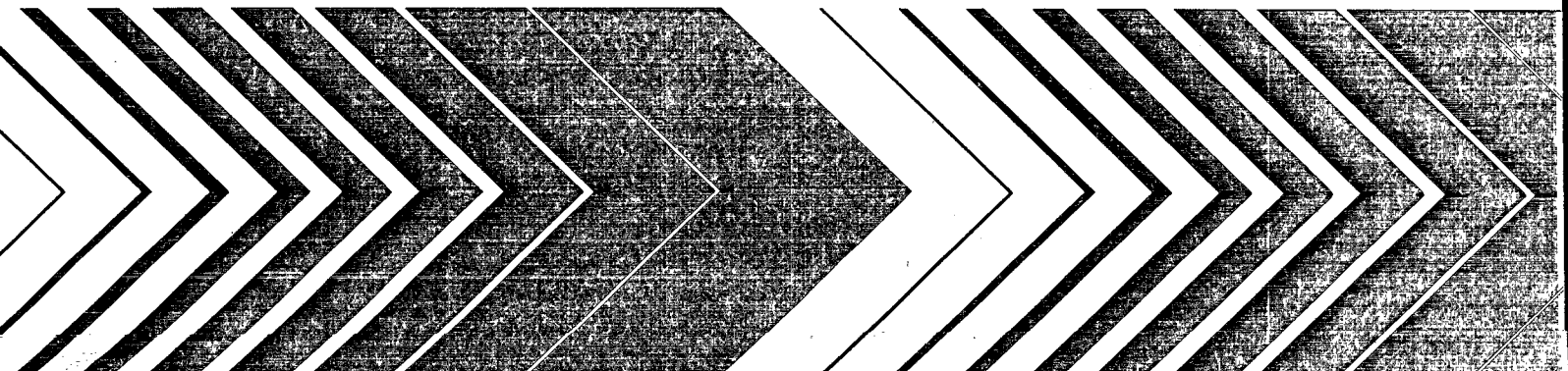
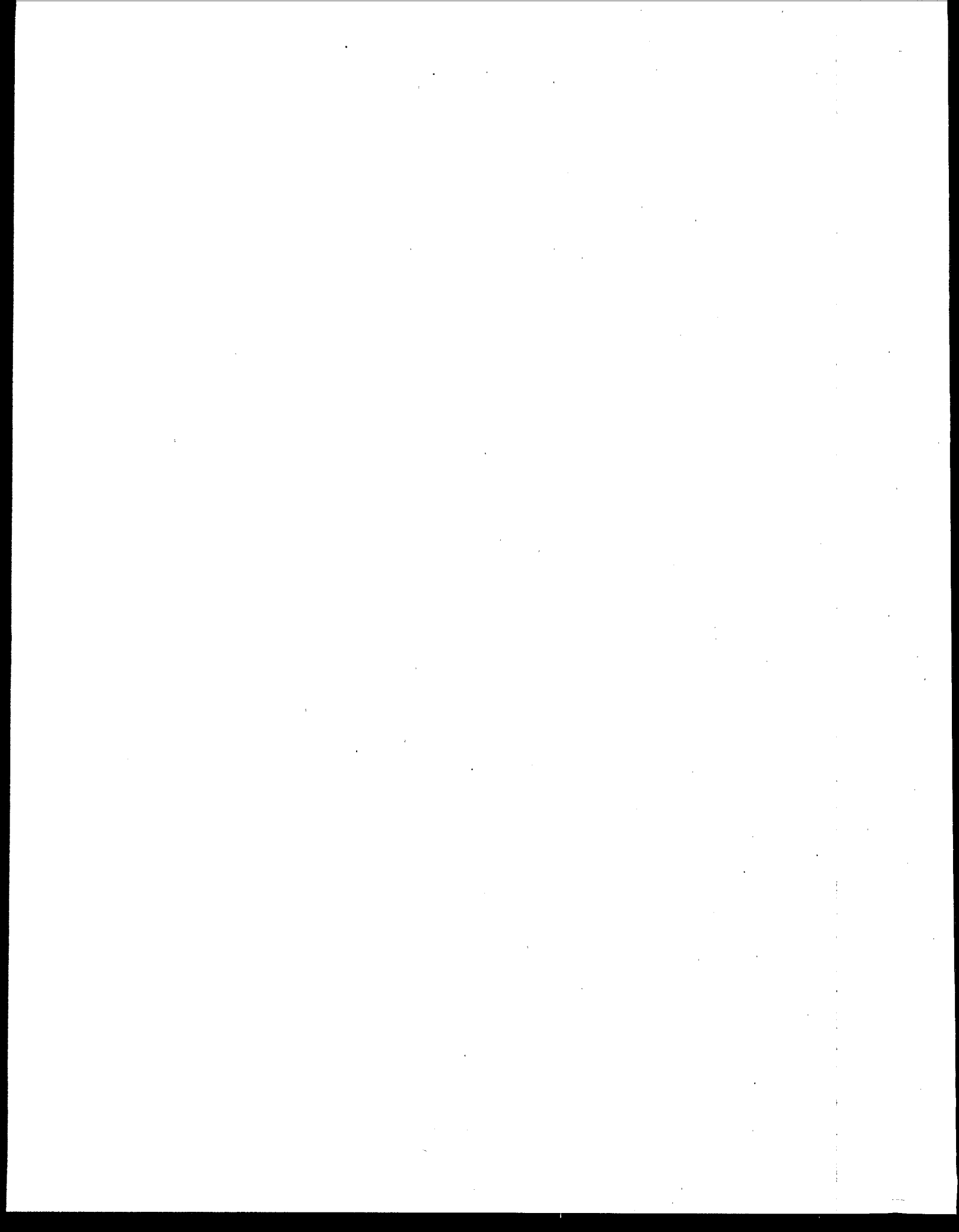




Laboratory Study on the Use of Hot Water to Recover Light Oily Wastes from Sands





EPA/600/R-93/021
February 1993

**LABORATORY STUDY ON THE USE OF
HOT WATER TO RECOVER LIGHT
OILY WASTES FROM SANDS**

by

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms, and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report presents the results of a laboratory study on the displacement of light oily wastes from sands using hot water. This study demonstrated that the use of hot water, even in the moderate temperature range of 20 to 50°C, can significantly improve the displacement of light, viscous oily wastes from sands. The main mechanism for the increase in oil recovery at higher temperatures is the reduction of the oil viscosity but numerical simulation results qualitatively indicate that the additional oil recovery at higher temperatures is greater than would be expected based on viscosity reduction alone. Hot water as a remediation technique for aquifers contaminated with oily wastes has the advantage of improving the removal of the waste without adding potentially harmful chemicals such as surfactants or other organic cosolvents to the aquifer.



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ABSTRACT

The wide range of subsurface contamination problems involving organic wastes will require a wide variety of remediation techniques in order to effectively and efficiently restore these sites. Thermal techniques are one means of increasing the recovery of organic wastes from the subsurface. This laboratory research project investigated the use of hot water to recover oily contaminants that are less dense than water, highly viscous at ambient temperatures, essentially nonvolatile, and not soluble in water. One dimensional displacement experiments were conducted at constant temperatures in the range from 10 to 50°C on two different silica sands using Inland 15 Vacuum Pump Fluid and distilled water for the displacing phase. These experiments showed approximately a ten percent increase in oil recovery over this range of temperatures. The major mechanism for the increased recovery appeared to be viscosity reduction, however, some additional recovery was achieved beyond that expected due to viscosity reduction alone. This increased recovery was likely due to shifts in the ratio of oil to water permeability at low water saturations that occurred as the temperature of the system increased. Attempts to simulate these results using the Buckley and Leverett equation with the assumption of a negligible capillary pressure gradient along the column were not successful. Transient temperature displacement experiments were also performed by placing the oil-saturated column in the incubator at 10°C and using water at 50°C to displace the oil. Although the average temperature in the column during these transient temperature experiments was approximately 32°C, the oil recovery was comparable to that found for a 40°C constant temperature waterflood. Thus, these experiments showed that the benefits of hot water in terms of enhanced oil recovery can be achieved under conditions which more closely resemble field conditions.

Capillary pressure-saturation curves, as well as the displacement experiments, showed that the residual water saturation increases with temperature, while the residual oil saturation decreases with temperature. Comparison of the capillary pressure for a given wetting phase saturation for different fluid pairs and for different temperatures show that the ratio of interfacial or surface tensions of the different fluid pairs or of the fluids at different temperatures cannot account for changes in the capillary pressure curves as the fluids and temperatures are changed.

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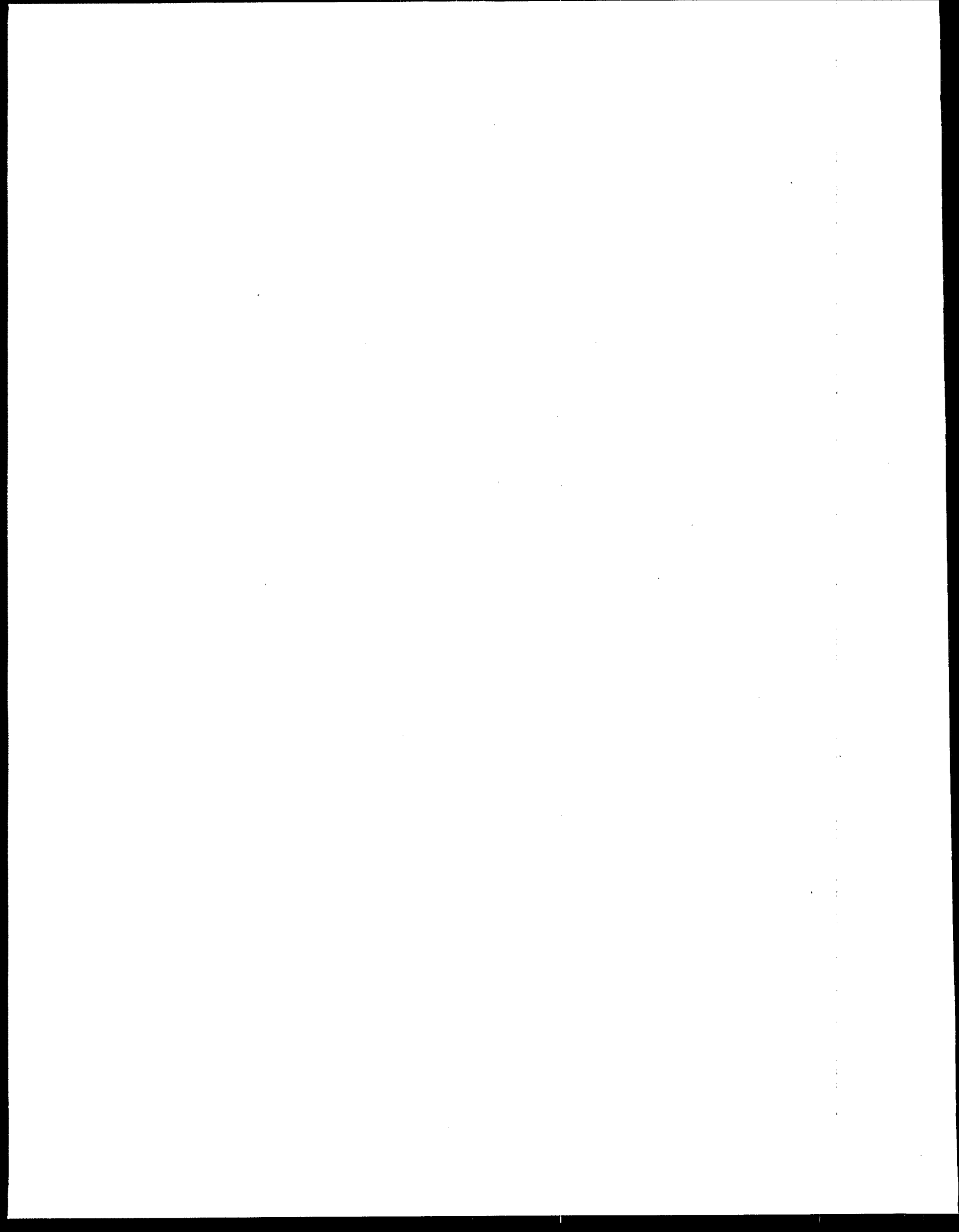
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SECTION 1

INTRODUCTION

Cases of soil and groundwater contamination by organic liquids that are immiscible with water are numerous and involve many different types of organic liquids. Site conditions vary significantly, also, making each site unique in the problems encountered there. Gasoline, jet fuel, crude oil, chlorinated organic solvents such as trichloroethylene, wood preserving chemicals such as creosote, and transmission fluids are some of the nonaqueous phase liquids (NAPLs) that have been found at contaminated sites as free organic phases. The properties of these fluids, such as density, volatility, viscosity, and water solubility, vary significantly, and therefore different remedial techniques will be required in dealing with these different contaminants. For example, volatile organics such as gasoline or jet fuel may be effectively remediated by vapor extraction or biodegradation. Pump-and-treat remediation techniques make use of the slight solubility in water that many organic liquids have and attempt to remove the organic in the water phase. Some NAPLs contained in the subsurface as a layer floating on the water table or resting on top of a confining layer can be recovered as a free product using wells or drains.

All of these methods can be made more effective and efficient by the addition of heat to the subsurface. Heat or steam can significantly increase the vapor pressure of many volatile or semivolatile organics and decrease their adsorption onto the solid phase, thereby increasing their recovery by vapor extraction methods. Since the solubility of most NAPLs in water increases with temperature, the application of heat in the form of hot water can increase the removal of slightly soluble NAPLs by methods such as pump-and-treat. As has been demonstrated many times by researchers in the petroleum industry, oil recovery as a free product can be enhanced by the use of hot water to displace the oil. Enhanced recovery by hot water can be attributed to a reduction in the viscosity of the oil and in some cases, changes in the permeability ratio of oil and water with temperature.

The purpose of this research effort is to further investigate the use of hot water for the displacement of oily contaminants from the subsurface. A literature review has been conducted into the effects of porous media properties and fluid properties on the displacement of oil by water and the effects of heat on the basic properties of the porous media-water-oil system that influence the flow of the fluids and, therefore, the displacement process. Available literature on the use of thermal methods for the recovery of oily contaminants is also reviewed. Laboratory displacement experiments were then conducted to study the effects of heat on the displacement process of an oil from porous media. Constant and transient temperature displacement experiments were run. In addition, properties of the oil and the porous media were determined independently as a function of temperature, and these properties were used in a mathematical description of the displacement process to try to predict the oil recoveries achieved in the constant temperature laboratory experiments and to further explore the effects of porous media and fluid properties on the displacement process.

This laboratory research is centered on the use of moderately hot water, with the expectation that the heat source will be waste heat from an industrial process. This limits the high temperature of the injected water to about 50°C, and 10°C is considered to be the ambient temperature of the groundwater. The types of oily contaminants of interest here are less dense than water, essentially nonvolatile over the temperature range of interest, and not appreciably soluble in water. The viscosity of these oils at ambient temperature is significantly greater than that of water, and decreases as the temperature is increased.

SECTION 2

LITERATURE REVIEW

Properties of Water Floods

Buckley and Leverett (1942) were some of the first researchers to describe, both verbally and mathematically, the simultaneous flow of two fluids in porous media and the factors which influence flow. They recognized that the flow of the fluids is dependent on the properties of the sand and the fluids, as well as the relative amounts of each of the fluids in the pore space. Because the oil and water flow simultaneously through the same pores, displacement of either phase can never be complete and the amount of oil displaced depends on the relative ease with which the two fluids flow.

For a linear, unidirectional displacement in a porous media, two phases to the displacement have been identified. The primary phase corresponds to the movement of a steep saturation bank or front of the displacing fluid. When the water reaches the far end of the porous media, water breakthrough is said to occur, and the displacement enters the subordinate phase. During the primary phase, only oil is displaced from the media, and it is produced at the same rate at which water is injected. During the subordinate phase, both oil and water are produced from the media, and the percent oil in the effluent gradually decreases.

For any porous media, the oil recovery during a water flood is largely dependent on the oil-water viscosity ratio. As the ratio increases, the primary displacement phase becomes less important and the subordinate phase becomes more important (Rapoport and Leas, 1953). Therefore, for higher viscosity oils, less oil is recovered during the primary phase of the displacement and the residual oil saturation is approached more gradually during the subordinate phase of the displacement (Buckley and Leverett, 1942).

Laboratory tests have shown that for injection velocities less than some threshold rate, the oil recovery at breakthrough will increase with increasing rate of water injection. This is due to the fact that water will build up at the effluent end of the column until the capillary pressure at the effluent face is zero before the water can exit from the column. This phenomenon is referred to as the "end effect." By increasing the flow rate, the length at the end of the column that is affected by the end effect is made smaller. Although the effect cannot be eliminated, it can be made negligible compared to the viscous forces. For flooding rates above the critical rate, the flood is said to be "stabilized." All stabilized floods yield the same relation between oil recovery and cumulative water injection (Rapoport and Leas, 1953).

The flooding rate needed to produce a stabilized flood is generally dependent on the properties of the porous media, in particular its permeability, the viscosity ratio, and the initial saturation distribution. For the cores tested by Rapoport and Leas (1953), stabilized floods required a scaling coefficient, defined as $LV\mu_w$, greater than 0.5 to 3.5 cp cm²/min, where L is the length of the core, V is the velocity, and μ_w is the viscosity of the water. However, they found that the value of the scaling coefficient required to reach a stabilized flood appears to increase with increasing permeability. Since the conditions under which stabilization is achieved vary from one core material to another, the flow rate needed to produce a stabilized flood must be determined experimentally for the system of interest.

Other factors which affect the efficiency of a waterflood for recovering oil include the wettability of the system and the interfacial tension between the phases. Wettability is defined as "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids." The fluid termed the wetting phase will occupy the small pores and contact the majority of the rock surface, while the nonwetting phase resides in the center of the larger pores. The wettability is dependent on the properties of the two immiscible fluids as well as the solid, and can range from strongly water wet to neutral wettability to strongly oil wet. For most water/oil/sand systems, the water is the wetting phase and oil is the nonwetting phase (Anderson, 1986).

The contact angle that the fluids form on a solid surface is a common measure of the degree of wettability of a system. Generally, where the contact angle is between zero and approximately 60 to 75°, the system is defined as water wet. When the contact angle is between 180° and 105 to 120°, the system is defined as oil wet. In the middle range of contact angles, a system is defined as neutrally wet, with no preference for either fluid (Anderson, 1986).

Mungan (1964) studied the effects of interfacial tension and wettability reversal on oil displacement. He found that reducing the interfacial tension of the system from 47 to 1.1 dynes/cm resulted in increased recovery and that the increase in recovery was greater if the displaced phase was the wetting phase (i.e., the system is oil-wet). Also, he found that reversing the wettability of the system from oil wet to water wet conditions resulted in some additional oil recovery, but neutral wettability did not increase oil recovery.

Warren and Calhoun (1955) studied the effects of wettability (in terms of $\cos \theta$, where θ is the contact angle), interfacial tension, porosity and permeability on oil recovery. They found that oil recovery at breakthrough is linearly correlated with $\cos \theta$, interfacial tension, and the square root of the permeability times porosity. Their results showed that interfacial tension and contact angle are more important than permeability and porosity in controlling breakthrough recovery. They found ultimate oil recovery to be inversely related to $\cos \theta$ and permeability. Thus, $\cos \theta$ has the opposite effect on breakthrough recovery that it has on ultimate recovery.

Wagner and Leach (1966) studied the effect of interfacial tension on displacement efficiency and found it to be dependent on the wetting conditions of the media. For oil wet systems, they found that the displacement efficiency was improved by lowering the interfacial tension. However, in the system they studied, the interfacial tension had to be smaller than the threshold value of 0.07 dynes/cm before an improvement in breakthrough recovery was observed. Below that level, small reductions in interfacial tension led to large increases in breakthrough recovery. This result is qualitatively consistent with that of Amaefule and Handy (1982), who found that oil/water relative permeability ratios were greatly affected by interfacial tension values lower than 0.01 dynes/cm. They theorize that the threshold interfacial tension level for improving displacement efficiency would depend on the pore size distribution of the soil.

Mathematical Description of Water Floods

Buckley and Leverett (1942) considered unidirectional flow through a small element of sand in a continuous sand body and, through a material balance, derived the expression for a water flood:

$$\left(\frac{dx}{dt} \right)_s = \frac{q_t}{\phi} \left(\frac{dF_w}{dS} \right)_s \quad (1)$$

where S =saturation (of the wetting phase), x =distance, t =time, q_t =the total flow rate, ϕ =porosity, and F_w =the fractional flow function for the wetting phase. This equation assumes that the capillary pressure gradient is negligible when compared to the pressure gradient, that both fluids flow under nearly the same potential gradient, and that the flow of each fluid can be described by Darcy's law. The fluids are assumed to be incompressible, which is equivalent to saying that the total flow does not vary with distance.

The fractional flow function, F_w , is assumed to be a function of saturation only, and under the conditions used to derive the above equation, i.e., negligible capillary pressure gradient and gravity effects, it can be approximated as:

$$F_w \approx f_w = \left(1 + \frac{\mu_n k_w}{\mu_w k_n} \right)^{-1} \quad (2)$$

where μ = viscosity, k = relative permeability, and the subscripts w and n refer to the wetting (water) and nonwetting (oil) phases, respectively. Thus, the fractional flow function and, therefore, the saturation of the porous media at a given location during a displacement are dependent on the ratio of viscosities and relative permeabilities of the two phases. If these ratios are known for the system of interest, the saturation with distance along the system and the amount of oil recovered can be determined for a given volume of water injection (Corey, 1986). Welge (1952) extended the theory of Buckley and Leverett to the calculation of permeability ratios and the corresponding fluid saturations from oil recovery data, and Johnson et al. (1959) extended this to the calculations of the relative permeability to oil and water as a function of saturation. Jones and Roszelle (1978) presented a graphical technique for calculating relative permeabilities that is equivalent to calculations based on the equations of Welge (1952) and Johnson et al. (1959).

Effects of Hot Water

Researchers within the petroleum industry have studied hot water displacement of crude and refined oils in the laboratory. Research efforts have generally involved unsteady state displacements of oils at constant temperatures. Willman et al. (1961) found that oil recovery by hot water injection was always greater than for cold water injection, and that hot water injection has its greatest advantage with heavier oils where viscosity reductions as the temperature is increased are significant. They attributed the increased oil recoveries for hot water floods to both viscosity reduction and thermal expansion of the oil, and found that ultimate recovery from a hot water flood can be predicted from the results of a cold water flood by accounting for the viscosity ratio at the higher temperature and the thermal expansion of the oil. The increases in oil recovery over the temperature range of 27°C to 166°C were 5.3 percent for a white oil with a viscosity of 138 cp at 27°C, seven percent for a crude oil with a viscosity of 8.2 cp, and 14.8 percent for a second crude oil with a viscosity of 6500 cp. Ultimate recoveries from the hot water floods at 166°C ranged from 55 percent to 67 percent.

