Recovery %PV = 59.3

Concentration	Secondary Recovery (percent PV)				Tertiary Recovery (percent PV)			
	0.4PV	1.0PV	2.0PV	2.4PV	0.5PV	1.0PV	1.5PV	2.0PV
1% N-22	35.0	46.3	60.5	64.5	64.5	71.0	77.0	82.0
3% N-22	35.3	47.0	62.5	65.5	64.5	71.0	77.0	82.0
10% N-22	37.0	53.5	67.0	71.0	64.5	71.0	77.0	82.0
0% N-22	34.5	∿45.0	∿59.0	∿64.0	∿64.5	∿69.2	∿73.2	∿77.5

Note: All figures ±0.5% (Excluding those for 0% N-22)

TABLE 20

ADDITIONAL OIL RECOVERIES USING MARASPERSE

Concentration	Additional Oil during Secondary Recovery (percent PV)				Additional Oil during Tertiary Recovery (percent PV)			
	0.4PV	1.0PV	2.0PV	2.4PV	0.5PV	1.0PV	1.5PV	2.0PV
1%	0.5	1.3	1.5	0.5	0	1.8	3.8	4.5
3%	0.8	2.0	3.5	1.5	0	1.8	3.8	4.5
10%	2.5	8.5	8.0	7.0	0	1.8	3.8	4.5

CHAPTER 6

DISCUSSION

DISCUSSION

The results of this investigation relate to the use of lignosulfonates (Marasperse N-22 and C-21) for enhanced oil recovery during the secondary and tertiary stages. The displacement tests were carried out at 1% (low), 3% (usually employed in micellar flooding operations with petroleum sulfonate) and 10% (high) concentrations of the Marasperse solutions. A wide concentration range was covered to obtain any possible gains in capillary and viscous effects which might lead to increased enhanced oil recovery. No attempt was made to study the adsorption of Marasperse on the sand particles.

Low interfacial tension and high viscosity are the desirable properties when investigating any chemical for use in enhanced oil recovery operations. Figs. 24 and 25 show that the major drop in surface and interfacial tensions occur for concentrations up to 1%. The degree to which interfacial tension is lowered, even at high concentrations, is small. Very low interfacial tensions using 1-3% petroleum sulfonates have been reported by Hill et al(19) and Knaggs et al(20). These led to high tertiary recoveries.

Marasperse lignosulfonates exhibited non-Newtonian pseudoplastic behaviour: the viscosity of the solutions decreased with an increasing rate of shear. The increase in viscosity even with high Marasperse concentrations is minimal and only a little improvement in mobility ratio between oil and Marasperse was observed. The relatively lower viscosity of the Marasperse solutions at high displacement velocities (i.e. at higher pressure drops and shear rates) led to rapid movement of the displacing fluid causing frontal-instability and viscous fingering to an extent comparable with that observed during water flooding. The breakthrough time and the pressure drop across the Core-Holder confirmed this conclusion. Similar effects have been reported by Lee and Claridge(5) when using polymer solutions (pseudoplastic) for improving areal sweep. Since the increase viscosity using polymer solutions is appreciable even with low concentrations, it does result in improved recoveries.

The results of flooding are shown in Table 17 for secondary recovery. Additional recovery of oil at low concentrations of Marasperse N-22 (1-3%) is about 2-3% but at high concentrations (10%) there is an additional recovery of 6-8%. Additional oil recovery is the difference between the oil recovered using Marasperse solutions and that recovered using waterflooding. Unfavorable mobility ratios, indicated by the pressure drop profile and the breakthrough time, caused a decrease in the displacement efficiency. The operating viscosity of the Marasperse solutions is a function of the shear stress in the pores of the porous medium. The shear stress during any secondary displacement varies because the pressure drop changes as the injection proceeds. At 2.4 PV injection, the shear stress is of the order of 0.5 dyne/cm^2 when using 10% N-22. This corresponds to a viscosity of approximately 1.5-1.6 cp.

at 25°C. At lower concentrations, the increase in viscosity over that of water is rather small. Therefore, the mobilities tend to be unfavorable, resulting in low additional recoveries. The absence of any increased viscosity is also substantiated by the fact that breakthrough at low concentrations (1-3%) occurred at about the same pore volume injection as for that of water. For 10% N-22, the breakthrough lag was equivalent to 0.03 PV. The major part of additional oil recovery was obtained between breakthrough and approximately 1 PV injection. Lee & Claridge(5) have reported similar improved areal sweep at 1 PV injection of polymer solution.

