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EFFECTS OF INTERFACIAL REACTION ON OIL
DISPLACEMENT
IN A HELE-SHAW CELL

BY

FAKHIR U. BAIG

A THESIS PRESENTED TO THE UNIVERSITY OF OTTAWA IN PARTIAL FULFILMENT OF
THE REQUIREMENT FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE
IN
CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF OTTAWA
OTTAWA, ONTARIO



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UNIVERSITÉ D'OTTAWA
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To my wife Saadia

ABSTRACT

An experimental study was conducted to examine the behaviour of reactive and non-reactive systems by displacement experiments of light paraffin oil/decane mixtures by water in a range of mobility ratios. Displacement experiments were performed in a Hele-Shaw cell, simulated a quarter of a reversed five-spot pattern. Displacement patterns produced by reactive and non-reactive systems were compared. It showed that the displacement patterns in the case of the reactive system were completely different from the non-reactive system. The recovery in the reactive system was always higher than in the non-reactive system. The recovery at breakthrough for both the reactive and non-reactive systems increased with the decrease in viscosity of oil. In the non-reactive system, total recovery at one hour after breakthrough increases with the decrease in oil viscosity and becomes constant at 63%, when the oil viscosity reaches 6.86 mPa.s, while in reactive system total recovery after one hour is nearly constant and independent of oil phase viscosity. The effect of the flow rate of injecting fluid was also investigated, but it did not have any significant effect on recovery in the range studied.

Displacement experiments were performed for both favourable and unfavourable mobility ratios. It was found that when mobility ratio was 0.04 (i.e. very favourable) the recoveries at one hour after breakthrough for the non-reactive system and the reactive system were almost the same, close to 100%. For unfavourable mobility ratios ranging from 26.7 to 1.0, the recovery was from 22.0% to 63.0% in the non-reactive system, while in the case of reactive system it was close to 100% in all the cases.

In another series of displacement experiments, a slug of alkaline solution was injected followed by viscous water-glycerine solution. It was found that for all oil solutions, the breakthrough recovery for both reactive and non-reactive systems was lower in the case with a viscous back up. After one hour however total recovery for the non-reactive system was higher in the case using a back up. In the case of the reactive system for 100% paraffin oil the recovery was lower in the case of back up, but at other viscosities the recovery was almost the same as in the case without back up.

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NOMENCLATURE

EOR	Enhanced oil recovery
IFT	Interfacial tension
N_{Ca}	Capillary number
r_w	Radius of five-spot pattern
u	Velocity
d	Diameter
k	Permeability
q	Flow rate
$\Delta\Phi$	Potential change
μ	Viscosity
ρ	Density
γ	Interfacial tension
p	Pressure
g	Acceleration due to gravity

Units

mPa.s	Viscosity
gm / mL	Density

Chapter 1

INTRODUCTION

The first petroleum shortage in North America occurred during the 1920's. Demand for fuel oil doubled and demand for gasoline almost tripled during the first half of that decade. It was this shortage of petroleum that gave birth to enhanced oil recovery research.

It is estimated that less than a third of the oil in reservoirs which were discovered in North America can be recovered economically by either primary production (initial flow of oil) or secondary production (by injection of water into the reservoir). The remaining large amount of petroleum represents the oil trapped underground due to the large capillary forces present in the small pore structure of the reservoir rock or the high viscosity of the crude.

More than one-half of world wide enhanced oil recovery (EOR) production is estimated to be in North America. It now seems certain that EOR processes will make a significant and growing contribution to oil recovery world wide, but particularly so in North America, where prospects for discovery of new, large oil fields are small and declining. Yet current recovery technology leaves approximately two-thirds of the discovered oil in the ground. This creates a very large and tempting target for improved recovery (George and Marvin, 1990).

Enhanced oil recovery is generally considered as the third, or last, phase of useful oil production and is sometimes called tertiary production. The first or primary phase of production begins with the discovery of an oil field. A typical reservoir, as shown in Figure 1, consists of a layer of porous rock, such as sandstone, bounded both above and below by an impervious rock formation, usually granite or shale. Over a period of millions of years, water, oil and gas accumulate in the porous medium and separate into fairly distinct layers due to gravity effects. The crude oil is trapped in the pores of the rock by natural forces resulting from viscosity, interfacial tension, and capillarity. These forces must be overcome in order for the oil to be produced.

1.1 STAGES OF PRODUCTION

1.1.1 *PRIMARY RECOVERY*

When a well is drilled through the impervious cap of an oil reservoir, a pressure sink is formed and the reservoir contents are able to flow to the wellhead at the surface due to the expansion of reservoir fluids. This production of oil by natural energy is called primary recovery and can occur by one of three principal drive mechanisms:

1. Solution gas drive.
2. Gas cap drive.
3. Water drive.

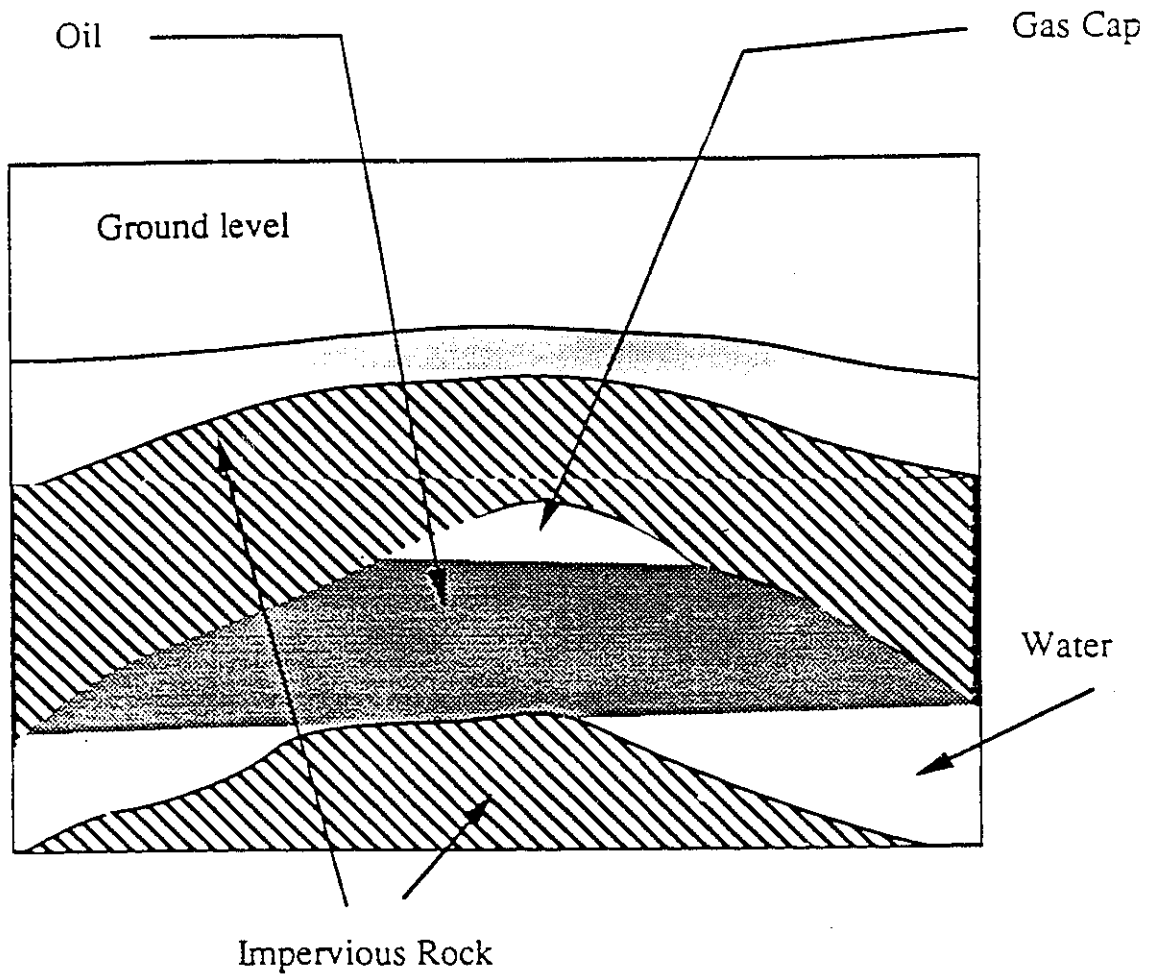


Figure 1: A typical oil reservoir

In a solution gas drive reservoir, the gases dissolved in the crude oil expand and come out of the solution as the pressure in the reservoir drops. This expansion of gases causes the oil to be driven towards the wellbore. As production continues, the pressure in the expanding gas is no longer sufficient to cause the oil to flow to the surface, and pumping is required for further oil production. In a solution gas drive reservoir, the primary recovery is usually quite low, on the average 5 to 25% of the original oil-in-place (Prince,1978). Another recovery technique (source of energy) for the production of oil is water encroachment from an adjoining aquifer, as a result of the lower pressure at the wellbore. The aquifer associated with a water drive reservoir is often much larger than the reservoir itself, and thus the energy supplied by the aquifer results in continued oil production over a long period of time. An effective water drive reservoir is characterised by a slow and gradual drop in reservoir pressure with time, and thereby a high recovery efficiency.

When the pressure in the reservoir is not high enough to maintain all the light hydrocarbon in solution , free gas collects in the porous medium above the oil, creating a gas cap drive reservoir. A drop in pressure at the wellbore causes the gas cap to expand and displace oil towards the production well. Also, this drop in pressure allows the gas dissolved in the oil to come out of solution which aids in forcing the oil towards the wellbore. Because the gas cap can expand considerably, the decline in reservoir pressure occurs more slowly than in a solution gas drive reservoir, and thus the oil recovery is higher, usually 20 to 40% (Prince,1978).

1.1.2 SECONDARY RECOVERY

Production of oil by the natural reservoir energy continues until this energy is depleted to the point where there is not sufficient force to drive the oil to the surface. At this point, it is necessary to supply energy from an external source for further production. This is accomplished by a technique known as pressure maintenance, in which a large volume of water, or sometimes gas, is injected into the reservoir through a separate well (Jha,1982).

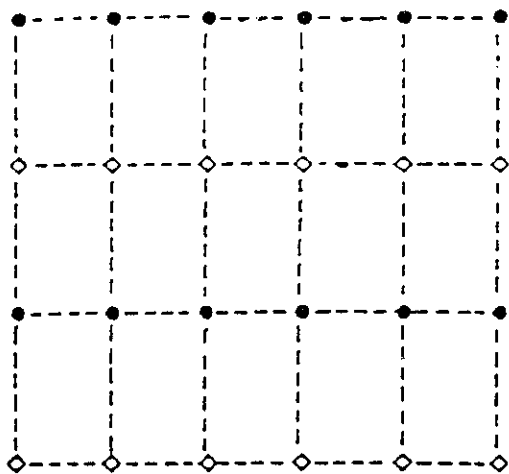
The injected fluid restores pressure in the reservoir, helps to keep the dissolved gases in solution (which maintains a low oil viscosity), and forces the oil through the porous rock to the production well. The injection of water results in a second harvest of oil, hence the name secondary recovery. In a water flooding operation, injection wells are drilled in a pattern around the production wells. Some typical patterns of well placement are shown in Figure 2. The most common pattern is the five-spot, which is actually a staggered line drive with the spacing between adjacent production wells and injection wells being the same. When water is injected into an oil reservoir, it displaces some of the oil remaining in the pores of the rock. This oil forms an oil bank which is then pushed towards the producing well. Secondary recovery techniques may produce 15 to 30% oil, which means that substantial quantities of oil are still trapped in the reservoir. This remaining oil can often be produced by various other methods, collectively known as Enhanced Oil Recovery techniques.

1.1.3 ENHANCED OIL RECOVERY OR TERTIARY RECOVERY

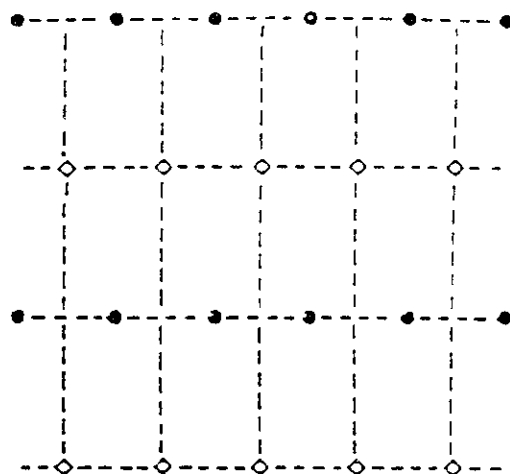
The term Enhanced Oil Recovery (EOR) has been defined in many ways. Jha(1982) uses this term to describe all the techniques used to increase the amount of oil obtained after primary recovery, thereby including water flooding as an EOR process. Within the many enhanced recovery techniques, there is a class of processes, known as tertiary processes, designed to recover oil, commonly described as residual oil, left in the reservoir after both primary and secondary recovery methods.

It has been estimated that United States's and Canada's crude oil reserves would be more than doubled if only ten percent of the oil, which is unrecoverable by other methods could be produced by some type of enhanced recovery process.

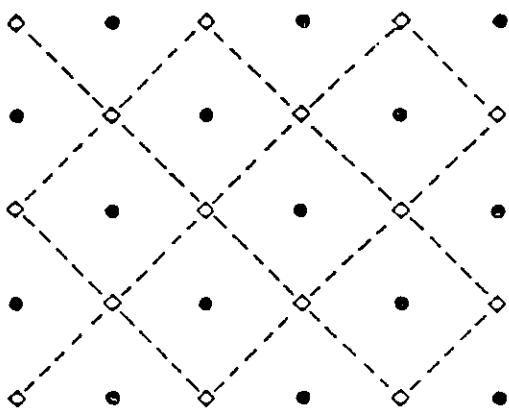
The technical and economic viability of an EOR process is dependent upon the oil saturation after primary recovery, the microscopic displacement efficiency and the volumetric sweep efficiency (Jha,1982).



Direct Line Drive



Staggered Line Drive



Five-Spot

- Production Well
- ◇ Injection Well
- Pattern Boundary

Figure 2 : Some typical patterns of well placement

These factors are in turn influenced by the past production history of the reservoir. The microscopic displacement efficiency is the fraction of the oil contacted by the injected fluid that is displaced or forced out of the pores in the reservoir rock. The oil left in the reservoir is called the residual oil and occurs in one of two forms. In a water-wet reservoir, the residual oil takes the form of droplets of oil surrounded by water and trapped in the pore spaces by interfacial forces. In an oil-wet reservoir the residual oil exists as a thin film spread on the reservoir rock.

The volumetric sweep efficiency, the product of the areal and vertical sweep efficiencies, is determined by the physical properties of the reservoir (permeability and porosity) as well as the mobility ratio of the injected fluid to the displaced fluid. Areal sweep efficiency is the fractional area of the field that is invaded by an injected fluid and vertical sweep efficiency is the fraction of the vertical section that is contacted by injected fluids.

The mobility of a fluid in a porous medium is a measure of the ease with which fluid flows through the medium, and is defined as the permeability of the formation to that fluid divided by the viscosity of the fluid.

$$\lambda = \frac{k}{\mu} \quad (1)$$

Mobility ratio can be defined as:

$$M = \frac{k_w/\mu_w}{k_o/\mu_o} \quad (2)$$

where k represents the permeability of each fluid and μ is the viscosity of each fluid.

There are two main objectives in order to improve oil recovery :

- a) To improve the microscopic displacement efficiency either by altering the forces that trap the oil in the rock pores, or by increasing the potential energy of the oil by increasing the pressure gradient in the reservoir or by solubilization of injected gas.
- b) To improve the sweep efficiency, and thus the portion of the reservoir contacted by the displacing fluid, by altering the mobility ratio or the flow paths developed during primary recovery.

In many cases, techniques which increase the displacement efficiency can actually reduce the sweep efficiency and therefore an optimal mix of these two objectives is required for a successful EOR application (Jha,1982). The choice of EOR process for a given reservoir depends on many factors, such as the geology and physical properties of the reservoir, and past production methods.

1.2 STATUS OF EOR PROJECTS IN NORTH AMERICA

Enhanced oil recovery methods hold promise for recovering a significant portion of the oil that will be left in the ground after conventional recovery. Conventional recovery includes primary recovery techniques and secondary recovery methods where fluids are injected to displace oil towards producing wells.

A study done for the U.S.Federal Energy Administration in 1974 indicated that tertiary oil recovery accounted for 3% of the total oil production in the United States and Canada, the remaining 97% being about equally divided between primary and secondary recovery.

On the one hand, the contribution of primary oil production continues to decline and currently amounts to about 40% of total U.S. oil production. On the other hand, both secondary and tertiary oil recovery methods have shown steady increases amounting to 52% and 8% respectively.

The trend is towards secondary and tertiary oil production, because oil fields in North America are aging and new discoveries are much smaller in size (George and Marvin, 1990).

1.2.1 NUMBER OF EOR PROJECTS AND PRODUCTION TRENDS IN NORTH AMERICA

The decade of the 1980's evidenced very rapid growth of oil production and in the number of active EOR projects in North America. In the United States EOR production more than doubled between 1980 and 1988, and the EOR production increased by a factor of six in Canada in the same period of time. The number of active EOR projects at that time about doubled in both countries. These trends are illustrated graphically in Figure 3 but do not include mining and in-situ recovery projects in the tar sands of Alberta, Canada.

Despite the downward oil price drift which began in 1981 and culminated with a sharp price decline late in 1986, both the EOR production and the number of active EOR projects increased steadily through 1986. After that, EOR production managed to retain the upward momentum, although a number of active EOR projects were reaching completion, and there were only a few new starts; operators concentrated on getting the most from their investment to limit potential losses due to the very low oil prices.

However, new EOR project starts declined steadily throughout the 1980's in the United States. The outlook for various technologies differs significantly. Steam injection has been and will remain by far the most commercially successful EOR technology. That is largely true in the United States, where nearly three-fourths of all EOR production in 1988 came from steam injection. The best candidates, however, have already been developed, and because the remaining prospective projects are in poorer reservoirs, they will likely not achieve the same degree of success as the first generation projects (George and Marvin, 1990).

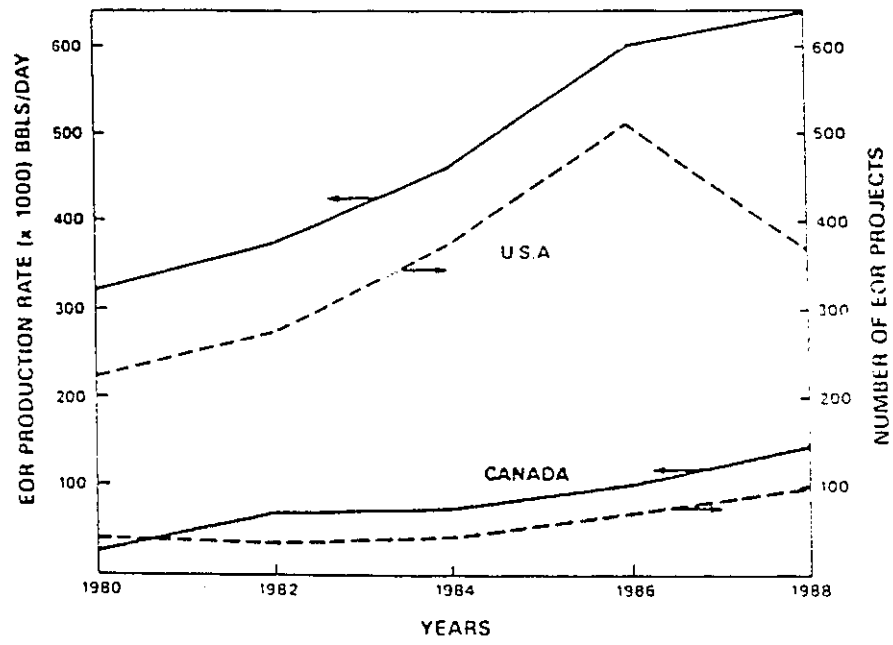


Figure 3 : EOR trends in North America

1.3 DIFFERENT METHODS OF EOR

EOE operations can be separated into three major types:

1. Thermal
2. Chemical
3. Miscible.

The objective of each is to recover as much oil as possible. The optimum application of each type is dependent upon reservoir characteristics including type of oil. Some of the EOR methods are described below.

1.3.1 *THERMAL METHODS*

1.3.1.1 **In-Situ Combustion**

In the in-situ combustion process, also known as fire flooding, air is injected into the oil reservoir through an injection well and the crude oil ignites either spontaneously or with the aid of a gas burner or resistance heater. As air injection continues, the combustion front moves away from the injection well, heating and displacing oil and water to the surrounding wells. At the combustion front, the connate (interstitial) water is vaporised and the oil is cracked leaving a residue of coke on the rock to maintain combustion. The steam produced in this manner moves ahead of the combustion front, condenses and mobilizes the oil into an oil bank which is pushed towards the production well. The portion of the reservoir swept by the front is then burned clean.

Often water is injected along with the air in a process known as wet combustion. The advantage of this is that the amount of heat transported to the region ahead of the combustion front is significantly increased (Gangoli and Thados, 1977). As a result of this, the oil viscosity is greatly reduced, improving oil recovery.

1.3.1.2 Steam Stimulation

This process is also called cyclic steam injection, steam soak , or huff and puff. Steam is injected into the reservoir through a production well (huff) for a period of several weeks to heat up the reservoir. The well is then shut-in for several days or weeks before production is resumed. During the shut-in period, the heat from the steam increases the reservoir temperature which decreases the oil viscosity and makes the mobility ratio more favourable. The oil is then produced (puff) until economic factors necessitate another steam injection. The production period is often up to one year in length, and is often followed by steam flooding.

1.3.1.3 Steam Flooding

In this process steam is injected into the reservoir through injection wells laid out in a pattern around the producing well . The steam mobilizes the oil and drives it towards the production wells. At the steam front, condensation occurs and a hot water bank is formed. The hot water causes thermal expansion of the crude oil and brings about a decrease in oil viscosity. Behind the steam front, oil is displaced by the vaporization of the lighter hydrocarbons and the resultant gas drive.

1.3.2 CHEMICAL AND MISCIBLE METHODS

1.3.2.1 Polymer Flooding

Polymer solutions have been used in three ways to increase oil recovery or to decrease water production.

1) Near-well polymer treatment has been performed in production wells and water injection wells. Production well treatments are designed to reduce fluid flow from zones producing excessive amounts of water. Injection well treatments are designed to reduce the volume of water that enters high permeability zones.

- 2) Polymer solutions which can be cross-linked within the formation have been used to plug high permeability zones at a substantial distance from the wellbore. The technique involves the injection of the polymer solution with an inorganic metal cation which will cross-link subsequently injected polymer molecules with the molecules already bound to the rock surface.
- 3) Polymer solutions may be injected for the purpose of reducing the mobility of the displacing fluid, thus improving the efficiency with which the reservoir crude oil is displaced (Lake, 1989).