Edmondson (1965) also found that oil recovery increased with increasing temperature for all the oils he tested and that the improvement in recovery with temperature was greater for oils which have a greater dependence of viscosity on temperature. For example, the two white oils he tested, No. 5 and No. 15, had viscosities of approximately 20 cp and 70 cp, respectively, at 38°C, and their viscosities decreased to 1.5 cp and 2.5 cp, respectively, at 149°C. The No. 5 white oil showed an increased recovery of 2.6 percent over this temperature range, while the No. 15 white oil recovery increased by 8.2 percent. He noted that these two white oils displayed a piston-like displacement with very little oil produced after water breakthrough, while the two crude oils tested had earlier breakthroughs and a very significant amount of subordinate oil production. These differences in waterflood history were found to hold true even when the distilled oil and crude oil had very similar viscosities. This difference in waterflood behavior Edmondson attributed to differences in interfacial tension: the distilled oil, with its piston-like displacement, had a significantly higher interfacial tension at 24°C (49 dynes/cm) than the crude oils (21 and 4.1 dynes/cm). However, the results of Warren and Calhoun (1955) would indicate that differences in contact angle (i.e., wettability of the media) may account for these differences in water flood history. Hot water displacements were also performed using two crude oils with different viscosity characteristics. Crude oil "A" had a viscosity of 80 cp at 22°C, which decreased to about 2.1 cp at 149°C. Crude oil "B" had viscosities of 100 cp at 66°C and 4 cp at 149°C. Both oils had approximately a 96 percent decrease in viscosity for the range of temperatures over which they were tested, but crude oil "A" showed a 20 percent increase in recovery while crude oil "B" had only a 12 percent increase in recovery. Thus, it appears that the water flood

history is affected in a complex way by viscosity, interfacial tension, and contact angle.

In contrast to the results of Willman et al. (1961), Edmondson found that the results of the hot water flood could not be predicted based solely on the viscosity of the oil or the oil-water viscosity ratio. He found that temperature had a significant effect on the relative permeability ratio, with the ratio (defined as k_w/k_o) characteristically increasing with temperature at low water saturations. However, the permeability ratio curves for the different temperatures crossed at permeability ratios of approximately one. He also found decreases in the residual oil saturation with temperature. These changes in the properties of the system with increasing temperature all contribute to an improvement in the performance of the hot water flood in comparison to a cold water flood.

Davidson (1969) also found that the relative permeability ratio increased with temperature at low water saturations and that the isothermal curves then crossed at some higher saturation. However, when he corrected his data for changes in the viscosity of the oil due to the dissolution of water into oil, he found that the permeability ratios were no longer temperature dependent above a threshold water saturation. The threshold water saturation above which the permeability ratio is independent of temperature was found to be dependent on the sand. These changes with temperature in the permeability ratio at lower saturations were attributed to variations in capillary forces and wettability with temperature.

Poston et al. (1970) confirmed the trends with temperature noted by Edmondson (1965): a decrease in residual oil saturation, a general increase in the permeability ratio, and a corresponding increase in oil recovery. Their research showed that the relative permeability to water in an unconsolidated sand at high water saturations increased significantly with temperature in the range of 24 to 104°C. Only slight increases in the relative permeability to water were observed as the temperature was increased from 104°C to 135°C. Their results also showed an increase in oil relative permeability with temperature for all oil saturations. These changes with temperature are all indicative of increasing water wetness and a reduction in capillary forces as the temperature increases. Their measurements showed that in general, both the interfacial tension and contact angle for the systems studied decreased as the temperature increased. However, these properties are not linearly related to temperature.

Sinnokrot et al. (1971) tested the theory of an increase in water wetness with increasing temperature by measuring the capillary pressure-saturation curves at different temperatures. For the sandstone/refined oil/water system, a strong temperature dependence was found, with the system showing an increase in water wetness at higher temperatures. However, a limestone core tested with the same refined oil and water showed no temperature dependence in its capillary pressure-saturation relationship.

Quettier and Corre (1988) also performed isothermal unsteady state displacement experiments at elevated temperatures. Unlike the results presented above, they found that the relative permeabilities to oil and water decreased with temperature. The ratio of the permeabilities was found to decrease at all saturations as the temperature increased, whereas the results of other researchers showed the ratios crossing at some saturation.

Weinbrandt et al. (1975) studied the effect of temperature on the relative and absolute permeability of sandstones and found that the experimental results were dominated by the increase in irreducible water saturation and decrease in residual oil saturation in response to an increase in temperature. Their curves for the permeability ratio are consistent with those of Quettier and Corre (1988) in that the curve is shifted to lower ratios for all saturations, i.e., the isothermal curves do not cross. This shift in the permeability ratio curve is the result of a significant increase in oil relative permeability with temperature and a slight decrease in water relative permeability with temperature. Although all of these changes are consistent with an increase in water wetness of the media and independent measurements of the contact angle confirm this, the authors state that they have difficulty accepting that the increase in water wetness is the only cause of the observed changes.

Several researchers have investigated the cause of the measured changes in relative permeability with temperature. Ehrlich (1970) attributed the changes to an increase in water wetness with temperature and developed a theoretical equation to describe the effect of temperature on

adsorption of surface active agents onto a solid surface. According to his theory, as the temperature increases the amount of surface active agents adsorbed onto the surface decreases, making the solid more water wet and causing the observed shifts in the relative permeability curves. Lo and Mungan (1973) also considered changes in wettability as the cause of shifts in relative permeability curves with temperature. However, of the three oils they tested, the one which showed the greatest change in contact angle with temperature, a 21° change, had almost no change in its relative permeability curves with temperature. Two other oils, which showed changes of 2 to 4° in the contact angle, showed much greater changes in relative permeability with temperature. Lo and Mungan attributed the observed changes in relative permeability with temperature to changes in the viscosity ratio.

Sufi et al. (1982) also disagreed with the theory of increasing water wetness as the temperature increases. They found that if the hot water flood was carried until completion (i.e., until no more oil could be recovered) instead of being stopped at a given water to oil ratio in the effluent, the "real" residual oil content was independent of temperature. They did find an increase in the irreducible water saturation with increasing temperature, but they attributed this to a decrease in viscous forces during the displacement. They also found that for a refined oil and distilled water flowing through clean, unconsolidated Ottawa sand, the relative permeabilities showed no dependence on temperature in the range from 21 to 86°C.

Martin et al. (1968) reported the results of a tertiary hot waterflood of a sand reservoir. The reservoir had been previously flooded out using water at the ambient temperature of 15°C. The injected hot water produced bottom hole temperatures at the injection wells ranging from 141°C to 167°C. In spite of severe channeling in the reservoir as indicated by temperature gradients and tracer tests, additional oil was produced from the reservoir. This additional oil, however, was produced at very high water to oil ratios, which suggests that the mechanism for oil displacement was not a more efficient displacement as would be expected by an increase in temperature, but a factor such as rate, pattern, rotation, or plugging, etc. At the end of the hot water flood, it was found that additional cold water injection scavenged the heat remaining in the reservoir and produced more oil.

Thermal Methods for the Recovery of Oily Contaminants

Recently, the use of thermal methods to recover oily contaminants from the subsurface has been investigated, and in some cases field trials of the techniques have been undertaken.

Stewart and Udell (1988) investigated the use of steam to displace immiscible organic phases from porous media. Volatile organics such as trichloroethylene, benzene, and toluene, as well as unleaded gasoline, which were initially present at approximately residual saturation, were completely removed using steam injection. The organic appeared at the effluent end of the column as a separate liquid phase just ahead of the steam front. A mineral oil was also treated by steam injection, but its removal was limited and occurred only as an oil-in-water emulsion which appeared in the effluent after steam breakthrough.

A process referred to as Contained Recovery of Oily Wastes (CROW™) has been developed at the Western Research Institute in Laramie, Wyoming. The basis of the process is the displacement of buoyant oily wastes using hot water. For dense wastes, steam injection is first used to reduce the density of the oil until it is buoyant. The main mechanism used for oil recovery is viscosity reduction, but the application of heat will also increase the vaporization of the volatile organic compounds and increase the solubility of some organics. In laboratory tests, this process recovered 60 to 70 percent of gas production contaminants and 84 to 94 percent of wood-treatment contaminants at the optimum waterflushing temperature. The process is effective at removing free products from soils but is not effective at substantially reducing contaminant levels in soils that contain only residual oils. In fact, the process will generally leave behind residual oil that may be above action levels and thus, require additional treatment.

The Western Research Institute has also investigated the use of hot water to remove a wood treating waste from soil by dissolution of the oil into the hot water. Laboratory tests on hot water

injection were run in the laboratory using undisturbed soil cores from the field. The initial content oil in the soil ranged from 2.7 percent to 4.3 percent, and the reduction in waste ranged from zero at 19°C to 60.9 percent at 82°C after the injection of 60 to 100 pore volumes of water. Increasing the pH of the injection water to increase the solubility of the oils was also investigated but was not found to significantly affect the waste removal rates for this contaminant. It appears that all of the oil recovered was dissolved in water; no separate-phase oil was displaced.

Summary of Previous Research

Although there is still considerable controversy and disagreement on the effects of hot water on the properties of a sand/water/oil system, previous research seems to indicate that several factors work simultaneously as the temperature is increased to improve oil production. These factors include a reduction in the oil to water viscosity ratio, a reduction in the interfacial forces, an increase in the irreducible water content, and a reduction in the residual oil saturation. Shifts in the ratios of relative permeabilities with temperature are sometimes found, and these could account for the increase in oil recovery beyond that expected based on the viscosity reduction alone. The changes in the residual saturations and permeabilities are indicative of a change in wettability of the system with temperature, and independent measurements of the contact angle with temperature have shown some increase in wettability with temperature for some systems. However, as was stated by Weinbrandt et al. (1975), it does not seem that wettability changes can account for all of the effects of temperature on these systems.

Different soil/water/oil systems seem to differ in their response to temperature which is probably due to differences in the relative importance of these various factors that are affected by temperature. Thus, different researchers have come to different conclusions on the effects of hot water on the properties of a soil/water/oil system.

The use of hot water to displace oils from porous media always increases recovery over that achieved with cold water. Generally, the amount of additional recovery with temperature is greater for more viscous oils which show a greater reduction in viscosity with temperature. It appears that the contact angle, or wettability of the system, determines the efficiency of the displacement process in terms of the percentages of the oil recovered before and after breakthrough, as well as other factors such as irreducible water content and residual oil content.

SECTION 3

EXPERIMENTAL METHODS

Three different types of experiments were conducted as part of this research. The first type of experiment was pressure-saturation curves for the sands/oil/water systems used in displacement experiments. These were measured at constant temperatures of 10 and 30°C. These curves provide information on the interfacial forces in the system and the pore size distribution of the sand, which can be used in expressions for the hydraulic properties of the soil. The second type of experiment was unsteady state displacement experiments at constant temperatures in the range from 10 to 50°C. The purpose of these experiments was to determine the effects of properties of the oil and the porous media on oil recovery at various temperatures. The third type of experiment was also unsteady state displacement experiments, but these were done under transient temperature conditions. The column was held at 10°C in a constant temperature incubator, and the oil was displaced from it using water at 50°C. These experiments more closely resemble the field situation where the area to be remediated will have to be heated by the hot water that is injected. They allow some observations on the flow of heat within the oil-saturated sand and help to give an idea of the heat input that would be required to achieve the benefits of hot water for oil recovery.

The oil used for all of these experiments was Inland 15 Vacuum Pump Fluid (Inland Vacuum Industries, Inc.). Its viscosity as a function of temperature at ten-degree increments was measured over the range of 10 to 50°C using a Brookfield LV series viscometer and a small sample adapter (Brookfield Engineering Laboratories, Inc.). The surface tension and interfacial tension against water were measured using a du Nouy Ring Tensiometer (Fisher Surface Tensiometer Model 20) by the method ASTM D-971. Again, measurements were made at ten-degree increments in the range from 10 to 50°C. The interfacial tension was measured immediately after the water and oil were mixed and then again after the interface had been allowed to age for approximately 6 hours. This was done to try to determine if the oil-water interfacial tension changed during the 6 hours that it takes to run the displacement experiments. Density measurements versus temperature and the percent volatiles versus temperature were also determined for this oil.

Two different silica sands were purchased from Gilson Company, Inc., for use in these experiments. The first was the very uniform 20/30 standard sand (Model Number HM-107) which is graded to pass the #20 (850 μm) sieve and be retained on the #30 (600 μm) sieve. The second sand was a mixture of equal weights of the density sand (HM-106), 20/30 standard sand, and graded standard sand (HM-108). This mixture, referred to as the "mixed" sand, had approximately one-third (by weight) of its grains in the range 0.85 to 0.50 mm, one-third in the range 0.50 to 0.25 mm, and one-third in the range 0.25 to 0.106 mm.

Capillary Pressure-Saturation Curves

The pressure-saturation curves at constant temperatures were measured by a method very similar to that used by Wilson et al. (1990) and is shown in Figure 1. The curves were measured for each of the sands for water/air and water/oil. The glass columns allowed for a soil column length of 5 cm and soil diameter of 5 cm. Tygon tubing was used to connect the column endpieces to the 25 ml burets. These columns were packed using a 95 cm long packer. The packer had a funnel at the top which held the soil and a funnel at the bottom which was slightly smaller in diameter than the column. Screens in the packer help to distribute the sand evenly in the column. During the packing, the sides of the column were tapped to compact the soil. The columns were then saturated with carbon dioxide before introducing deaired water, and approximately 5 pore volumes of water were passed through the column to dissolve and displace the carbon dioxide. Once the columns were saturated, they were placed in the incubator to equilibrate to the desired temperature before data

collection was initiated. The curves were measured at both 10 and 30°C.

For the water/oil experiments, oil was introduced at the top of the column once the sand was saturated with water, and the heights of the fluids were adjusted until the oil sat directly on top of the soil to start the experiment. For the water/air curves, nothing was attached to the top endpiece of the column, and air was allowed to enter the soil as the water was displaced. Drainage curves were

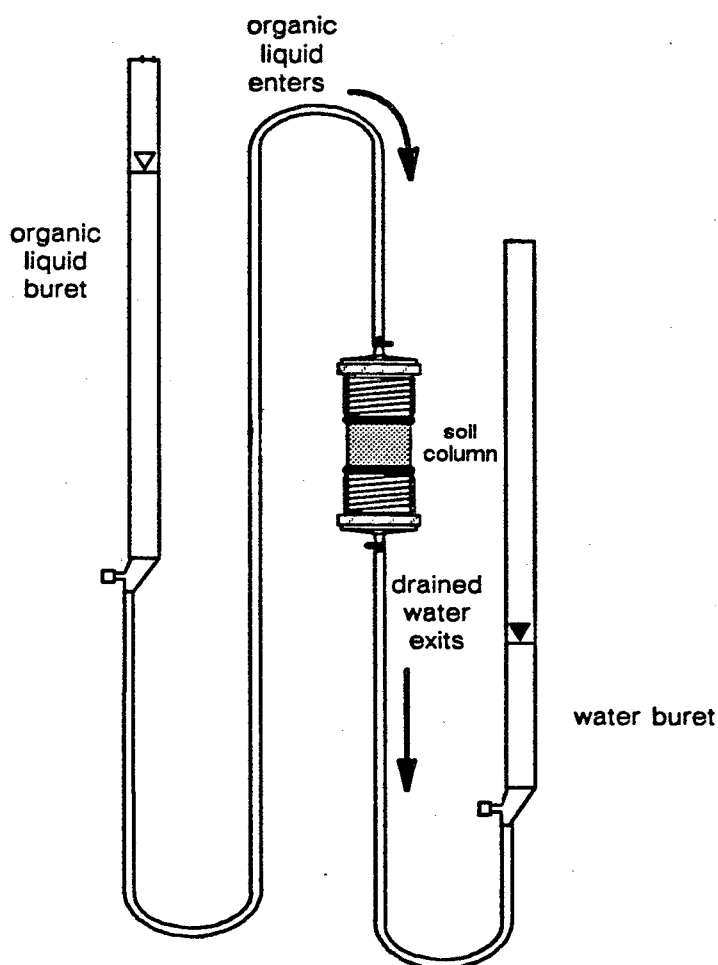


Figure 1. Schematic of experimental apparatus for capillary pressure-saturation curves (after Wilson et al., 1990).

measured by moving the water buret down (or the oil buret up in the case of the oil/water systems) and then allowing the fluids in the system to equilibrate. The volumes of fluids in each buret and the heights of the liquid levels relative to the center of the soil column were measured for each equilibrium point. Once the system reached residual saturation of water, the direction of movement of the burets was reversed. The reduction in the capillary pressure allowed water to re-imbibe into the soil, and the wetting curve was measured. The wetting curve was continued to a final capillary pressure of approximately zero.

Displacement Experiments

The columns used for the displacement experiments were 304 stainless steel, 45.7 cm long and 7.5 cm in diameter. The removable stainless steel endpieces, which contained stainless steel porous plates, were held in place using threaded rods which extended through the column. The columns were packed by the same method used to pack the column for the pressure-saturation curves. After the column was packed, carbon dioxide was allowed to flow through the column for approximately 1.5 hours. After this time, deaired water was introduced to the column, and approximately 4 pore volumes of water were passed through it to fully dissolve the carbon dioxide and remove it from the column. The column was then placed in the incubator, and the system was allowed to equilibrate to the temperature to be used for the run.

The experimental apparatus used for the constant temperature displacements is shown in Figure 2. Two pressure transducers (Omega PX-800 series) were connected to the column through valves that screwed into the column 5.3 cm from each end. These transducers were connected to a data collection system within an IBM-compatible computer. The tensiometers were fritted glass discs that fit into the end of the valve and were held in capillary contact with the soil. A diaphragm metering pump (ProMinent Gamma/4 Model 1201) was used for pumping water or oil into the column. A fraction collector (Isco Retriever IV) was used to collect the column effluent in a series of test tubes. This is essentially the same experimental design used by researchers in the oil industry for unsteady state displacements (see for example, Willman et al., 1961; Quettier and Corre, 1988; and Rapoport and Leas, 1953); and it was also used by Wilson et al. (1990) for oil displacement experiments.

Once the column and its contents had equilibrated to the temperature of the run, water at this temperature was pumped through the column and the pressure drop along the column was recorded to determine the hydraulic conductivity of the sand. After this the oil, which had also been equilibrated to the temperature to be used for the run, was pumped through the column to displace the water. Oil pumping was continued until no additional water was being displaced from the column. At this time, the pump was cleaned and then connected to the water bottle, and water displacement of the oil was initiated. For the constant temperature experiments, the displacing water was at the same temperature as the rest of the system. The flow rate used in these experiments was approximately 17 to 18 ml/min. The fraction collector was set to collect for 1.4 minutes in each test tube, so that each tube collected approximately 24 to 25 ml of effluent. The volume of water and oil in each tube was determined. Water displacement was continued until at least 10 pore volumes of water had passed through the column.

For the transient temperature experiments, essentially the same procedure was used, with the addition of four thermocouples (Type T thermocouples from Omega Engineering) at equal spacing along the length of the column to record the temperature during the displacement. The IBM-compatible PC recorded the temperature data from the thermocouples as well as the pressure readings from the transducers during these displacements. The water used to displace the oil was brought to 50°C in a water bath, while the column was held within the incubator at 10°C. This laboratory setup is shown in Figure 3.

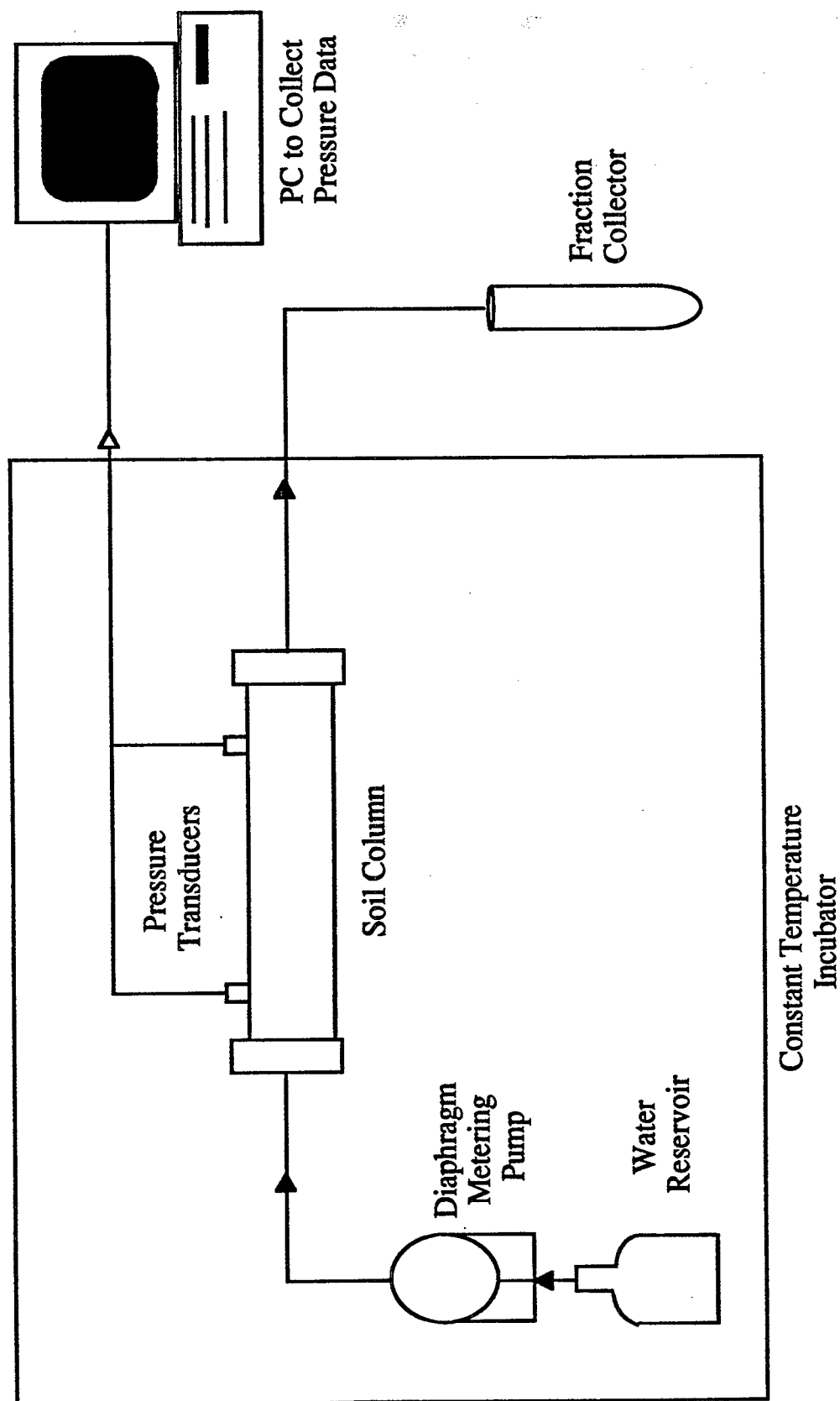


Figure 2. Schematic of experimental apparatus for constant temperature displacement experiments.