The water oil ratios (WOR) at 2.4 PV injection of Marasperse solutions are approximately 10, 13.5, 15.5 for 1%, 3% and 10% respectively and for the case of waterflooding (1.5% NaCl) the WOR is 8.4. This demonstrates that the additional oil recovery utilizing Marasperse solutions was obtained between breakthrough and about 1.0 PV. A lower WOR of 8.4 for the waterflooding run shows that the recovery of oil is spread over a longer time. Table 19 shows that low pore volumes of Marasperse could be injected at the secondary stage to obtain additional recoveries. As reported by Kalfoglou(14), such a preflush also reduces the adsorption of the expensive petroleum sulfonate in the tertiary stage.

When employing Marasperse for the tertiary stage of recovery, a small amount of additional oil (app. 4%) was recovered. Figs. 19-21 show the recoveries for cores flooded with Brine (1.5% NaCl) up to approximately 2 PV, followed by flooding with Marasperse employing 1%, 3% and 10% N-22. All these flooding results show that after breakthrough of Marasperse in the effluent, the additional oil recovery, although more than for an extended Brine flood, was rather low. The Marasperse solutions tend to travel in the more permeable aqueous channels created during the secondary waterflooding stage. Since the pressure drop remains constant during injection of Marasperse solutions, the additional oil recovery is attributed to the small amount of oil released, and subsequently emulsified, because of a reduction in the interfacial tension. A time lag equivalent to 0.17 PV for the breakthrough also indicates small improvement in the areal sweep efficiency. Conventional micellar flooding involves the use of petroleum sulfonates, which can solubilise oil and render low interfacial tensions with crude oil(18). This leads to 100% tertiary oil recovery from sand parks. Use of emulsions for EOR has been reported in the literature (18,22). All of these methods are based upon the presence of soluble oil in the displacing fluid which is miscible with the crude oil. Since Marasperse solutions do not have any solubilising capability for oils, emulsions externally made from the oil and Marasperse solutions may show improved recoveries when used as displacing fluids.

The results of waterflooding of cores saturated with oils of different viscosities are shown in Table 16 and

Figs. 12-15. Toluene and Kerosene showed high breakthrough and ultimate recoveries with only a slight chanelling effect. For oil No. 2, the recovery after breakthrough was low and high water-oil ratios were observed. For oil No. 4, the viscous fingering effects were more pronounced and yielded a breakthrough displacement efficiency of only 32.7%. The recovery after breakthrough was substantial and would have yielded more oil had the injection been continued beyond 2 PV, as shown by the relatively high oil content in the effluent (low WOR) at 2 PV.

CHAPTER 7

CONCLUSIONS

CONCLUSIONS

The following conclusions have been reached from this investigation:

1. Marasperse solutions yield small reductions in interfacial tension when used in varying concentrations (1%-10%).
2. Marasperse solutions are pseudoplastic in nature. The increase in viscosity, even for higher concentrations, is not appreciable with regard to producing favorable mobility ratios.
3. Addition of sodium chloride to Marasperse solutions leads to a fall in viscosity.
4. Results of sandpack flooding experiments, using Marasperse solutions directly, indicate that Marasperse solutions yield approximately 7% additional oil.
5. Marasperse solutions, when used for displacing residual oil, tend to follow the aqueous channels which result from water flooding.

CHAPTER 8

RECOMMENDATIONS

RECOMMENDATIONS

The following recommendations are made with regard to continuation of this work:

(i) Since the interfacial tension between oil and lignosulfonates cannot apparently be reduced to the desirable level of about 0.05 dynes/cm, a study should be carried out using other conventional surfactants or additives. Such combinations of surfactants could give desirable interfacial tensions and an optimum mix of lignosulfonates and conventional surfactants (for example petroleum sulfonates) could possibly be established.

(ii) When mixing additives with lignosulfonates for the purpose of obtaining ultra-low interfacial tensions, crude oils should be used, since the presence of certain chemicals in the crude oil may undergo surface reaction with the surfactant-additive system.

(iii) After an optimum mix of lignosulfonates and petroleum sulfonates has been established, the study may be extended to the use of Berea sandstone cores for displacement tests.

(iv) Since Marasperses are strong emulsion stabilisers, further study should be conducted using externally made emulsions of the Marasperse and the oil under consideration. The presence of oil in this displacing fluid could lead to higher additional recoveries.