1.3.2.2 Carbon Dioxide Drive

Injection of CO₂ into oil reservoirs may initiate oil displacement by a number of mechanisms. Although not usually miscible with reservoir oil upon initial contact, CO₂ creates a miscible front and miscibility is initiated by extraction of significant amounts of heavier hydrocarbon (C₅ to C₃₀) by CO₂. Carbon dioxide may also be useful in heavy oil reservoirs where thermal methods may not be applied.

1.3.2.3 Surfactant Flooding

Also known by the names micellar-polymer flooding, low tension water flooding, and microemulsion flooding, this method typically involves the injection of a slug of surfactant containing fluid, followed by polymer-thickened water, and finally ordinary brine. Despite the very high displacement efficiency of the micellar solution, micellar/polymer flooding is not profitable today because of the high cost of chemicals (George and Marvin, 1990).

1.3.2.4 Alkaline Flooding

A water flood may be converted to an alkaline flood by adding one to five weight percent of sodium hydroxide to the injected water. Other alkaline agents which have been used include

sodium orthosilicate, sodium metasilicate, and sodium carbonate. The pH of the injected solution usually ranges from 11 to 13. Polymers are sometimes added to increase viscosity. The chemical and physical processes which occur during alkaline flooding are not completely understood. The injected chemicals evidently react with acidic components of the reservoir crude, lowering surface tension between the oil and water phases. Other processes that could contribute to oil recovery include emulsification and entrapment of oil in the water phase, and changes in rock wettability.

A crude oil must contain acidic components, if it is to react with an injected alkaline solution. Acidity of oil is usually specified by an "acid number", defined as the number of milligrams of potassium hydroxide required to neutralize one gram of oil. Acid number should be determined on a sample of oil that is free from any chemical additives or dissolved acidic gases (H_2S or CO_2).

Alkali, when injected, can also reduce concern over calcium and magnesium ion interactions with the anionic surfactant. Sodium silicate keeps both calcium and magnesium out of solution better than sodium hydroxide or sodium carbonate does, but sodium silicate and sodium hydroxide are consumed in the reservoir by reaction with kaolinite clay much more than sodium carbonate. As with most enhanced recovery methods, low crude oil prices limit severely the current chances of economic success.

Progress is being made on lowering the cost of alkaline flooding. Surfactant loss to the reservoir is substantially lower under alkaline conditions. Whether viewed as alkaline-enhanced surfactant flooding or cosurfactant-enhanced alkaline flooding, the field results are encouraging (Nelson, 1989).

1.4 OBJECTIVE OF THE CURRENT RESEARCH

Hornof and Bernard (1992) performed some preliminary displacement experiments of heavy oil by alkaline solution in a Hele-Shaw cell. It was found that the displacement patterns in the case of alkaline flooding were fundamentally different from those seen for water flooding. Furthermore, for water flooding, oil recovery was found to decrease with increasing oil viscosity. For alkaline flooding, this was also observed at breakthrough time; however the total recovery after 1 hour was much higher and not affected by the oil viscosity. While water flood mobilized almost no more oil after breakthrough, alkaline flooding kept on producing more oil and such oil mobilization was visually observed.

In this research a Hele-Shaw cell (see chapter 4 for detail) was used to visualize the displacement patterns using a light paraffin/n-decane mixture. The geometrical structure of the Hele-Shaw cell is quite different from the capillary network found in three-dimensional reservoir rock. However, experimental work (Saffman and Taylor, 1958; Paterson, 1981) has shown that fingering patterns observed in Hele-Shaw cells are quite similar to those observed in actual porous media. Paraffin oil was used because the viscosity of paraffin oil is higher than low viscosity oils, because of that different viscosities were obtained by diluting the paraffin oil with n-decane to simulate various viscosities of crude oil.

The main objective of this research was to compare and study the reactive system (light paraffin oil + n-decane + linoleic acid [10 mM] displaced by alkaline solution [25mM]) and the non-reactive system (light paraffin oil+ n-decane displaced by distilled water).

The specific objectives of the research are as follows:

- 1) To compare the reactive and non-reactive system as a function of oil viscosity.
- 2) To compare the reactive and non-reactive system under different flow rates.
- 3) To compare the reactive and non-reactive system under favourable mobility ratio.

As the work progressed, a series of experiments was added, in which a slug of low-viscosity aqueous displacing phase was followed up by injecting a viscous back-up solution. This was also performed to enhance oil recovery.

Chapter 2

LITERATURE SURVEY

The effect of interfacial reaction on viscous fingering has so far been paid little attention. Such situations are encountered in caustic (alkaline) flooding of crude oil. The injected alkali reacts at the water-oil interface with naturally-occurring acids in the crude oil producing surface-active materials. It has been shown that this results in time dependent (dynamic) interfacial tension at the oil-water interface (Nasr-El-Din et al., 1990).

One of the factors to be considered when dealing with alkaline flooding is the acid content of the crude oil. If the oil has a low acid content (i.e. low acid number) then the amount of surfactants produced from the alkali/acid reaction is not enough to significantly lower the interfacial tension (IFT). Synthetic surfactants can be added to alkali/oil systems to lower their IFT (Krumrine et al., 1982).

Mobility control is another factor which determines the effectiveness of alkaline flooding in recovering waterflood residual oil, especially with viscous oils. A significant increase in oil recovery was observed in many laboratory tests when a polymer was co-injected with an alkali (Alam and Tiab, 1988; Nasr-El-Din and Hawkins, 1991).

The precise mechanism for the reactions between caustic reagents with acidic oil is still largely unclear, i.e. the mechanism of interfacial reaction of alkaline solution when displacing acidic oils in the cell. In the visualization of two immiscible fluids, when one fluid displaces another one in the presence of chemical reactions in the cell, the experimenter is faced with complicated problems. Some of these difficulties are:

1) The volume ratio of the two phases (displacing and displaced phases) is time dependent, i.e. it is not constant.

2) Chemical reactions occur in large three dimensional surface areas. This means that the interface of the displacing phase with the displaced phase is not a simple two dimensional surface area. Three dimensional surface areas are more complicated to analyze than two dimensional surface areas.

3) Since the mobility ratio of the displacing phase to the displaced phase is higher than one, there is viscous fingering and convective diffusion at the interface. Sharma and Yen (1989) suggested that the sequence of events (diffusive convection, chemical reaction, diffusive convection) gives rise to relative maxima and minima of IFT as dictated by the relative kinetics of each step.

4) Mass transfer of both chemical reactants from the bulk phase to the interface and vice versa.

All of the above problems make it difficult to conclude a reliable quantitative analysis of interfacial reaction inside the cell, where the displacing phase comes into contact with the displaced phase. Mass transfer of surface active species from the bulk phases to the interface and vice versa. Jennings (1974) postulated that the reduction in the interfacial tension, due to the interfacial reaction between the alkali in the aqueous phase and the acidic components in the oil, causes emulsification of crude oil in-situ. This emulsion phase tends to lower water mobility, and

consequently dampen the tendency towards viscous fingering. For tertiary recovery, several mechanisms have been postulated for oil recovery by alkaline flooding (Cooke et al., 1974) including: emulsification and entrainment, wettability reversal (oil-wet to water-wet) wettability reversal (water-wet to oil-wet), and emulsification and entrapment. Castor et al., (1981) added emulsification and coalescence as an important mechanism in systems which spontaneously form unstable water/ oil emulsions.

2.1 MECHANISMS OF ALKALINE OIL RECOVERY

2.1.1 *EMULSIFICATION AND ENTRAINMENT*

Reisberg and Doscher (1957) believed that this process was the result of a lowering of interfacial tension between the crude oil and the displacing alkaline solution. However, they concluded that caustic flooding was not economically feasible due to the large amount of caustic necessary because of adsorption and reaction with the reservoir rock.

2.1.2 *WETTABILITY REVERSAL (OIL-WET TO WATER-WET)*

The second mechanism responsible for improved oil recovery presented by Johnson (1976) is a change in rock wettability from oil-wet to water-wet. Wagner and Leach (1959) concluded that this change in wettability during a waterflood will result in an increase in oil recovery over that obtained where no wetting change occurs. They achieved this wettability reversal through the addition of certain chemicals, including acids, bases, and some salts, that changed the injection water pH. They also found that the higher the oil viscosity the greater the percentage improvement obtained with this wettability reversal over conventional waterflood recovery.

2.1.3 WETTABILITY REVERSAL (WATER-WET TO OIL-WET)

A third mechanism by which caustic solutions might improve oil recovery was first reported in 1974 by Cooke et al. Their investigation showed that some types of porous media could be changed from water-wet to oil-wet by the adjustment of injection water pH, salinity, and temperature. They also observed that certain combinations of caustic and salt were able to both cause this wettability change and lower the crude oil-water interfacial tension to very low values.

This change in wettability from water-wet to oil-wet causes the trapped residual oil, originally discontinuous in the porous medium, to be converted to a continuous wetting phase, thereby making a flow path for the trapped oil to the production well. Due to the low interfacial tensions present, an emulsion of water droplets in the now continuous oil phase forms. These emulsion droplets tend to become trapped in the porous medium and thus induce a high pressure gradient which is able to overcome the capillary forces retaining the oil in the reservoir, these forces having been already reduced by the low interfacial tension.

2.1.4 EMULSIFICATION AND ENTRAPMENT

Jennings (1974) proposed an alternative to the wettability reversal mechanism by which the injection of caustic solutions can significantly improve the recovery of certain oils. This mechanism involves the drastic reduction of oil-water interfacial tension by the caustic activation of potentially surface-active organic acids naturally occurring in some crude oils. This reduction in interfacial tension causes in-situ emulsification of residual oil. The emulsion thus formed tends to move downstream with the flowing caustic and becomes entrapped by pores that are too small for the emulsion droplets to penetrate.

The entrapment of the emulsion droplets lowers the injection water mobility, lowers the tendency towards viscous fingering, and improves both vertical and areal sweep efficiencies. The emulsified oil, once trapped in the pore throats, is not recovered and the ultimate residual oil saturation is not

significantly affected by caustic injection. Therefore this mechanism would be primarily of importance in reservoirs containing highly viscous oils where sweep efficiency is poor. In these types of reservoirs, any improvement in sweep efficiency, caused by a more favourable mobility ratio, would be more important economically than the recovery of residual oil left after a water-flood.

2.1.5 EMULSIFICATION AND COALESCENCE

Another mechanism for alkaline oil recovery is emulsification and coalescence. It was proposed by Castor et al. (1981). As with the emulsification and entrainment and emulsification and entrapment mechanisms, the first stage in this mechanism is accomplished by the in-situ formation of surfactants which promote emulsification of the oil. However, in the emulsification and coalescence mechanism unstable water-in-oil emulsions are formed by the injection of calcium hydroxide. The calcium hydroxide acts to swell the residual oil and increase its apparent saturation. Because of this swelling, adjacent oil ganglia contact each other and coalesce to form localized regions of high oil saturation that have an increased oil permeability. There is also evidence that the emulsification and entrainment and the emulsification and entrapment mechanisms can aid the coalescence phenomena to increase oil recovery.

Alkaline flooding can be viewed as a two stage process (Castor et al., 1981), the first stage serving to mobilize residual oil by altering its configuration in the pore space, either through IFT reduction or wettability alteration with the second stage being the macroscopic displacement of the mobilized residual oil.

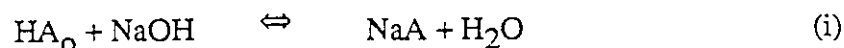
Nelson (1982) treated alkaline flooding as a special case of surfactant flooding. Using commercial surfactants to augment the in-situ produced surfactant, they applied the principle of optimal salinity (Reisberg and Doscher, 1957) to design of alkaline floods to determine the appropriate

concentrations of alkali and added surfactant which would provide optimum phase behaviour for the system.

2.2 SYSTEM CHEMISTRY

Borwankar (1986) and Sharma (1989) employed a system chemistry in which the crude oil acids were represented by one hypothetical single species labelled 'HA'. Another common element was the formation of surface inactive complexes due to the reaction between excess sodium ions and the surface active anions. Borwankar, however contended that the surface-inactive complex was partitioned preferentially to the oil phase while Sharma argued that the inactive species remained in the interface showing little or no tendency to desorb either to the oil or to the aqueous phases (Ramakrishnan and Wasan, 1983).

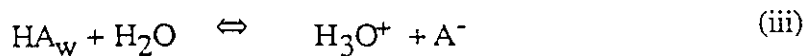
The overall hydrolysis and extraction is given by:



The distribution of the molecular acid between the oleic and aqueous phase is given by:



The dissociation of acid in the aqueous phase is given by:



The distribution between the oleic and aqueous phase is represented by:

$$K_D = \frac{C_{HAo}}{C_{HAw}} \quad (\text{iv})$$

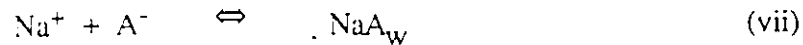
The corresponding dissociation constant being:

$$K_A = \frac{(C_{H_3O^+})(C_{A^-})}{(C_{HAw})} \quad (\text{v})$$

Addition of alkali in the aqueous phase leads to a reduction in H_3O^+ governed by:

$$K_w = (C_{H_3O^+})(C_{OH^-}) \quad (\text{vi})$$

where K_w is the dissociation constant for water. The repartitioning of the species A^- to the oil phase is described by



Aspects of the envisaged system chemistry have been also presented by Chiwetelu et al. (1990).

The dynamic analysis he proposed consists of the following steps:

1. Transport of the reacting species from the bulk to the interface, essentially by convective diffusion. Convection currents are particularly significant in the vicinity of the interface due to Marangoni instabilities.

2. Interfacial reactions and the associated equilibria leading to the formation of the surface-active soap species.
3. Transport of the reaction products from the interface to the bulk phases by convection diffusion.
4. Surfactant adsorption and desorption resulting in time-dependent changes in surface excess concentration and consequently interfacial tension.

The primary objective of Chiwetelu's work was to obtain a mechanistic interpretation of the dynamic interfacial tension arising from simple reacting systems. The dynamic interfacial tension predicted by the model compared favourably with the experimental data over a wide range of acid and caustic concentrations.

Chapter 3

THEORY

3.1 HELE-SHAW CELL

A Hele-Shaw cell has been used as an analog of two-dimensional isotropic homogeneous porous media. The Hele-Shaw cell involves flow in thin gaps. It was first described by Hele-Shaw (1889). The Hele-Shaw cell has also been used to study two-phase displacements (Saffman and Taylor, 1958). However, in spite of a considerable amount of work on the solution of such two-phase flow problems, a rigorous derivation of the equations and boundary conditions has not been completed to date. The Hele-Shaw theory for single-phase flow results in the following equations relating the depth-averaged pressure and two-dimensional velocity fields (Park and Homsy, 1984).

$$\nabla \cdot \mathbf{u} = 0, \quad (3)$$

$$\nabla p = -A\mu\mathbf{u} - \rho\mathbf{g} \quad (4)$$

with $A = 3/b^2$, where b is the gap half-width. Saffman and Taylor (1958) have discussed modification of the Hele-Shaw theory for the special case in which there is a wetting film of constant thickness c on the solid surface when there are two phases present.

In the case in which one fluid displaces another fluid in a horizontal smooth Hele-Shaw cell, for example, if the oil displaced by the water has a constant pressure p then the pressure in the water and velocity field in the water is described by:

$$\mathbf{u} = -\frac{k}{\mu} \nabla p \quad (5)$$

For a smooth Hele-Shaw cell with a gap 'b', $k = b^2/12$, with the incompressibility condition $\nabla \cdot \mathbf{u} = 0$, this becomes

$$\nabla^2 p = 0 \quad (6)$$

For two immiscible fluids with interfacial tension γ the pressure jump across the fluid interface is

$$p_i - p = \gamma \kappa \quad (7)$$

where κ is the curvature of the interface

$$\kappa = (2/b) + (1/R) \quad (8)$$

Here the displaced phase is assumed to be completely expelled by the displacing phase and has a zero contact angle to the plate, and R is the radius of curvature of the projection of interface on the plate.

The kinematic condition at the interface is

$$\mathbf{u} \cdot \mathbf{n} = (-k/\mu) \mathbf{n} \cdot \nabla p \quad (9)$$

where \mathbf{n} is the unit vector normal to the projected curve of the interface on the horizontal plane.

3.2 RELATIONSHIP BETWEEN HELE-SHAW CELL AND POROUS MEDIA

The Hele-Shaw cell has been used as an analog of porous media by many researchers to visualise the displacement patterns of various fluids. Although the Hele-Shaw cell is quite different in structure from the actual porous media, experimental research has shown that the fingering patterns observed in the Hele-Shaw cell are quite similar to those observed in actual porous media (Saffman and Taylor, 1958; Paterson, 1981).

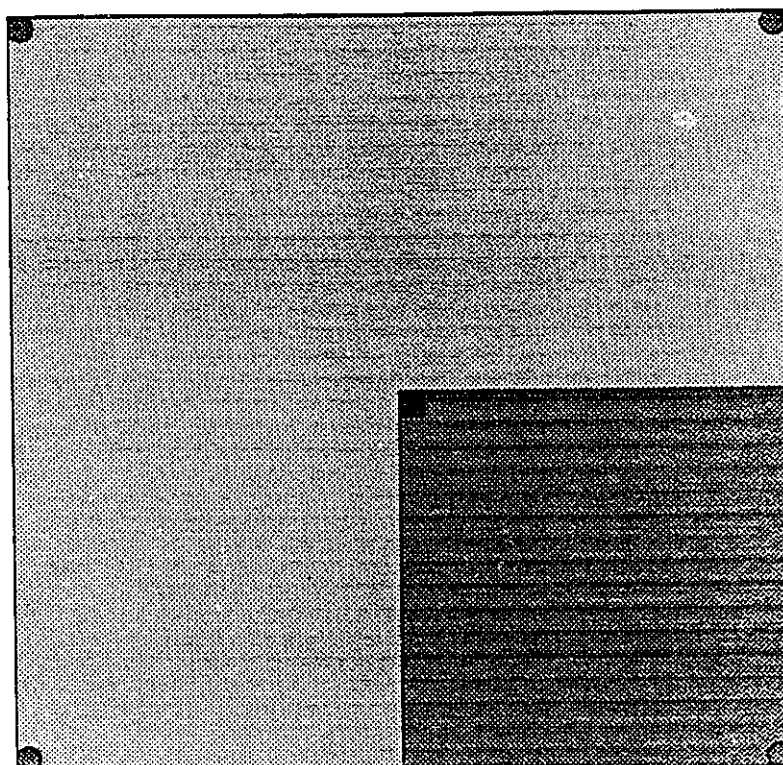
The pattern in which the injection well and the producing wells are arranged is an important factor when using enhanced oil recovery techniques. One of the most commonly used configurations is the reversed five-spot pattern. Reversed five-spot patterns consist of four injection wells and one production well in the center as shown in Figure 4. The Hele-Shaw cell used in these experiments has a square structure and diagonal flow pattern, and is used to simulate a quarter of the reversed five-spot pattern.

Caudle (1968), suggested on the basis of his research that, no matter how large the reservoir, the injection or withdrawal of fluid at any point will create potential gradients and fluid movement throughout the entire system of connected fluid-filled pore space. The flow rate in five-spot pattern can be given as:

$$q = \frac{7.67 h k \Delta\Phi}{2[\ln(d/r_w) - 0.619] \mu} \quad (10)$$

where

$$\Phi = p + \rho gh \quad (11)$$



- Injection well
- Production well

Figure 4 : The reversed five-spot pattern

Chapter 4

EXPERIMENTAL STUDIES

4.1 EQUIPMENT USED

In this investigation a Hele-Shaw cell was used to perform the displacement experiments. The cell consisted of two tempered glass plates of dimensions of 30x30 cm, arranged in parallel, separated by a gap of 0.0067 cm. Metal spacers at the corners were used to constant spacing of the plates. This provides an interplate space of 6.03 cm^3 , which is equivalent to the pore space or pore volume. The pore volume is defined as the area of the Hele-Shaw cell times the distance between the plates of Hele-Shaw cell. Two metal tubes were inserted at opposite corners of the cell, providing it with an injection inlet and producing outlet. Two holes were drilled at the other two opposite corners of the cell, which were secured with tight-fitting teflon plugs during an experiment. The purpose of the holes was to make it easier for the cleaning process to be carried out.

The pump used in the experiments was a syringe pump (Model 341- Sage Instruments Co). The pump was capable of producing a range of flow rates from 0.22 mL/min to 0.81 mL/min with a 30 mL glass syringe. The experimental setup is shown in Figure 5. Plastic tubes of 1/8" ID were used to connect the syringe to the injection inlet of the cell and to evacuate the cell from the producing outlet into a 10 mL measuring flask. For all experiments, the displacement patterns were photographed with an automatic camera at different stages of displacement.

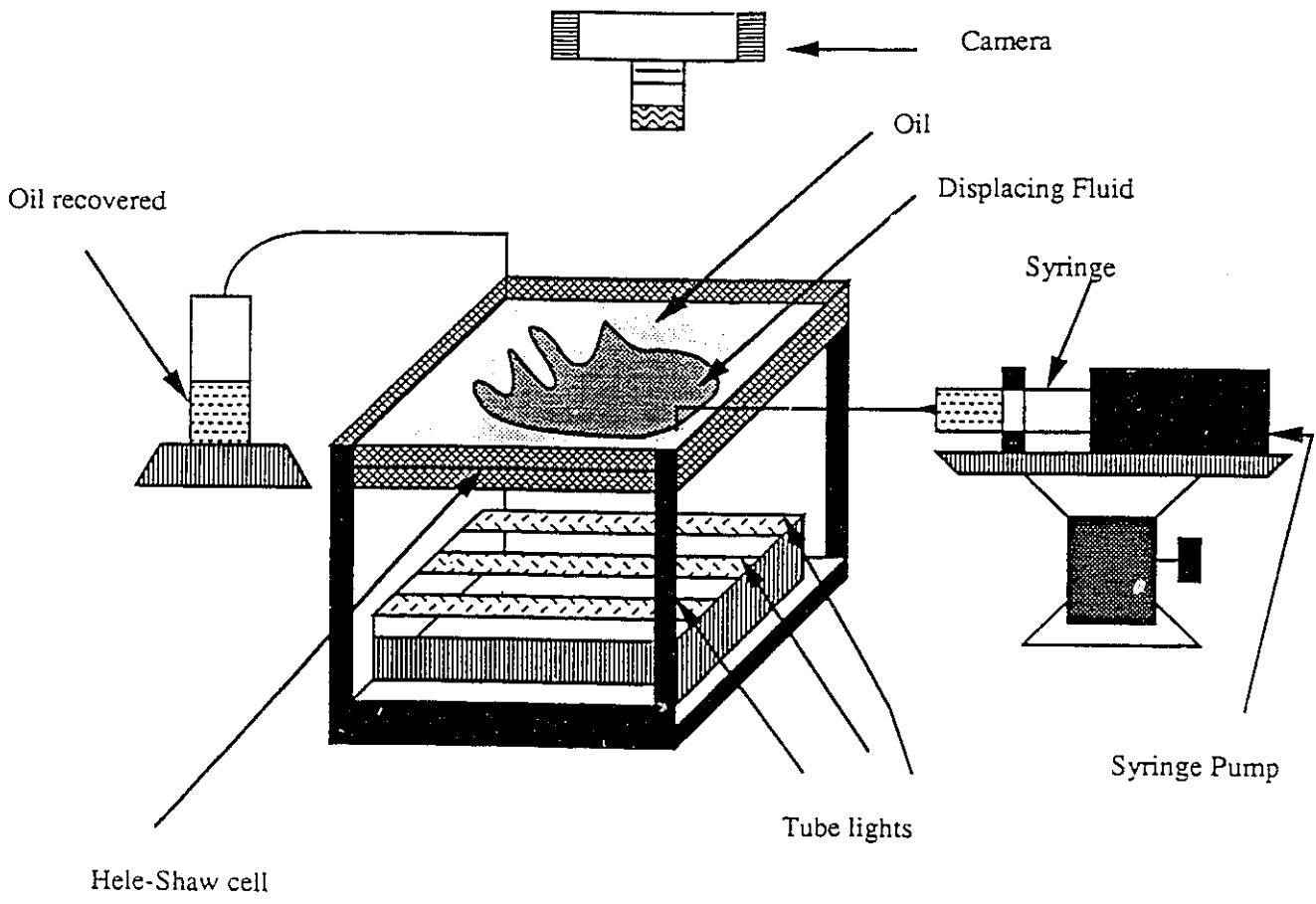


Figure 5: Experimental setup

4.2 PREPARATION OF SOLUTIONS

The oil used in these experiments is a mixture of light paraffin oil and n-decane. The light paraffin oil has a viscosity of 23.73 mPa.s. This oil is diluted with n-decane to form solutions of various viscosities. The solutions made had viscosities ranging from 23.73 mPa.s (pure light paraffin oil) to 0.80 mPa.s (pure n-decane). The relation between the viscosity and light paraffin oil percentage can be seen in Figure 6.