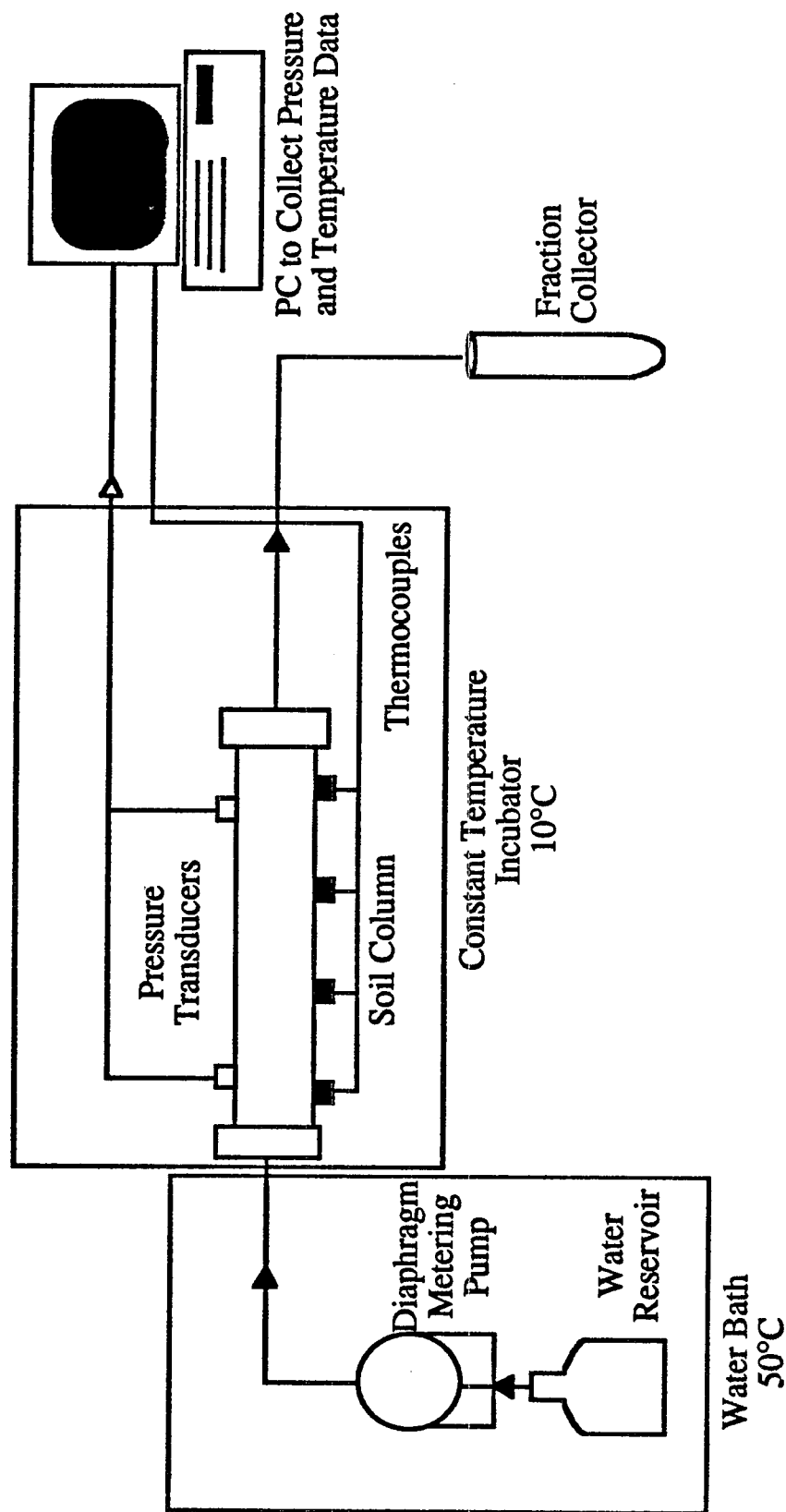


Figure 3. Schematic of experimental apparatus for transient temperature displacement experiments.

SECTION 4

EXPERIMENTAL RESULTS

Properties of Inland 15 Pump Oil

The density, viscosity, surface tension and interfacial tension of Inland 15 Pump Oil were measured as a function of temperature. The density measurements show the oil to be less dense than water, with an approximately linear decrease in density with temperature in the range of 10 to 50°C. This relationship is shown in Figure 4. The viscosity versus temperature for the oil is shown in Figure 5. The viscosity shows an approximately exponential decrease with temperature, which is the expected relationship between liquid viscosity and temperature (Atkins, 1986). Over this relatively moderate range in temperature, the viscosity of the oil decreases by more than 86 percent. Also shown in this graph is the ratio of water viscosity to oil viscosity versus temperature.

Table 1 shows the results from the surface and interfacial tension measurements with temperature for Inland 15 oil. All of the values reported here are the average of at least three measurements. Results of surface tension measurements on water are included in this table. The averaged surface and interfacial tension measurements versus temperature are graphed in Figure 6. These results show that the measured surface tensions for water with temperature are approximately 2 to 8 percent lower than published values for these temperatures. The surface tension of the oil does not show a consistent trend with temperature. When the surface tension measurements at different temperatures were compared using the Student t-test, the measured values at each of the higher temperatures were found to be different from the value measured at 10°C at the 98 percent confidence level. At 20 and 30°C, the surface tension of the oil increases slightly, but as the temperature was increased further the surface tension decreased substantially.

The interfacial tension between water and oil was measured both coming up through the interface (water to oil) and going down through the interface (oil to water). The interfacial tension values measured by these two methods do not differ significantly. Because the measurements made going down through the interface are more consistent (i.e., have smaller standard deviations), these values will be used for further comparisons. These measurements show that the water/oil interfacial tension does not change significantly with temperature over the 40 degree range of temperatures of interest here.

| | 10°C | 20°C | 30°C | 40°C | 50°C |
|-------------------|------------------|------------------|------------------|------------------|------------------|
| water/air | 71.17 ± 0.833 | 70.47 ± 1.743 | 69.98 ± 0.466 | 64.07 ± 0.694 | 63.73 ± 0.783 |
| oil/air | 29.22 ± 0.401 | 30.34 ± 0.649 | 30.18 ± 0.444 | 26.37 ± 0.311 | 25.25 ± 0.222 |
| water/oil up | 42.23 ± 5.236 | 41.97 ± 3.952 | 37.55 ± 4.386 | 40.77 ± 7.585 | 39.19 ± 1.890 |
| water/oil down | 39.96 ± 1.846 | 40.03 ± 0.344 | 40.03 ± 0.344 | 39.70 ± 0.880 | 39.59 ± 0.320 |
| water/oil aged | 35.79 ± 1.092 | 34.34 ± 0.735 | 34.54 ± 0.505 | 33.97 ± 0.825 | 33.30 ± 0.337 |

Table 1. Surface and interfacial tensions for water and Inland 15 Pump Oil versus temperature.

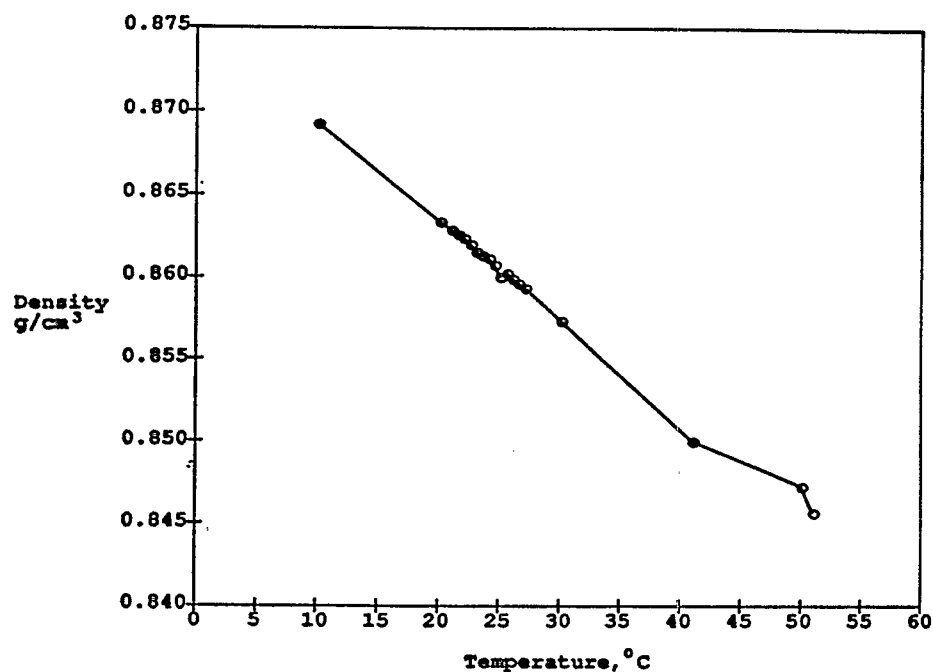


Figure 4. Density versus temperature relationship for Inland 15 Vacuum Pump Oil.

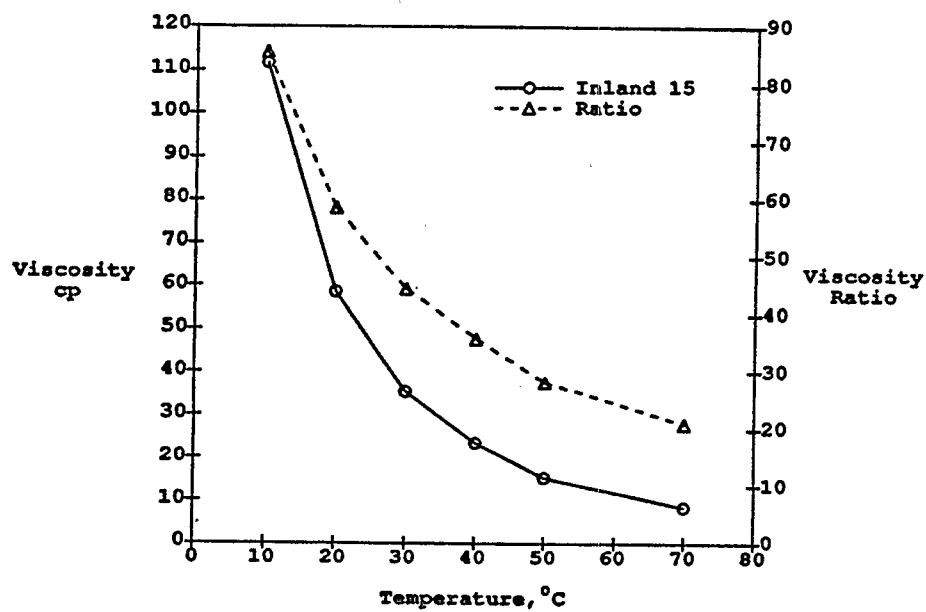


Figure 5. Viscosity versus temperature relationship for Inland 15 Vacuum Pump Oil and the viscosity ratio, μ/μ_w , versus temperature.

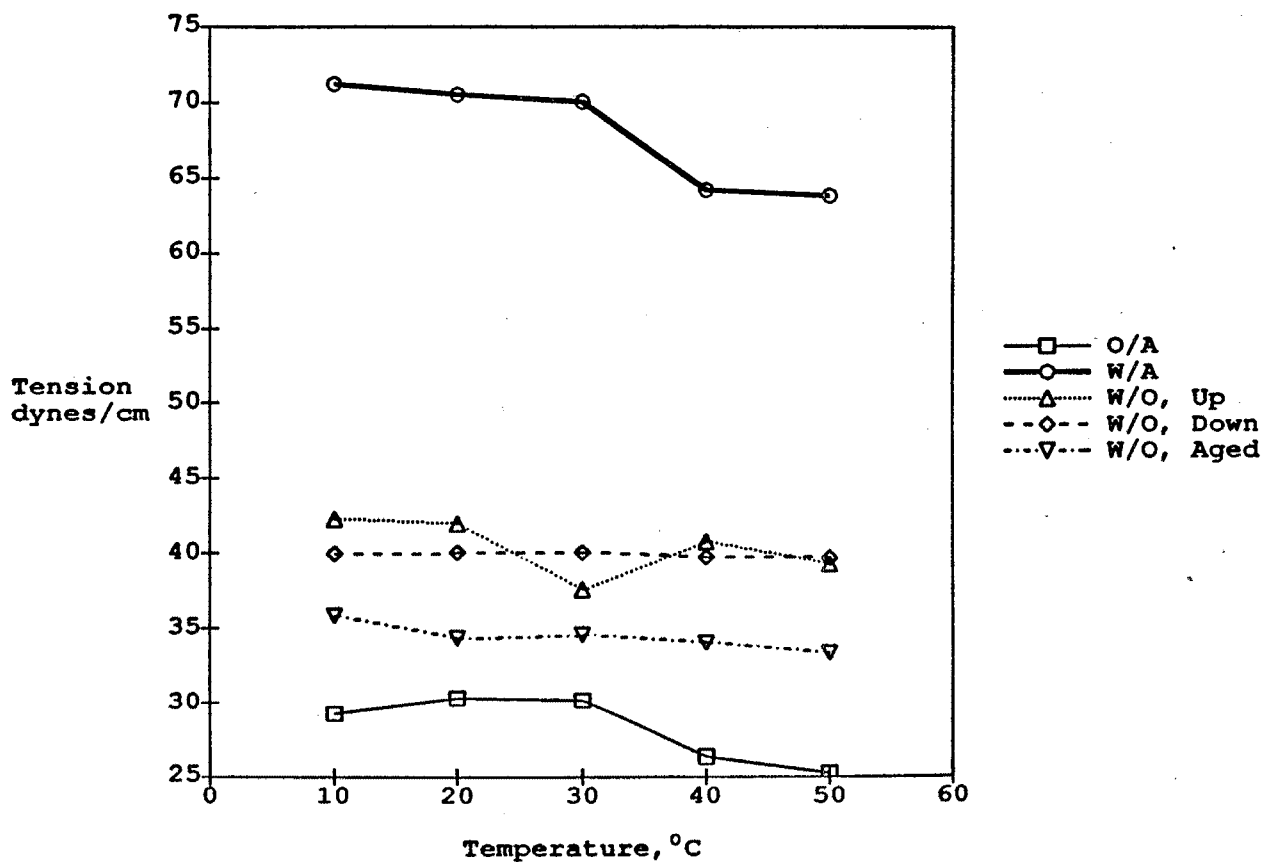


Figure 6. Surface and interfacial tensions versus temperature: Oil/air surface tension (O/A); Water/air surface tension (W/A); Oil/water interfacial tension, measured going up through the interface (O/W, Up); Oil/water interfacial tension, measured going down through the interface (O/W, Down); Oil/water interfacial tension, measured going down through the interface, after interface had aged for approximately six hours (O/W, Aged).

Mercer and Cohen (1990) state that the interfacial tension for crude oil-water systems decreased by approximately 0.055 dynes/cm per degree C, and other researchers have found the interfacial tension of alkanes to decrease linearly with temperature at a rate of 0.122 to 0.089 dynes/cm per degree (McCaffery, 1972). Other researchers, such as Poston et al. (1970) and Lo and Mungan (1973) found that different oils had different temperature relationships. Although the oils did generally show a decrease in interfacial tension with temperature increase, in the lower temperature ranges the interfacial tension sometimes remained constant with temperature or showed a slight increase. Small changes in interfacial tension with temperature that would be consistent with the findings of these researchers generally could not be measured by the surface tensiometer technique used here over the small temperature range of interest.

After the oil/water interface had been allowed to age for approximately 6 hours, a second measurement of interfacial tension was made going down through the interface, and these values are also shown in Table 1 and Figure 6. These measurements show that the interfacial tension significantly decreases with time. This finding led to additional measurements of interfacial tension with time at 10 and 30°C, and the results of these measurements are shown in Figure 7. This graph shows that the interfacial tension decreases approximately exponentially over about a 5 day period, then appears to stabilize. The stable interfacial tension values are significantly different from the interfacial tension measured on the newly formed interface, however, the stable interfacial tensions measured at 10 and 30°C do not differ significantly from each other at the 99 percent confidence level. Reisberg and Doscher (1956) and McCaffery (1972) also found the interfacial tension of water and oil to change over time, but their systems generally stabilized in far less time. McCaffery's systems were stable after about 10 minutes, while 3 out of 4 crude oil/water systems studied by Reisberg and Doscher were stable within approximately 60 minutes. However, the pendant drop method they used for making the measurements, which uses a much smaller volume of oil than the surface tensiometer method used here, likely accounts for the difference in the times required for the interfaces to stabilize.

Intrinsic Permeability

Before beginning the displacement experiments, water at the temperature to be used for the experiment was pumped through the column and the pressure drop along the column was measured to determine the intrinsic permeability of the sand. However, difficulties were encountered in the pressure measurements, and this data was actually collected for only a few of the experiments. The average and standard deviation of the calculated intrinsic permeabilities for the 20/30 and mixed sands were $6.27 \times 10^{-6} \text{ cm}^2 \pm 7.06 \times 10^{-6}$ and $5.26 \times 10^{-7} \text{ cm}^2 \pm 3.40 \times 10^{-7}$, respectively. Not surprisingly, the mixed sand, which has somewhat smaller grain sizes, showed a slightly lower intrinsic permeability than the 20/30 sand. However, the Student t-test shows that the difference between the means is not significant. Some researchers (Weinbrandt et al. 1975; Casse and Ramey, 1979) have found the intrinsic permeability of sandstones, when measured with water, to decrease as the temperature is increased. Figure 8 shows the intrinsic permeabilities measured here plotted as a function of temperature. This graph shows a trend of decreasing permeabilities as the temperature is increased for the 20/30 sand, but no apparent trend with temperature for the mixed sand. The variation with temperature displayed by the 20/30 sand is not statistically significant.

Capillary Pressure-Saturation Curves

Before discussing the experimental results for the capillary pressure-saturation curves, a brief discussion is provided to define some of the terms used in describing these curves.

When two immiscible fluids occupy the pore space of a porous medium at hydrostatic equilibrium the two fluids will have different pressures, and the pressure difference between the two fluids determines the configuration of the fluid-fluid interface within the pores. The fluid with the

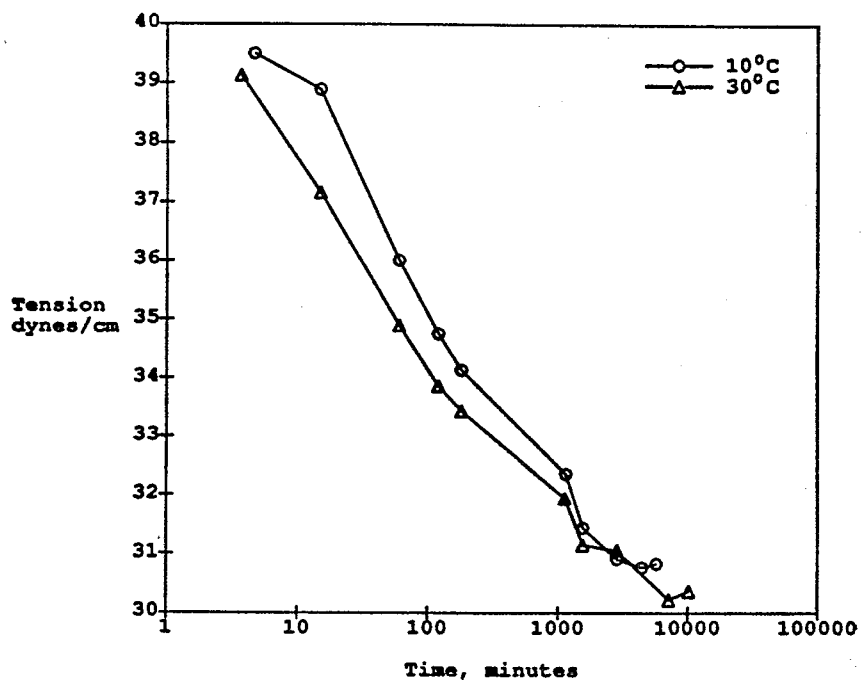


Figure 7. Interfacial tension of water and oil versus time at 10 and 30°C.

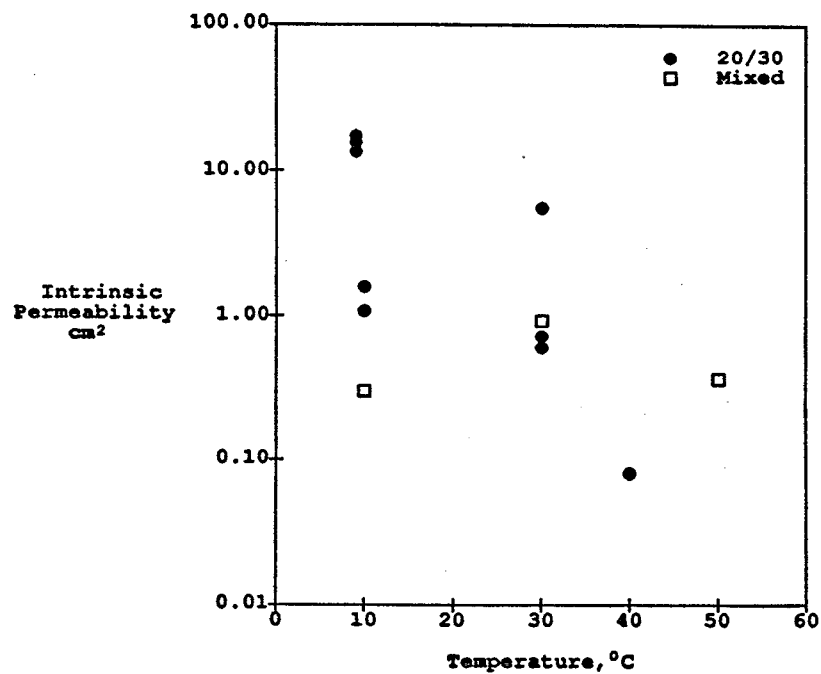


Figure 8. Intrinsic permeability of the 20/30 and mixed sand versus temperature.

greater affinity for the solid occupies the smaller pore spaces and usually also coats the surface of the solids. This fluid is the wetting phase and is always at a lower pressure than the nonwetting phase, which occupies the larger pore spaces. As the pressure difference between the fluids increases, the fluid-fluid interface will have a smaller radius of curvature, which forces it into the smaller pores of the media. Larger pores, consequently, are drained of the wetting fluid. Thus, a capillary pressure-saturation curve is a rough measure of the distribution of pore sizes in the porous medium.