CHAPTER 9

NOMENCLATURE

NOMENCLATURE

A: Pattern area

A_c: Cross-sectional area of porous medium, cm^2

A_S: Swept area

A_{SB} Swept area at breakthrough

d: Density of the upper phase (oil), gm/cc

D: Density of the lower phase (aqueous), gm/cc

E_a: Areal sweep efficiency, %

E_d: Displacement efficiency, %

f: Fraction of a fluid in the flowing system

Δh: Fall in level of the injection fluid reservoirs, cm.

k: Relative permeability of the medium to fluid, darcy

K: Permeability of the medium (single phase), darcy

K_o, K_w: Permeability of oil and water during their simultaneous flow.

L: Length of porous medium, cm.

M: Mobility ratio

p: Pressure of fluid in the porous medium, atmospheres

p_c: Capillary pressure, atmospheres

P: Apparent surface/interfacial tension, dynes/cm

ΔP: Pressure differential, atmospheres

q: Volumetric flow rate, cc/sec.

$r_1 r_2$: Principal radii of curvature, cm.

Re: Reynolds number

R_B: Oil recovery at breakthrough, %

R_V: Ultimate recovery for given pore volume injection,%

S: Saturation of the porous medium with respect to a fluid

t: Time, sec.

t_B: Breakthrough time, sec.

V_o: Volume of oil recovered at any time, cc

V_w: Volume of water recovered at any time, cc

V_B: Volume of oil recovered at Breakthrough, cc

V_C: Internal Volume of Core-Holder, cc

V_p: Pore volume, cc

V_T: Total volume of oil in the core-holder, cc

V_u: Ultimate volume of oil recovered, cc

V_w: Actual total water injected in the core-holder, cc

W_s: Weight of sand filled in core-holder, Kgm

x: Distance along the length of the porous medium, cm

ρ: Density of fluid, gm/cm^3

μ: Viscosity of fluid, centipoise

δ: Average sand grain diameter, cm

ρ_s: Density of sand, gm/cc

ϕ: Porosity

γ: Surface/interfacial tension, dynes/cm

SUBSCRIPTS

w: Water or aqueous/wetting phase

o: Oil phase

nw : Non-wetting phase

CHAPTER 10

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Aronofsky, J.S., "Mobility Ratio-Its Influence on Flood Pattern During Water Encroachment", Trans. AIME (1952), Vol. 195, 15-24.

2. Dyes, A.B., Caudle, B.H. and Erickson, R.A., "Oil Production After Breaktrhough-As Influenced by Mobility Ratio", Trans. AIME (1954), 201, 81.

3. Pye, D.J., "Improved Secondary Recovery by Control of Water Mobility", J. Pet-Tech (August 1964) 911-916.

4. Patton, J.T., Coats, K.H. and Colegrove G.T., "Prediction of Polymer Flood Performance", Society of Petroleum Engineers Journal, (March 1971) 72-84.

5. Lee, K.S., Claridge, E.L., "Areal Sweep Efficiency of Pseudoplastic Fluids in a Five-Spot Hele-Shaw Model", Society of Petroleum Engineers Journal (March 1968), 52.

6. De Groot, M., "Flooding Process for Recovering Oil from Subterranean Oil Bearing Strata", US Patent No. 1, 823, 439 (1934).

7. Holbrook, O.C., "Surfactant-Water Secondary Recovery Process", US Patent No. 3, 006, 411 (1961).

8. Bobek, J.E., Mattax, C.C. and Denekes, M.O., "Reservoir Rock Wettability-Its Significance and Evaluation," Trans. AIME (1958) Vol. 213, 155-160.

9. Wagner, O.R., Leach, R.O., "Improving Oil Displacement Efficiency by Wettability Adjustment," Trans. AIME (1959), 216, 65.

10. Mungan, N., "Certain Wettability Effects In Laboratory Waterfloods," J. Pet. Tech. (February 1966) 247-252.

11. Dranchuk, P.M., Scott, J.D. and Flock, O.L., "Effects of the Addition of Certain Chemicals on Oil Recovery During Waterflooding", J. Can. Pet. Tech., July 1974.

12. Ehrlich, R. and Wygal, R.J., Jr., "Interaction of Crude Oil and Rock Properties With the Recovery of Oil by Caustic Waterflooding", Society of Petroleum Engineers Journal (August 1977) 263-269.

13. De Groot, M. and Monson, L.T., "Flooding Process for Recovering Fixed Oil from Subterranean Oil Bearing Strata", US Patent No. 1, 823, 440 (1931).