For the reactive system linoleic acid (10 mM) was added to the oil solution. NaOH (25mM) solutions were prepared freshly before every run, the reason being that NaOH degrades with time due to absorption of carbon dioxide present in the air.

In the experiments performed to observe the recovery percentage under the favourable mobility ratio, water/glycerine solutions were prepared with viscosities of 5,15, and 20 mPa.s.

4.3 MEASUREMENT OF PHYSICAL PROPERTIES

The kinematic viscosity of each solution was determined using a Cannon-Fenske Routine Viscometer of type 150 (Model K35) and type75 (Model A122) having a viscometer constant of 0.0367 and 0.008 centistokes/sec respectively. The temperature was kept constant at 25 °C.

The viscometer was immersed in a viscosity bath (Temp-Tral from Precision Scientific Co.) Kinematic viscosity was measured by recording the time required by the fluid inside the viscometer to drop, due to gravity, from one marking to the other. This is called efflux time, and it is measured using an electric timer (Precision Scientific Co.). The kinematic viscosity is equal to the efflux time, in seconds, multiplied by the viscometer constant, in centistokes/sec.

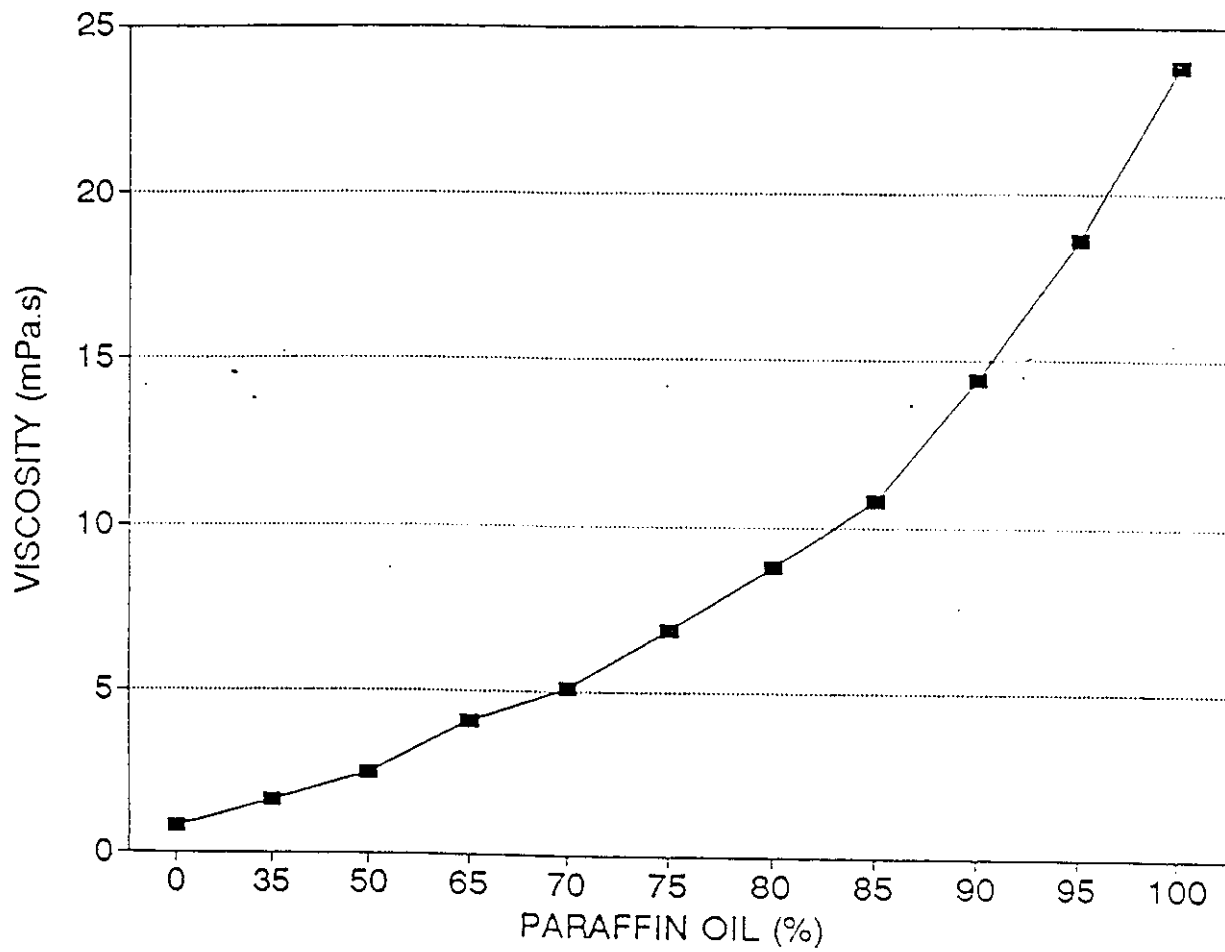


Figure 6: Viscosity of light paraffin oil / n-decane mixtures

The actual viscosity of the oil solution is equal to the kinematic viscosity multiplied by the density of the solution. The viscosity was measured in centipoise which is equivalent to mPa.s in the SI system, mPa.s's will be use throughout the text. To estimate the experimental error of viscosity measurements, the viscosities and densities were measured three times and the mean value was taken. The standard deviation was calculated by using SAS system and can be seen in the Appendix B.

4.4 DYE USED

Dyes were added to the displacing fluids to visualise the fingering patterns. Three different types of dyes were used to differentiate between the reactive and non-reactive systems. The dyes used are as follow:

1. Red food dye: A water based food dye (Club House, McCormick Canada Inc.). 2mL of dye/100mL of water was used.
2. Black Ink : A common ink of black color (Carter's, Dennison Manufacturing Canada Inc.) was used. The amount used was 2mL of ink/100mL of water.
3. Congo red dye: A powder dye (Fisher Scientific Co.) was used. The amount used was 250 mg of dye/100 mL of water.

4.5 EXPERIMENTAL PROCEDURE

The cell was first filled with the oil to be displaced. After filling the cell, it was checked to make sure that no leak was present. The syringe pump was arbitrarily adjusted at the minimum flow rate (0.22 mL/min) for 30 mL glass syringe. The timer was started at the point when the displacing

fluid entered into the cell, and was stopped at the time when the fluid reached the outlet. This is called breakthrough time. The displaced oil was collected in a 10 mL graduated cylinder and that amount of displaced oil was subtracted from the total oil injected. This volume was the recovery at breakthrough. The experiment was kept running for one hour after breakthrough. The volume of the oil collected at the end of 1 hour represented the total recovery after 1 hour.

The displacement patterns were photographed with an automatic camera at four different stages, arbitrarily selected as follows:

1. when the displacing fluid entered into the cell.
2. when the displacing fluid reached the centre of the cell.
3. when the displacing fluid reached the production outlet (breakthrough).
4. One hour after the breakthrough.

Cleaning of the cell after every run was a major and important task. The cell first had to be emptied of its oil and its displacing fluid. Several injections of acetone and methanol were required to dissolve the oil sticking to the glass plates inside the cell. The cell was then filled again with methanol which was sucked out by using a water vacuum pump (water aspirator) and then dried out by using compressed air.

Chapter 5

RESULTS AND DISCUSSION

A total of nine series of experiments were performed, which are as follows:

1. The first series consisted of initial experiments designed so as to obtain general information about the differences between displacements in the reactive and non-reactive systems. The effect of dye on displacements was also investigated.
2. The second and third series was a comparison between the reactive and non-reactive systems respectively at unfavourable mobility ratio (such as normally encountered in the field).
3. The fourth and fifth series was a comparison between the reactive and non-reactive systems respectively using different flow rates of displacing fluid.
4. The sixth and seventh series was a comparison between the reactive and non-reactive systems at favourable mobility ratios.
5. The eighth and ninth series was a comparison between the reactive and non-reactive systems in which oil was displaced by a finite amount of an intermediate aqueous fluid followed by a viscous water/glycerine solution.

The results obtained in the above experiments are compared and discussed below.

5.1 COMPARISON OF REACTIVE AND NON-REACTIVE SYSTEMS IN THE FIRST SERIES OF EXPERIMENTS

The first series consisted of four experiments. The flow rate was kept constant at 0.22 mL/min for each of the four experiments. In the first experiment, pure oil was displaced by distilled water. In the second experiment acidic (10 mM linoleic acid) oil was displaced by distilled water. In the third experiment pure oil was displaced by NaOH solution (25 mM). In the non-reactive system, the three experiments mentioned above, no chemical reaction could occur at the interface. In the fourth experiment acidic oil (10 mM) was displaced by NaOH solution (25 mM). This was the reactive system. The results of the four experiments can be seen in Table 1 in the Appendix A. The purpose of this series was to compare the reactive and non-reactive systems as to recovery percentage and displacement patterns. In this series of experiments three different dyes (Black Ink, Red Food dye and Congo Red dye) were used for both the reactive and non-reactive systems. It was found that the dyes did not have any significant effect on the recovery percentage and on the displacements.

In the four experiments mentioned above, it was observed that the reactive system (the fourth experiment) produced a completely different displacement pattern from the other three experiments. Many minute fingers were formed. A few fingers dominated and reached the outlet of the cell (production well). New fingers kept forming and sweeping the oil out of the cell after the breakthrough. However, in the non-reactive systems (the first three experiments) the pattern observed was very different. A few fingers formed which penetrated through the oil. One finger subsequently elongated then reached the production well and provided a channel for the water. The water then kept flowing through this single channel and additional fingers were not formed. These preliminary experiments provided evidence that the presence of either acid or alkali alone, without the other reactive counterpart, did not have any significant effect on the recovery or the displacement pattern. As a result subsequent research involved only a comparison of the non-reactive (oil-displaced-by-water) system and the reactive (acidic-oil-displaced-by-NaOH-solution) system. To estimate the experimental error, the reactive system experiment was repeated five times and the standard

deviation for the recovery percentage was calculated by using SAS programme as shown in the Appendix B.

5.2 EFFECT OF VISCOSITY ON REACTIVE AND NON-REACTIVE DISPLACEMENTS

The experiments discussed here constitute the second and third series of experiments dealing with reactive and non-reactive displacements respectively. A total of 22 experiments were performed for the reactive and non-reactive systems. The second series of experiments was performed using an aqueous alkaline solution (25 mM NaOH) as the displacing fluid to displace acidic (10 mM linoleic acid) light paraffin oil/n-decane mixture. Black ink was used as a dye for the alkaline solution. The third series of experiments was performed using distilled water as the displacing fluid to displace non-acidic light paraffin oil/n-decane mixture. Food dye was used as a dye for the distilled water. All experiments were performed at the same flowrate (0.22 ml/min). The results of the experiments are shown in Tables 4 and 5 (Appendix A). The time required for breakthrough, recovery at breakthrough and the total recovery are expressed as a function of oil viscosity. Figure 7 compares the oil recovery at breakthrough for reactive and non-reactive displacement, as a function of oil viscosity. It is found that oil recovery at breakthrough is inversely related to oil viscosity i.e. if the viscosity of oil is decreased oil recovery increases at breakthrough.

5.2.1 BREAKTHROUGH RECOVERY AND RECOVERY AFTER 1 HOUR

From Tables 4 and 5 it can be seen that for all oil compositions the recovery at breakthrough of the reactive system is always higher than the non-reactive system. The recovery at breakthrough for the non-reactive system increases with the decrease in viscosity of oil. The total recovery for the non-reactive system increases with the decrease in oil viscosity after breakthrough and becomes constant at 63% when the oil viscosity reaches 6.86 mPa.s, but in the reactive system total recovery after 1 hour is almost independent of oil viscosity. The recovery at breakthrough and recovery after 1 hour in a non-reactive displacement is influenced by the mobility ratio. The relation between the recovery and the oil viscosity can be seen in Figures 7 and 8.

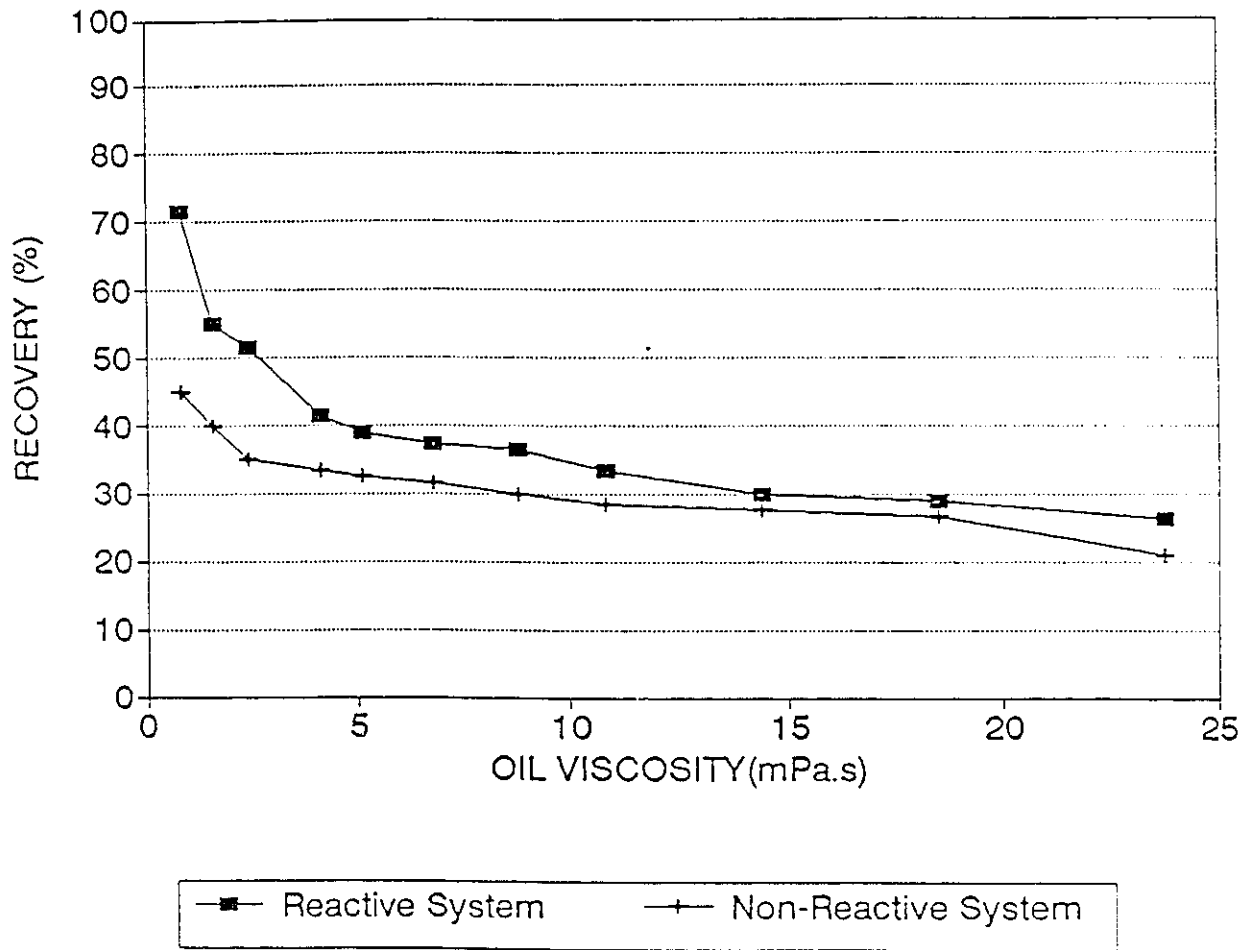


Figure 7: Recovery at breakthrough as a function of oil viscosity

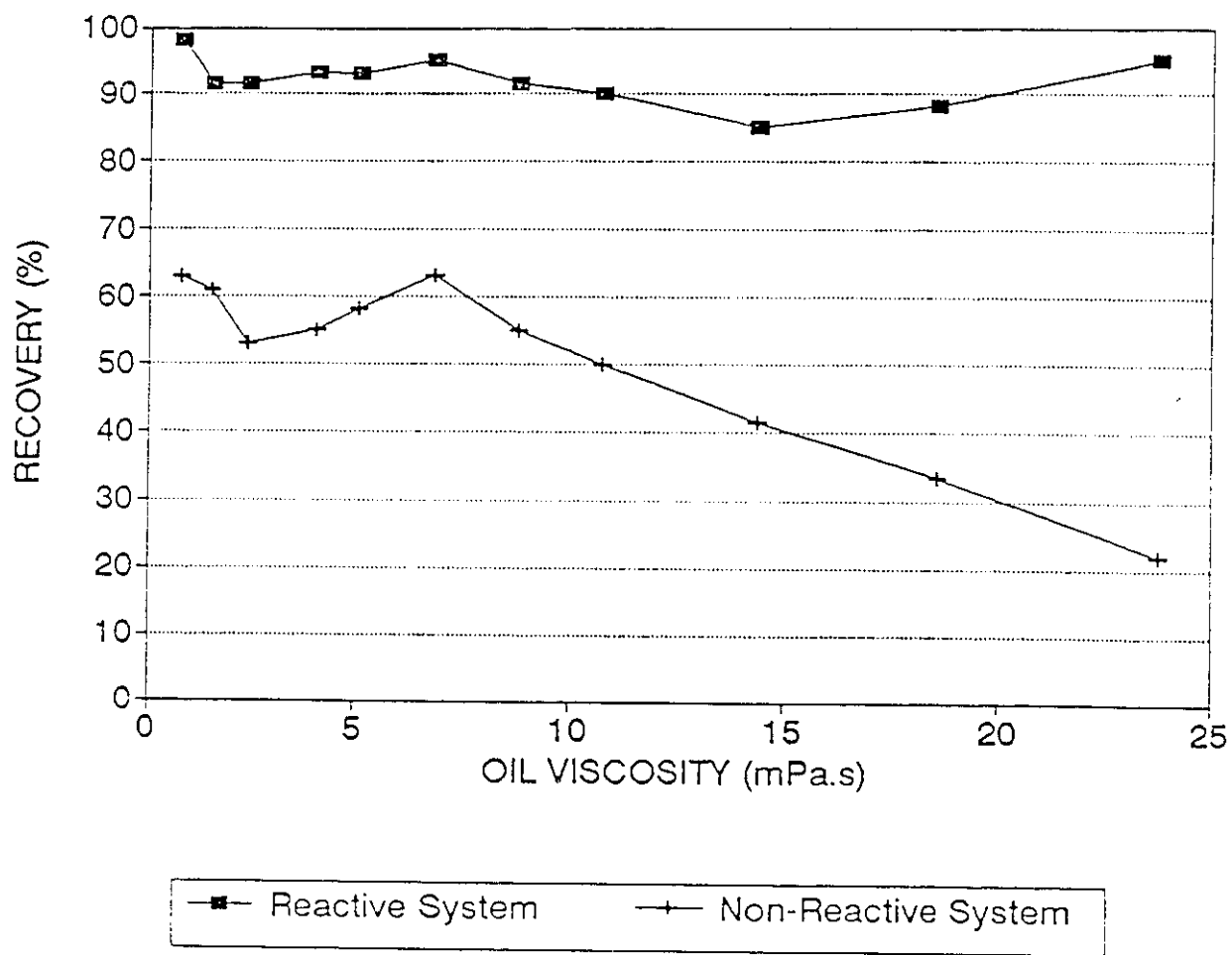


Figure 8: Recovery at 1 hour after breakthrough as a function of oil viscosity

5.2.2 DISPLACEMENT PATTERNS

The displacement front observed in the reactive systems is fundamentally different from the non-reactive systems. In the non-reactive system at higher oil viscosities the displacing front breaks up into a few big fingers. The fingers located near the diagonal between the injection and producing well elongate as the front gets closer to breakthrough. These fingers move ahead faster than the main front, and enter the producing well. After breakthrough the number of fingers is related to the viscosity of the oil. In the oil of higher viscosity, the number of fingers formed was lower than in the case of the oil of lower viscosity because of the better mobility ratio in the latter case. In the case of the reactive system for all oil solutions, the displacing front breaks up very early in the displacement into numerous tiny fingers, which are very close to each other. The fingers located near the diagonal between the injection and producing wells elongate in all directions as the front gets closer to the production well. This is the reason why recovery at breakthrough for the reactive system is higher than in the non-reactive system. Some of the photographs of these patterns can be seen in Figures 9 to 15.

5.2.3 TIME REQUIRED FOR BREAKTHROUGH

Table 6 (Appendix A) compares the time required for breakthrough for the reactive and non-reactive displacement. As the oil viscosity decreases the time required for the breakthrough for both types of displacement increases and therefore the recovery also increases. This behaviour was observed in both the reactive and non-reactive systems. The only difference was the size of the fingers in the reactive system as discussed above. The relation between time at breakthrough and the oil viscosity can be seen in Figure 16.