Capillary pressure-saturation curves are normally measured by initially completely saturating the pore spaces with the wetting fluid, at which point the capillary pressure is zero. As the capillary pressure is increased incrementally, the wetting phase will be drained from the media when the capillary pressure exceeds that required for the nonwetting phase to penetrate into the largest pore opening of the media. This capillary pressure is often called the displacement pressure. As the capillary pressure is increased further, the drainage portion of the capillary pressure-saturation curve is defined. Eventually a point is reached where further increases in capillary pressure no longer drain more of the wetting phase from the media. The remaining wetting phase saturation is called the residual or irreducible wetting phase.

If at this point the capillary pressure is incrementally reduced, the wetting or imbibition portion of the capillary pressure-saturation curve is measured. Due to the irregularities in the pore shapes and distributions the fluid-fluid interface during imbibition does not encounter the same pore shapes that were available during drainage, and thus a different curve, lower than the drainage curve, is defined. This phenomena is called "hysteresis", and results in the capillary pressure corresponding to a given wetting phase saturation during imbibition to be lower than during drainage. Or from the other viewpoint, for a given capillary pressure, the wetting phase content during drainage will be higher than during imbibition. Further information on capillary pressure-saturation curves can be obtained from Corey (1986) and Melrose (1965).

Pressure-saturation curves were measured at 10 and 30°C for both the 20/30 sand and the mixed sand for water/air and water/oil. At 30°C, three repetitions of each of the curves were measured, while at 10°C one water/air curve for each soil and duplicates of the water/oil curves were measured. For unconsolidated sands, pressure-saturation curves are very sensitive to the packing of the soil as well as grain size and grain size distribution, so replicate curves vary to some degree. Representative curves of each type will be presented in this section in order to make qualitative comparisons between curves. The variation between replicate curves is reflected in the standard deviations of the parameters for these curves (see Discussion of Results).

Figure 9 shows a comparison of the water/air curves at 10°C for the two sands. The rapid change in saturation of the 20/30 sand as the pressure is increased (once it is past the displacement pressure) is typical for a sand with uniform pore sizes. The greater pressure needed to initiate desaturation of the mixed sand, its steeper slope, and the greater irreducible water saturation indicate smaller pore sizes in general and a somewhat wider range of pore sizes. Figures 10 and 11 show the pressure saturation curves for water/oil and water/air at 10°C for each of the sands. These graphs show that the pressure saturation curves for the water/oil system have essentially the same shape as the corresponding water/air curves, but have lower displacement pressures than the water/air curves. At this temperature, it appears that the water/oil system for both sands have a slightly lower irreducible water saturation than the water/air systems.

Figures 12 and 13 show the water/air pressure-saturation curves at 10 and 30°C for the 20/30 and mixed sands, respectively. Both sands show lower drainage curves at the higher temperature, but the two sands show different effects of temperature on the residual water saturation. For the 20/30 sand, the residual water saturation is essentially the same for both temperatures, however, the mixed sand has a lower residual water saturation at the higher temperature. However, the three replicates of the water/air curves at 30°C for each of the sands showed considerable variation, particularly in terms of residual water saturations. When the residual water saturations for the three replicates are averaged and compared to the residuals found at 10°C, the residuals are found to be essentially the same. For both sands, there is a lower residual air saturation at 30°C than at 10°C. Also, both sands show a decrease in hysteresis with temperature for the water/air system at higher temperatures.

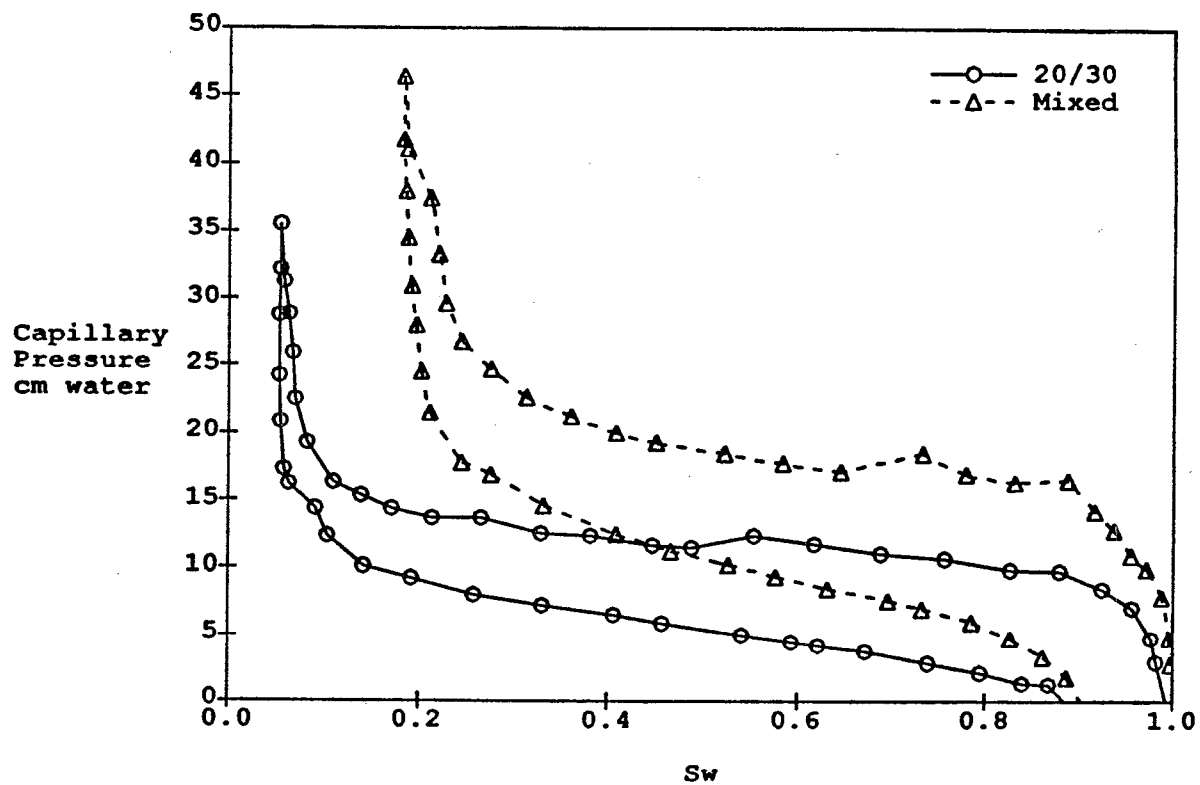


Figure 9. Capillary pressure-saturation curve for water/air systems for the 20/30 sand and mixed sand at 10°C.

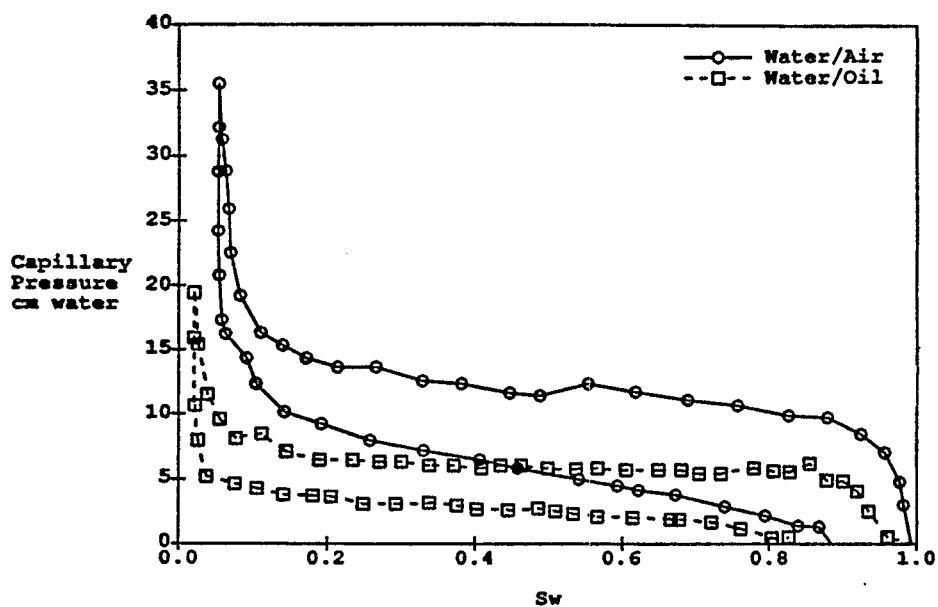


Figure 10. Capillary pressure-saturation curve for the 20/30 sand for the water/air and water/oil system at 10°C.

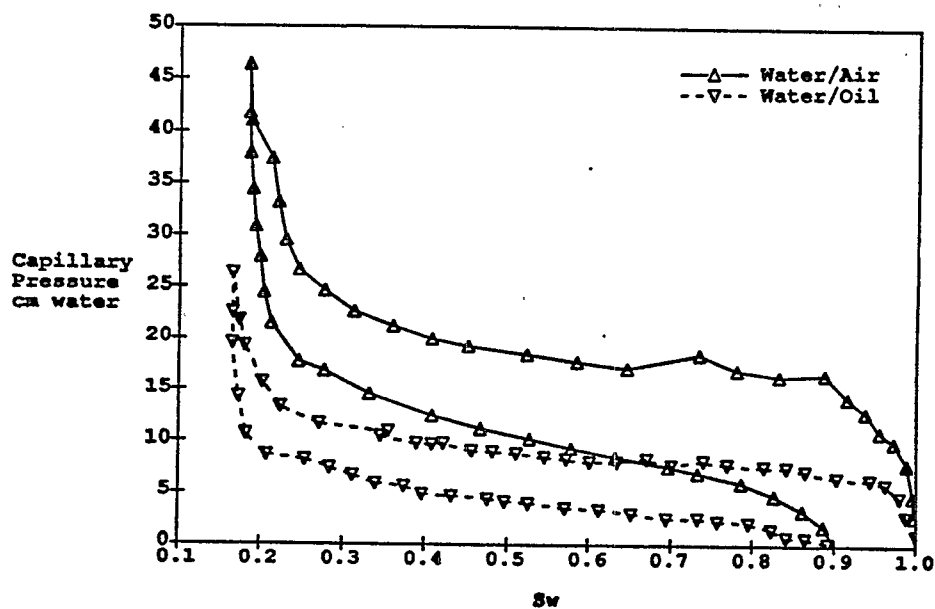


Figure 11. Capillary pressure-saturation curve for the mixed sand for the water/air and water/oil system at 10°C.

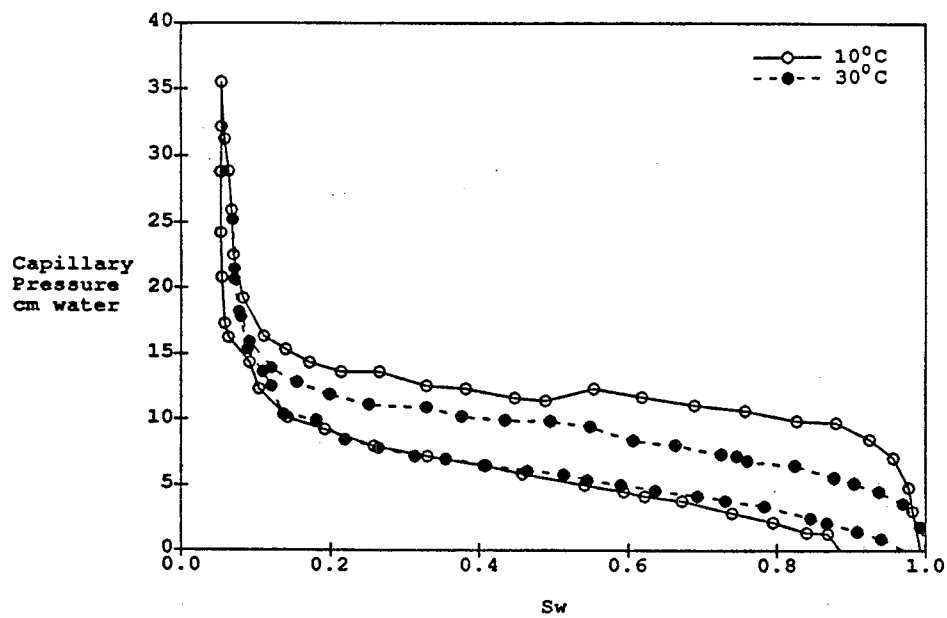


Figure 12. Capillary pressure-saturation curve for the 20/30 sand for the water/air system at 10 and 30°C.

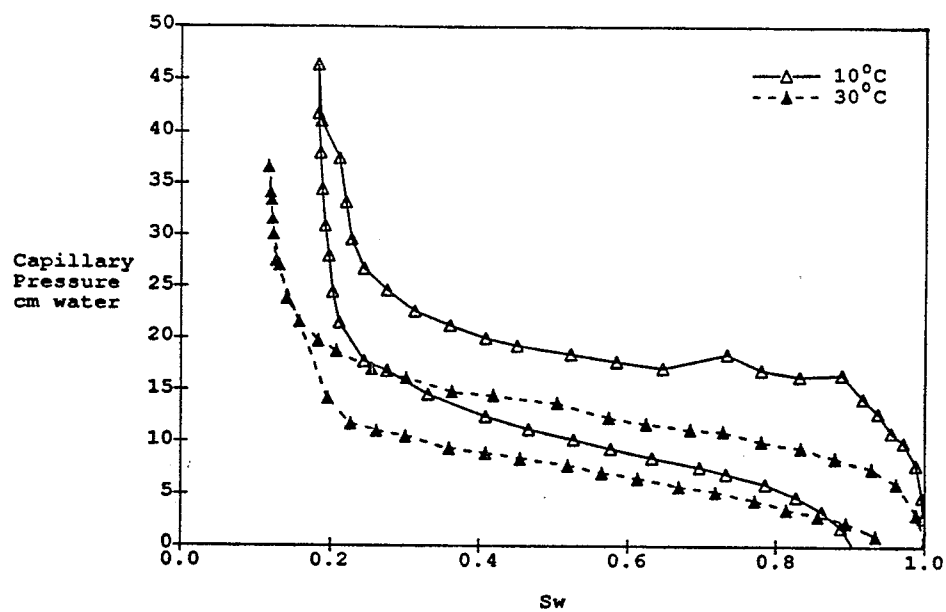


Figure 13. Capillary pressure-saturation curve for the mixed sand for the water/air system at 10 and 30°C.

Increases in irreducible water saturation and reductions in hysteresis with temperature increase are consistent with the results of Sinnokrot et al. (1971) for sandstone cores with a refined oil and distilled water.

The water/oil curves at 10 and 30°C for the two sands are shown in Figures 14 and 15. There is very little difference in these curves with temperature, which is consistent with the lack of a change in the interfacial tension over the temperature range used here for this water/oil system. There are, however, some significant differences in the residual saturations at the two temperatures. Both sands showed a significantly higher residual water saturation at the higher temperature, and a significantly lower residual oil content.

The effects of different fluid pairs or changes in temperature on irreducible water saturations and residual oil saturations does not seem to be well-established. The data of Parker et al. (1987) seems to show a change in the residual water saturation for different fluid pairs, with a trend toward lower residual water saturations for systems with lower surface or interfacial forces. However, in their mathematical description of the capillary pressure-saturation relationship, they chose to ignore these small differences and consider the term for residual wetting fluid to be independent of fluid properties and saturation history. Haridasan and Jensen (1972), when studying water-air systems, found that the water content at near zero pressure heads was higher at lower temperatures (i.e., the residual air content increased with increasing temperature). The data of Hopmans and Dane (1986a,b) seems to show lower irreducible water contents at higher temperatures. Sinnokrot et al. (1971) found the irreducible water saturation for sandstone cores to increase with temperature, while the limestone core showed no change in irreducible water saturation with temperature. Their sandstone cores showed decreases in residual oil content with increasing temperature, but the limestone core showed an increase in residual oil saturation with temperature. Demond and Roberts (1991) found increases in the residual water contents with decreases in the interfacial forces, but also showed that the residual saturation can be influenced by the drainage rate.

The data presented here generally is in agreement with the findings of lower irreducible water saturations with lower interfacial forces and with higher temperature. The lower residual air and oil contents found at higher temperatures is in disagreement with the results of Haridasan and Jensen (1972), but in agreement with the results of Sinnokrot et al. (1971) for the sandstone cores.

Constant Temperature Displacements

Oil Recovery. For the 20/30 sand, the constant temperature displacement experiments were run at temperatures of 10, 20, 30, 40, and 50°C. For the mixed sand, displacement experiments were run at 10, 30 and 50°C. Throughout each experiment, the initial oil saturation in the column and the percent oil recovered versus the volume of water injected were determined. The recovered volumes given are the average of at least two displacement experiments for each temperature. The variation in the percent oil recovery between replicate displacement experiments was generally low, ranging from one to two percent at low temperatures and with a maximum variation of about 5 percent at high temperatures.

Table 2 shows the volume of oil recovered versus the pore volumes of water injected at each temperature for both sands. Each experiment had a slightly different initial oil volume, so the percent oil recovered of each experiment was used to determine a volume recovered based on an average initial oil volume for each experiment. The greatest percent increase in recovery for each constant temperature experiment is at breakthrough, with increases of as much as 30 percent for the 20/30 sand and 50 percent for the mixed sand. The percent additional recovery in the 1 to 5 pore volumes of injected water range is usually higher than the percent of additional recovery at 10 pore volumes. For the 20/30 sand, the increased recovery at 50°C is approximately 22 percent, while the mixed sand showed a 17 to 20 percent increase in recovery over the same temperature range.

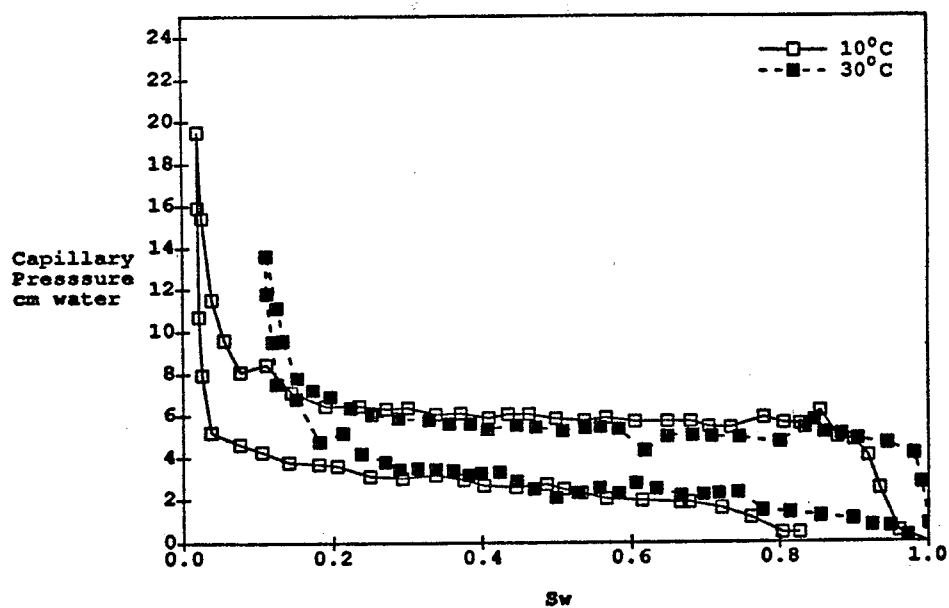


Figure 14. Capillary pressure-saturation curve for the 20/30 sand for the water/oil system at 10 and 30°C.

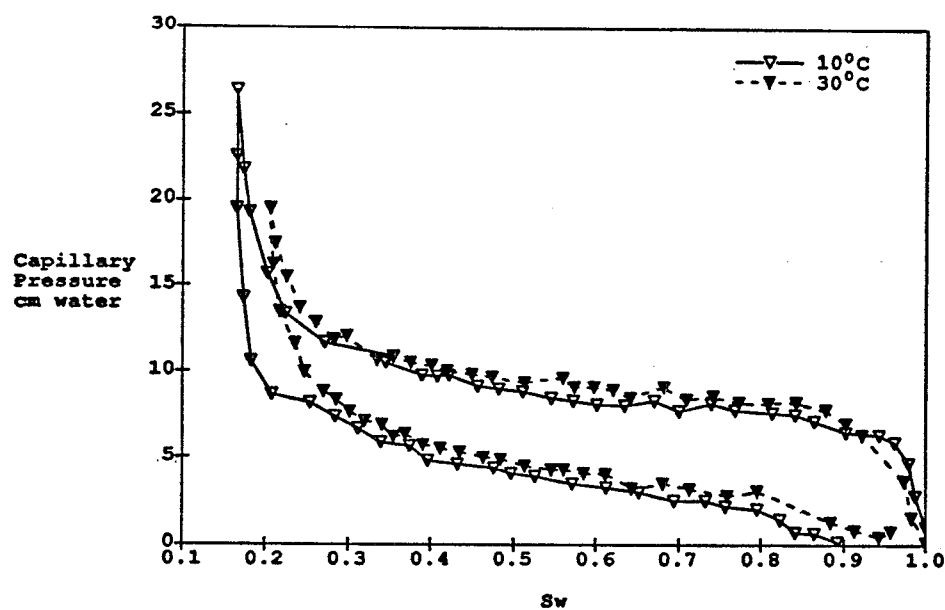


Figure 15. Capillary pressure-saturation curve for the mixed sand for the water/oil system at 10 and 30°C.