14. Kalfoglou, G., "Lignosulfonates as Sacrificial Agents in Oil Recovery Processes", US Paten No. 4006779 (1975).

15. Parker, H., US Patent No.3384171 (1968).

16. Atkinson, H., US Patent No. 1,651,311 (1927).

17. Ojeda, E., Preston, F.W., and Calhoun, J.C., Jr., "Correlations of Oil Residuals Following Surfactant Floods", Prod. Monthly, 18, No. 2, (Dec. 1953), 20.

18. Gogarty, W.B. and Tosch, W.C., "Miscible-Type Waterflooding: Oil Recovery with Micellar Solutions," J. Pet. Tech. (December 1968) 1407-1414.

19. Hill, H.J., Reisberg, J. and Stegemeier, G.L., "Aqueous Surfactant Systems for Oil Recovery", J. Pet. Tech. (February 1973) 186-194.

20. Knaggs, E.A., Nussbaum, M.L., Carlson, J.B. and Guenzani, R.C., "Petroleum Sulfonate Utilization in Enhanced Oil Recovery Systems," paper SPE 6006 presented at SPE-AIME 51st Annual Fall Technical Conference held in New Orleans, Oct. 3-6, 1976.

21. Gogarty, W.B., "Status of Surfactant or Micellar Methods", J. Pet. Tech. (Jan. 1976) 93-102.

22. Healy, R.N. and Reed, R.L., "Immiscible Microemulsion Flooding", Society of Petroleum Engineers Journal (April 1977) 129-139.

23. Jones, S.C. and Dreher, K.D., "Cosurfactants in Micellar Systems Used for Tertiary Oil Recovery", Society of Petroleum Engineers Journal (June 1976) 161-167.

24. Bae, J.H. and Petrick, C.B., "Adsorption/Retention of Petroleum Sulfonates in Berea Cores", Society of Petroleum Engineers Journal (October 1977) 353-357.

25. Lawson, J.B. and Dilgren, R.E., "Adsorption of Sodium Alkyl Aryl Sulfonates on Sandstone", Society of Petroleum Engineers Journal, (February 1978) 75-82.

26. The Oil and Gas Journal, April 3, 1978, 46.

27. Herbeck, E.F., Heintz, R.C. and Hastings, J.R., "Fundamentals of Tertiary Oil Recovery", Energy Communications, Dallas (1977).

28. Anderson, E.V., "Enhanced Oil Recovery: Big Chemical Potential", Chemical and Engineering News (Jan. 24, 1977) 12-13.

29. Doscher, T.M., "Tertiary Oil Recovery and Chemistry", Chemtech. (April 1977) 232-239.

30. Salathiel, R.A., "Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks", Journal of Petroleum Technology (Oct. 1973) 1216-1224.

31. Treiber, L.E., Archer, D.L. and Owens, W.W., "A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs", SPEJ (December 1972), 531-540.

32. Chemicals from Wood, Bulletin No. 131, American Can Company, Greenwich, Conn. (USA).

33. Marasperse for Stabilizing Oil-in-Water Emulsions Bull. 119-R, American Can Company, Greenwich, Conn. (USA).

34. Rothrock, R., Jr., "Residual Oil Determination Key to Economic Enhanced Recovery", Petroleum Engineer, November 1977, 18-19.

35. Collins, R.E., "Flow of Fluids Through Porous Materials", Reinhold Publishing Corporation, New York (1961), 142.

36. Frick, T.C. and Taylor, R.W., "Petroleum Production Handbook" Volume II Reservoir Engineering, McGraw-Hill (1962).

37. Scheidegger, A.E., "The Physics of Flow Through Porous Media" University of Toronto Press, 3rd Edition (1972).

38. Larsen, R.G. and Hirasaki, G.J., "Analysis of the Physical Mechanisms in Surfactant Flooding", Society of Petroleum Engineers Journal, (February 1978), 42-58.

39. Tickell, F.G., Mechen, O.E. & McCurdy, M.C., "Some Studies on the Porosity and Permeability of Rocks", AIME 1933, 250-260.

40. Wyman, R.E., "Tertiary Recovery Presents Challenge to Produce More Crude from Older Fields", Oil Week (Dec. 2, 1974); 12-15.

APPENDICES

APPENDIX A

Calibration of Feed Pump

The Feed Pump was calibrated for different stroke lengths and a calibration curve made covering the entire range. Following two methods were used to measure the capacity

(i) Measure the drop in liquid level from calibrated vessel

(ii) Measure the quantity collected from the discharge side of the pump.