Reactive System

Non-Reactive System

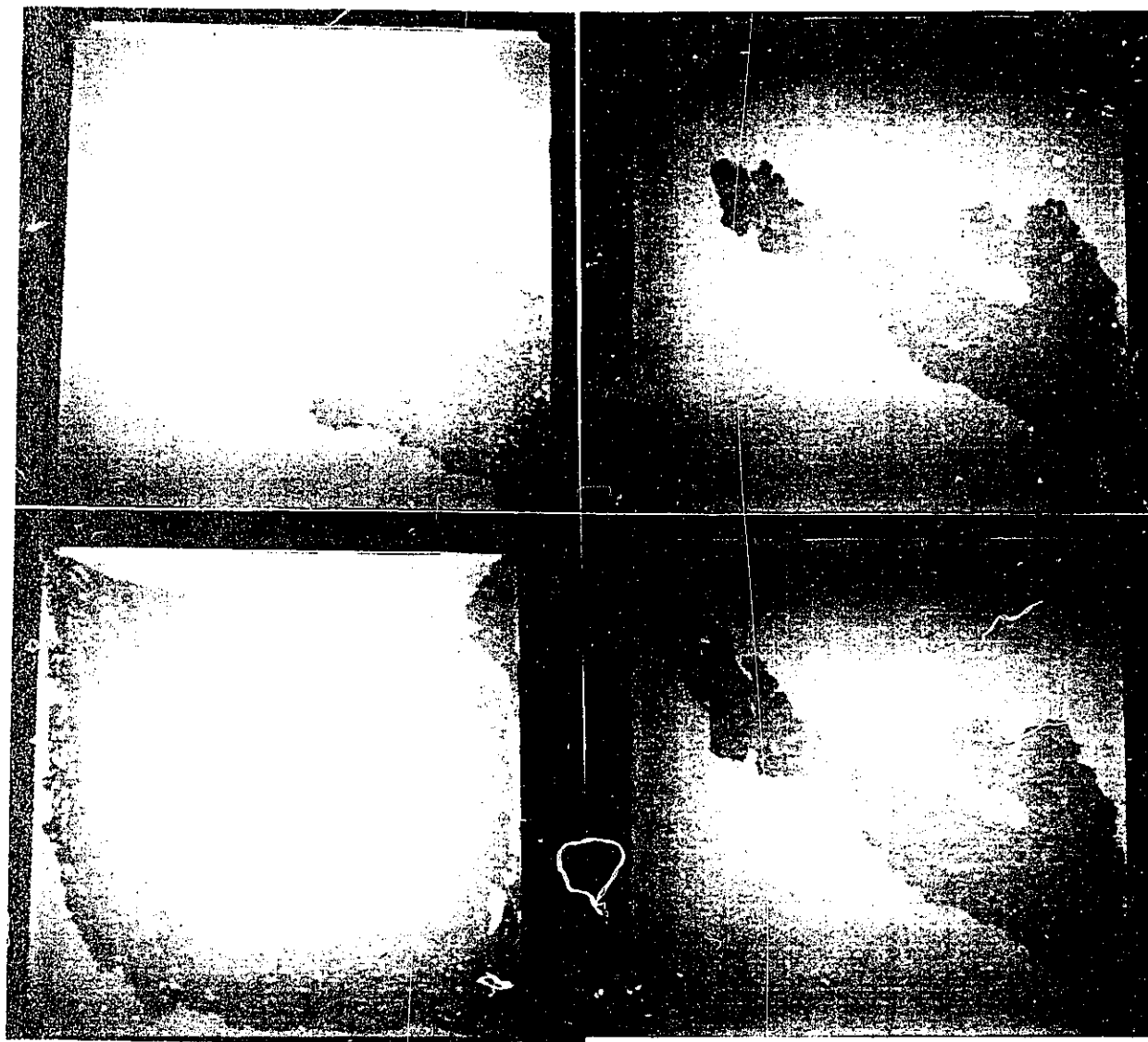


Figure 9 : Comparison between the displacement of acidic (10 mM linoleic acid) light paraffin oil (23.79 mPa.s) by alkaline solution (25 mM NaOH) and the displacement of light paraffin oil (23.79 mPa.s) by distilled water.

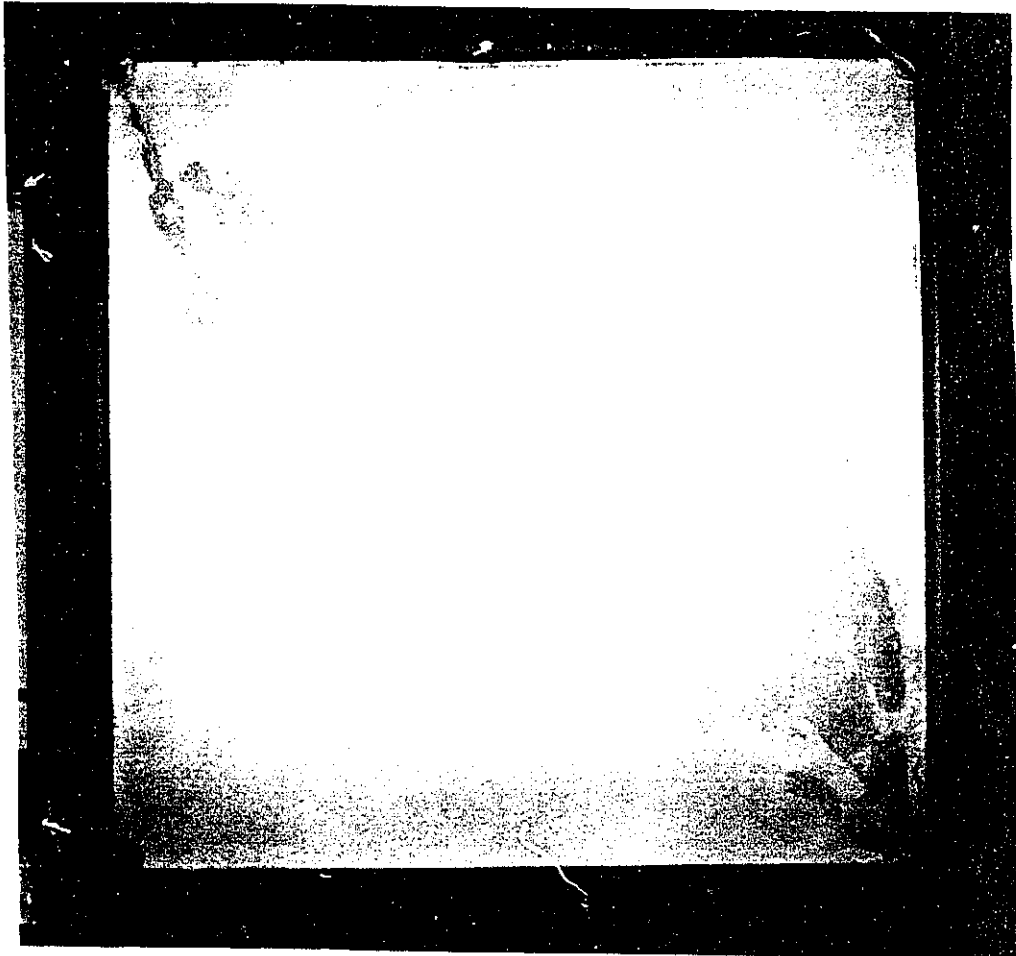


Figure 10: Displacement of light paraffin oil with a viscosity of 23.79 mPa.s by distilled water (Non-reactive system) after 1 hour of breakthrough.

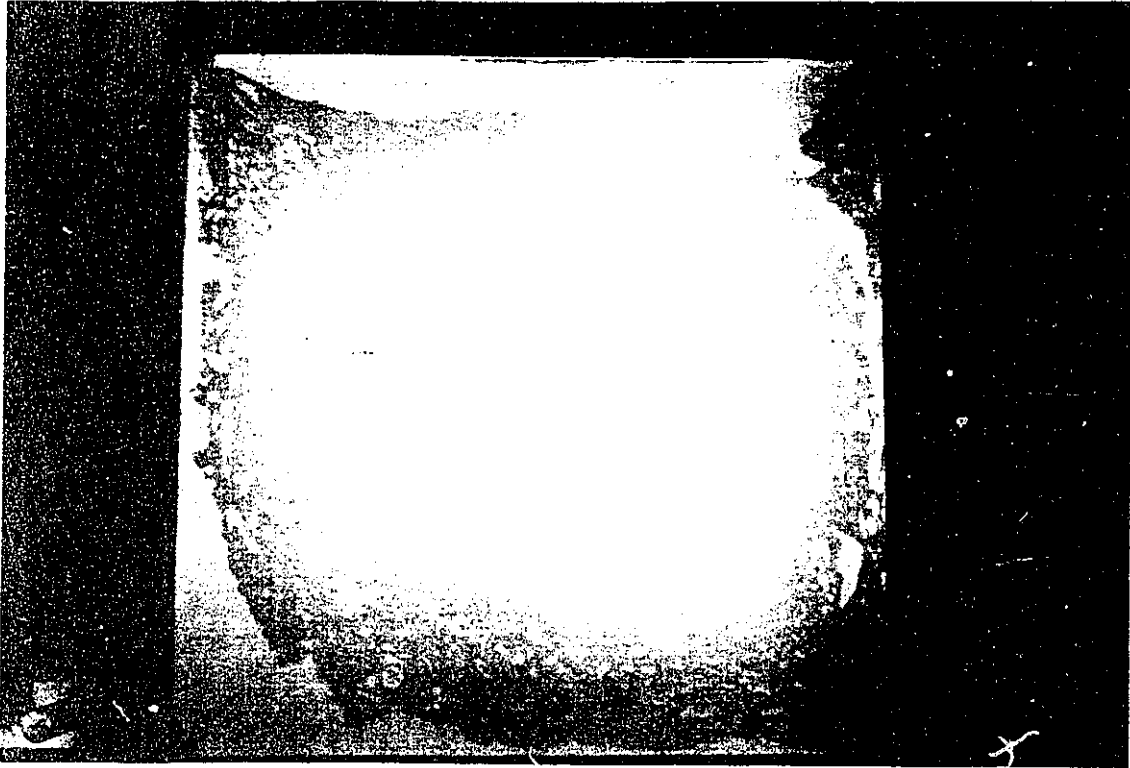


Figure 11: Displacement of acidic light paraffin oil with a viscosity of 23.79 mPa.s by alkaline solution (Reactive system).

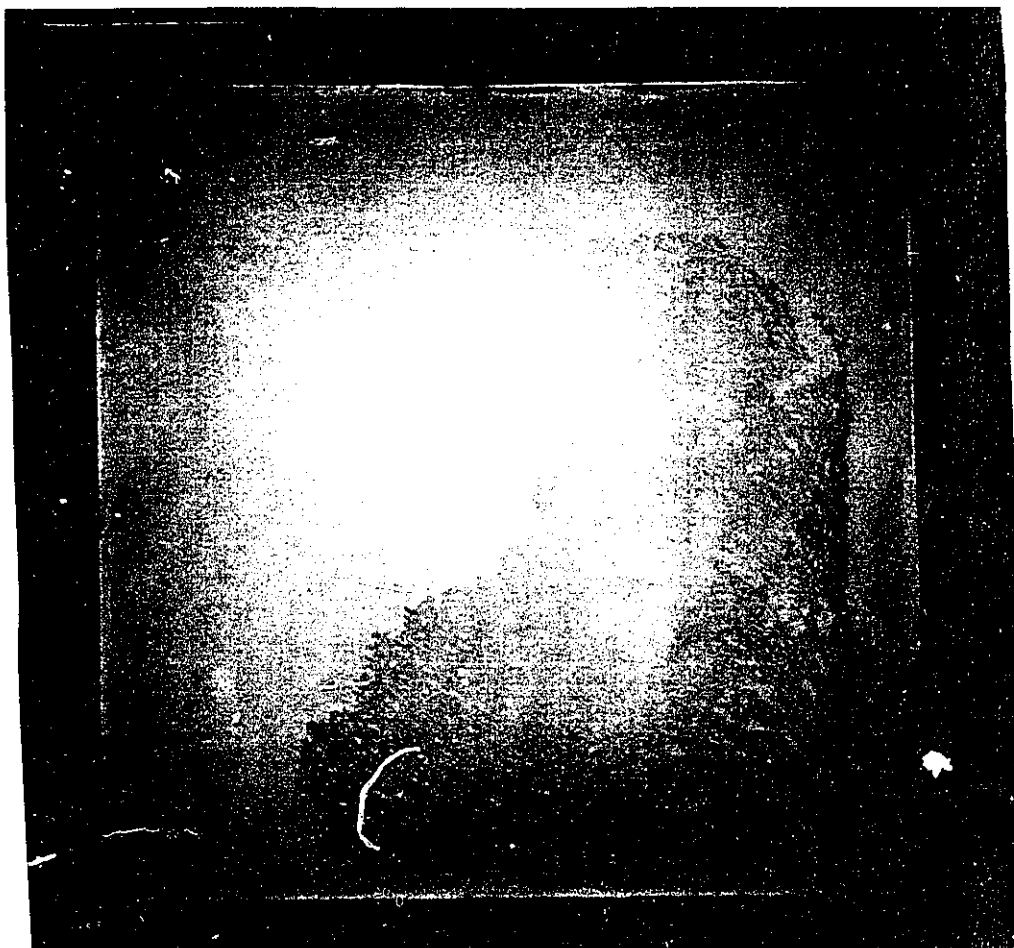


Figure 12: Displacement of light paraffin oil / n-decane mixture with a viscosity of 14.42 mPa.s by distilled water (Non-reactive system)

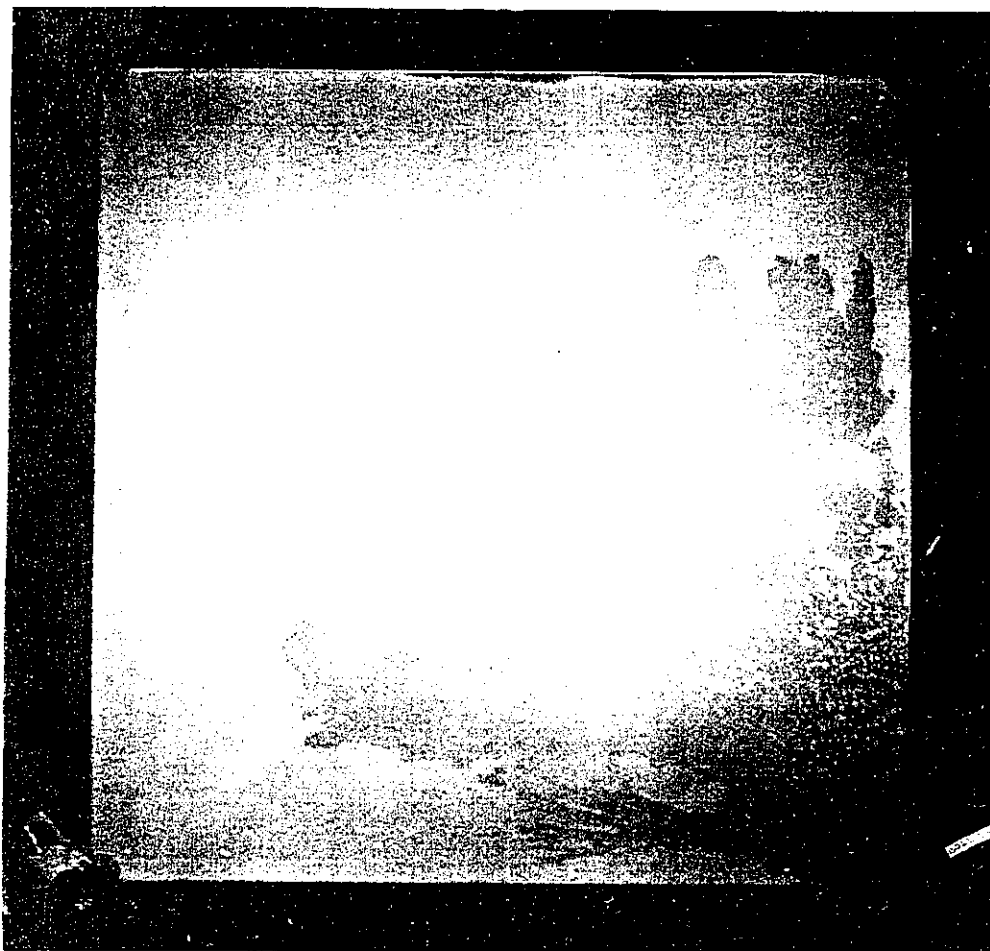


Figure 13: Displacement of acidic light paraffin oil / n-decane mixture with a viscosity of 14.42 mPa.s by alkaline solution (Reactive system).

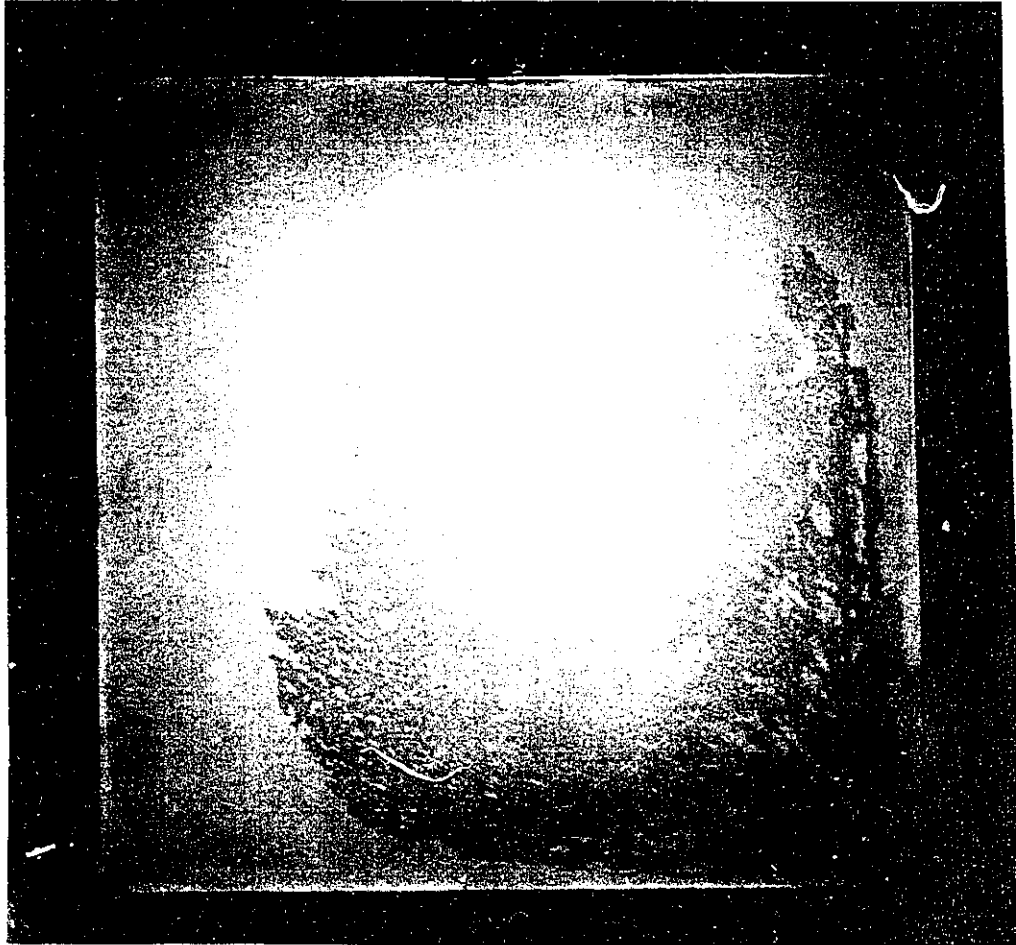


Figure 14: Displacement of light paraffin oil /n-decane mixture with a viscosity of 5.10 mPa.s by distilled water (Non-reactive system)



Figure 15: Displacement of acidic light paraffin oil /n-decane mixture with a viscosity of 5.10 mPa.s by alkaline solution (Reactive system).

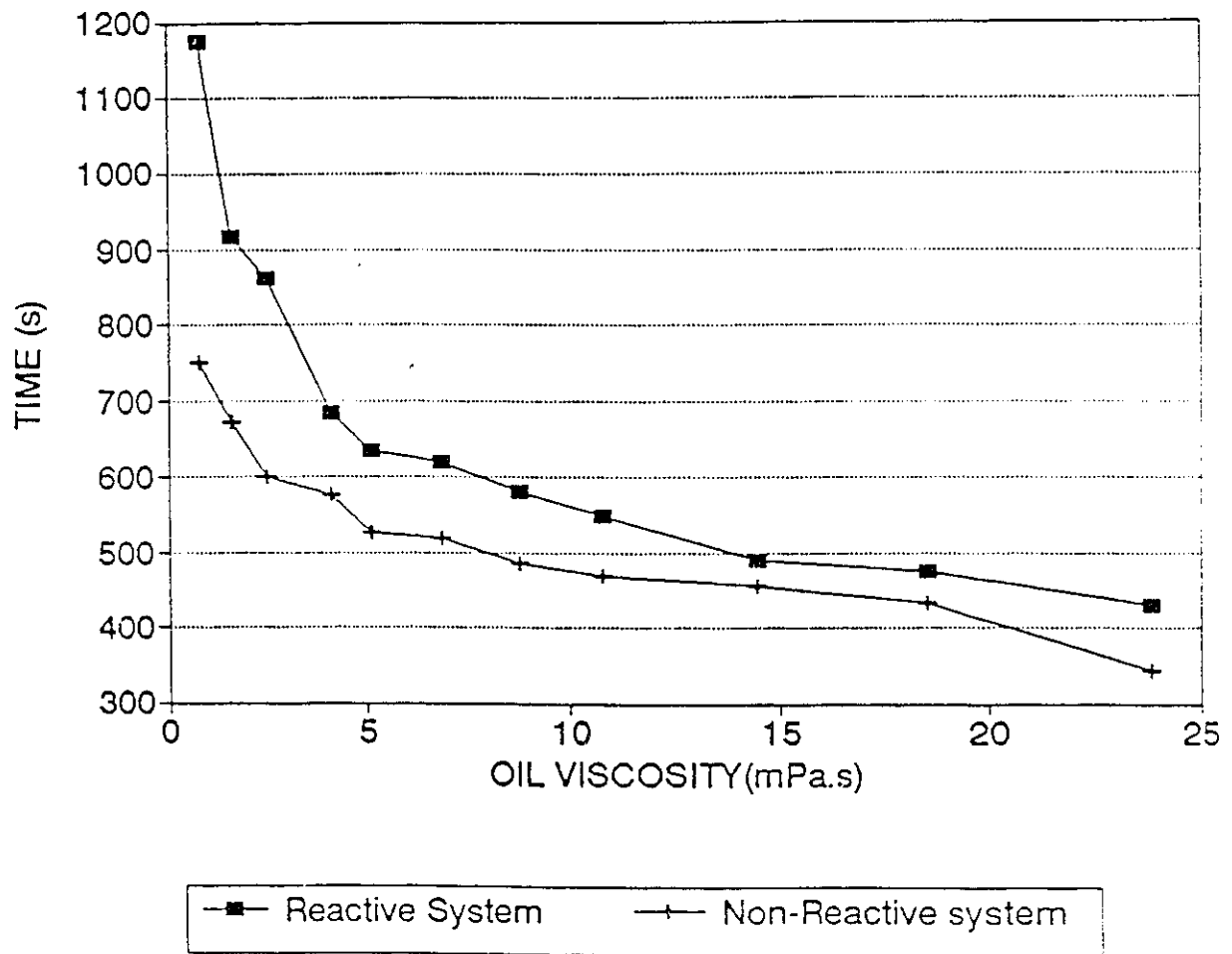


Figure 16 : Time at breakthrough as function of oil viscosity

5.3 REACTIVE AND NON-REACTIVE DISPLACEMENTS AT DIFFERENT FLOW RATES

The experiments discussed here constitute the fourth and fifth series of experiments dealing with reactive and non-reactive displacements respectively. The purpose of this investigation was to study the effect of flow rate. The recovery percentage and the displacement patterns of the reactive and the non-reactive systems was observed at three different flow rates. The three different flow rates were 0.16 mL/min , 0.22 mL/min and 0.32 mL/min. A total of six experiments were performed for reactive and non-reactive systems.