20/30 SAND

| | 10°C | 20°C | 30°C | 40°C | 50°C | Transient |
|-----------------|-------|-------|-------|-------|-------|-----------|
| Breakthrough | 159.0 | 191.6 | 187.7 | 187.7 | 205.9 | 176.2 |
| 1 Pore volume | 248.0 | 268.2 | 273.8 | 281.2 | 302.0 | 256.7 |
| 2 Pore volumes | 289.0 | 308.5 | 314.7 | 332.2 | 349.5 | 310.5 |
| 3 Pore volumes | 308.3 | 328.9 | 337.5 | 361.2 | 376.7 | 339.8 |
| 4 Pore volumes | 324.4 | 346.1 | 355.0 | 384.1 | 394.8 | 363.7 |
| 5 Pore volumes | 336.6 | 359.3 | 368.6 | 401.2 | 408.2 | 379.07 |
| 10 Pore volumes | 382.5 | 395.7 | 411.0 | 446.2 | 439.1 | 418.7 |

MIXED SAND

| | 10°C | 30°C | 50°C | Transient |
|-----------------|-------|-------|-------|-----------|
| Breakthrough | 146.1 | 204.4 | 219.1 | 172.3 |
| 1 Pore volume | 254.6 | 300.3 | 317.8 | 268.2 |
| 2 Pore volumes | 304.6 | 346.3 | 363.0 | 316.0 |
| 3 Pore volumes | 331.0 | 368.1 | 389.6 | 351.2 |
| 4 Pore volumes | 349.7 | 381.5 | 408.0 | 373.3 |
| 5 Pore volumes | 362.3 | 393.2 | 423.0 | 389.7 |
| 10 Pore volumes | 404.3 | 428.1 | 457.1 | 434.4 |

Table 2. Volume of oil recovered versus the pore volumes of water injected at each of the temperatures for the 20/30 and mixed sands

The percent oil recovered as a function of the pore volumes of water injected are shown in Figures 16 and 17 for the 20/30 and mixed sands, respectively, at each of the temperatures used for the displacements. These graphs show a steady increase in the percent oil recovered as the temperature increases. On the basis of the recovery as a percentage of the initial oil saturation, the increase in recovery at 50°C over the recovery at 10°C is about 10 percent for each soil.

The flow rate used for all of the displacements was approximately 17 to 18 ml/min. This flow rate was checked in the scaling coefficient determined by Rapoport and Leas (1953) to see if it should produce a stabilized flood. The permeability of the sands used here is similar to the permeability of the cores used in determining these coefficients, so the values needed for stabilization should be similar. For these floods, the velocity is $17 \text{ cm}^3/\text{min} \div 44.18 \text{ cm}^2 = 0.385 \text{ cm/min}$, and the value of the scaling coefficient for a 10°C flood is $45 \text{ cm} \times 0.385 \text{ cm/min} \times 1.307 \text{ cp} = 22.98 \text{ cp cm}^2/\text{min}$. For the 50°C flood, the scaling coefficient is $9.62 \text{ cp cm}^2/\text{min}$. Therefore, the flow rates used for these experiments should have been sufficient to minimize the end effect and produce a stabilized flood. If the floods were not stabilized, then the smaller value of the scaling coefficient at 50°C should have caused a decrease in the oil recovery.

Some researchers (Stewart and Udell, 1988; Bennion and Thomas, 1983) have found that emulsions are formed when hot water or steam are used to displace oil from porous media. The formation of emulsions would adversely affect efforts to recycle the water and would likely increase the amount of treatment that the water would require before it could be discharged. However, visual inspection of the column effluent showed that emulsions were never formed in the displacement experiments reported here.

The initial oil saturations in the column, the final oil saturation, the percent oil recovery at breakthrough and after the injection of 10 pore volumes, and the percent oil recovery between breakthrough and 10 pore volumes are shown in Table 3. The initial oil saturation of the column was determined by a material balance on the volume of oil pumped into the column and the volume recovered during the oil pumping phase. For a couple of experiments at low temperatures, the material balance showed that more oil was contained in the column than the calculated total pore volume of the sand. This was most likely due to errors in determining the bulk density of the sand in the column which were caused by loss of sand during the packing and by differences in the volumes of the columns. It is estimated that these errors could cause as much as 5 percent error in the calculated pore volumes of the sand columns. Thus, the volume of oil contained in the column is considered the more reliable estimate of pore volume. However, both the estimate of the initial oil saturation in the column at the beginning of the displacement and the calculated initial oil volume in the column show a trend to higher irreducible water saturations as the temperature is increased. Lo and Mungan (1973) also found higher irreducible water saturations at higher temperatures.

In comparing oil recovery data, two points on these curves will generally be compared: the recovery at water breakthrough and the recovery after the injection of 10 pore volumes of water. For both sands, the oil recovery at breakthrough and after the injection of 10 pore volumes of water increased as the temperature increased. It is interesting to note that both soils seemed to have a fairly consistent oil recovery between breakthrough and 10 pore volumes of water injection independent of temperature. Consistently more oil was recovered from the mixed sand than from the 20/30 sand, which is consistent with the results found in the numerical simulations (see Simulation of Experimental Results). However, neither sand shows a degree of increase in recovery that is as great as the decrease in the viscosity.

Figure 18 shows the recovery at breakthrough and after the injection of 10 pore volumes of water versus the viscosity ratio (μ_o/μ_w) for both sands. Generally, the oil recovery at breakthrough is linearly related to the viscosity ratio. The oil recovery after the injection of 10 pore volumes of water, however, seems to show greater increases as the viscosity ratio becomes smaller. Note, though, that the viscosity ratio versus temperature relationship, shown in Figure 5, does not continue to decrease significantly with further increases in temperature. Thus, as the viscosity ratio approaches one, significant increases in oil recovery are achieved with only small further reductions in the viscosity

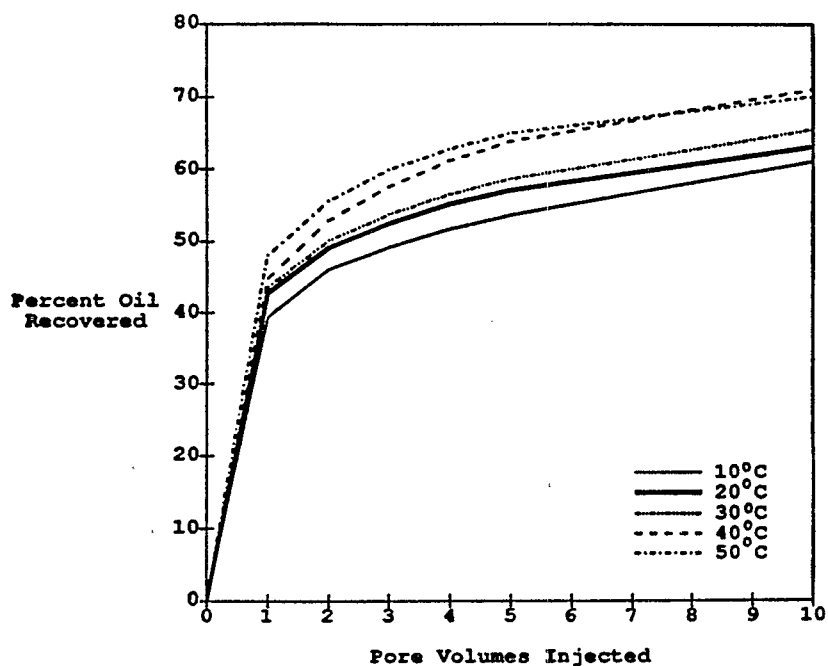


Figure 16. Oil recovery curves versus pore volumes of water injected for the 20/30 sand for constant temperature displacements at 10, 20, 30, 40 and 50°C.

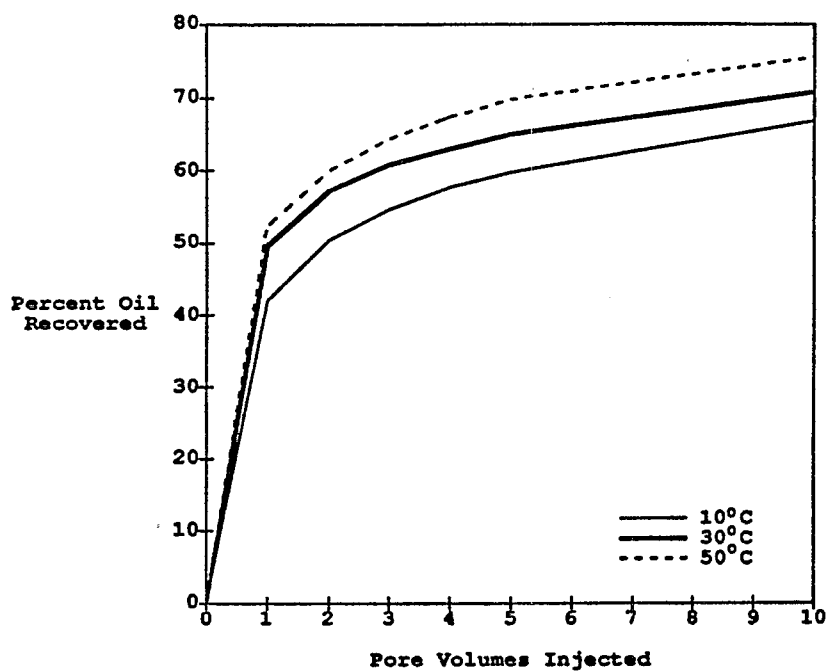


Figure 17. Oil recovery curves versus pore volumes of water injected for the mixed sand for constant temperature displacements at 10, 30, and 50°C.

20/30 Sand

| | 10°C | 20°C | 30°C | 40°C | 50°C | Transient |
|---|-------|-------|-------|-------|-------|-----------|
| Initial Oil Saturation | 1.000 | 0.998 | 0.984 | 0.989 | 0.978 | 0.987 |
| Final Oil Saturation | 0.391 | 0.384 | 0.344 | 0.295 | 0.299 | 0.297 |
| Percent Recovery at Breakthrough | 24.68 | 27.04 | 28.94 | 28.94 | 32.82 | 27.51 |
| Percent Recovery at 10 Pore Volumes | 60.88 | 62.98 | 65.41 | 71.01 | 69.89 | 65.40 |
| Recovery Between Breakthrough and 10 Pore Volumes | 36.20 | 35.94 | 36.47 | 42.07 | 37.07 | 37.89 |

Mixed Sand

| | 10°C | 30°C | 50°C | Transient |
|---|-------|-------|-------|-----------|
| Initial Oil Saturation | 0.982 | 0.983 | 0.975 | 0.994 |
| Final Oil Saturation | 0.331 | 0.291 | 0.232 | 0.255 |
| Percent Recovery at Breakthrough | 22.93 | 32.70 | 33.32 | 27.93 |
| Percent Recovery at 10 Pore Volumes | 66.79 | 70.71 | 75.50 | 70.44 |
| Recovery Between Breakthrough and 10 Pore Volumes | 43.86 | 38.01 | 42.18 | 42.51 |

Table 3. Initial oil saturation, final oil saturation, percent recovery at breakthrough, percent recovery after the injection of 10 pore volumes of water, and the recovery between breakthrough and 10 pore volumes of injection for the constant temperature and transient temperature displacements

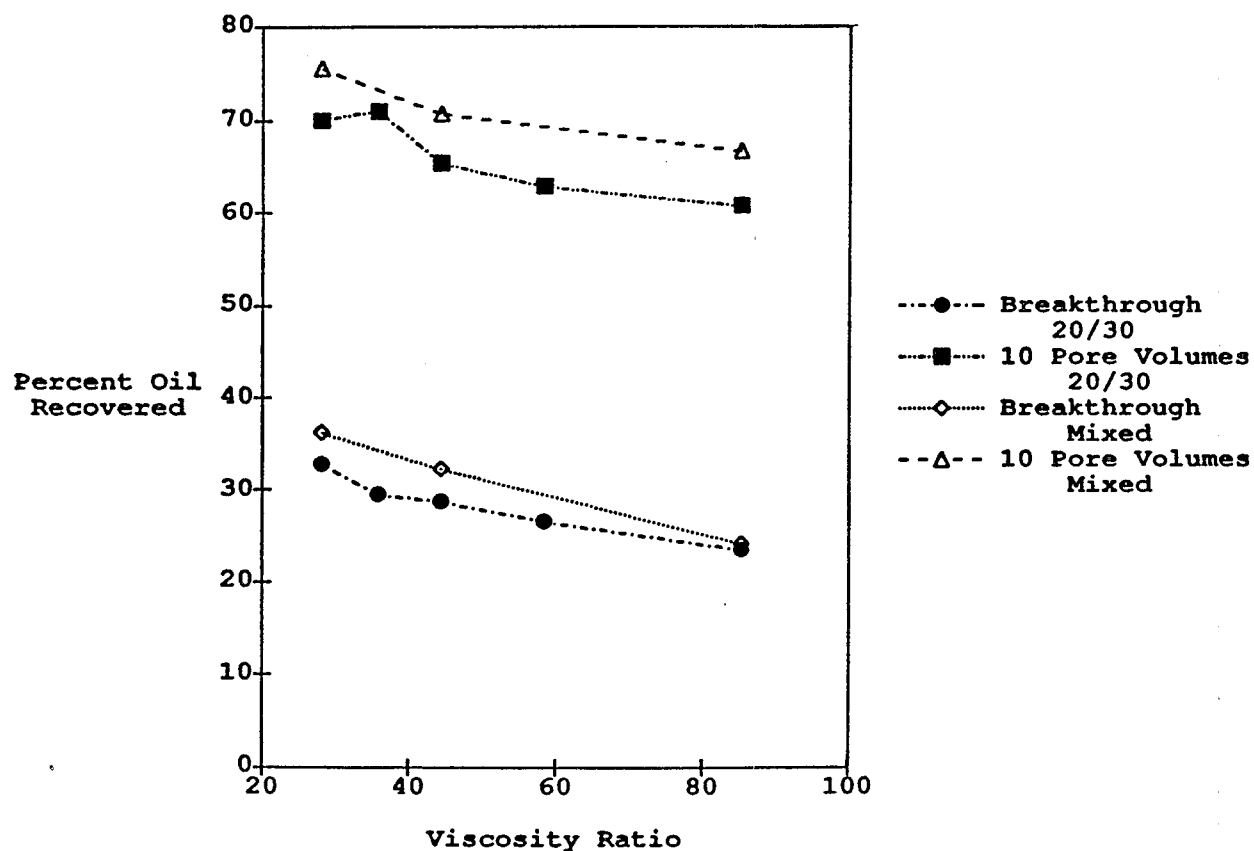


Figure 18. Percent oil recovered at breakthrough and after the injection of 10 pore volumes of water versus the viscosity ratio for the 20/30 sand and the mixed sand for constant temperature displacements.

ratio. Graphs showing an even greater increase in recovery at lower oil viscosities were made based on the laboratory data of Edmondson (1965).

These recoveries can be compared at least in a qualitative way with the recoveries of other researchers. Willman et al. (1961) found 2 to 15 percent increases in recoveries of oil when the temperature was raised from 26 to 165°C, while Edmondson (1965) found 12 to 20 percent increases in oil recovery for temperature increases from 24 to 149°C (these percent recoveries are based on the initial volume of oil in the column). Comparing the recoveries achieved here to those recoveries which were achieved with much larger increases in temperature shows that these results are generally better than the results achieved by others. The ultimate recoveries found here are also similar to or better than those found by the other researchers. Johnson's (1991) recoveries of 60 to 70 percent for coal gasification wastes and 84 to 94 percent for wood treating wastes are about the same or better than the ultimate recoveries achieved here, but information of the temperatures used and increased recoveries achieved by the use of hot water is not provided. Stewart and Udell (1988) essentially did not recover any of a viscous mineral oil using steam injection. All of these results fit into Mercer and Cohen's (1990) estimate of primary recovery removing 30 to 40 percent of the NAPL and secondary/tertiary recovery removing possibly an additional 30 to 50 percent, leaving 10 to 40 percent of the NAPL in the subsurface.

Figure 19 shows the oil saturation remaining in the column at the end of the displacement experiments. For the 20/30 sand at ambient temperature (10°C), approximately 39 percent of the pore space was still saturated with oil, and at 50°C, 30 percent of the pore space still contained oil. For the mixed sand, the residual oil saturation went from 33 percent at 10°C to 23 percent at 50°C. Although these are significant reductions in the residual oil contained in the column, these saturations are most likely still higher than cleanup goals for the soil or aquifer. Comparing these oil saturations after 10 pore volumes of water throughput to the residual oil saturations found in the wetting curve of the pressure-saturation curves shows that the remaining oil saturations in the displacement experiments were significantly higher than the residual found for the system at static equilibrium.

Calculations were made to determine the water to oil ratio in the effluent during approximately the last pore volume of the displacement and are shown in Table 4. Although there is considerable variation between duplicate experiments, there is a trend for both soils to achieve the most favorable water to oil ratios at temperatures of 20 to 30°C. Also, the mixed sand always has better ratios for a given temperature than the 20/30 sand. With the assumption that the water to oil ratio in the effluent remains the same as the displacement is continued, then the pore volumes of throughput needed to achieve the residual saturations found in the columns under static equilibrium conditions can be estimated. These calculations show that at 10°C, approximately 28 additional pore volumes of water would be needed to reach the true residual oil saturation, while the mixed sand would require about 6 additional pore volumes of throughput. At 30°C, both sands would require slightly more throughput (30.4 and 17 pore volumes, respectively) to reach the significantly lower residual oil saturations, even though the water to oil ratios are more favorable in the 30°C displacements. However, it must be kept in mind that these are probably low estimates of the pore volumes of throughput needed, because the water to oil ratio will most likely increase slowly as the displacement continues.

Various researchers have developed correlations between the residual nonwetting phase remaining in a column after a waterflood and the capillary number, which is the ratio of viscous and capillary forces during the displacement. Several different but essentially equivalent definitions for capillary number have been used in these correlation. Larson et al. (1981) reviewed the published data on residual nonwetting phase saturations, and found that the results could be correlated using a capillary number, N_{ci} , defined as

$$N_{ci} = \frac{k \Delta P}{L \gamma} \quad (3)$$

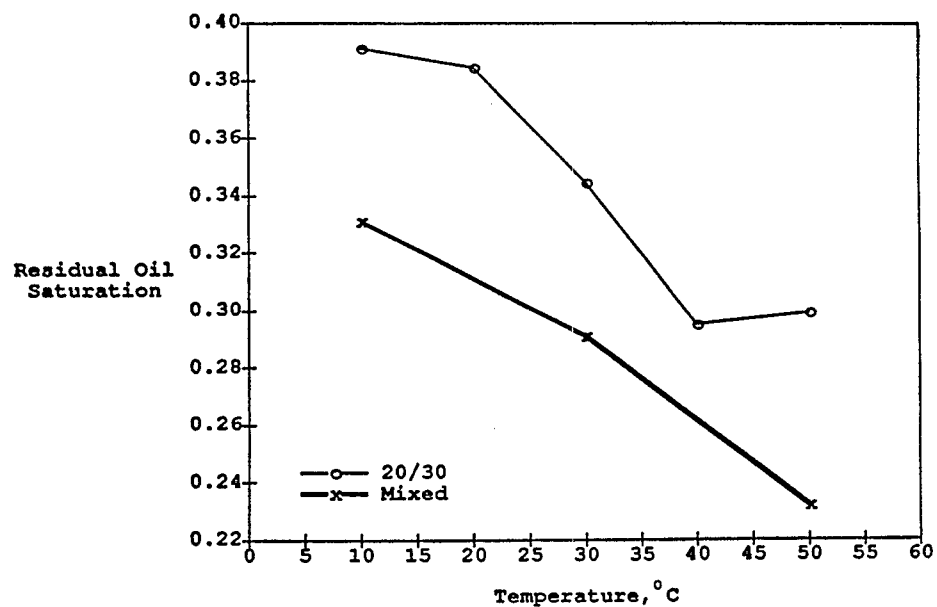


Figure 19. Residual oil saturation for the constant temperature displacement experiments after the injection of 10 pore volumes of water versus the temperature for the 20/30 sand and mixed sand.

| Temperature | 20/30 Sand | Mixed Sand |
|-------------|------------|------------|
| 10°C | 117.3 | 72.71 |
| 20°C | 90.59 | |
| 30°C | 96.86 | 66.41 |
| 40°C | 121.86 | |
| 50°C | 138.41 | 135.55 |
| Transient | 121.81 | 81.40 |

Table 4. Water to oil ratios in the column effluent during the tenth pore volume of the displacement

where k is the intrinsic permeability of the porous media, ΔP is the pressure drop, L is the length of the column, and γ is the interfacial tension. These correlations showed that for most porous media the residual nonwetting phase saturation decreased approximately exponentially with increasing capillary number after a certain threshold capillary number, in the range of 10^{-4} to 10^{-5} , had been exceeded. At lower capillary numbers as are typical of waterflood displacements in petroleum reservoirs, the residual nonwetting phase saturation approaches a limiting saturation, the value of which is dependent on the media. The capillary numbers calculated for these experiments based on this definition of the capillary number show that for the 10°C experiments, the capillary number is in the range where significant reductions in the residual oil saturation may be expected. For 50°C experiments, which had pressure drops which are more than an order of magnitude lower than the pressure drops in the 10°C experiments, the capillary number of the order 10^{-5} , would indicate that the oil saturation was not reduced beyond the limiting saturation. This definition of capillary number would predict lower residual saturations at lower temperatures, and thus does not appear to be applicable to these experiments.

A brief review of the definitions used for capillary number by other researchers shows that most of these definitions would lead to the same result of a decreasing capillary pressure as the temperature increases. The definition used by Lefebvre du Prey (1973) shows the expected result for these experiments of an increasing capillary number with increasing temperature, but has no way of predicting differences in the residuals found in different sands. The definition of capillary number used by Leverett (1939) allows for differences in residuals for different sands, and shows an increase as the temperature increases. His definition of capillary number is

$$N_{C2} \equiv \frac{P_d(L)}{\Delta P D} \quad (4)$$

where P_d is the displacement pressure for the sand/water/oil system, D is the average pore diameter defined as $5.63 \times 10^{-4} (k/\phi)^{1/2}$, and all other symbols are as defined previously. A plot of residual oil saturation (the final oil saturation at the completion of the displacement) versus the capillary number is shown in Figure 20. This plot contains the results from both the constant and transient temperature displacements for both sands. Although there is scatter in the data, the downward trend in saturation as the capillary number increases is shown. Some of the scatter is likely due to the fact that the final saturation at the end of the displacement experiment was used rather than a true residual oil saturation, and the actual number of pore volumes of water injected for each displacement varied slightly.

Pressure Data. The two pressure transducers, one at each end of the column, were used to measure the pressure in the water phase during the displacement experiments. However, in some of the experiments, problems were encountered in trying to establish a hydraulic connection between the water in the column and the pressure transducer. This caused the pressure transducers to record unrealistic pressures. The most common problem was the recording of a higher water pressure at the effluent end of the column than was recorded at the influent end. Just over half of the displacement experiments showed higher pressures at the downstream end of the column at some time during the experiment, but there was no consistent pattern in these pressure profiles. Several of the displacement experiments had very erratic pressure readings. For some of these, the pressure reading could be smoothed and then used for further calculations. Only pressure profiles that show a greater pressure at the upstream end of the column are presented.