The calibration curve for the Feed Pump is given in Fig. 30.

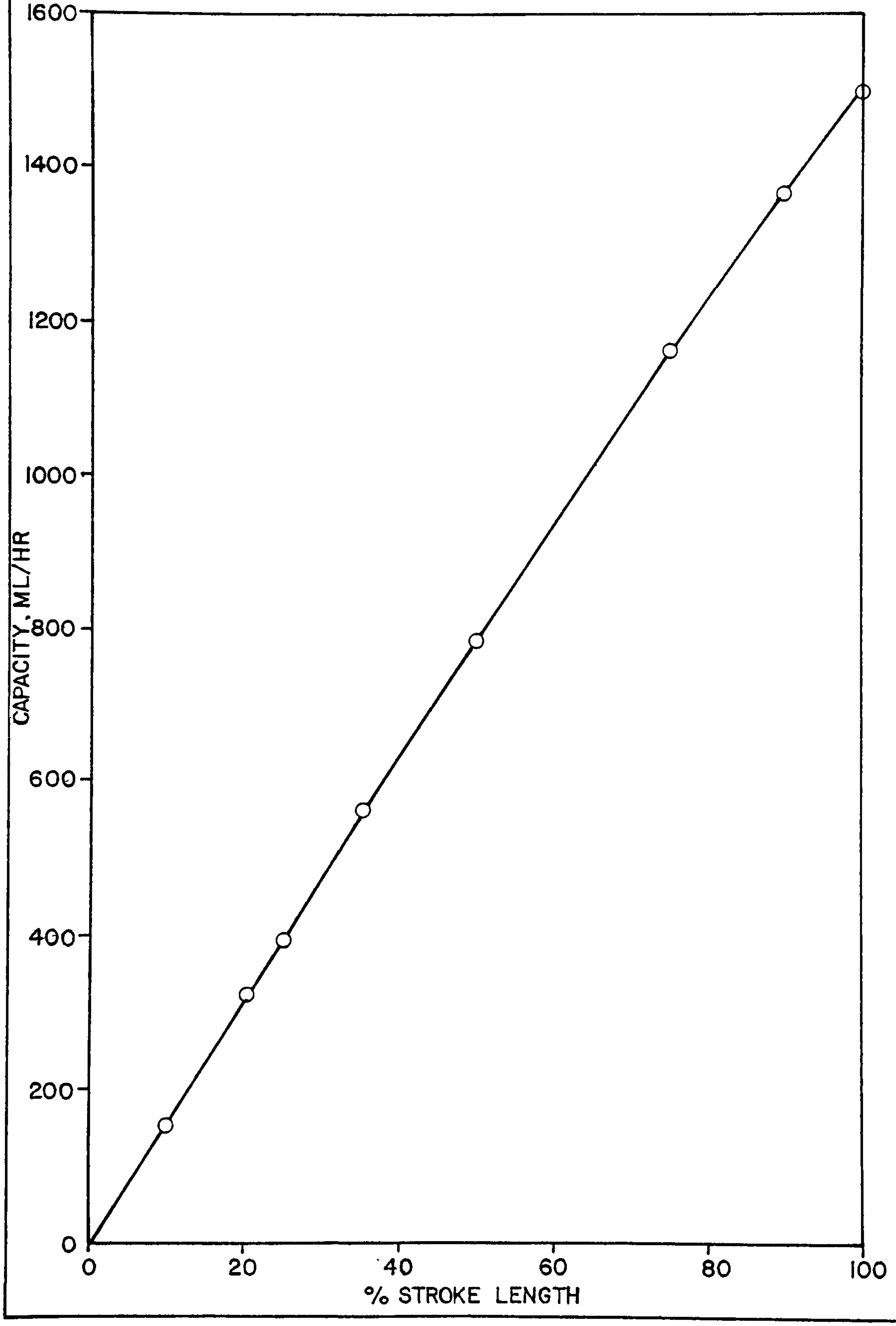


FIG. 30 CALIBRATION CURVE FOR FEED PUMP

APPENDIX B

LEAKAGE TEST

A leakage test was performed before saturation of bed with oil. A typical leakage test when the core-holder and the associated piping were isolated from the vacuum pump is shown in Table 21.

TABLE 21

TYPICAL LEAKAGE TEST FOR CORE HOLDER

Atmospheric pressure: 758.2 mm Hg.