The fourth series of experiments was performed using an aqueous alkaline solution (25 mM NaOH) as the displacing fluid to displace acidic light paraffin oil (10 mM linoleic acid). In this series the acidic oil/n-decane mixture with a viscosity of 8.80 mPa.s was arbitrarily chosen as the oil phase. Congo red dye was used as a dye for the displacing fluid.

The fifth series of experiments was performed using distilled water as the displacing fluid to displace non-acidic light paraffin oil/n-decane mixture. The same dye as above was used for the displacing fluid.

5.3.1 BREAKTHROUGH RECOVERY AND RECOVERY AFTER 1 HOUR

From Tables 7 and 8 (Appendix A) it can be seen that for all three flow rates the recovery at breakthrough for the reactive system is almost the same as the recovery for the non-reactive system, regardless of the time, which decreased with the increase in flow rates at the breakthrough.

The recovery at 1 hour after breakthrough in the case of the reactive system is always much higher than for the non-reactive system. In the non-reactive system the recovery became almost constant, around 55%, while in the case of the reactive system total recovery after 1 hour was nearly complete and independent of flow rate. The relation between the recovery and the flow rate can be seen in Figures 17 and 18.

5.3.2 DISPLACEMENT PATTERNS

The displacement patterns observed for non-reactive system at all three different flow rates i.e. 0.16 mL/min, 0.22 mL/min and 0.32 mL/min were different until the breakthrough; after the breakthrough, the patterns became quite similar in all three cases.

For reactive systems, the displacing front breaks up very early in the displacement into numerous tiny fingers which are very close to each other. In the case of the 0.16 mL/min flow rate the fingers elongate in all directions as the front gets closer to the production well, while in the case of 0.32 mL/min, the fingers located near the diagonal between the injection and producing wells elongate essentially only in the direction of the production well. After 1 hour, the final patterns are quite similar as in the case of other flow rates.

In the case of the non-reactive systems at the flow rate of 0.16 mL/min, the displacing front breaks up into a few big fingers. The fingers located near the diagonal between the injection and producing well elongate as the front gets closer to breakthrough. These fingers move ahead faster than the main front, and enter the producing well. In the case of 0.32 mL/min the displacing front breaks up into a few fingers, but only one big finger located near the diagonal between the injection and producing well elongates as the front gets closer to breakthrough. After 1 hour the patterns were very similar as in the case of other flow rates.

5.3.3 TIME REQUIRED FOR BREAKTHROUGH

It can be seen from Table 7 (Appendix A) that as the flow rate increases, the time at breakthrough decreases; However, there is no drastic effect on the recovery. The recovery at breakthrough is quite similar in all cases. The relation between the time at breakthrough and the flow rate can be seen in Figure 19.

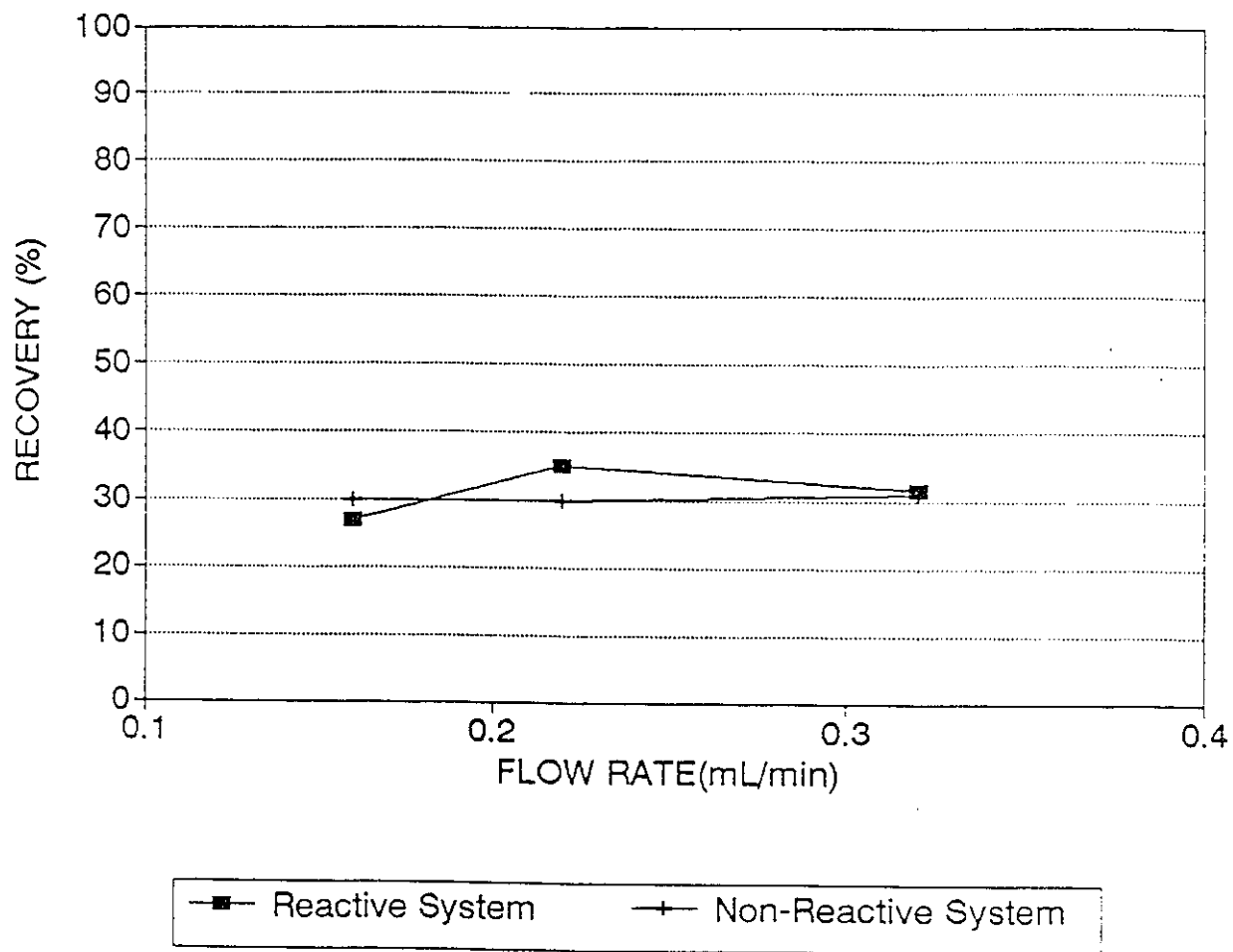


Figure 17: Recovery at breakthrough as a function of flow rate

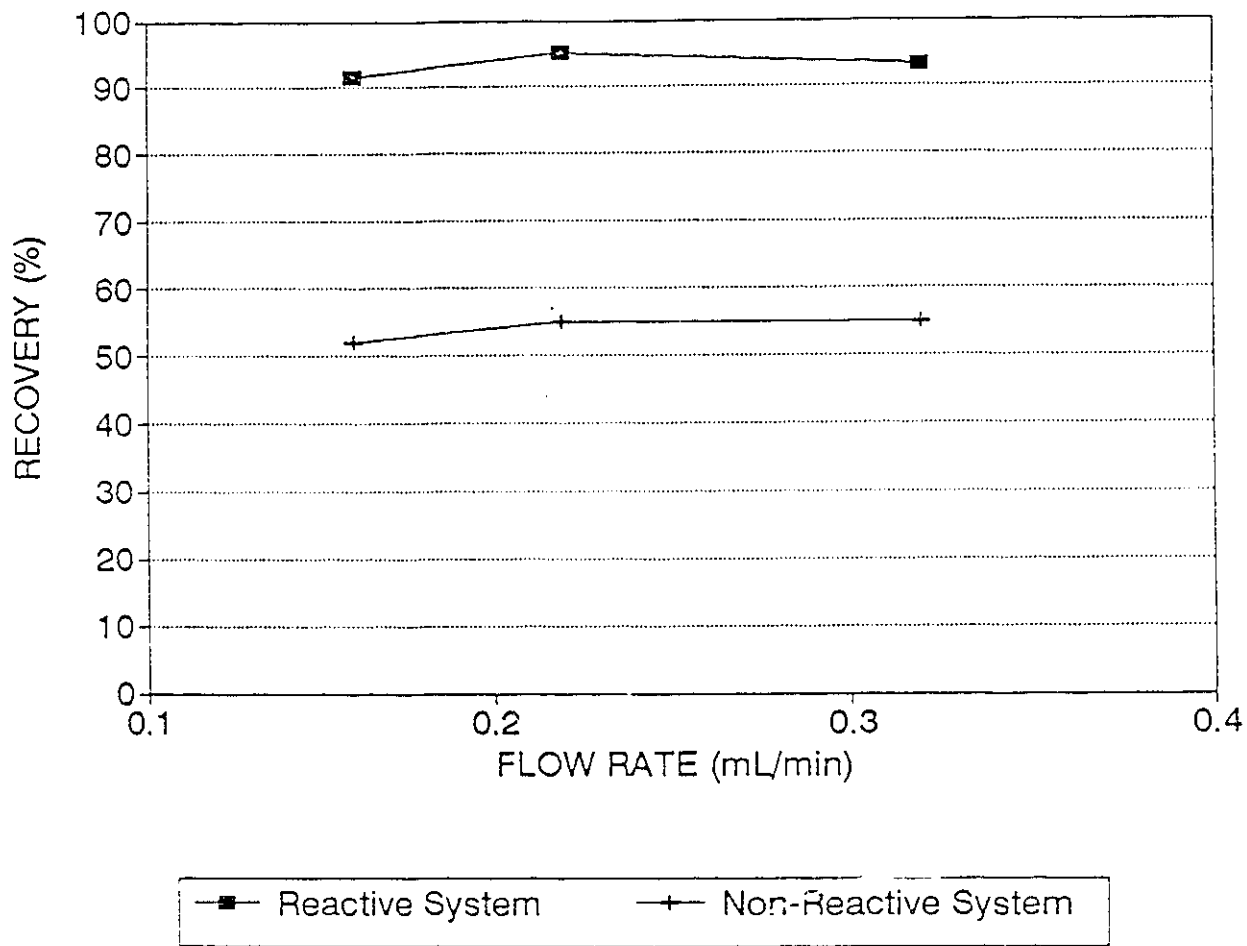


Figure 18: Recovery at 1 hour after breakthrough as a function of flow rate

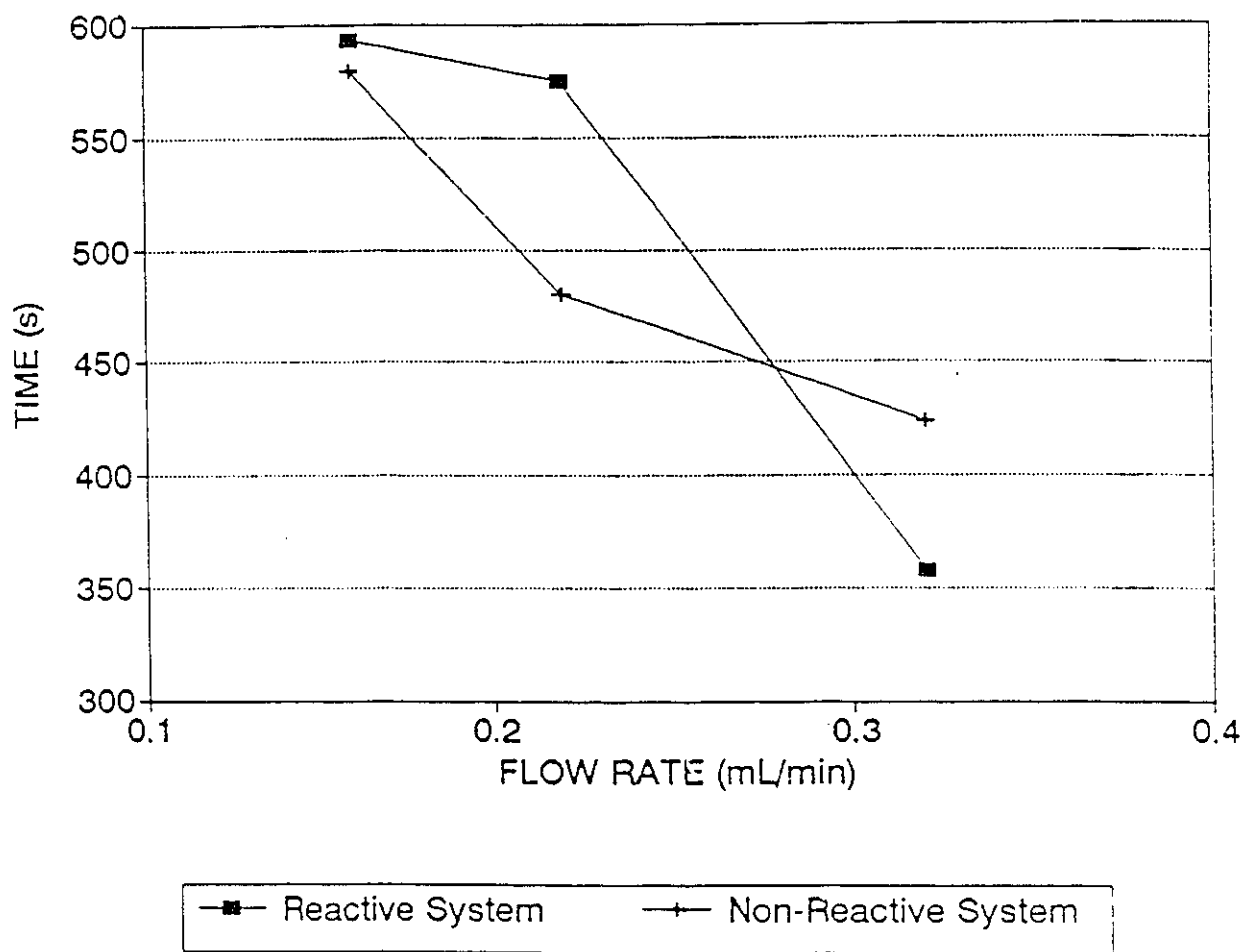


Figure 19: Time at breakthrough as a function of flow rate

5.4 REACTIVE AND NON-REACTIVE DISPLACEMENT AT FAVOURABLE MOBILITY RATIOS

The purpose of this investigation was to study and observe the displacement patterns and the percentage recovery in the reactive and the non-reactive systems under favourable mobility ratios. A total of six experiments were performed for the reactive and the non-reactive system.

The sixth series of experiments was performed using an alkaline water/glycerine solution (25 mM NaOH) as the displacing fluid to displace acidic n-decane. Aqueous solutions of three different viscosities (20.0, 12.2 and 5.3 mPa.s) were used to displace acidic n-decane. The seventh series of experiments was performed using a water-glycerine system as the displacing fluid to displace n-decane. In this non-reactive system, the same three aqueous solutions of different viscosities were also used as in the sixth series. The comparison between the reactive and the non-reactive system can be seen in Figure 20. The relation between the recovery and the viscosity of water/glycerine solution can be seen in Figures 21 and 22.

The parameters recorded in the experiments were breakthrough time, recovery at breakthrough, total recovery after 1 hour of breakthrough and displacement pattern. The results of the experiments are shown in Tables 9 and 10 (Appendix A). The relation between the recovery and the mobility ratio can be seen in Figures 23 and 24.

5.4.1 BREAKTHROUGH RECOVERY AND RECOVERY AFTER 1 HOUR

From Tables 9 and 10 (Appendix A), it can be seen that at breakthrough, the recovery observed in the case of the reactive system at a low viscosity of the displacing fluid is higher than for the non-reactive system, while at a higher viscosity the recovery at breakthrough is almost the same. Similarly, total recovery after 1 hour is very high - almost 100%.

5.4.2 DISPLACEMENT PATTERNS

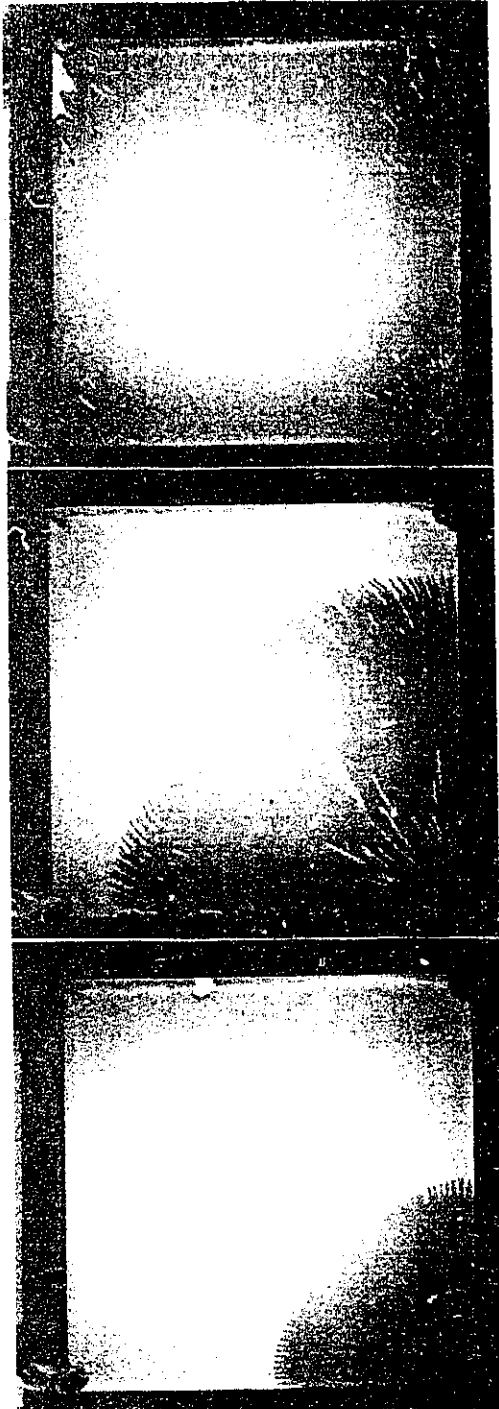
The displacement front observed in reactive systems is once again different from non-reactive systems. In non-reactive systems it is observed that instead of having fingers created along the front of the displacing fluid, a few dominant fingers exist, that grow and reach the producing well. Because of the favourable mobility ratio, after 1 hour of flooding, the displacing fluid displaces all the oil from the cell. In the case of the reactive system there were many tiny and uniform fingers in the beginning but after 1 hour past breakthrough, because of the highly favourable mobility ratio, the displacing fluid also displaced all the oil from the cell. Some of the photographs of these patterns can be seen in Figures 25 and 26.

5.4.3 TIME REQUIRED FOR BREAKTHROUGH

The time at breakthrough for the reactive and non-reactive systems increases with the increase in the viscosity of the displacing fluid. This is consistent with the higher recoveries observed. At a low viscosity of the aqueous phase, breakthrough time for the reactive system is higher than for the non-reactive system but at a higher viscosity, the breakthrough time is almost the same. This is due to the highly favourable mobility ratio.

It can be seen from Table 9 (Appendix A) that recovery at breakthrough is very much dependent upon the mobility ratio i.e. the lower the mobility ratio, the higher the recovery and the higher the time for breakthrough. This is in agreement with the expected behaviour for either the Hele-Shaw cell or a porous medium (Chen, 1987). The relation between time at breakthrough and viscosity of water/glycerine solution can be seen in Figure 27.