Figure 21 shows an example of the pressure at the influent and effluent ends of the column during a displacement experiment. This displacement experiment was with 20/30 sand and was carried out at 20°C . At time zero, water pumping was initiated. Pressure readings at each transducer were recorded every 10 seconds. The maximum pressure corresponds to the time when water breakthrough at the effluent occurs. This sharp increase in the pressure drop across the column just

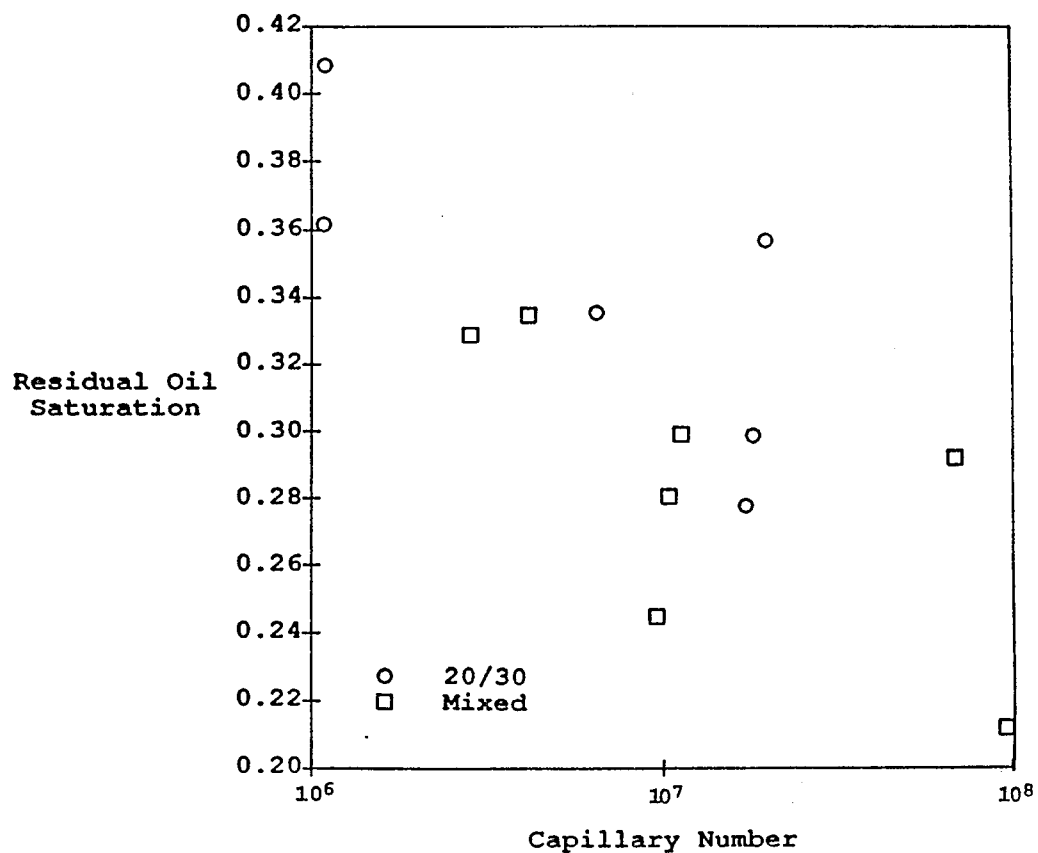


Figure 20. Residual oil saturation in the displacement experiments versus the capillary number as defined by Leverett (1939). Data points are for both the 20/30 and mixed sand for the constant and transient temperature displacement experiments.

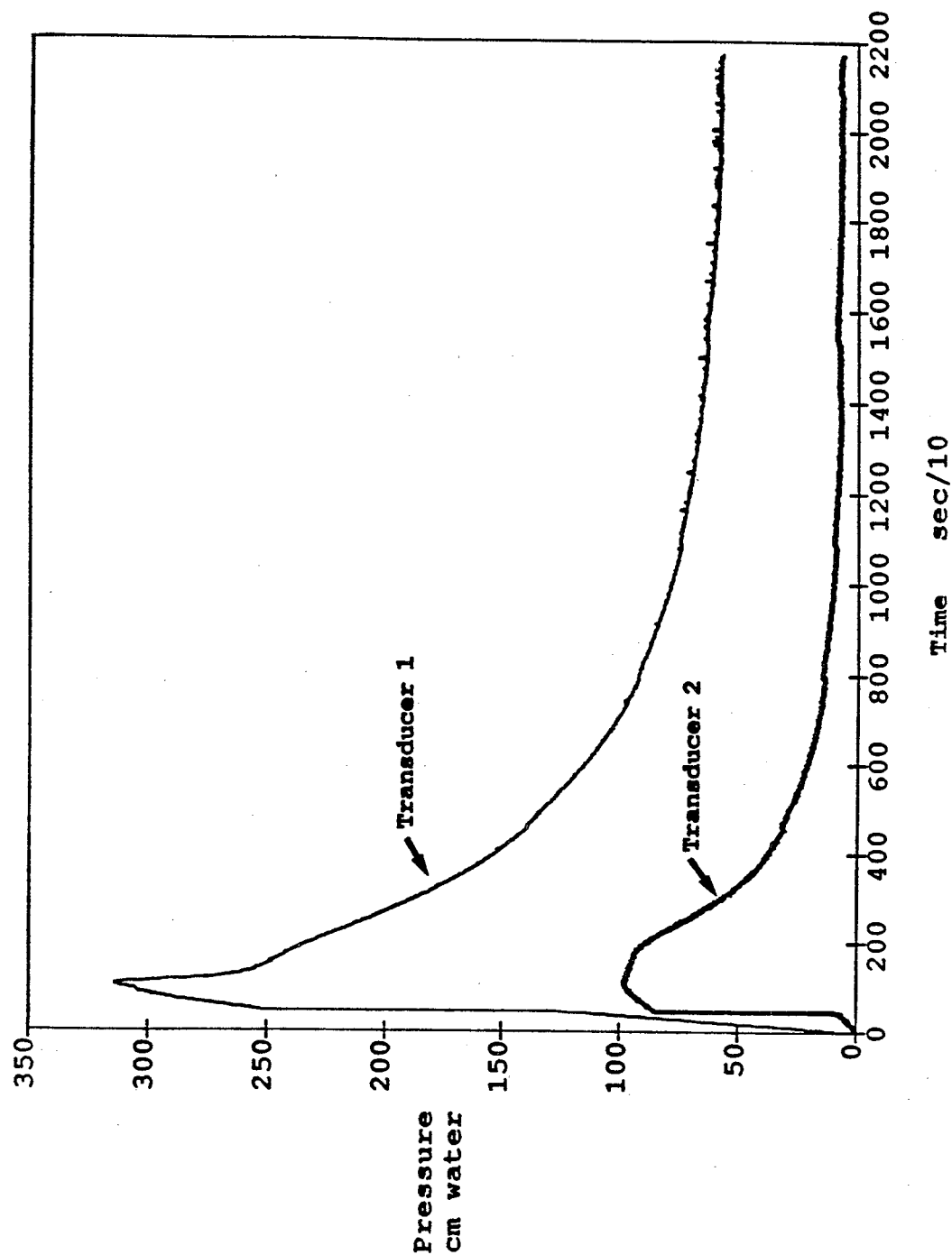


Figure 21. Pressure in the water phase during a 20°C constant temperature displacement experiment using the 20/30 sand. Transducer 1 was 5.3 cm from the influent end of the column, and Transducer 2 was 5.3 cm from the effluent end of the column.

before breakthrough is consistent with the results of Quettier and Corre (1988).

Figure 22 shows the pressure drops at 10, 30, and 50°C for the mixed sand. This graph shows the significant decline in the maximum pressure drop along the column as the temperature is increased and consequently the viscosity of the oil is decreased. Note also the significant decline in the pressure drop at the higher temperatures for the subordinate phase of the displacement.

Transient Temperature Displacements

For the transient temperature displacements, the column was placed in the constant temperature incubator which was held at 10°C. Oil at 10°C was used to displace the water initially contained in the column. As soon as the column was saturated with oil, water at 50°C was used to displace the oil. The pressure and pressure drop along the column were recorded during the displacement, as well as the temperature at four locations along the column.

The oil volume recovered versus pore volumes of water injected for the transient temperature experiments is given in Table 2, and the percent recoveries are shown in Figures 23 and 24 for the 20/30 and mixed sands, respectively. Also shown on these graphs is the oil recovery curve at 10 and 50°C from the constant temperature experiments for purposes of comparison. Table 2 shows that the recovered oil volumes for the transient temperature experiments are somewhat better than the recoveries for the 30°C waterfloods. Because the initial oil saturations for these experiments was somewhat lower than the initial oil saturations for the 10°C constant temperature experiments, the final oil saturation at the end of the transient temperature displacement is similar to that for a 40°C constant temperature waterflood (see Table 3). Thus, under conditions which more closely resemble those that would be found in a field situation where hot water is used to displace oil from an aquifer that is at ambient temperature, the benefits in terms of enhanced oil recovery by using hot water were realized.

The pressure drop along the column during a transient temperature displacement is shown in Figure 25. Again, problems were encountered in getting the pressure data, but it appears from Figure 25 that the maximum pressure during these transient temperature displacements was at least as high as measured in the 10°C constant temperature displacements. Comparing Figure 25 to the pressure drop curve in Figure 22 for a 10°C constant temperature displacement shows that the pressure drop during the subordinate phase of the displacement is much lower than in the ambient temperature displacements. Therefore, the apparent advantage of less pressure needed to drive the displacement at higher temperatures was not actually realized until the subordinate phase of the transient temperature displacement.

The temperatures in the column, in the incubator, and of the displacing water are shown in Figure 26. Each of these temperatures were recorded every 10 seconds. The figure shows that the heat loss in the column is fairly significant, limiting the high temperature in the column to less than 40°C, and dropping off fairly quickly and uniformly along the column to a low temperature of around 30°C near the effluent end. The graph seems to indicate that very little heat travels in front of the water bank, but the temperature at any place along the column reaches its equilibrium temperature fairly quickly once the water front reaches it. Undoubtedly, the stainless steel column used during these experiments moved heat away from the sand faster than would occur in a field situation because of the significantly higher thermal diffusivity of stainless steel than sand. Attempts were made to lessen the heat loss by insulating the column. This insulation increased the temperature along the column by at most 2°C, and did not seem to have a significant effect on oil recovery.

Stewart and Udell (1988) report theoretical and experimental temperature data for steamflood displacements. Heat loss during their one-dimensional column experiments was eliminated by adding heat to the outside of the column when the steamfront reached that section of the column. Their experiments and theoretical calculations showed some heat moving in front of the steam front. However, temperature profiles with depth in an oil reservoir during a hot water flood reported by Martin et al. (1968) show that the temperature is not constant with depth, indicating significant heat

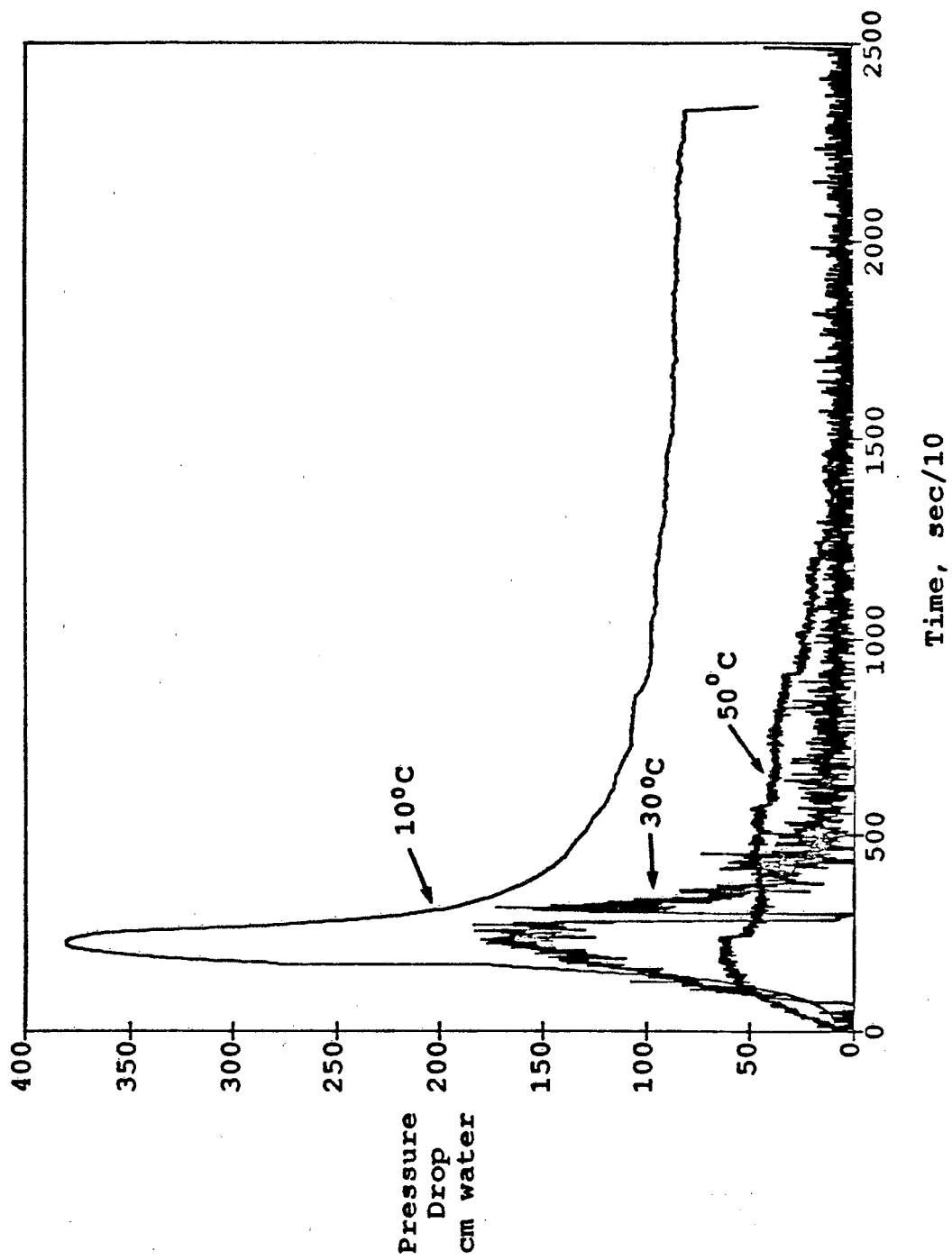


Figure 22. Pressure drop along the column during constant temperature displacement experiments at 10, 30, and 50°C for the mixed sand.

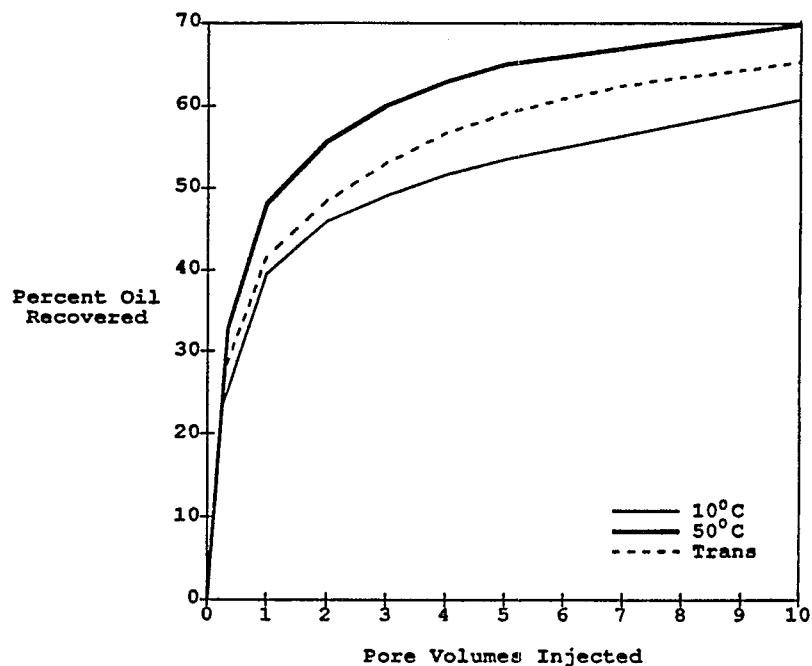


Figure 23. Percent oil recovery versus the pore volumes of water injected for the 20/30 sand for 10 and 50°C constant temperature displacements and for the transient temperature displacements.

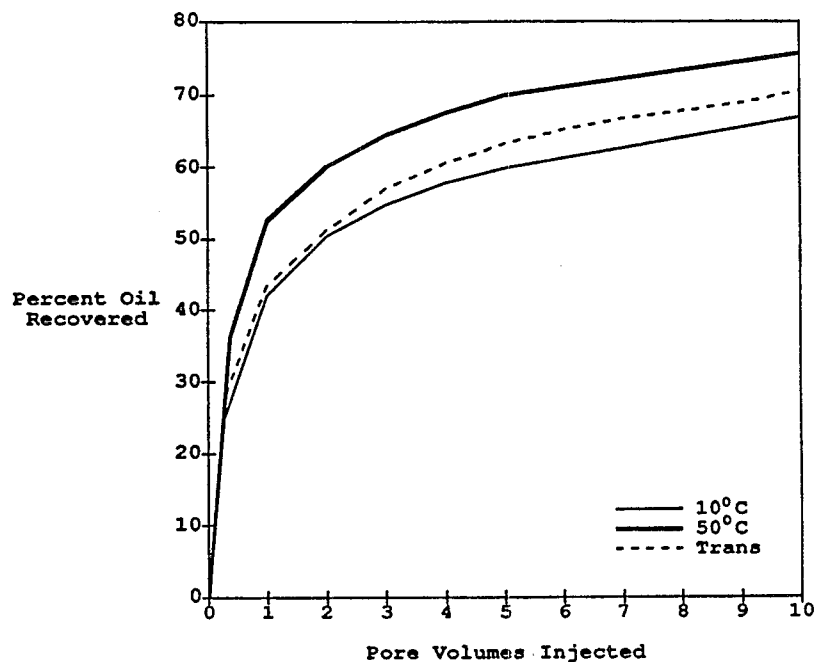


Figure 24. Percent oil recovery versus the pore volumes of water injected for the mixed sand for 10 and 50°C constant temperature displacements and for the transient temperature displacements.

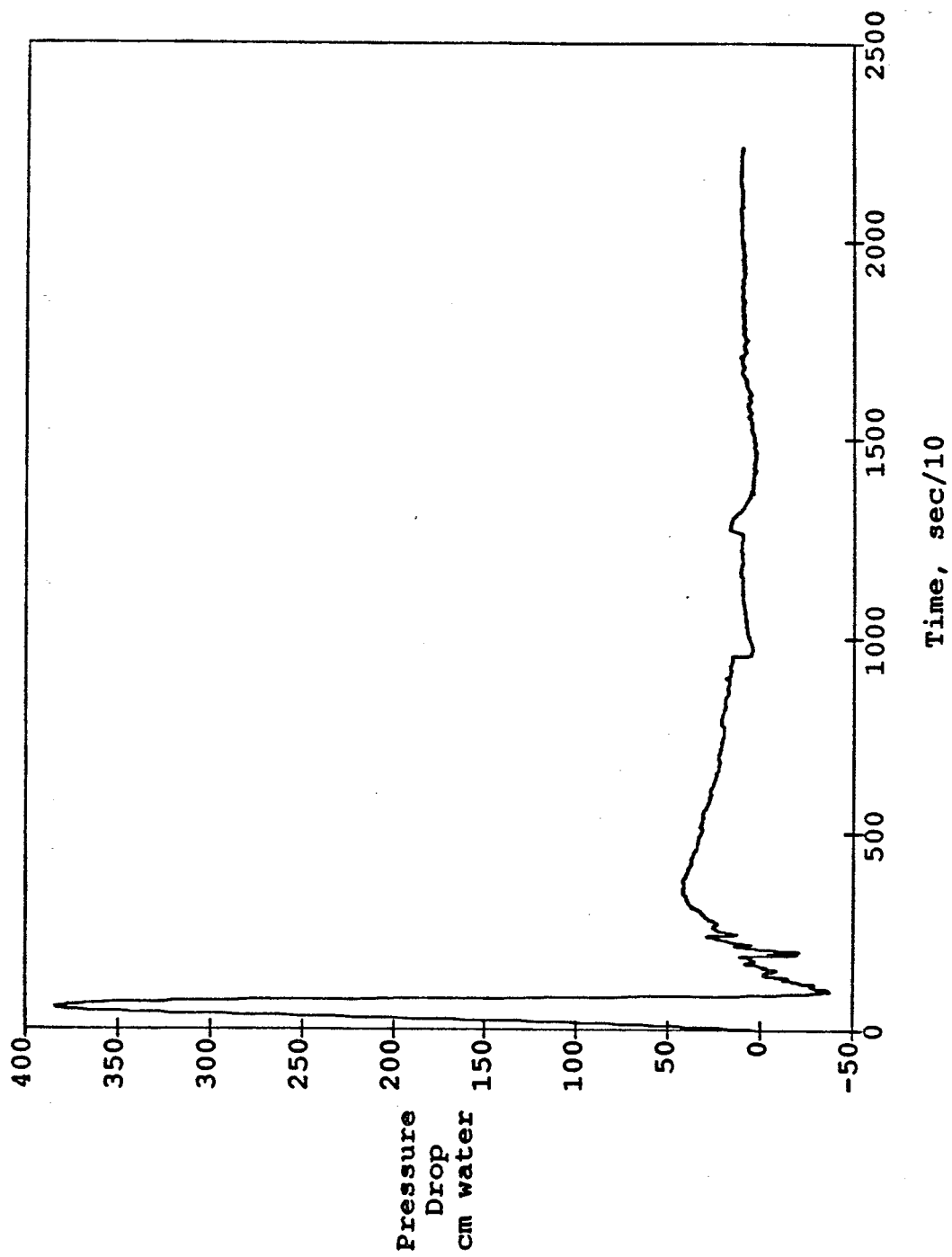


Figure 25. Pressure drop along the column during a transient temperature displacement for the mixed sand.