Time Minutes	Manometer Reading		Vacuum Reading cm Hg
	Right	Left	
0	37.7	38.1	75.8
4	37.7	38.1	75.8
8	37.7	38.1	75.8
12	37.7	38.1	75.8
16	37.7	38.1	75.8
20	37.6	38.0	75.6
24	37.5	37.9	75.4
28	37.5	37.9	75.4
30	37.5	37.9	75.4

APPENDIX C

EXPERIMENTAL DATA

All displacements runs were taken for an injection rate of 385-390 ml/hr. Ottawa sand with specifications as shown in Table 10, was used. The displacement runs, therefore, were based on a constant porosity, pore volume and initial oil saturation. All runs were conducted at 24±0.5°C.

TABLE 22

WATERFLOODING RUNS FOR VARIOUS OILS USED

Run No.	Oil	Displacing Fluid	Approximate Pore Volumes Injected	Breakthrough PV
1	Toluene	Water	2	0.934
2	Kerosene	Water	2	0.942
3	Oil No.2	Water	2	0.855
4	Oil No.4	Water	2	0.327

TABLE 23

EXPERIMENTAL DATA FOR OIL NO. 4 AND MARASPERSE SOLUTIONS

Run No.	Displacing fluid	Approximate pore volume injected	Breakthrough pore volume	Oil Collected (pore volume)	
				Breakthrough	Ultimate
5	1% N-22 1.5% NaCl	2.4	0.344	0.316	0.658
6	3% N-22 1.5% NaCl	2.5	0.352	0.323	0.669
7	10% N-22 1.5% NaCl	2.7	0.379	0.346	0.740
8	1.5% NaCl	4.0	0.350	0.327	0.770
9a	1.5% NaCl	2.0	0.357	0.327	0.590
9b	1% N-22	2.0	0.489	0.0605	0.240
10a	1.5% NaCl	2.0	0.360	0.327	0.589
10b	3% N-22	2.0	0.497	0.059	0.239
11a	1.5% NaCl	2.0	0.352	0.324	0.591
11b	10% N-22	2.0	0.532	0.0605	0.240

TABLE 24

DATA FOR ABSOLUTE PERMEABILITY OF CORE-HOLDER

Temperature: 23.8°C

Pump Setting %	Flow Rate ml/hr.	Manometer Reading Rm, cm
10	156	2.92
20	323	5.95
25	394	7.67
35	562	10.42
40	647	12.19
50	789	14.86
60	942	17.78
70	1087	20.42
80	1225	23.27
90	1353	25.81
100	1500	28.30