Reactive System



Non-Reactive system

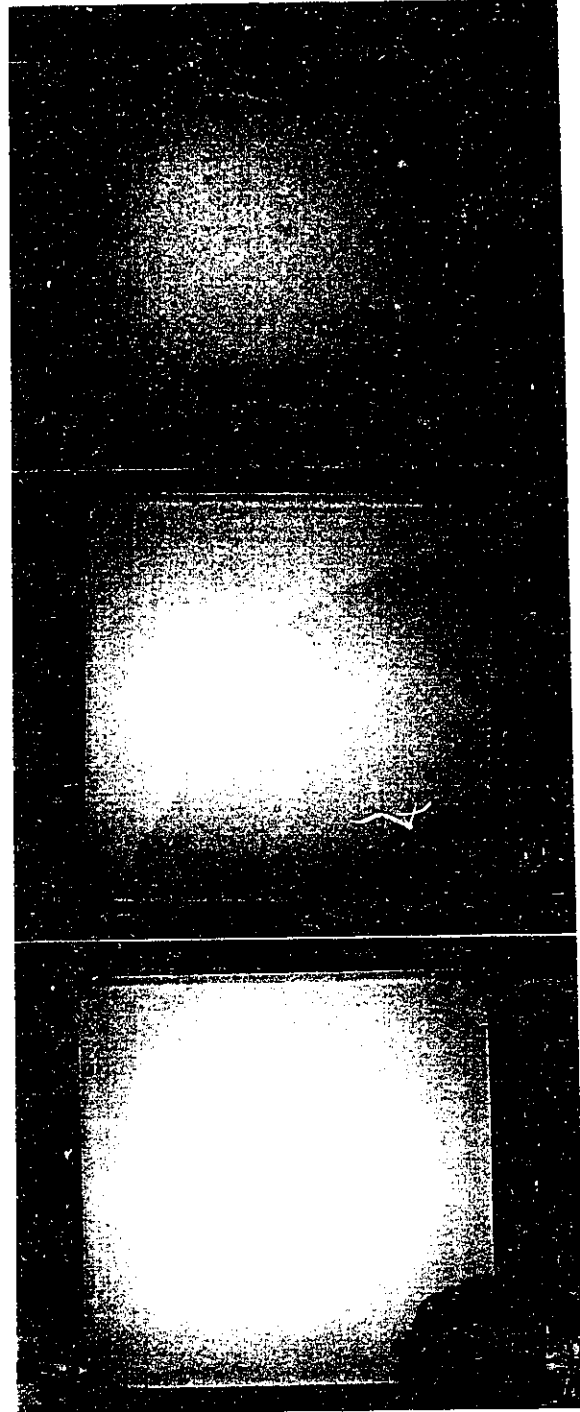


Figure 20 : Comparison between reactive and non-reactive system under favourable mobility ratio

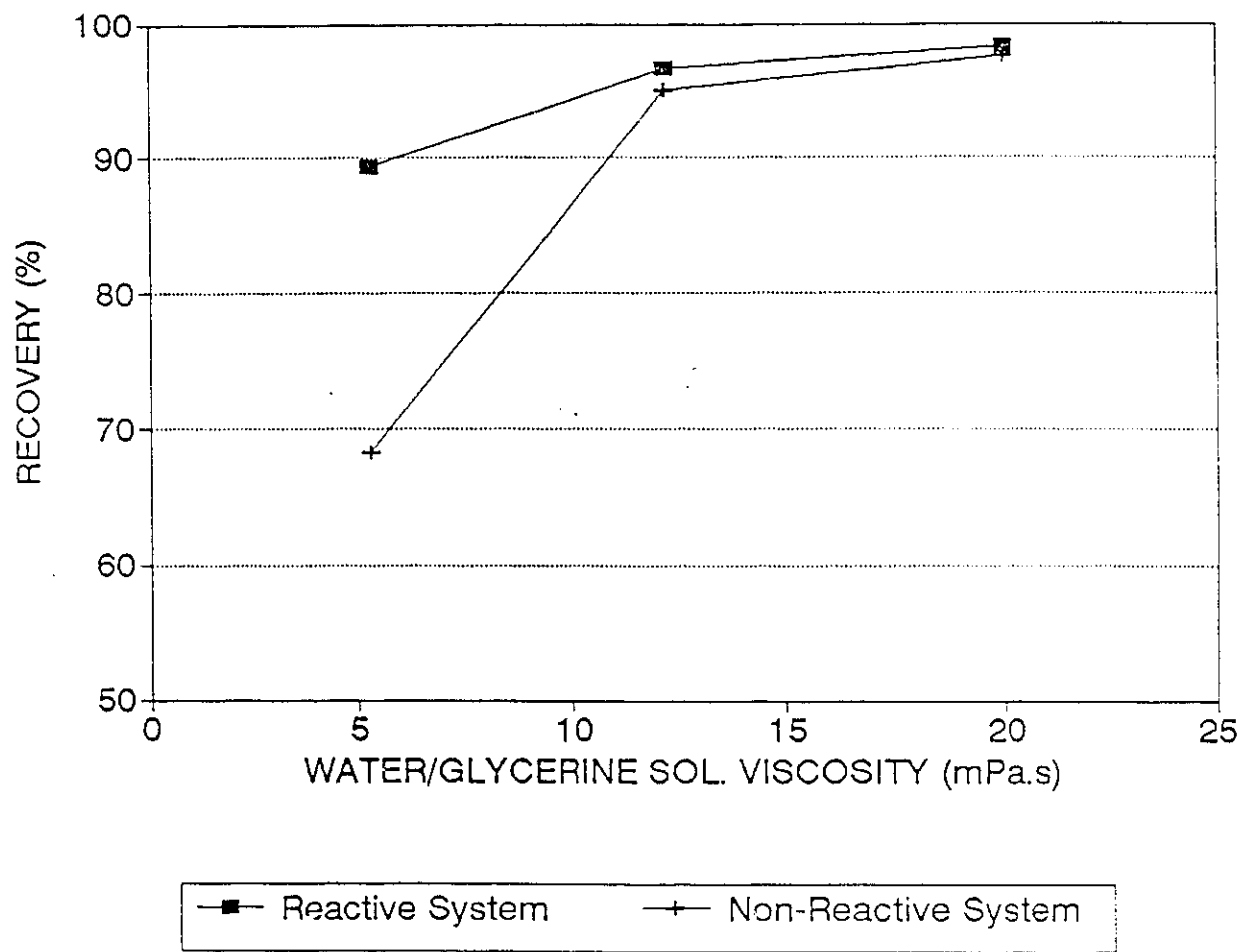


Figure 21: Recovery at breakthrough as a function of water/glycerine solution viscosity

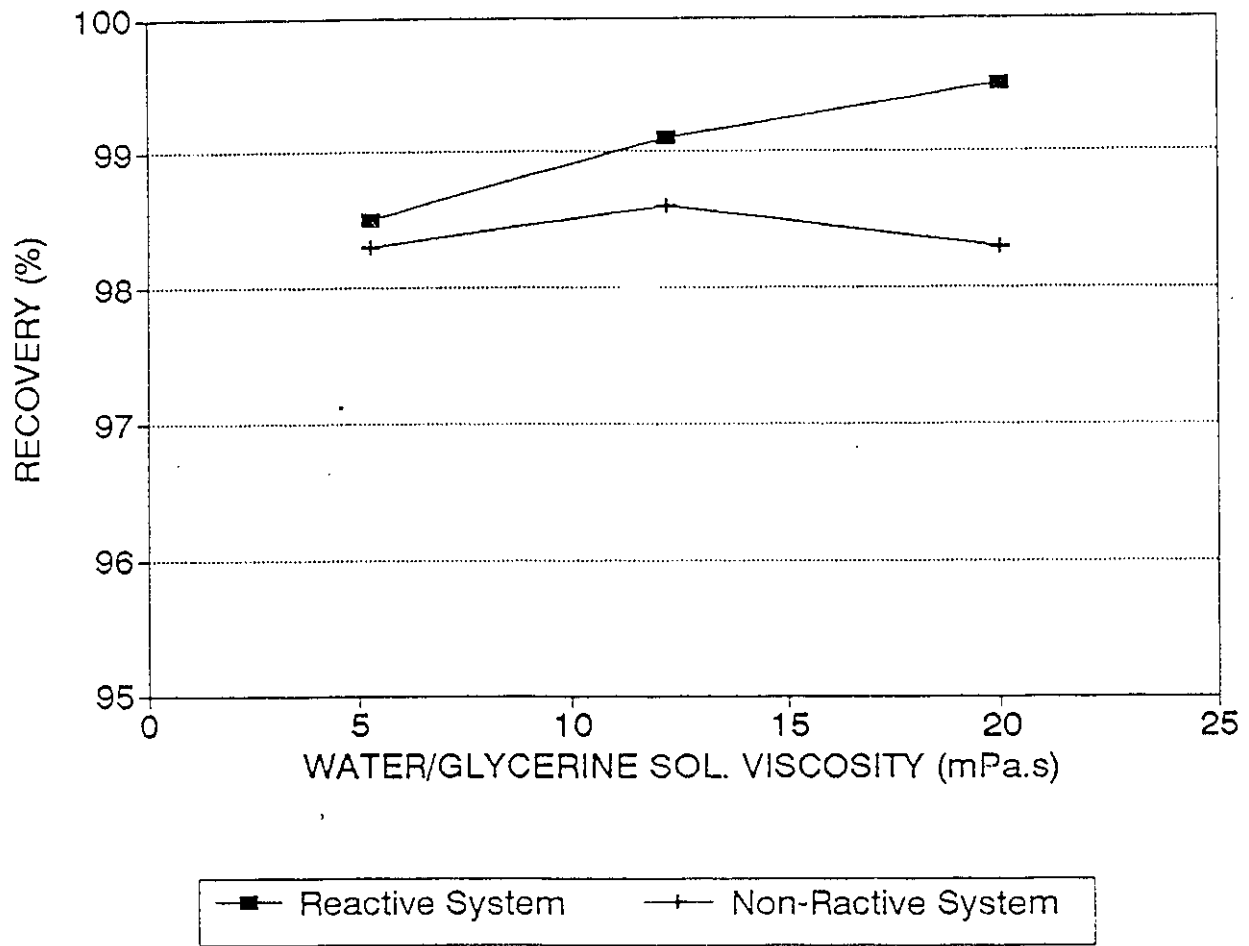


Figure 22: Recovery at 1 hour after breakthrough as a function of water/glycerine solution viscosity

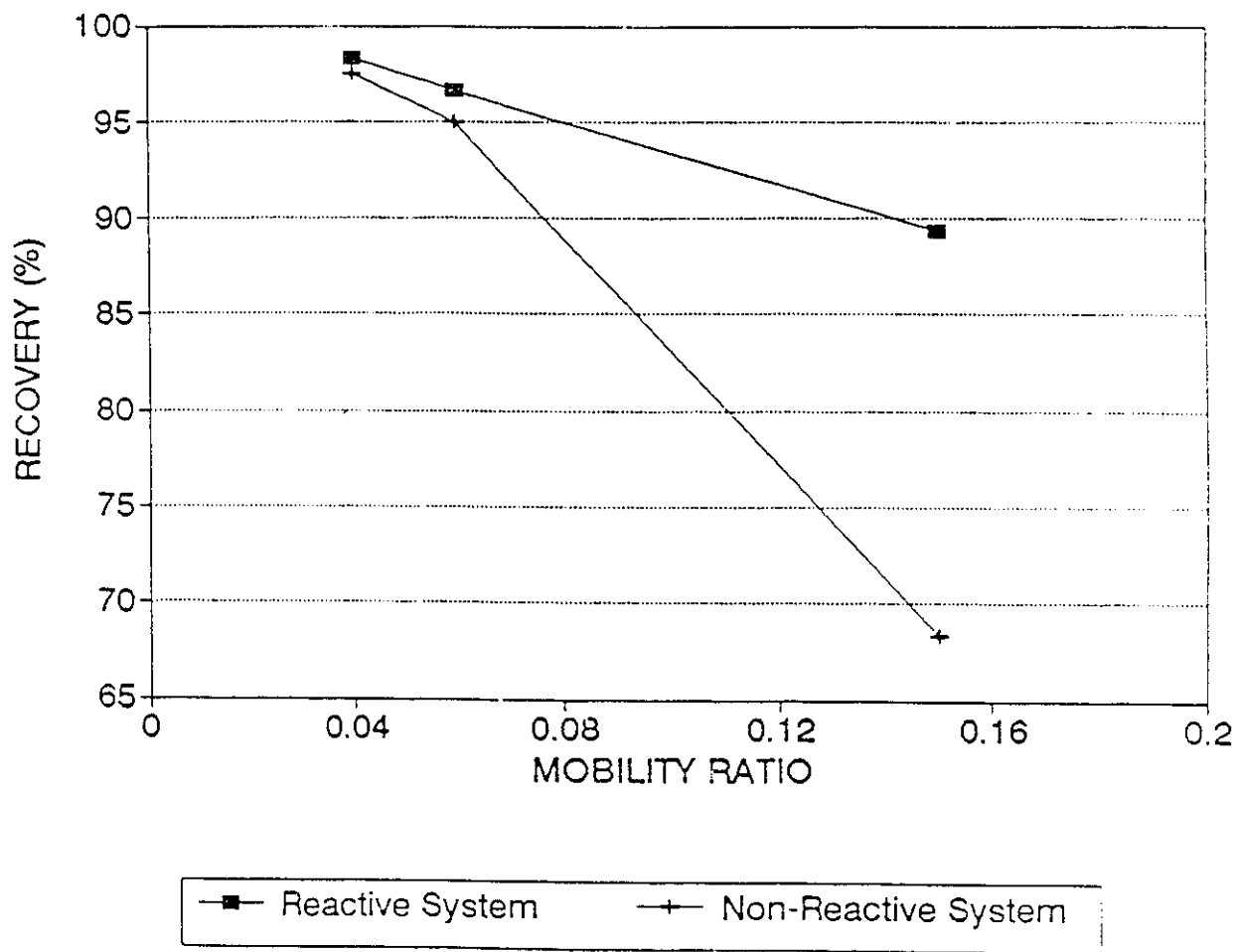


Figure 23: Recovery at breakthrough as a function of mobility ratio

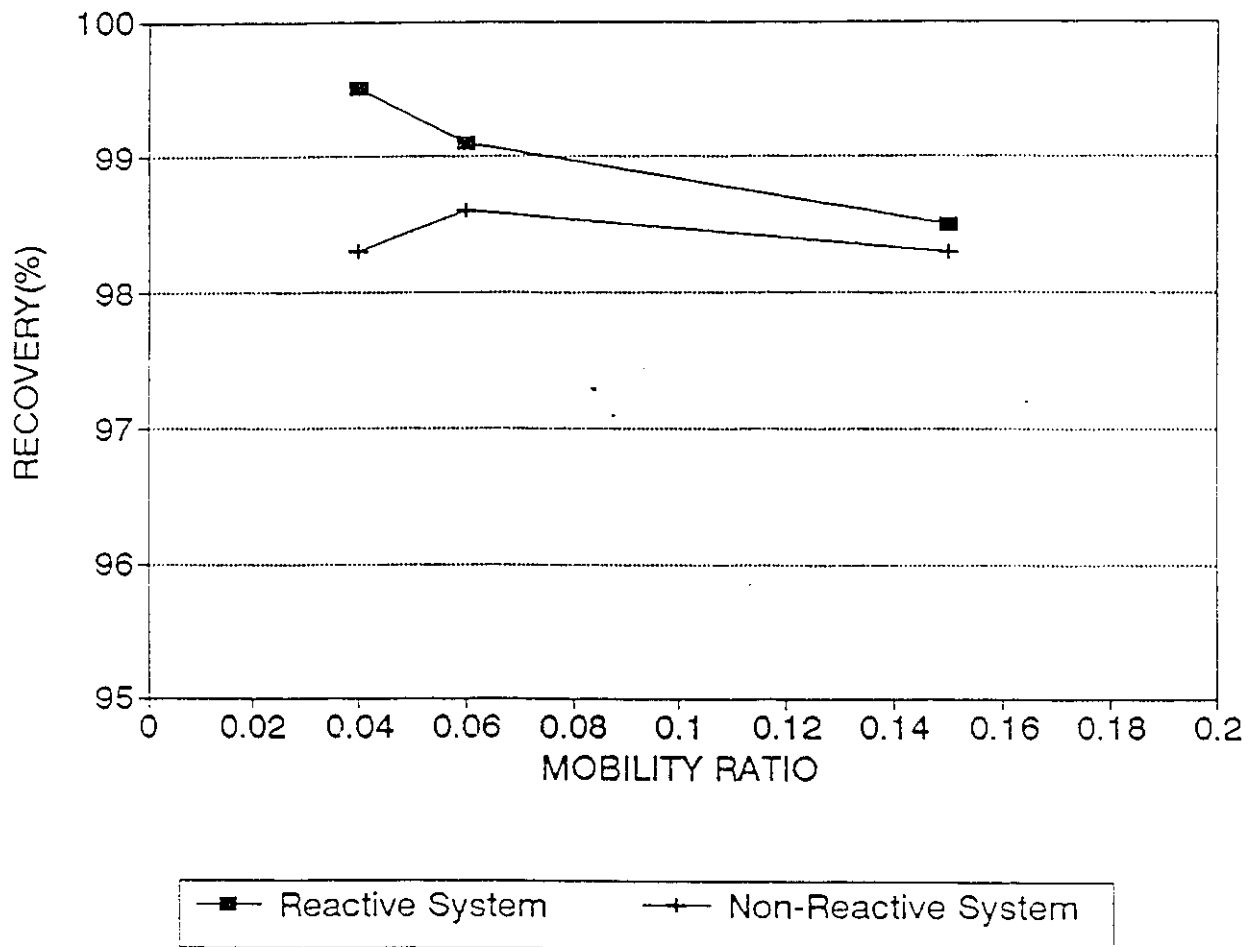


Figure 24: Recovery at 1 hour after breakthrough as a function of mobility ratio

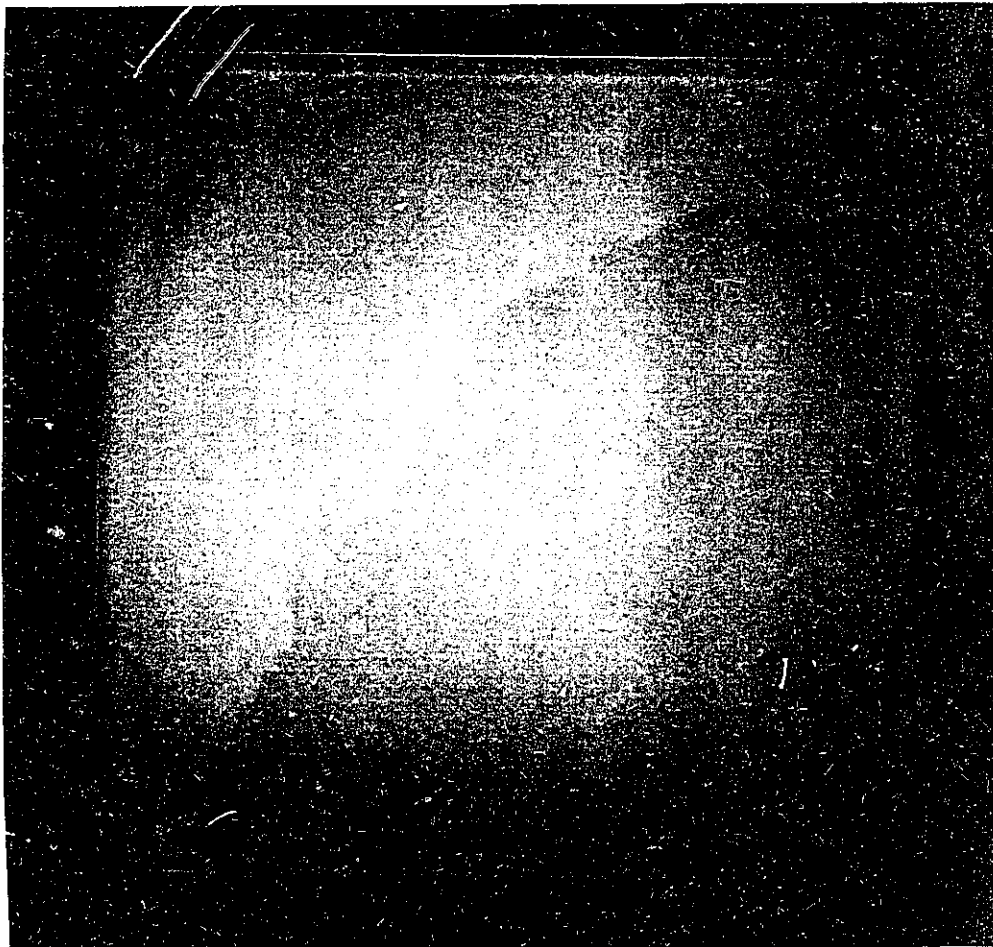


Figure 25: Displacement of n-decane by water-glycerine solution with a viscosity of 12.25 mPa.s (Non-reactive system)

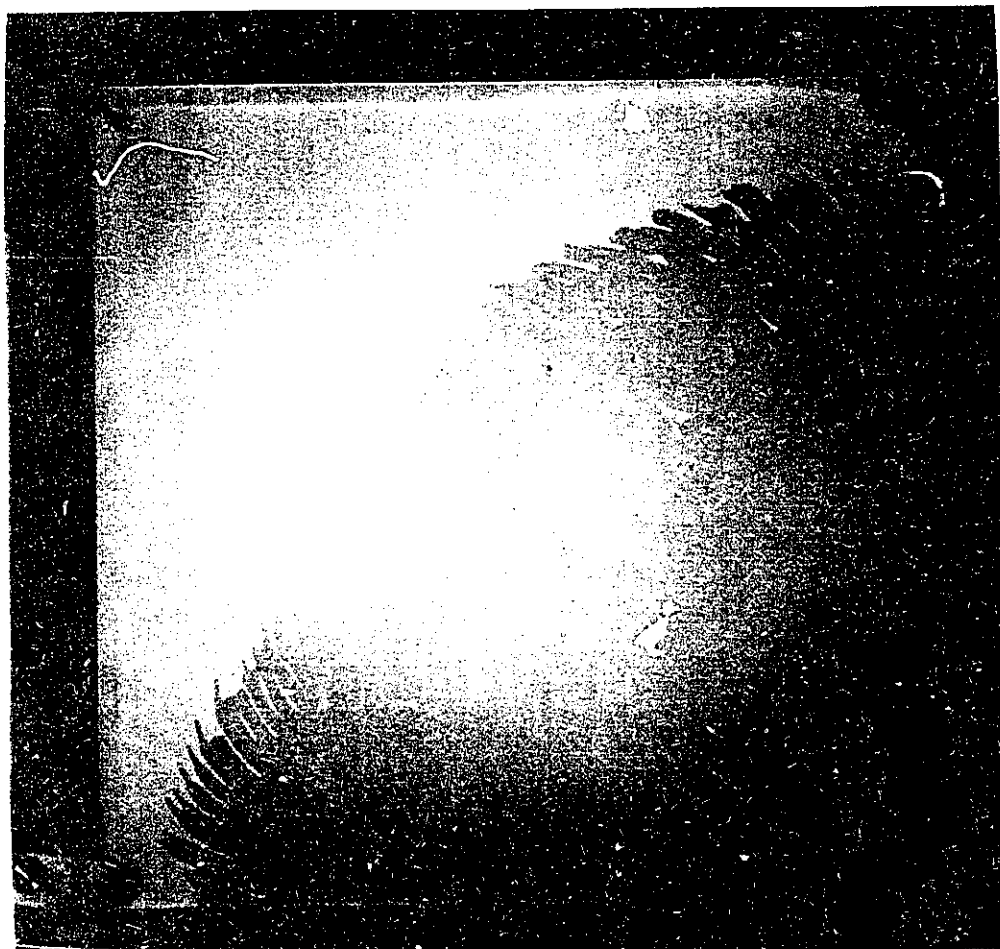


Figure 26: Displacement of acidic n-decane by alkaline water-glycerine solution with a viscosity of 12.25 mPa.s (Reactive system)

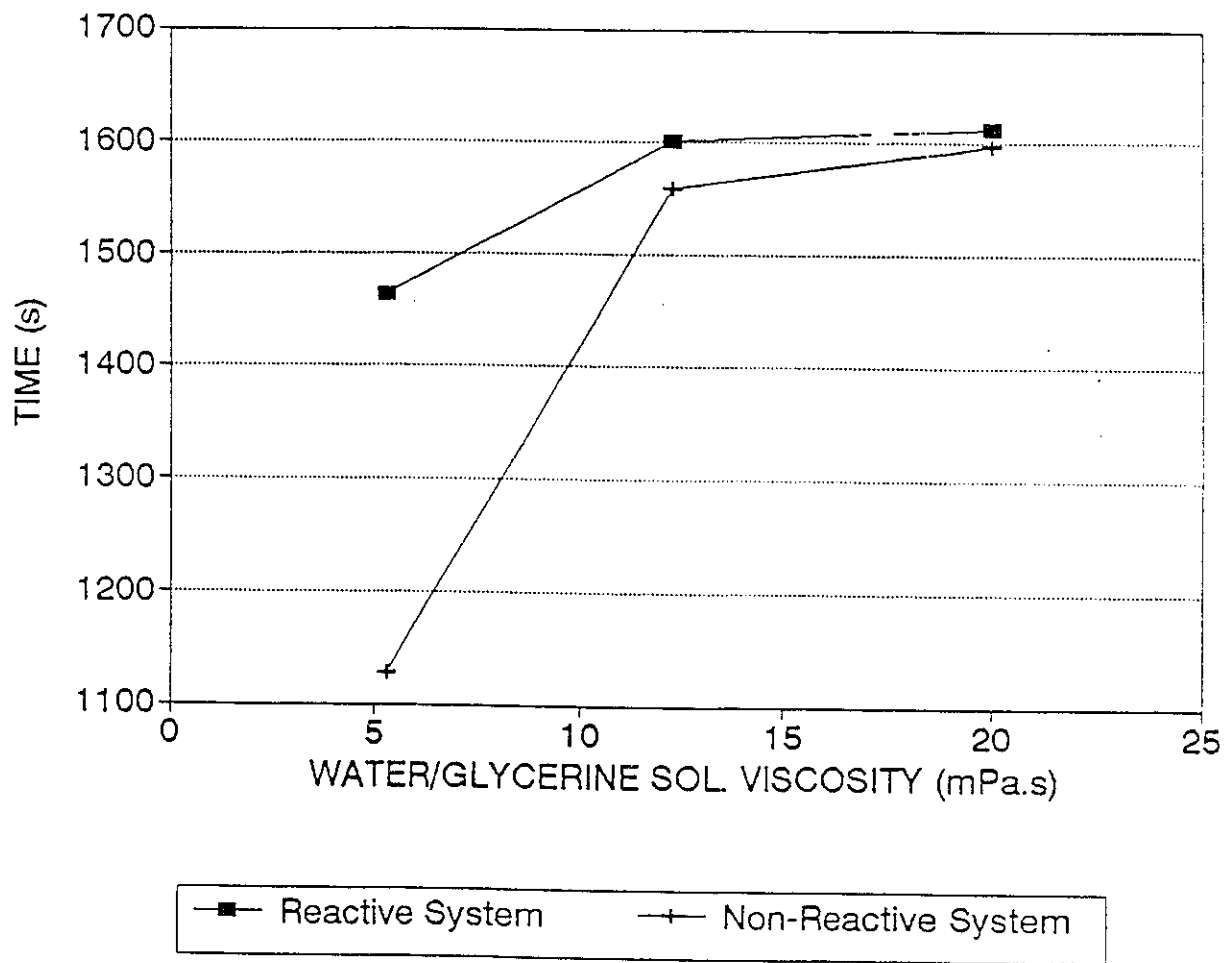


Figure 27: Time at breakthrough as a function of water/glycerine solution viscosity

5.5 DISPLACEMENT OF LIGHT PARAFFIN OIL BY ALKALINE SLUG BACKED UP BY VISCOUS WATER-GLYCERINE SOLUTION

A number of laboratory studies have since been reported which study the application of alkali/polymer or alkali/surfactant/polymer flooding to various reservoir systems. Indeed, the use of such combined chemicals has become the state-of-the-art in chemical flooding.