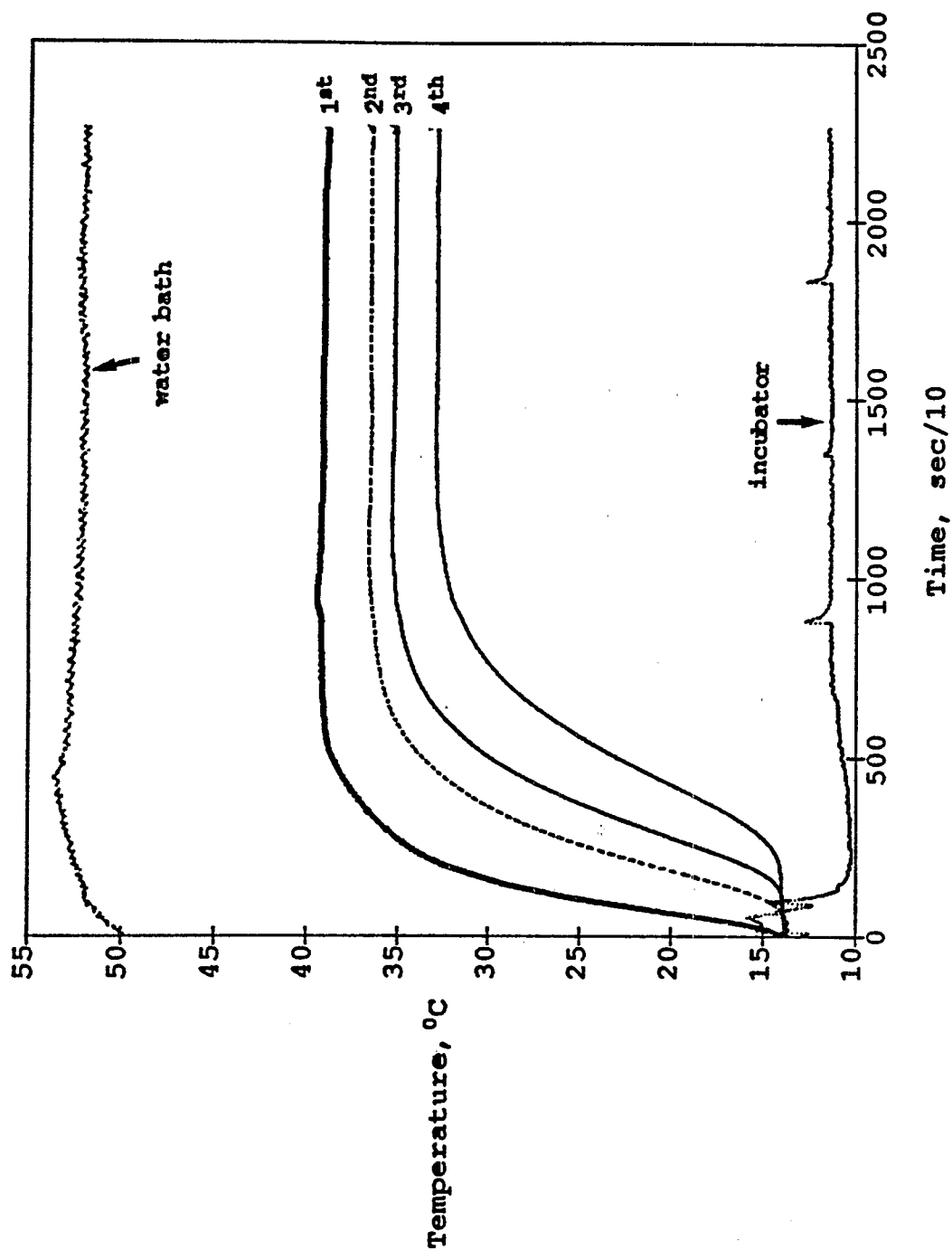


Figure 26. Temperature in the incubator, the hot water bath, and at each of the thermocouples along the column (1st, closest to the influent; 4th, farthest from the influent) during a transient temperature displacement for the mixed sand.

loss to the media surrounding the reservoir. The highest temperature they found in the reservoir was 93°C, which is significantly less than the injection water temperature of 177°C. Thus, the decline in temperature along the column observed in these transient temperature experiments is to be expected, but the degree of heat loss is likely accelerated by the high heat conduction of the stainless steel column. Because of this and the fact that we cannot predict the heat loss that will occur in the field, it is not possible to extrapolate this data directly to field situations.

SECTION 4

DISCUSSION OF RESULTS

Capillary Pressure-Saturation Curves

The Brooks and Corey (1964) and van Genuchten (1980) equations for describing the hydraulic properties of soil were fit to the capillary pressure-saturation curves by the program RETC (van Genuchten et al., 1991), which uses a nonlinear least-squares parameter optimization method to estimate the coefficients in these hydraulic models from the retention data. For most of the curves, good fits of both equations were found, with R^2 values greater than 0.95. Both parametric equations use four parameters: S_m , the maximum saturation to the wetting phase; S_r , the residual saturation of the wetting phase; P_o , a characteristic pressure; and N , the exponent of the equation. The best fit parameters for these equations for the various retention curves measured at constant temperatures are given in Table 5. Where replicate curves were measured, the parameters given in the table are averages of the replicates.

Generally, the results show that the exponent values (N) for each of the soils do not change with the temperature nor with the fluid pair in the pores (i.e., the exponents are essentially the same for a given soil for both water/air and water/oil systems at both temperatures). This would be expected since the exponent is related to the pore size distribution of the soil, which should be only a function of the sand and its packing but not the temperature or the properties of the fluids contained in the pores.

According to the methods proposed by Batycky et al. (1981) and Lenhard and Parker (1987), the capillary pressures-saturation relationship for a given soil and fluid pair can be scaled to the pressures for different fluid pairs based on the ratio of the interfacial tensions. The expression can be given as:

$$\frac{P_c^{ow}}{P_c^{aw}} = \frac{\gamma^{ow}}{\gamma^{aw}} \quad (5)$$

where P_c is capillary pressure, γ is interfacial tension, and the superscripts ow and aw stand for oil-water and air-water, respectively. Lenhard and Parker (1987) found this scaling to work fairly well for several fluid pairs in different soils. Demond and Roberts (1991), however, found that the ratio of interfacial tensions was always lower than the measured ratio of displacement pressures; i.e., the measured displacement pressures are higher than would be predicted based on the ratio of interfacial tensions. Morrow (1976) found that the measured ratios of capillary pressures was generally lower than the predicted ratio. He brought the measured and predicted ratios into agreement by including the cosine of the apparent contact angle on the left side of equation 5. The apparent contact angle was consistent with the values of the advancing and receding contact angles measured on a roughened surface as a function of the intrinsic contact angle of the fluid/fluid interface on the solid.

The results found here generally show higher ratios of capillary pressures than would be predicted based on the ratio of interfacial tensions when the interfacial tension of the fresh interface is used. However, when the ratio of the interfacial tensions is based on the measured stable interfacial tension, then the ratio of capillary pressures for the drainage portion of the curves generally are lower than the predicted ratio, while the imbibition portion of the curve remains at higher capillary pressure ratios than predicted. This result may indicate a continued change in the interfacial tension with time and/or a change in the wettability of the media.

| | Water/Oil | | Water/Air | |
|--------------------------------------|----------------|---------------|---------------|---------------|
| 10°C Averages | | | | |
| van Genuchten | Drainage | Imbibition | Drainage | Imbibition |
| N | 11.539 ± 2.700 | 4.180 ± 0.627 | 9.797 | 3.045 |
| P _o (cm H ₂ O) | 5.557 ± 0.575 | 2.263 ± 0.405 | 11.589 | 4.856 |
| θ _s | 0.323 ± 0.002 | 0.278 ± 0.009 | 0.333 | 0.294 |
| θ _r | 0.007 ± 0.001 | 0.000 ± 0.000 | 0.019 | 0.000 |
| Brooks-Corey | | | | |
| N | 4.643 ± 0.797 | 1.604 ± 0.259 | 5.153 | 1.362 |
| P _o (cm H ₂ O) | 4.855 ± 0.568 | 1.554 ± 0.327 | 10.301 | 3.422 |
| θ _s | 0.310 ± 0.011 | 0.267 ± 0.003 | 0.318 | 0.282 |
| θ _r | 0.000 ± 0.000 | 0.000 ± 0.000 | 0.019 | 0.000 |
| 30°C Averages | | | | |
| van Genuchten | Drainage | Imbibition | Drainage | Imbibition |
| N | 12.671 ± 0.858 | 3.580 ± 0.200 | 5.840 ± 0.784 | 4.010 ± 0.182 |
| P _o (cm H ₂ O) | 5.548 ± 0.256 | 1.982 ± 0.486 | 8.869 ± 0.135 | 5.346 ± 0.241 |
| θ _s | 0.325 ± 0.000 | 0.318 ± 0.001 | 0.328 ± 0.005 | 0.309 ± 0.018 |
| θ _r | 0.048 ± 0.007 | 0.044 ± 0.012 | 0.035 ± 0.031 | 0.039 ± 0.019 |
| Brooks-Corey | | | | |
| N | 4.481 ± 0.962 | 1.421 ± 0.131 | 2.313 ± 0.676 | 1.768 ± 0.319 |
| P _o (cm H ₂ O) | 4.810 ± 0.032 | 1.488 ± 0.320 | 6.768 ± 0.552 | 4.042 ± 0.429 |
| θ _s | 0.302 ± 0.024 | 0.297 ± 0.007 | 0.319 ± 0.003 | 0.296 ± 0.024 |
| θ _r | 0.027 ± 0.006 | 0.025 ± 0.010 | 0.020 ± 0.035 | 0.029 ± 0.031 |

Table 5A. Parameters for the Brooks and Corey (1964) and van Genuchten (1980) equation determined from the capillary pressure-saturation curves at temperatures of 10 and 30°C for the 20/30 sand (where more than one curve was measured for a given sand/wetting phase/nonwetting phase system, the parameters given are the average of the replicates and the standard deviation of the measurements is also given)

| | Water/Oil | | Water/Air | |
|--------------------------------------|----------------|---------------|----------------|---------------|
| 10°C Averages | | | | |
| van Genuchten | Drainage | Imbibition | Drainage | Imbibition |
| N | 9.133 ± 2.296 | 3.328 | 9.967 | 4.109 |
| P _o (cm H ₂ O) | 8.359 ± 0.097 | 3.344 | 18.210 | 8.291 |
| θ _s | 0.348 ± 0.011 | 0.305 | 0.352 | 0.314 |
| θ _r | 0.050 | 0.058 | 0.066 | 0.066 |
| Brooks-Corey | | | | |
| N | 4.417 ± 0.839 | 1.005 | 4.949 | 1.425 |
| P _o (cm H ₂ O) | 7.260 ± 0.182 | 2.081 | 15.934 | 6.413 |
| θ _s | 0.333 ± 0.003 | 0.298 | 0.346 | 0.304 |
| θ _r | 0.050 ± 0.012 | 0.018 | 0.066 | 0.002 |
| 30°C Averages | | | | |
| van Genuchten | Drainage | Imbibition | Drainage | Imbibition |
| N | 10.754 ± 1.517 | 3.910 ± 0.491 | 6.743 ± 0.906 | 4.123 ± 0.408 |
| P _o (cm H ₂ O) | 7.694 ± 1.117 | 3.039 ± 0.621 | 13.937 ± 1.766 | 7.822 ± 0.837 |
| θ _s | 0.334 ± 0.001 | 0.325 ± 0.011 | 0.338 ± 0.005 | 0.328 ± 0.024 |
| θ _r | 0.065 ± 0.005 | 0.064 ± 0.007 | 0.063 ± 0.020 | 0.060 ± 0.018 |
| Brooks-Corey | | | | |
| N | 4.290 ± 0.338 | 1.604 ± 0.413 | 2.982 ± 1.029 | 1.287 ± 0.240 |
| P _o (cm H ₂ O) | 6.581 ± 1.022 | 2.236 ± 0.318 | 11.278 ± 1.895 | 5.165 ± 0.877 |
| θ _s | 0.327 ± 0.006 | 0.313 ± 0.007 | 0.326 ± 0.005 | 0.321 ± 0.020 |
| θ _r | 0.059 ± 0.012 | 0.046 ± 0.012 | 0.050 ± 0.043 | 0.029 ± 0.026 |

Table 5B. Parameters for the Brooks and Corey (1964) and van Genuchten (1980) equation determined from the capillary pressure-saturation curves at temperatures of 10 and 30°C for the mixed sand (where more than one curve was measured for a given sand/wetting phase/nonwetting phase system, the parameters given are the average of the replicates and the standard deviation of the measurements is also given)

Philip and de Vries (1957) and Wilkinson and Klute (1962) developed expressions for the effect of temperature on retention curves, both of which can be shown to be equivalent to the expression above for the effect of interfacial tension on capillary pressure. However, Wilkinson and Klute (1962), Haridasan and Jensen (1972), and Hopmans and Dane (1986a&b) found that the measured effects of temperature on the retention curve was much greater than that predicted by theory. The only explanation that has been offered for the changes with temperature is based on the effect of temperature on the dissolved and entrapped air in the soil water (Peck, 1960). For the pressure-saturation curves measured here, the effect of temperature on the water/oil curves is approximately what would be predicted based on this theory, i.e., no significant change in the pressure-saturation curves over this range of temperatures. However, the effect of temperature on the water/air curves is significantly greater than would be predicted although with the method employed here for measuring the curves, air entrapment should not have occurred.

Calculation of Permeabilities and Permeability Ratios

Data on oil recovery and pressure drop from unsteady state displacement experiments as those conducted here can be used to calculate the ratio of oil permeability to water permeability at the effluent face of the column. This calculation is based on the Buckley-Leverett (1942) equation, and the first step is to calculate the fractional flow function for water, F_w , from the fractions of water and oil in the column effluent versus the volume of water injected:

$$F_w = \frac{dQ_w}{dQ_i} \quad (6)$$

where Q_w is the cumulative outflow of water and Q_i is the cumulative inflow. If it is assumed that capillary pressure and gravity effects are negligible, then F_w is approximately equal to f_w as given in equation (2). From equation (2), the ratio of oil permeability to water permeability can be calculated at different times (i.e., different injected water volumes) throughout the displacement process. Using a material balance technique developed by Welge (1952), the water saturations corresponding to the fractional flow functions can be determined, and the relationship of the ratio of oil permeability to water permeability versus saturation is established. This calculation was carried out for each of the displacement experiments, and examples of the resulting curves are shown in Figures 27 and 28 for the 20/30 and mixed sands, respectively. These curves show a shift in the permeability ratios with temperature at low water saturations, but all ratios become essentially the same at water saturations greater than about 0.35 for the 20/30 sand and 0.55 for the mixed sand. This result of shifts in the permeability ratios at low saturations is consistent with the results of Davidson (1969). There is not much difference in these curves for the two different sands, but the mixed sand curves lie slightly above the curves for the 20/30 sand. However, the sharp increase in pressure to the wetting phase that occurred just before water breakthrough in the laboratory experiments may be an indication that capillary end effects were significant (Quettier and Corre, 1988), and this would affect the permeability ratios calculated from the above equation.

Linear, unsteady state displacement experiments have been used by researchers in the petroleum industry for determining the relative permeability to water and oil as a function of saturation by a technique developed by Johnson et al. (1959). Jones and Roszelle (1978) developed a graphical technique to calculate the relative permeabilities that is equivalent to the method of Johnson et al., and this technique was used to calculate the relative permeability to each phase as a function of saturation. Since this method required data on the pressure drop during the displacement, only the displacements where reliable pressure data were collected could be used to calculate the relative permeabilities. The results for the 20/30 and mixed sand are given in Figures 29A and B, and

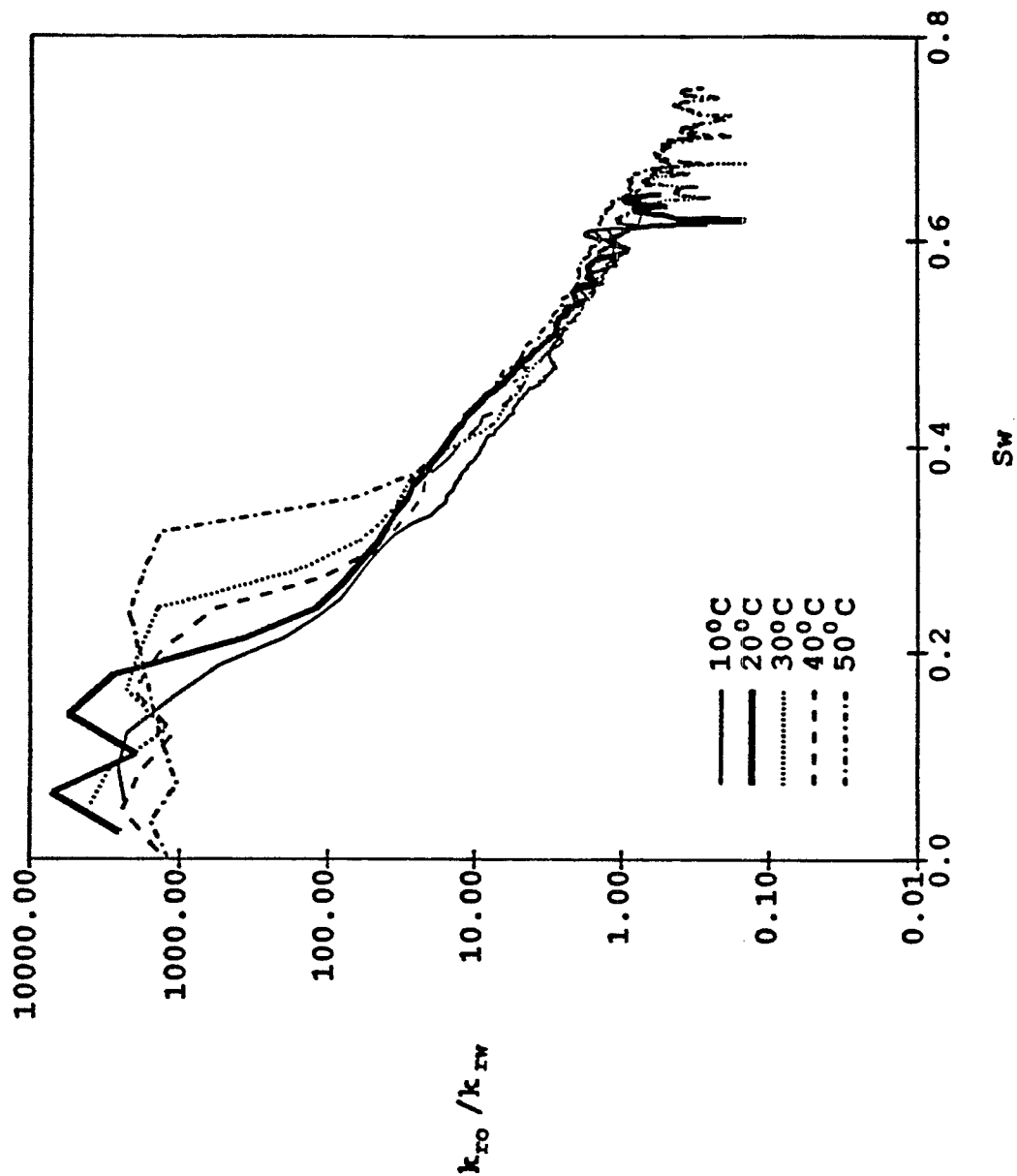


Figure 27. Permeability ratio (k_{ro}/k_{rw}) versus water saturation for the 20/30 sand at temperatures of 10, 20, 30, 40 and 50°C as determined by the Welge (1952) method from the constant temperature displacement data.

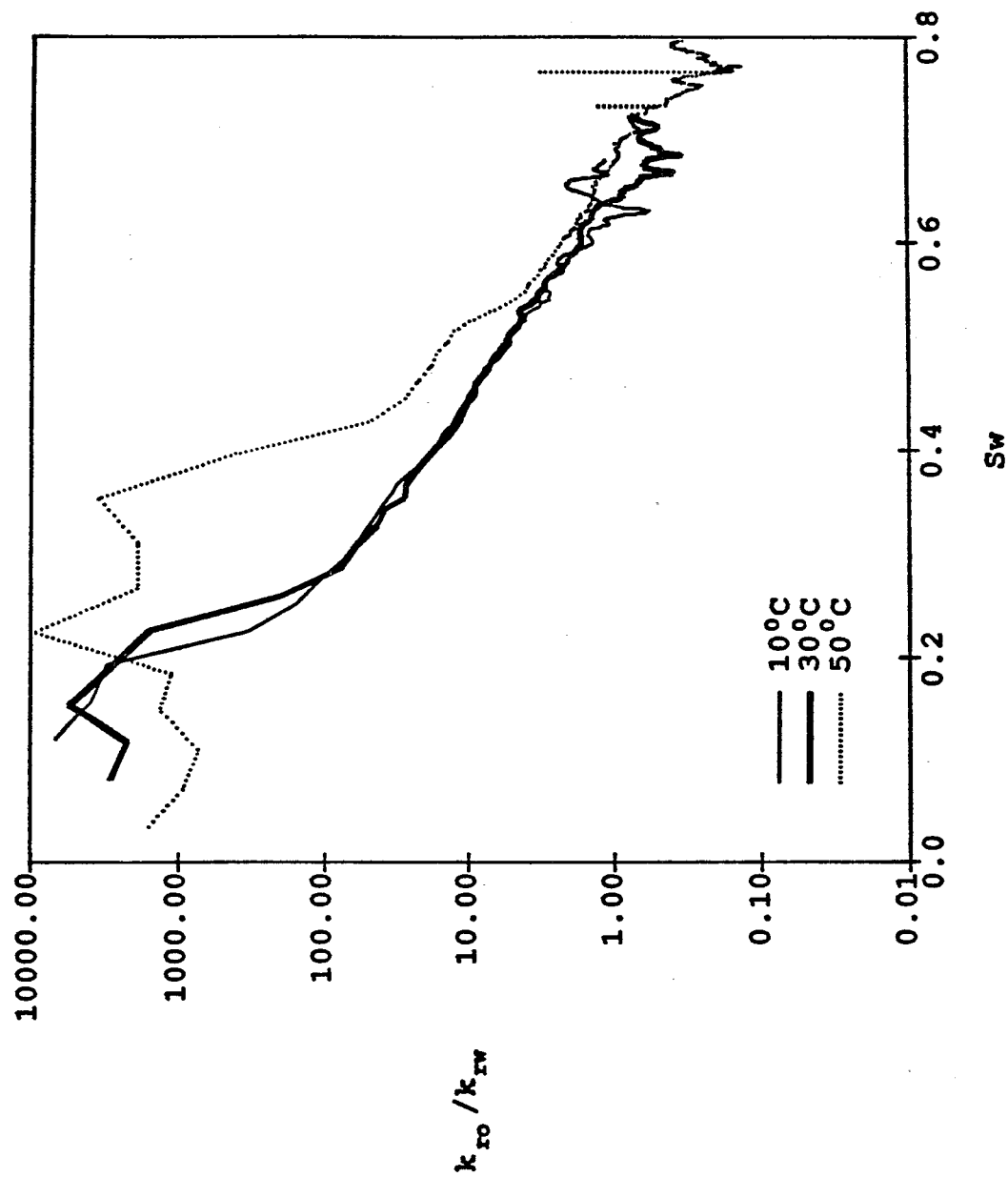


Figure 28. Permeability ratio (k_{ro}/k_{rw}) versus water saturation for the mixed sand at temperatures of 10, 30 and 50°C as determined by the Welge (1952) method from the constant temperature displacement data.