Manometer Fluid D-8325, Meriam, Sp. Gr. 1.75

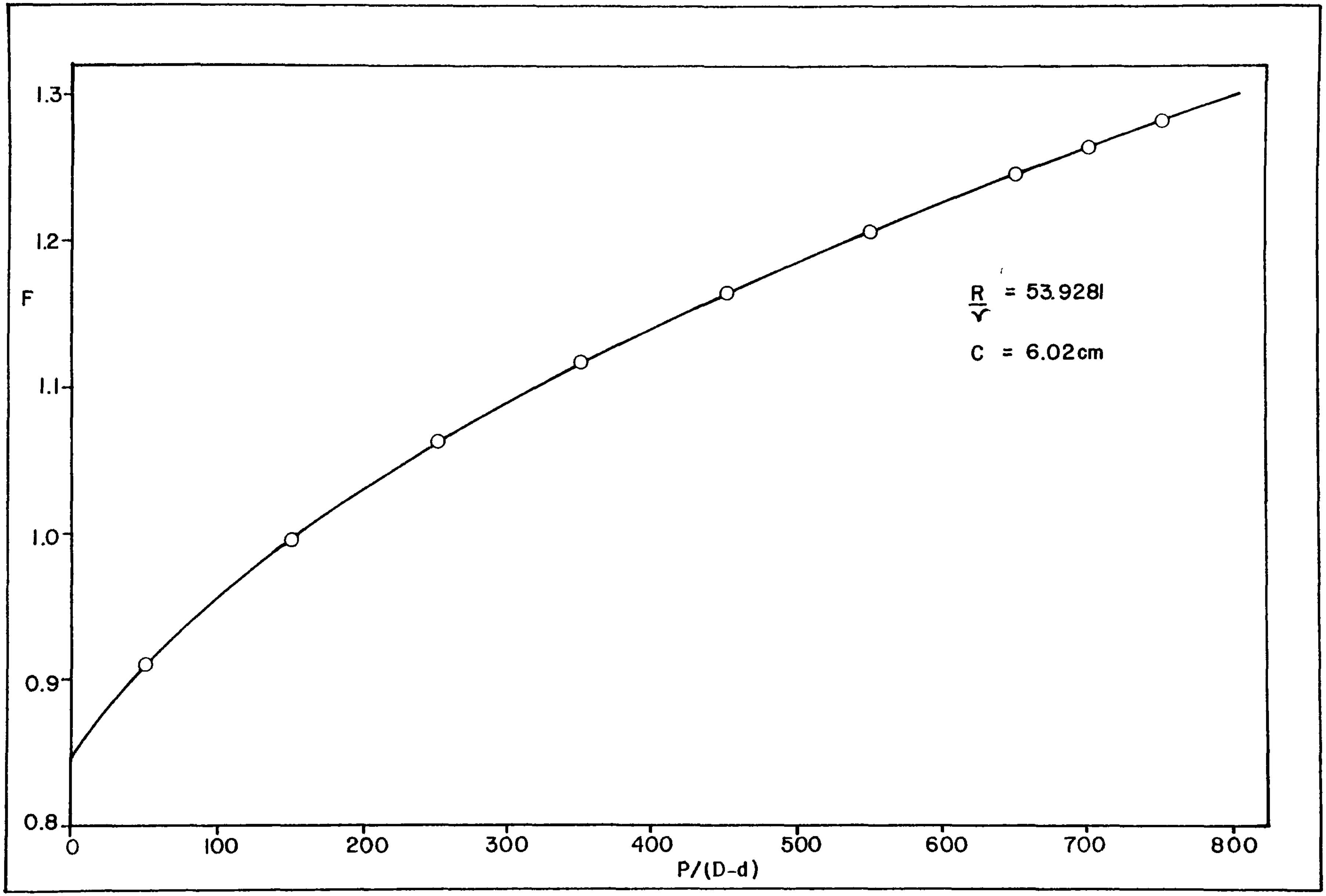


FIG. 31 $\frac{P}{D-d}$ Vs F FOR AUTOTENSIOMAT

APPENDIX D

SAMPLE CALCULATION

The experimental data pertaining to Run No. 9 is used below for this calculation.

1. Porosity, Pore volume

a) $\phi = 1 - \frac{W_s}{V_c x \rho_s}$

$\phi = 1 - \frac{4559}{2595.8x2.6502} = 0.3373$

b) $V_p = \phi V_c$

$= 0.3373x2595.8$

$= 876$ ml

c) $V_T = 19.3\ (\Delta h)$

$= 19.3x46.8$

$= 903$ ml

Actual volume = V_T - Volume of Oil in piping, windows

= 903-17

= 886 ml

2. Recovery

Actual Volume of Oil recovered at breakthrough = 300-13

$V_B = 287$ ml

Actual Volume of Oil recovered after 2PV = 530-13=517 ml

$$R_B = \frac{V_B}{V_p} x100 = \frac{287}{876} x100 = 32.7\%$$

$$R_V = \frac{V_u}{V_p} x100 = \frac{517}{876} x100 = 59.02\%$$

3. Volume Balance

(i) Water Injected = Pumping Rate x Time

= 389x4.63

= 1800 ml

(ii) Water Injected = Cross-Sectional Area x Fall in Level

= 283.54x6.3

= 1787 ml

Water Injected = 1793 ml (average)

(iii) Actual Water to the pores = 1793-7

= 1786 ml

(iv) Recovered Oil = 530 ml

Water = 1225 ml

(v) Volume in downstream piping = 17 ml

Inlet Volume = 1786 ml

Outlet Volume = 1225+530+17=1772 ml

4. Actual Breakthrough Time

Actual Breakthrough Time = Time noted - Time for the outlet length of the piping

= 2987-60

= 2927 sec

= 48.8 min.

5. Velocity in Pores and Chanelling

$$\text{Velocity in pores} = \frac{389}{21.3} \times \frac{1}{0.3373} \quad \frac{cm}{hr.}$$

= 54.14 cm/hr.

Breakthrough time for no chanelling $= \frac{121.7}{54.14}$ hrs.

$= 135$ min.

6. Pore Volume Calculations

Pore volume - 876 ml

Pumping Rate = 389 ml/hr = 6.48 ml/min.