The most efficient application in alkali/polymer process requires simultaneous injection of alkali and polymer. This permitted both mobilization of residual oil by lowering interfacial tension and displacement of the oil by formation of an oil bank. Another possibility is to inject the viscous polymer solution after first injecting a finite amount of the alkaline solution.

In this investigation a series of experiment was performed in the Hele-Shaw cell by displacing the light paraffin oil by an alkaline slug backed up by a viscous water/glycerine solution. The main objective of this investigation was to compare the displacement patterns and the recovery percentage of the reactive and the non-reactive systems. In the reactive system, acidic (10mM linoleic acid) light paraffin oil/n-decane mixture was displaced by an alkaline slug (25 mM NaOH) backed up by a viscous water/glycerine solution. In the non-reactive system light paraffin oil/n-decane mixture was displaced by distilled water backed up by viscous water/glycerine solution.

5.5.1 REACTIVE AND NON-REACTIVE DISPLACEMENT BACKED UP BY VISCOUS WATER-GLYCERINE SOLUTION

Six experiments were performed for reactive and non-reactive systems. The eighth series of experiments was performed by injecting 2mL of alkaline solution (25 mM NaOH) as an intermediate displacing fluid, backed up by a viscous water-glycerine solution with a viscosity of 20 mPa.s., to displaced acidic light paraffin oil/n-decane mixture having viscosities of 23.3, 14.4 and 8.8 mPa.s. Congo red dye was used to differentiate between the displacing fluid and the

displaced fluid. The ninth series of experiments was performed by using 2mL of distilled water as an intermediate displacing fluid, backed up by a viscous water-glycerine solution with a viscosity of 20.0 mPa.s., to displaced light paraffin oil/n-decane mixture with the viscosities of 23.3, 14.4 and 8.8 mPa.s. Red food dye was used to differentiate between the displacing fluid and the displaced fluid.

5.5.2 BREAKTHROUGH RECOVERY AND RECOVERY AFTER 1 HOUR

From Tables 11 and 12 (Appendix A), it can be seen that for all oil compositions the recovery at breakthrough of the reactive system is always higher than the non-reactive system. The recovery at breakthrough for the non-reactive system increases with decreasing oil viscosity. This behaviour is similar to that observed in flooding experiments without viscous backup.

It was also noticed that the recovery at breakthrough for the non-reactive system was even lower than the non-reactive system without backup. The recovery at one hour after breakthrough in the reactive and the non-reactive system (when the oil viscosity was 23.8 mPa.s) was 16.6% and 15% respectively. The recovery at 1 hour after breakthrough for the non-reactive system was 58.3% and the recovery for the reactive system was 83.3%. The latter recovery was lower than the other two cases, i.e. 93% to 100%.

The reason for the low recovery was that the mobility ratio between the slug and the oil was not favourable. The viscous fluid initially pushed the alkaline slug and then viscous fluid bypassed alkaline slug and connected with the oil to be displaced from the sides. Because of the favourable mobility ratio on the sides, the viscous fluid went through the sides for breakthrough, and left the alkaline slug, in the middle of the cell. After one hour it swept most of the oil because of the high viscosity, but left some traces of the alkaline solution in the middle of the cell.

5.5.3 DISPLACEMENT PATTERNS

The displacement front observed in the reactive system is fundamentally different from the non-reactive system. In the non-reactive system it was observed that the water/glycerine solution forced the water into the middle of the cell forming an island. The water/glycerine solution then started to penetrate around the island and eventually swept all the water and oil with it out of the cell due to its high viscosity.

In the reactive system the alkaline solution started to form many minute fingers penetrating the oil and slowly advancing forward. The water/glycerine solution then swept all the alkaline solution and oil out of the cell, leaving no islands behind. Selected photographs of the patterns can be seen in Figures 28 and 29.

5.5.4 TIME REQUIRED FOR BREAKTHROUGH

It can be seen from Table 11 (Appendix A) that, as the viscosity of the oil decreases, the time at breakthrough increases and the recovery also increases. The reason was that the mobility ratio decreases with the decrease in viscosity of the light paraffin oil. The relation between the time at breakthrough and the oil viscosity can be seen in Figure 30.

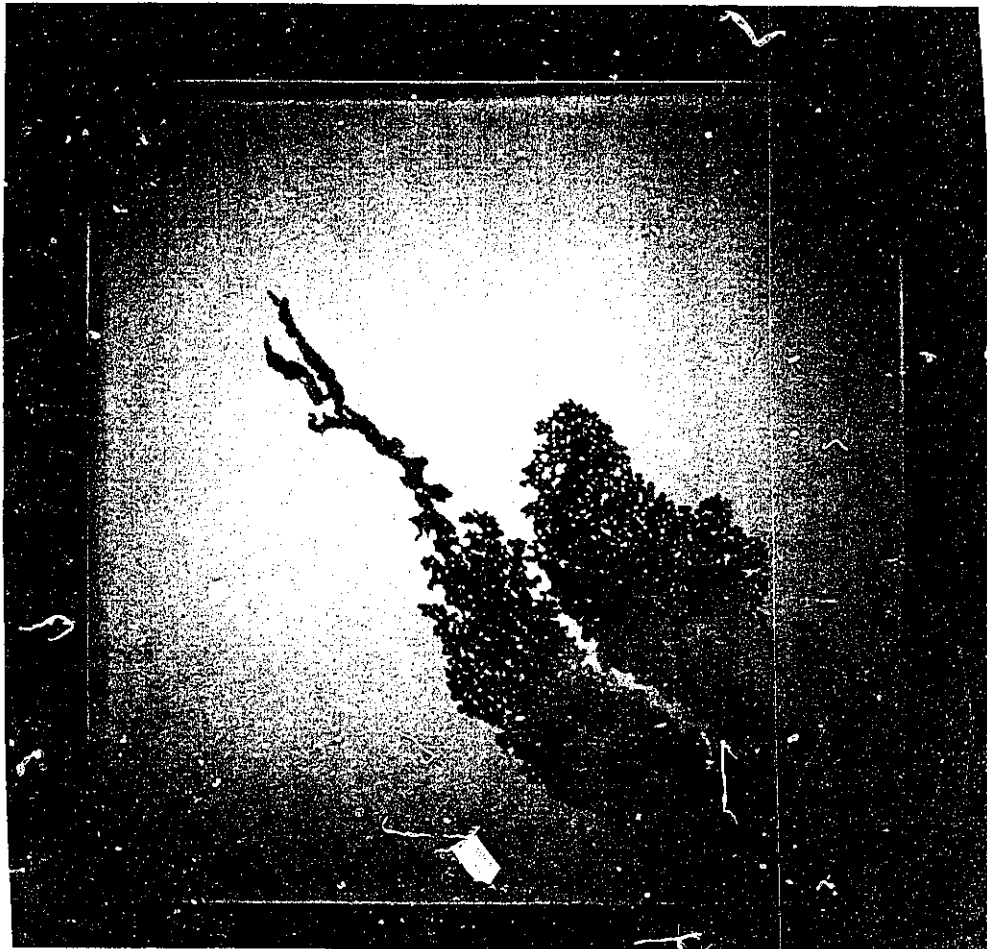


Figure 28: Displacement of light paraffin oil /n-decane mixture with a viscosity of 14.42 mPa.s by distilled water backed up by water-glycerine solution with a viscosity of 20.0 mPa.s (Non-reactive system)

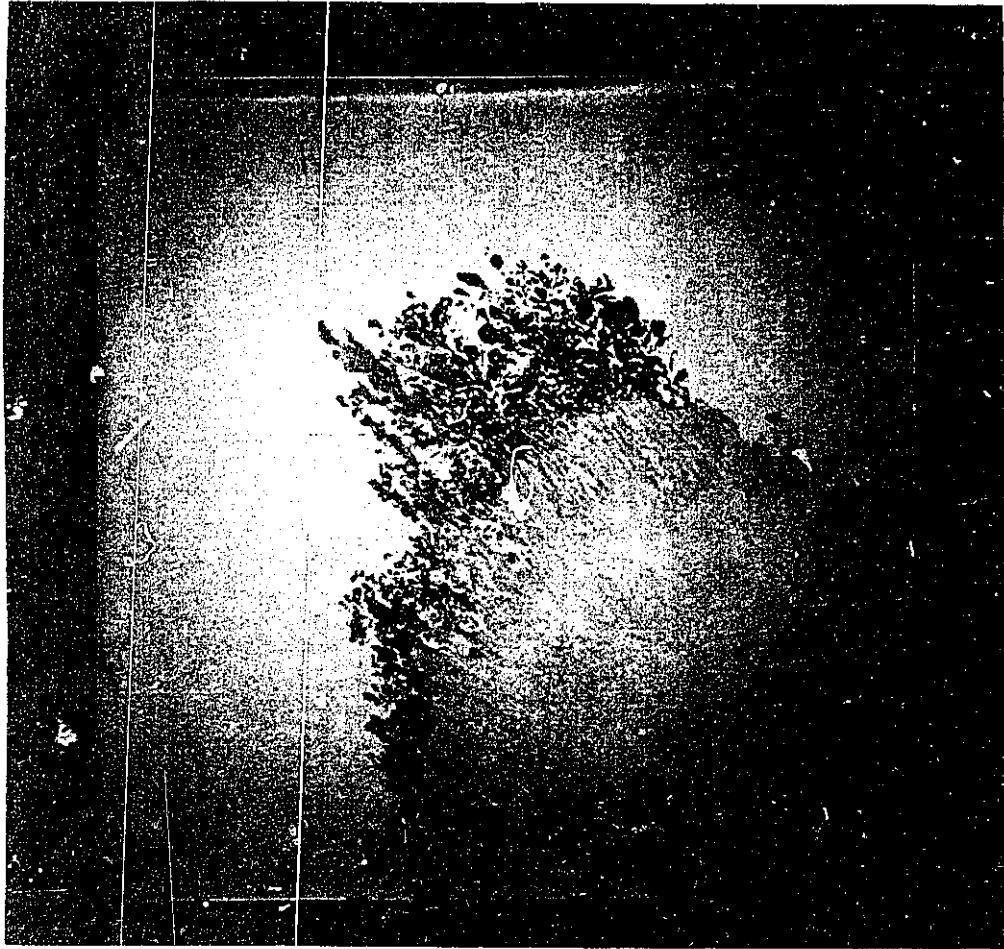


Figure 29: Displacement of acidic light paraffin oil /n-decane mixture with a viscosity of 14.42 mPa.s by alkaline slug backed up by water-glycerine solution with a viscosity of 20.0 mPa.s (Reactive system)

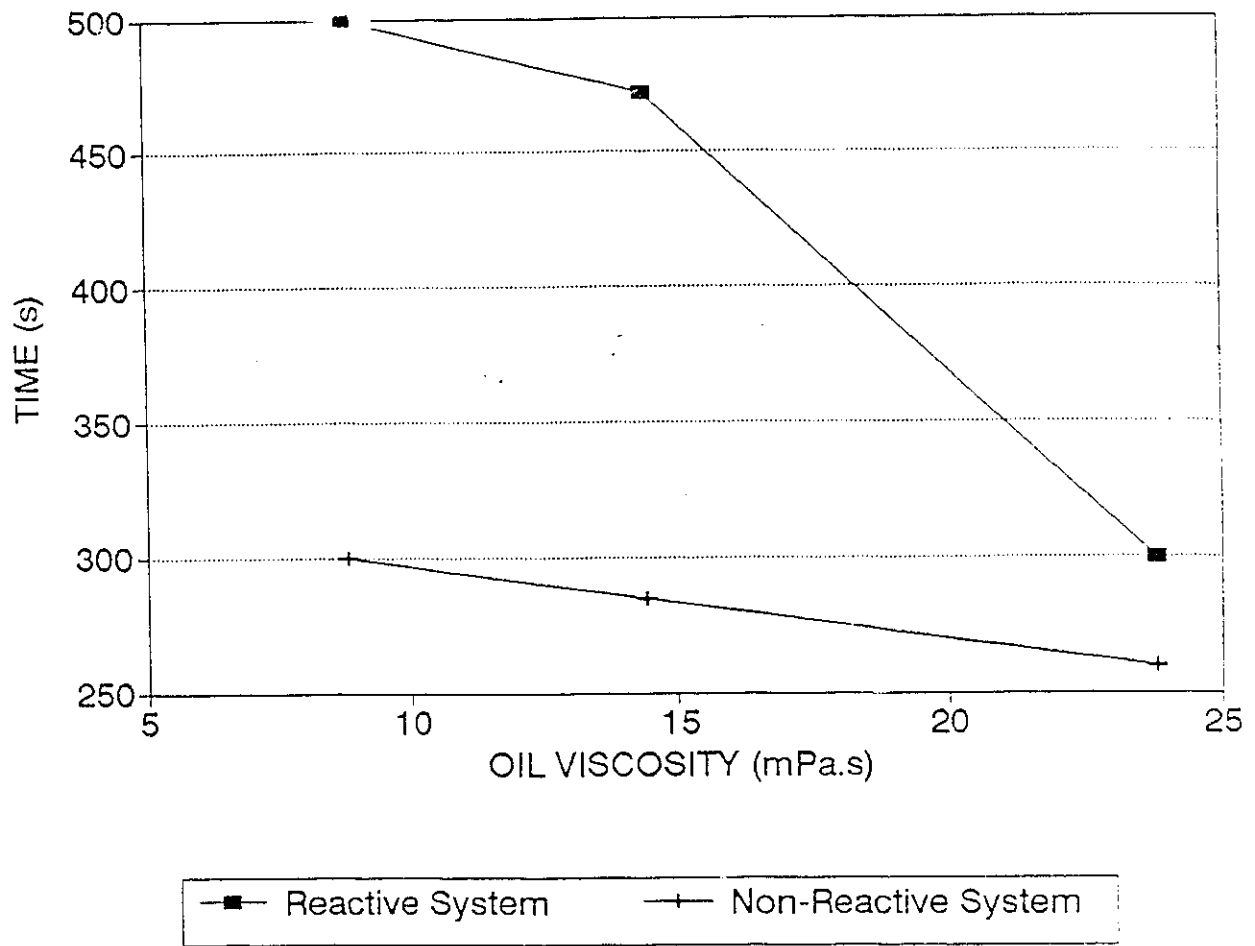


Figure 30 : Time at breakthrough as a function of oil viscosity

5.6 COMPARISON OF RESULTS WITH OTHER RESEARCHERS

The chemical reaction at the interface of oil and displacing fluid plays a large role in alkaline flooding. In addition to lowering the interfacial tension, it can change wettability, promote emulsification and entrainment of the oil and thereby lower its bulk-phase viscosity. Many researchers have investigated different aspects of interfacial chemical reactions. In this research the effect of the interfacial chemical reaction on the percentage recovery was studied. It was noted that the significant differences between the displacement patterns for the reactive system and non-reactive system could be a consequence of the lowering of interfacial tension between the two phases i.e. oil and alkaline solution. This occurred because in the reactive system, lowering of the IFT caused an increase in the number of fingers observed in the displacement patterns in comparison with the non-reactive system. In the reactive system at the interface of the displacing aqueous alkaline solution and the acidic oil, the interfacial reaction formed a surface active agent. The formation of the surface active agent as a result lowered the IFT, as mentioned above.

The other factors which also affected the oil recovery were convection, molecular diffusion and adsorption of the reactants at the interface. The molecular diffusion took place from alkaline aqueous solution and from acidic light paraffin oil towards the interface. Adsorption of the reactant also occurred at the interface. The comparison between the reactive and non-reactive system can be seen in Figure 9. Nasr-El-Din et al. (1990) had conducted similar investigation of displacements in model porous media. The displacement patterns that were observed in the reactive system in this research were very similar to the displacement patterns observed in the reactive system in a radial cell by Nasr-El-Din et al.

England and Berg (1971) suggested a diffusion model to describe the transfer of surface active agents across a liquid-liquid interface and the presence of an activation barrier to adsorb and / or desorb the chemical reactants. Ramakrishnan and Wasan (1983) related the IFT reduction to the concentration of the surface active species. Sharma and Yen (1989) had discussed the dissociation of acid species.

At different flow rates, the finger patterns were completely different. At a constant flow rate, in the case of the reactive system the finger patterns were different from those of the non-reactive system because of the reduction of IFT between the oil phase and the aqueous phase. Park and Homsy (1985) studied the effect of viscosity of the immiscible fingers in a radial cell. They found that in the displacement experiments, as the viscosity of oil increased, the fingers became narrower and further branching occurred. This behaviour was very similar to the behaviour observed in the Hele-Shaw cell conducted in this work as mentioned above.

Chen (1989) studied the growth of radial viscous fingers in a radial cell. He found that the displacements of oil were similar in all directions. As may be observed in figure 4, in the reversed five-spot pattern, the injection well is located at the centre of four production wells. The location of the injection well can help the injecting fluid to move in all directions. Consequently one might assume that the effect of interfacial reaction will also be the same in all directions. However, because of the complex porous structure of the reservoir, one could not predict the actual direction of the flow; it could flow in one direction or in all directions depending on the nature of the reservoir rock and the fluids.

It was observed in experiments by Saffman and Taylor (1958) that the unstable interface gives rise to fingers of the less viscous fluid penetrating into the more viscous fluid. They were using a linear cell geometry.

The shape of the fingers between the two fluids depends on the capillary number, which can be given as:

$$N_{Ca} = \frac{(\mu u)}{\gamma} \quad (12)$$

The capillary number depends on the ratio of the distance between the two plates and the width of the Hele-Shaw cell. A third parameter, the ratio of the two viscosities, also affects the shape of the fingers. If N_{Ca} was not too large, it was observed by Saffman and Taylor (1958), Park and Homsy (1985) and others that the flow developed into a single steady-state finger which moved through the cell with constant velocity u . For larger values of the capillary number, the interface branched into a number of different fingers. In the reactive system reduction of IFT decreased the capillary number. However, the interface branched into a numerous tiny fingers.

5.7 PROPOSED EXPLANATION OF OBSERVED BEHAVIOUR AND POSSIBLE APPLICATIONS OF THIS RESEARCH

In this research the effect of the interfacial reaction between immiscible liquids is studied. The process consists of the generation of a surface-active agent by an interfacial reaction of an aqueous solution of NaOH with linoleic acid dissolved in oil. The surface-active agent thus generated can be adsorbed at the oil-water interface and can lower the interfacial tension (IFT) between the oil and the injected alkaline solution. The adsorption of surfactant may be expected to affect the wettability of the glass plates of the Hele-Shaw cell. The IFT is a function of the concentration of the active species at the interface. The concentration of these species at the interface depends on their rates of adsorption and desorption. If the rate of desorption was much lower than the rate of adsorption, then the active species will accumulate at the interface. This accumulation of the active species will cause the IFT to drop significantly. As the concentration of the active species at the interface

increased, however, the desorption rate also increased due to the higher concentration gradient present. As a result, the concentration of the active species at the interface diminished and the IFT rose again.

Other researchers have conducted similar investigation by using radial and linear cells. In the radial cells, the interface velocity at a given injection flow rate was maximum at the inlet and decreased as the displacing fluid moved forward. In linear cells the interface velocity at a given injection flow rate remained the same throughout the displacement. In the Hele-Shaw cell used in the present work the interface velocity was maximum at the inlet and decreased as the displacing fluid moved forward but, the flow rate increased again towards the outlet. The difference between the radial cell, linear cell and the cell used in this research can be seen in Figure 31. The reversed five-spot pattern Hele-Shaw cell has its own advantages. It is a very efficient pattern. Mahaffey and Rutherford (1965) found that reversed five-spot pattern's sweep efficiency was much higher than the other patterns.

Displacement sweep efficiency is defined as the amount of oil displaced divided by amount of oil contacted by the displacing agent. It can range between 0.0 and 1.0 efficiency . The rate at which the displacement sweep efficiency approached 1.0 was strongly affected by the type of displacing fluid and the amount of the oil to be displaced. If the displacement was such that the displacing fluid would contact all the oil initially present in the media, the volumetric sweep efficiency would be unity, where the volumetric sweep efficiency is defined as the volume of oil contacted by the displacing agent divided by volume of oil originally in place.

The results dealing with the effect of flowrate are not conclusive. There was no significant effect on the recovery percentage after one hour of breakthrough. The patterns were completely different at the breakthrough. In all the cases the final patterns were quite similar. More experiments would be necessary to determine the dependence of oil recovery on flow rate.

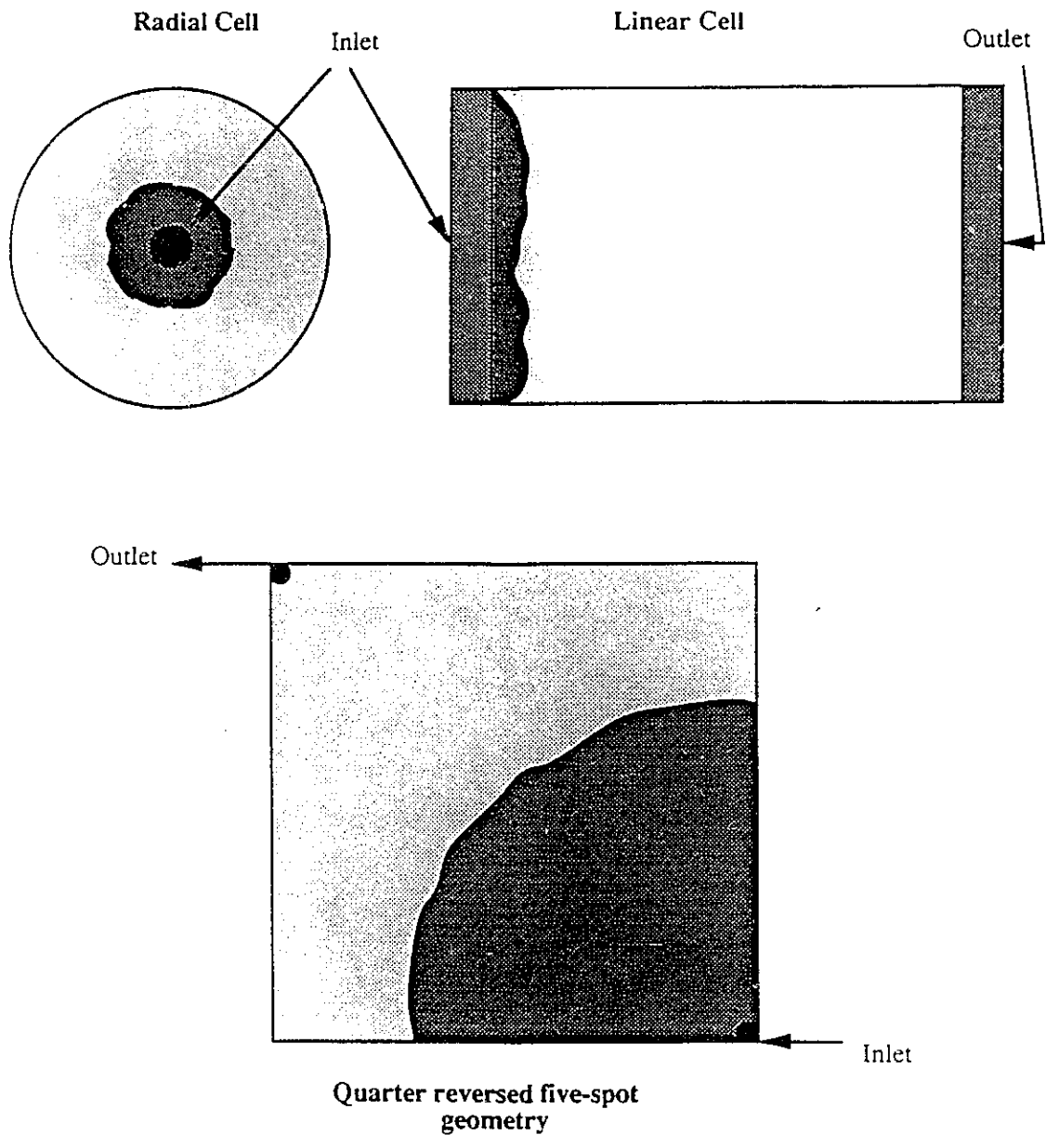


Figure 31: Comparison between radial , linear and quarter reversed five-spot geometry

Favourable mobility ratio (i.e. the case in which the viscosity of the displacing fluid was higher than the viscosity of the displaced fluid) played an important role in the recovery regardless of the size of the fingers. In the case of reactive system there were many tiny but uniform fingers in the beginning. However, after breakthrough, because of the favourable mobility ratio, the displacing fluid displaced all the oil from the cell. In the case of the non-reactive system the only difference was the pattern of the fingers. There were very few fingers at the moving front, and all the oil was displaced from the cell at one hour after breakthrough.

In the experiments in which the alkaline solution was followed by a viscous water/glycerine solution, it was observed that there was an improvement in the sweep efficiency of the displacement due to the high viscosity of the water/glycerine solution. In the reactive system the alkaline solution started to form many minute fingers which penetrated the oil and slowly advanced forward, but there was no uniformity between the fingers. The water/glycerine solution did not have any acidic species, therefore, no reaction took place between the alkaline solution and the water/glycerine solution. In these experiments, water/glycerine solution was used to simulate a polymer pusher solution. The purpose was to study the effect of an interfacial reaction in conjunction with a high viscosity solution. In actual practice, the use of glycerine, because of high cost, is not feasible. However, on laboratory scale, experiments showed that the interfacial reaction in conjunction with a high viscosity back-up could improve oil recovery.

All the experiments were performed twice and an average value was taken. It was noted that all the experiments were reproducible in terms of finger patterns and in percentage recovery. The relative permeability aspects of a real porous media were absent in such a cell. It is also to be noted that the laboratory displacement, because of the small size of the displacement system employed, was invariably stable, while field systems, because of the large size of a field-scale system, are generally unstable. The same experiments could be performed in a Hele-Shaw cell with a porous media. The displacement patterns may behave somewhat differently in the porous media. It cannot be predicted how accurately such a system will behave in terms of displacing patterns and percentage recovery.

The injection of alkaline solution should improve the acidic oil recovery as compared with water injection in the oil well, but as discussed in an earlier chapter, the recovery also depends on the well patterns, geometry of the reservoir, rock wettability and other factors. Sodium hydroxide was used as an alkaline agent to recover the oil. This is an inexpensive and readily available alkali, but the possible advantages of using NaOH cannot be predicted at this point. In the practical application, many other factors come into play, and need to be studied further.

As discussed in the objectives of this research, Hornof and Bernard (1992) conducted some displacement experiments by using heavy oil. It was found in this research that the displacement patterns of the model system (light paraffin oil / n-decane mixture) was similar to the heavy oil. Consequently, it may be concluded that the present results obtained with a simple model system (light paraffin oil / n-decane mixture) are relevant to displacements of real crude oil by alkaline solution.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. Recovery in the reactive system is always higher than in the non-reactive system.
2. In both the reactive and non-reactive systems, the recovery at breakthrough is a function of oil viscosity.
3. The total recovery at 1 hour after breakthrough in the non-reactive system is a function of oil viscosity, while in the case of the reactive system it is independent of oil viscosity.
4. The time required for breakthrough is longer in the case of the reactive system; it is a function of oil viscosity for both the reactive and the non-reactive systems.
5. Flow rate does not have a significant effect on the recovery in both the reactive and the non-reactive systems in the range investigated.
6. At a favourable mobility ratio, the recovery in both the reactive and non-reactive systems is very high.
7. Recovery in the reactive system is always higher than the non-reactive system when using an intermediate low-viscosity displacing fluid, backed up by a viscous water-glycerine solution.

RECOMMENDATIONS

1. The experiments carried out in this research can be performed in actual porous media in order to compare recoveries and displacement patterns.
2. Instead of a viscous water/glycerine solution a polymer solution can be used as a back up.

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APPENDIX - A

TABLE 1

NON-REACTIVE AND REACTIVE SYSTEMS IN THE FIRST SERIES OF EXPERIMENTS

SYSTEMS	BREAKTHROUGH TIME (s)	RECOVERY AT BREAKTHROUGH (%)	RECOVERY AFTER 1 HOUR (%)
DISPLACEMENT OF PARAFFIN OIL BY WATER (NON-REACTIVE)	345	20.0	21.0
DISPLACEMENT OF ACIDIC PARAFFIN OIL BY WATER (NON-REACTIVE)	349	20.5	21.0
DISPLACEMENT OF PARAFFIN OIL BY ALKALINE SOLUTION (NON-REACTIVE)	340	20.0	21.0
DISPLACEMENT OF ACIDIC PARAFFIN OIL BY ALKALINE SOLUTION (REACTIVE)	430	26.0	95.0

TABLE 2

# RUNS	1	2	3	4	5
TIME AT BREAKTHROUGH (s)	600	605	599	600	585
RECOVERY AT BREAKTHROUGH (mL)	2.2	2.2	2.2	2.2	2.1
RECOVERY AFTER 10 min (mL)	3.0	3.0	3.0	3.0	3.0
RECOVERY AFTER 20 min (mL)	3.6	3.8	3.5	3.5	3.4
RECOVERY AFTER 30 min (mL)	4.0	4.0	4.0	4.0	4.0
RECOVERY AFTER 40 min (mL)	4.5	4.5	4.5	4.4	4.4
RECOVERY AFTER 50 min (mL)	5.1	5.0	5.0	5.1	5.0
RECOVERY AFTER 60 min (mL)	5.6	5.6	5.5	5.7	5.6

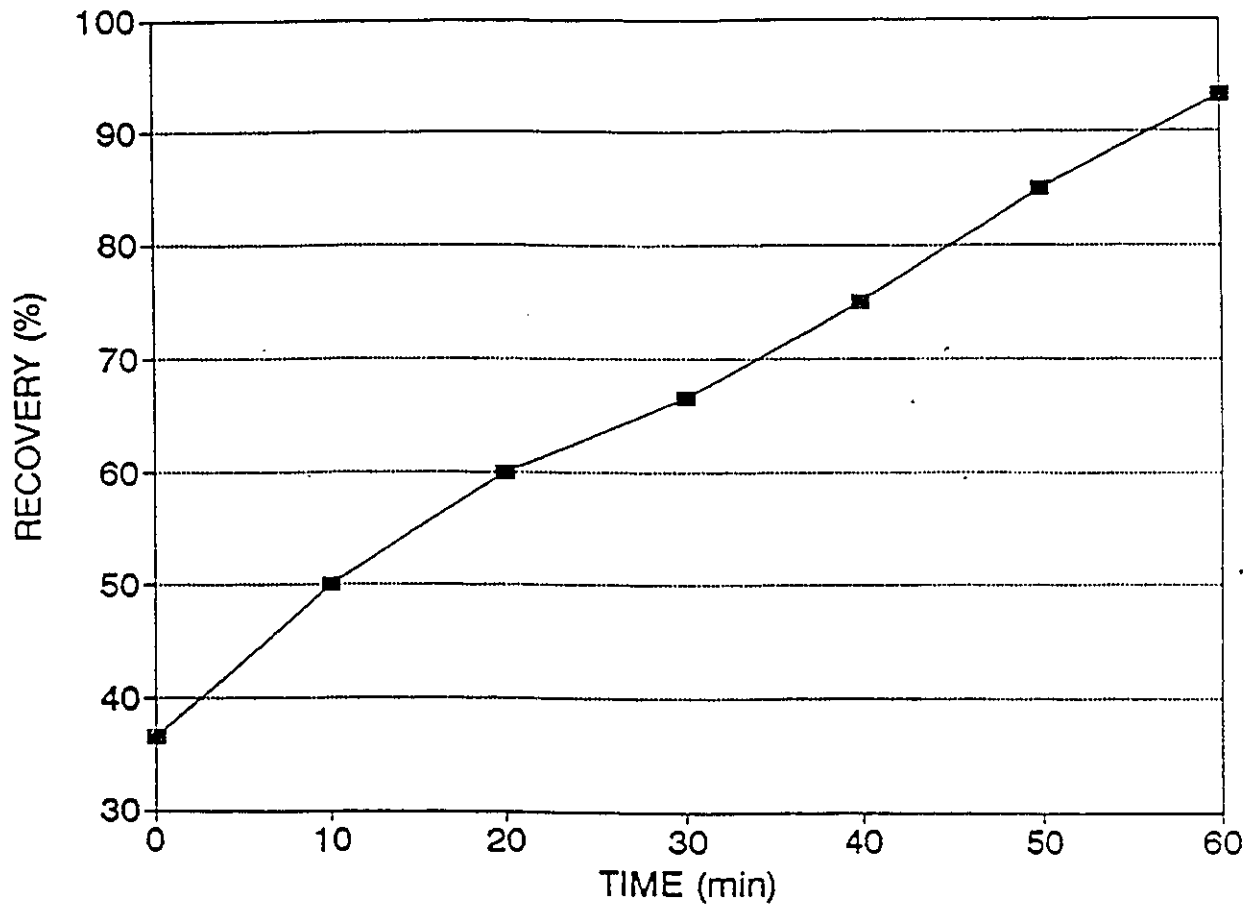


Figure 32 : Recovery after breakthrough with the progression of time

TABLE 3

VISCOSITY OF LIGHT PARAFFIN OIL-n-DECANE MIXTURES

LIGHT PARAFFIN OIL (%)	VISCOSITY (mPa.s)
Paraffin oil	23.79
95	18.57
90	14.42
85	10.80
80	8.80
75	6.86
70	5.10
65	4.09
50	2.48
35	1.60
n-decane	0.80

TABLE 4

RECOVERY AT BREAKTHROUGH FOR REACTIVE AND NON-REACTIVE SYSTEMS
IN THE SECOND AND THE THIRD SERIES OF EXPERIMENTS

OIL VISCOSITY (mPa.s)	MOBILITY RATIO	RECOVERY AT BREAKTHROUGH (%)	
		NON-REACTIVE	REACTIVE
23.79	26.71	21.0	26.2
18.57	20.85	26.6	29.0
14.42	16.16	27.5	30.0
10.80	12.12	28.3	33.3
8.80	9.88	30.0	36.6
6.86	7.70	31.6	37.3
5.10	5.72	32.6	38.9
4.09	4.59	33.3	41.6
2.48	2.78	35.0	51.6
1.60	1.79	40.0	55.0
0.80	0.89	45.0	71.6

TABLE 5

RECOVERY AT 1 HOUR AFTER BREAKTHROUGH FOR REACTIVE AND
NON-REACTIVE SYSTEMS
IN THE SECOND AND THE THIRD SERIES OF EXPERIMENTS

OIL VISCOSITY (mPa.s)	MOBILITY RATIO	TOTAL RECOVERY AFTER 1 HOUR (%)	
		NON-REACTIVE	REACTIVE
23.79	26.71	22.0	95.0
18.57	20.85	33.3	88.3
14.42	16.19	41.6	85.0
10.80	12.12	50.0	90.0
8.80	9.88	55.0	91.6
6.86	7.70	63.3	95.0
5.10	5.72	58.3	93.3
4.09	4.59	55.0	93.3
2.48	2.78	53.0	91.6
1.60	1.79	61.0	91.6
0.80	0.89	63.0	98.0

TABLE 6

TIME AT BREAKTHROUGH FOR REACTIVE AND NON-REACTIVE SYSTEMS IN THE
SECOND AND THIRD SERIES OF EXPERIMENTS

OIL VISCOSITY (mPa.s)	MOBILITY RATIO	TIME AT BREAKTHROUGH NON-REACTIVE SYSTEM (s)	TIME AT BREAKTHROUGH REACTIVE SYSTEM (s)
23.79	26.71	345	430
18.57	20.85	435	475
14.42	16.19	456	490
10.80	12.12	470	549
8.80	9.88	487	580
6.86	7.70	520	620
5.10	5.72	527	635
4.09	4.59	576	685
2.48	2.78	600	861
1.60	1.79	672	918
0.80	0.89	750	1173

TABLE 7

RECOVERY AT BREAKTHROUGH FOR REACTIVE AND NON-REACTIVE SYSTEMS AT
DIFFERENT FLOW RATES IN THE FOURTH AND FIFTH SERIES OF EXPERIMENTS

FLOW RATE (mL/min)	TIME AT BREAKTHROUGH (s)		RECOVERY AT BREAKTHROUGH (%)	
	NON-REACTIVE	REACTIVE	NON-REACTIVE	REACTIVE
0.16	579	593	30.0	28.3
0.22	480	575	30.0	35.0
0.32	485	358	31.0	32.6

TABLE 8

RECOVERY AT 1 HOUR AFTER BREAKTHROUGH FOR REACTIVE AND NON-REACTIVE SYSTEMS AT DIFFERENT FLOW RATES IN THE FOURTH AND FIFTH SERIES OF EXPERIMENTS

FLOW RATE (mL/min)	TOTAL RECOVERY AFTER 1 HOUR (%)	
	NON-REACTIVE SYSTEM	REACTIVE SYSTEM
0.16	53.0	91.6
0.22	55.0	95.0
0.32	55.0	93.3

TABLE 9

RECOVERY AT BREAKTHROUGH FOR REACTIVE AND NON-REACTIVE SYSTEMS BY
DISPLACEMENT OF n-DECANE BY WATER-GLYCERINE SOLUTION IN THE SIXTH
AND SEVENTH SERIES OF EXPERIMENTS

SOLUTION MOBILITY VISCOSITY RATIO (mPa.s)		TIME AT BREAKTHROUGH (s)		RECOVERY AT BREAKTHROUGH (%)	
		NON-REACTIVE	REACTIVE	NON-REACTIVE	REACTIVE
5.30	0.150	1128	1464	68.3	89.4
12.25	0.065	1559	1601	95.0	96.6
20.00	0.040	1597	1612	97.5	98.3

TABLE 10

RECOVERY AT 1 HOUR AFTER THE BREAKTHROUGH FOR REACTIVE AND
NON-REACTIVE SYSTEM
FOR DISPLACEMENT OF n-DECANE BY WATER-GLYCERINE SOLUTION IN THE SIXTH
AND SEVENTH SERIES OF EXPERIMENTS

SOLUTION VISCOSITY (mPa.s)	MOBILITY RATIO	TOTAL RECOVERY AFTER 1 HOUR (%)	
		NON-REACTIVE	REACTIVE
5.30	0.1509	98.3	98.5
12.25	0.0653	98.6	99.1
20.00	0.0400	98.3	99.5

TABLE 11

RECOVERY AT BREAKTHROUGH FOR REACTIVE AND NON-REACTIVE SYSTEMS
 BY DISPLACEMENT OF LIGHT PARAFFIN OIL/n-DECANE BY ALKALINE SOLUTION
 FOLLOWED BY WATER/GLYCERINE SOLUTION IN THE EIGHTH AND NINTH SERIES
 OF EXPERIMENTS

OIL VISCOSITY (mPa.s)	TIME AT BREAKTHROUGH (s)		RECOVERY AT BREAKTHROUGH (%)	
	NON-REACTIVE	REACTIVE	NON-REACTIVE	REACTIVE
23.79	260	300	15.0	16.60
14.42	285	472	16.6	28.33
8.80	300	500	18.3	30.00

TABLE 12

RECOVERY AT 1 HOUR AFTER BREAKTHROUGH FOR REACTIVE AND
 NON-REACTIVE SYSTEMS
 BY DISPLACEMENT OF LIGHT PARAFFIN OIL/n-DECANE BY ALKALINE SOLUTION
 FOLLOWED BY WATER-GLYCERINE SOLUTION IN THE EIGHTH AND NINTH SERIES
 OF EXPERIMENTS

OIL VISCOSITY (mPa.s)	MOBILITY RATIO ALKALI/OIL	MOBILITY RATIO BACKUP SOL/OIL	TOTAL RECOVERY AFTER 1 HOUR (%)	
			NON-REACTIVE	REACTIVE
23.79	26.71	1.189	58.3	83.3
14.42	16.19	0.721	83.3	93.3
8.80	9.88	0.440	96.3	100.0

APPENDIX - B

DETERMINATION OF EXPERIMENTAL ERROR

A series of experiments was performed to estimate the experimental error. Six experiments were performed, each by using acidic light paraffin oil/n-decane mixture (10 mM linoleic acid) displaced by alkaline solution (25 mM) under the same flow rate. In each experiment the recovery reading were taken at 10 minutes intervals.

The standard deviation for recovery was calculated by SAS programme and found to be 1.5%. The graph in Figure 31 shows the recovery with the progression of time. The results of the experiments are shown in Table 2. The standard deviation for the viscosity and density of the light paraffin oil / n-decane mixture were also calculated by using SAS programme.

THE STANDARD DEVIATION FOR RECOVERY PERCENTAGE OF LIGHT
PARAFFIN OIL / N-DECANE MIXTURES

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	2.1800000	0.0447214	2.1000000	2.2000000

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT 10 MIN AFTER BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	3.0000000	0	3.0000000	3.0000000

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT 20 MIN. AFTER BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	3.5600000	0.1516575	3.4000000	3.8000000

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT 30 MIN. AFTER BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	4.0000000	0	4.0000000	4.0000000

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT 40 MIN AFTER BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	4.4600000	0.0547723	4.4000000	4.5000000

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT 50 MIN. AFTER BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	5.0400000	0.0547723	5.0000000	5.1000000

THE SAS SYST

ANALYSIS VARIABLE : RECOVERY AT 60 MIN AFTER BREAKTHROUGH

N	Mean	Std Dev	Minimum	Maximum
5	5.6000000	0.0707107	5.5000000	5.7000000

THE STANDARD DEVIATION FOR THE VISCOSITY OF LIGHT PARAFFIN
OIL / N- DECANE MIXTURES

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	23.7933333	0.0450925	23.7500000	23.8400000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 95% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	18.5700000	0.0300000	18.5400000	18.6000000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 90% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	14.4200000	0.0200000	14.4000000	14.4400000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 85% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	10.8000000	0.0200000	10.7800000	10.8200000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 80% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	8.8000000	0.0200000	8.7800000	8.8200000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 75% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	6.8600000	0.0100000	6.8500000	6.8700000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 70% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	5.1000000	0.0100000	5.0900000	5.1100000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 65% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	4.0900000	0.0200000	4.0700000	4.1100000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 50% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	2.4800000	0.0200000	2.4600000	2.5000000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF 35% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	1.6000000	0.0300000	1.5700000	1.6300000

THE SAS SYST

ANALYSIS VARIABLE : VISCOSITY OF PURE N-DECANE

N	Mean	Std Dev	Minimum	Maximum
3	0.8000000	0.0100000	0.7900000	0.8100000

THE STANDARD DEVIATION FOR THE DENSITY OF LIGHT PARAFFIN OIL /
N - DECANE MIXTURES

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8490000	0.0010000	0.8480000	0.8500000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 95% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8480000	0.0010000	0.8470000	0.8490000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 90% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8410000	0.0020000	0.8390000	0.8430000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 85% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8350000	0.0020000	0.8330000	0.8370000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 80% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8300000	0.0010000	0.8290000	0.8310000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 75% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8200000	0.0010000	0.8190000	0.8210000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 70% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8150000	0.0010000	0.8140000	0.8160000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 65% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.8100000	0.0040000	0.8060000	0.8140000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 50% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.7870000	0.0020000	0.7850000	0.7890000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF 35% LIGHT PARAFFIN OIL

N	Mean	Std Dev	Minimum	Maximum
3	0.7200000	0.0020000	0.7180000	0.7220000

THE SAS SYST

ANALYSIS VARIABLE : DENSITY OF PURE N-DECANE

N	Mean	Std Dev	Minimum	Maximum
3	0.6700000	0.0020000	0.6680000	0.6720000