$\therefore$ PV Injected $= \frac{\text{Rate x Time}}{\text{PV}} = \frac{6.48}{876}$ x Time

where Time is in minutes for every collection of known volume

PV produced $= \frac{V_o}{876}$ for oil

$= \frac{V_w}{876}$ for water

7. Recovery Data:

The oil recovery data is shown in Table 25.

TABLE 25

OIL RECOVERY DATA

PV Injected (Water/Surfactant)		PV produced		Oil Recovery %	WOR
		Oil	Water		
0	0	0	0	0	0
0.0224	0	0	0	0	0
0.1449	0.1225	0.1142	0	10.67	0
0.2577	0.2353	0.2283	0	23.09	0
0.3692	0.3468	0.3425	0	33.50	0
0.4829	0.4605	0.3664	0.0902	35.16	3.76
0.5967	0.5743	0.3870	0.1838	37.22	4.56
0.7138	0.6914	0.4076	0.2774	39.27	4.56
0.8310	0.8086	0.4269	0.3722	41.21	4.88
0.9472	0.9248	0.4450	0.4679	43.04	5.17
1.0629	1.0405	0.4635	0.5640	44.86	5.25
1.1786	1.1562	0.4818	0.6598	46.69	5.25
1.4696	1.4472	0.5251	0.9018	51.03	5.58
1.5852	1.5628	0.5422	0.9989	52.74	5.67
1.7014	1.6790	0.5594	1.0959	54.45	5.67
1.8247	1.8023	0.5754	1.1998	56.05	6.5
1.9402	1.9178	0.5902	1.2991	57.53	6.7
2.0540	2.0316	0.6050	1.3984	59.02	6.7

Calculations of Permeability

Flow Rate ml/hr.	Manometer Reading Rm,	Pressure Drop $\Delta P = Rm \times 0.7284, atm \times 10^3$
156	2.92	2.13
323	5.95	4.33
394	7.67	5.59
562	10.42	7.59
647	12.19	8.88
789	14.86	10.82
942	17.78	12.95
1087	20.42	14.87
1225	23.27	16.95
1353	25.81	18.80
1500	28.30	20.61

Slope of straight line through $= 0.0137581 \times 10^{-3} \frac{\text{atm}}{(\text{ml/hr})}$

origin using least square fitting

$$\text{Slope} = \frac{\mu L}{KA}$$

$$K = \frac{0.9185}{21.29} \times 60.96 \times \frac{1}{0.0137581 \times 10^{-3}}$$

$$K = 53.10 \text{ Darcy.}$$

$$\text{Reynolds Number, } R_e = \frac{q.\rho\delta}{UA_c\phi}$$

$$= \frac{q.(0.9973)}{0.9142 \times 21.3} \times \frac{0.3512}{10} \times \frac{100}{0.3373}$$

$$= 0.5333(q)$$

$$\text{Maximum Reynold No, } R_e = 0.5333 \times \frac{1500}{3600} = 0.222$$

$$\text{Operating Reynold No, } R_e = 0.5333 \times \frac{390}{3600} = 0.058$$

Calculation of Shear Stress in the Pores

For visometer,

Shear stress $= \frac{\text{Torque}}{2\Pi R^2 L}$, R, radius of spindle, cm
L, length of spindle, cm

$$\text{Shear stress} = \frac{6.737\ (\text{Dial Reading})}{2\Pi\ (1.26)^2 \times 9.07}$$

$$\text{Shear stress} = 0.07446\ (\text{DR})$$

For the porous medium,

Hydraulic Radius for a porous bed is given by

$$R_h = \frac{\phi\ D_p}{6(1-\phi)},\quad D_p: \text{ mean particle diameter}$$

$$\text{Shear stress} = R_h \quad \frac{\Delta P}{2L}$$

$$\text{Shear stress} = \frac{\phi\ D_p}{6(1-\phi)} \cdot \frac{\Delta P}{2L}$$

$$\text{Shear stress} = \frac{0.3373 \text{x} 0.3512}{6 \text{x} (1-0.3373)} \times \frac{1}{10} \times \frac{(1.55 \text{x} 1.033 \text{x} 1000 \text{x} 980)}{76.0} \text{x} \frac{1}{2} \times \frac{1}{2 \text{x} 30.54}$$

Shear stress $= 0.504$ dyne/cm^2

This shear stress corresponds to a dial reading of 6.77 and a viscosity of ∿1.6 cp at 25°C for Marasperse solution of 10% N-22 and 1.5% NaCl.