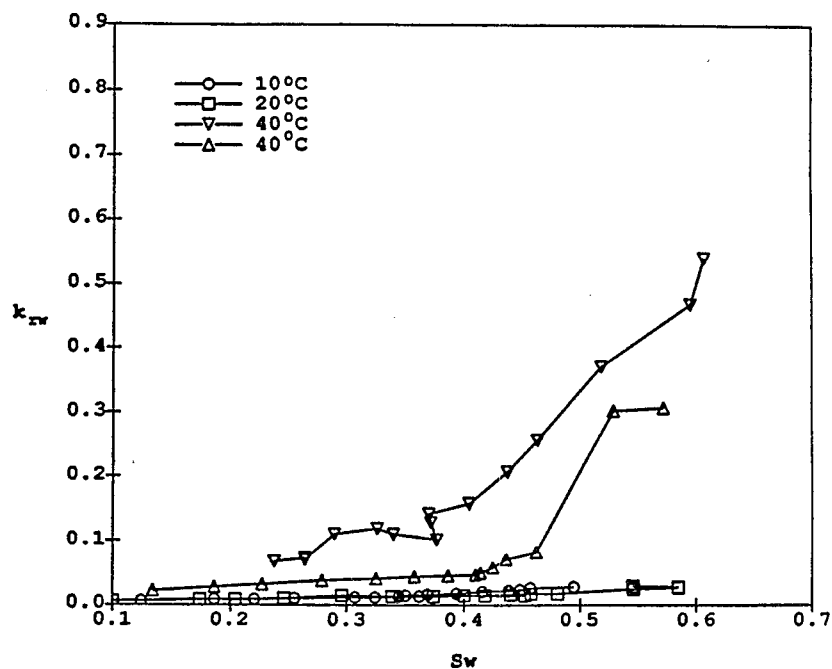


Figure 29A. Relative permeability to water versus water saturation for the 20/30 sand at temperatures of 10, 20 and 40°C as determined by the method of Jones and Roszelle (1978) using the constant temperature displacement data.

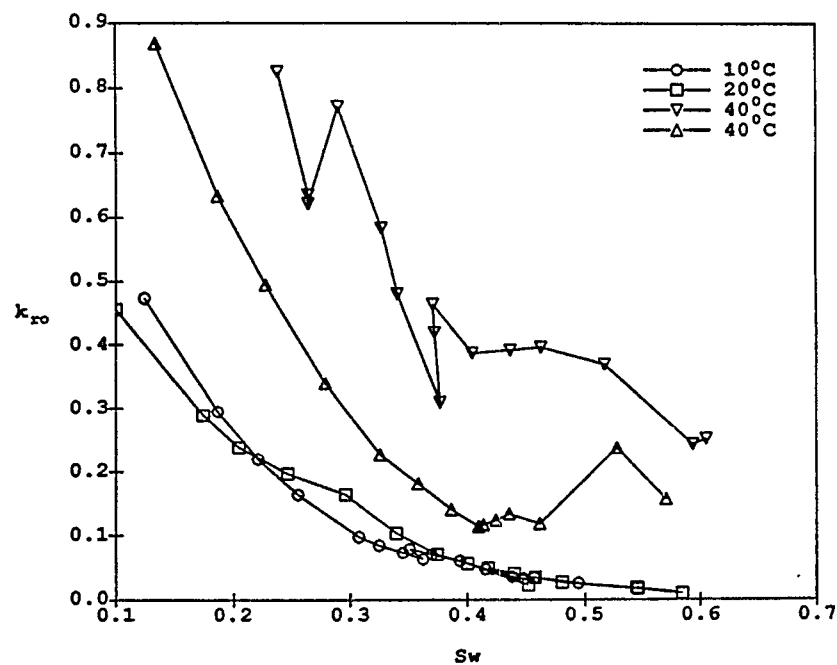


Figure 29B. Relative permeability to oil versus water saturation for the 20/30 sand at temperatures of 10, 20 and 40°C as determined by the method of Jones and Roszelle (1978) using the constant temperature displacement data.

Figures 30A and B, respectively. For the 20/30 sand, there is no measurable temperature effect on the oil and water permeabilities when going from 10 to 20°C (see Figures 29A and B). However, the permeabilities calculated for 40°C are significantly higher than those at lower temperatures. Also, the two duplicates at this temperature show significant variations between the experiments. The results for the mixed sand show better consistency for experiments run at the same temperature and, again, a significant increase in the relative permeability as the temperature is increased from 10 to 30°C.

The ratio of the relative permeabilities calculated from these individual relative permeabilities is shown in Figures 31 and 32. These figures show essentially no effect of temperature on the permeability ratios. When the ratios in Figures 31 and 32 are compared to the ratios determined from the Welge (1952) technique given in Figures 27 and 28, it can be seen that although the ratios as determined by the two methods are close at high water saturations, the ratios differ by approximately one and a half to two orders of magnitude at the lower water saturations. It is difficult to determine which method is more accurate just based on these calculations.

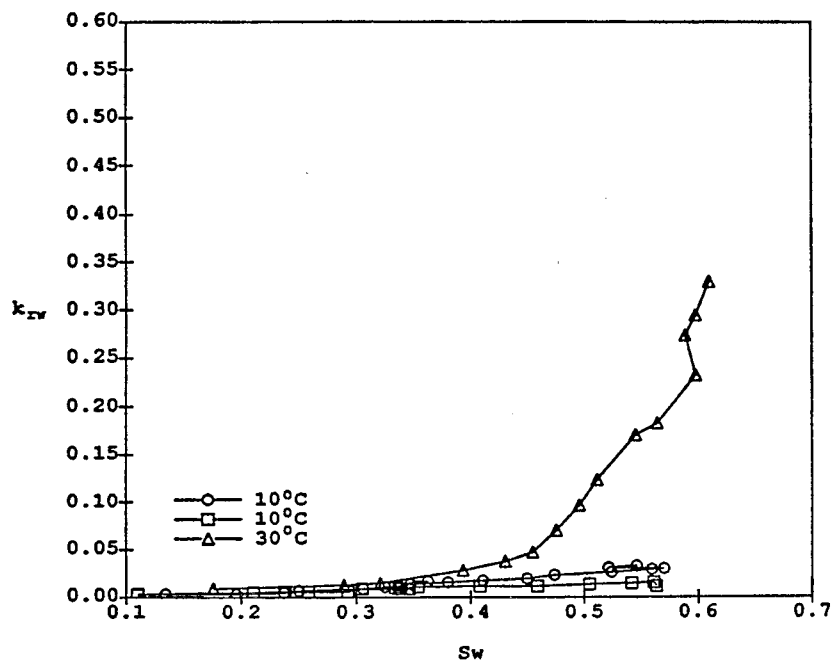


Figure 30A. Relative permeability to water versus water saturation for the mixed sand at temperatures of 10 and 30°C as determined by the method of Jones and Roszelle (1978) using the constant temperature displacement data.

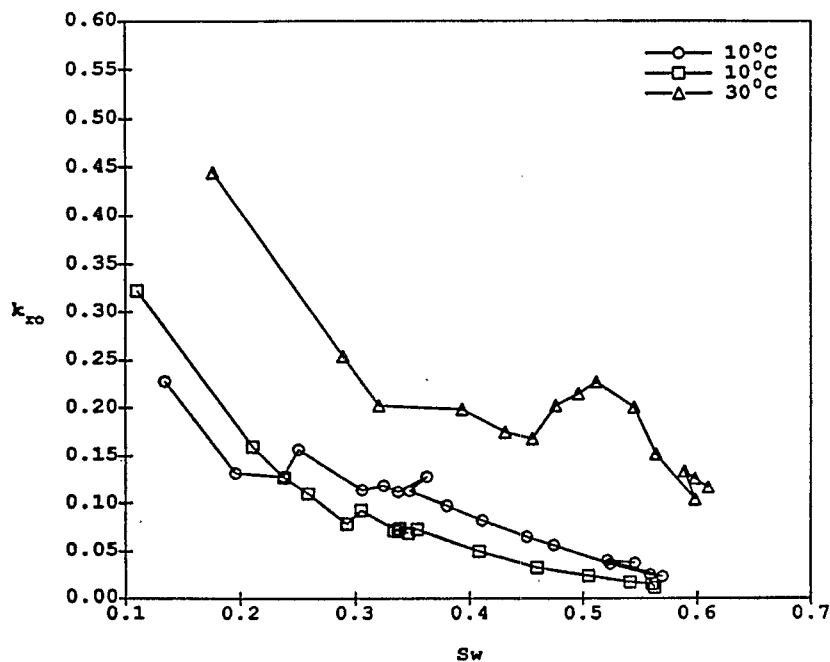


Figure 30B. Relative permeability to oil versus water saturation for the mixed sand at temperatures of 10 and 30°C as determined by the method of Jones and Roszelle (1978) using the constant temperature displacement data.

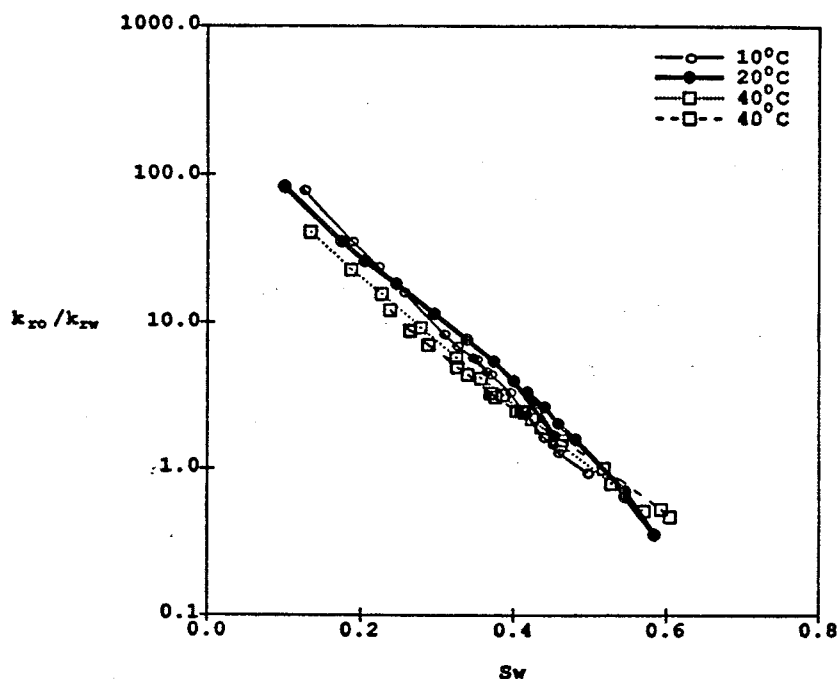


Figure 31. Permeability ratios (k_{ro}/k_{rw}) versus water saturation for the 20/30 sand at temperatures of 10, 20 and 40°C as determined by the method of Jones and Roszelle (1978) using the constant temperature displacement data.

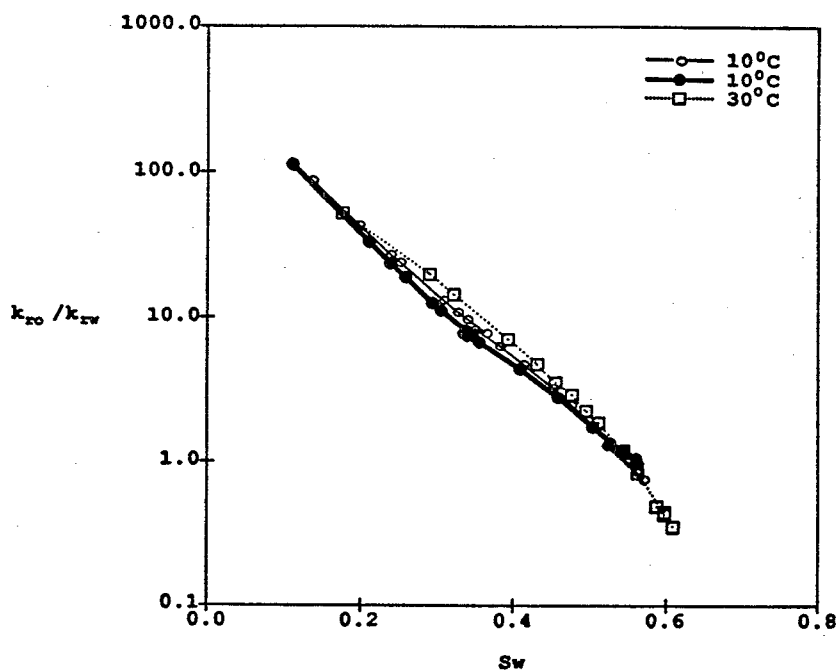


Figure 32. Permeability ratios (k_{ro}/k_{rw}) versus water saturation for the mixed sand at temperatures of 10 and 30°C as determined by the method of Jones and Roszelle (1978) using the constant temperature displacement data.

SECTION 5

SIMULATION OF EXPERIMENTAL RESULTS

Modeling of the displacement process can aid in predicting the results of a displacement to be expected with different soils or different properties of the oil and water, and can therefore help in determining if the process of hot water displacement can be expected to be beneficial for a given system and the optimum conditions for the displacement. However, fully describing the heat and fluid flow, even in a one-dimensional displacement, would require a sophisticated numerical simulator. Time constraints on this project did not allow the development of such a simulator. Therefore, modeling efforts were limited to the use of the Buckley-Leverett (1942) equation in an attempt to describe the oil recovery from the displacement processes at constant temperatures.

Integration of the Buckley-Leverett equation, which is given as equation 1, with respect to time yields

$$(X)_s = \frac{Q_d(t)}{\phi A} \left(\frac{dF_w}{ds} \right)_s \quad (7)$$

where A is the cross-sectional area of flow and all other terms are as defined previously. If the conditions of negligible capillary pressure and gravity effects are met, then the fractional flow function, F_w , can be estimated as given in equation 2. Examination of this equation shows that the properties of the fluids and porous media that influence flow are the viscosity ratio of the fluids and their permeability ratio. The viscosities of the fluids were measured independently of the displacement experiments as a function of temperature. Determination of the permeability ratio, however, is not as straightforward. This ratio is a function of the saturation of each phase, and consequently must be determined over the range of saturations that occur during the displacement process. Two different approaches have been taken to calculate the permeability ratios as a function of saturation, one based on the results of the capillary pressure-saturation curves and the other based on the oil recovery data.

The first approach used was to predict the relative permeability to each phase based on the equation by Brooks and Corey (1964) and van Genuchten (1980) for the hydraulic properties of soils. The parameters needed for these equations have been estimated from the capillary pressure-saturation data and are listed in Table 5. Since the displacement of oil by water is a wetting process, the parameters for the wetting curves were used in all cases. Two different theories, that of Burdine (1953) and Mualem (1978), have been used to estimate the relative permeability functions based on the relationship for capillary pressure-saturation. Therefore, from the two sets of parameters in Table 5 for each of the sands, four sets of relative permeability versus saturation curves can be generated. In each case, the parameters used to estimate relative permeability are the exponent N , the residual water saturation, and the residual oil saturation (i.e., the maximum water saturation). Although both the Brooks and Corey and van Genuchten equations fit the retention data quite well, the permeability ratios and the oil recovery predicted by these equations are very different. Since very few measurements of relative permeability versus saturation have been made for systems of interest in oil contamination situations, it is not known which of these expressions yields the best estimates of relative permeability.

Examples of the permeability ratios are shown in Figure 33. These ratios were calculated using the average parameters found for the 20/30 and mixed sand for a water/oil system at 10°C. The theory of Burdine was used with the Brooks and Corey equation to develop the expressions for relative permeability and the theory of Mualem was used with the van Genuchten equation, as the oil recovery curves generated using these expressions were found to come closer to the experimental curves. For all the parameters used, the curves for the permeability ratios generated by the Burdine and Mualem

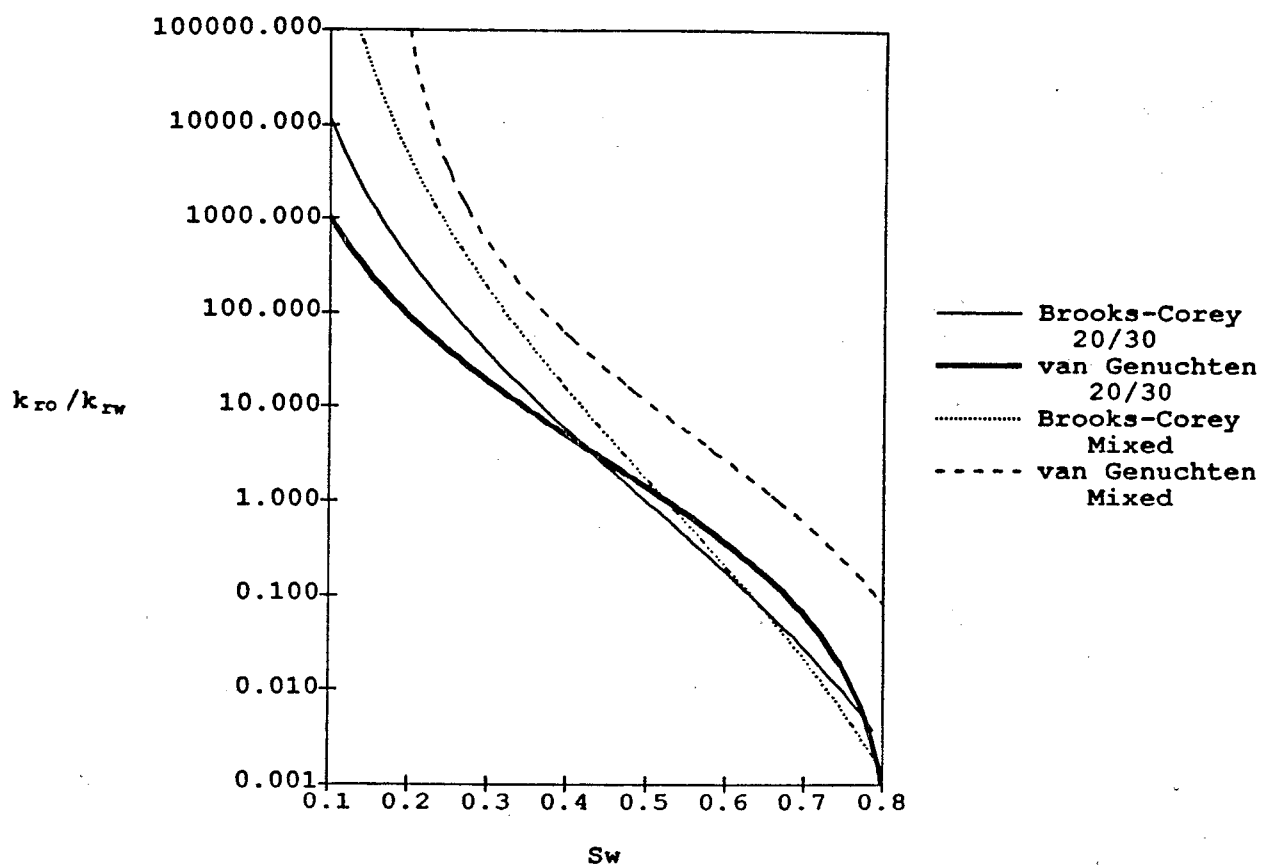


Figure 33. Permeability ratios (k_{ro}/k_{rw}) versus water saturation for the 20/30 and mixed sands as determined using the Brooks and Corey (1964) equation and the theory of Burdine (1953) and the van Genuchten (1980) equation and the theory of Mualem (1978) and the parameters determined from the capillary pressure-saturation data.

theories for the same set of parameters are basically parallel to each other and slightly offset. The Brooks and Corey equation always generates the steeper ratio of permeabilities, which seems to lead to oil recovery curves in which little oil is predicted to be recovered after breakthrough. The less steep ratio curve generated by the van Genuchten equation produces greater oil recovery after breakthrough. It appears that lower permeability ratios at low water saturations produce earlier breakthroughs.

When these simulated oil recovery curves are compared to the experimental curves at 10°C (see Figures 34 and 35), it can be seen that none of these permeability ratios, when used with the fractional flow function defined by equation 2 in the Buckley-Leverett equation, can simulate the experimental curves with a good degree of accuracy. For the 20/30 sand, the recovery predicted by the van Genuchten equation using the theory of Mualem after the injection of approximately 10 pore volumes is close to that determined in the laboratory, but the predicted breakthrough is much later than was found in the experiments. For the mixed sand, the simulated curve does not fit the data well at breakthrough or after the injection of 10 pore volumes.

The relative permeability ratios were also calculated based on the average parameters found in the pressure-saturation curves for the sands at 30°C. These ratios show a shift to higher ratios for a given saturation. This shift in the permeability ratio will predict greater oil recoveries when used in the Buckley-Leverett equation.

The second approach taken was to use the permeabilities ratios and the permeability to each phase calculated from the displacement data to calculate the fractional flow function in the equation. To do this, a straight line on a semi-log scale was fit to the permeability ratio data by linear regression and this equation was used to calculate the permeability ratio-saturation relation within the fractional flow function. Because there are a large number of data points for the permeability ratio generated by the Welge method and most are at high water contents, interpolation was used to calculate the ratios at saturation intervals of 0.025 over the range of saturations in the column during the displacement, and these values were used for a least-squares regression to determine the line that best fit the data. For the Jones and Roszelle estimates of relative permeability, all the data points were used in the linear regression analysis.

The permeability ratios calculated from the individual permeabilities that were determined using the method of Jones and Roszelle (Figures 31 and 32) did not produce oil recovery curves using the viscosity ratio at 10°C. Mathematically, the low permeability ratio at high water saturations produces such a low flow of oil that the water cannot displace it from the column. The higher permeability ratios found by the Welge method does produce oil recovery curves, and these oil recovery curves are also shown in Figures 34 and 35. These ratios also predict a much later breakthrough than was found in the laboratory experiments and significantly greater recoveries after the injection of 10 pore volumes of water.

The most obvious possible reason for the lack of agreement between the measured and simulated oil recoveries at 10°C is that there were significant capillary pressure gradients in the columns during the experiments, which are not accounted for by the Buckley-Leverett equation. However, a comparison of the capillary pressure saturation curves for these sands with the measured pressure drop along the column during the displacements show that the pressure drop along the column was significantly greater than any capillary pressure gradients that were present. Another possibility is that the waterfloods were not stabilized, even though the scaling criteria proposed by Rapoport and Leas (1953) was met. A third possibility is the occurrence of fingering during the displacements which would account for the earlier breakthrough. Additional work is needed to be able to incorporate the effects of capillary pressure gradients into the mathematical expressions, either by a method similar to that used by Quettier and Corre (1988), or that used by McWhorter and Sunada (1990).

Despite these problems, some qualitative information can still be gained from these simulations, since the simulated oil recovery curves based on either approach are qualitatively consistent with the laboratory results in the respect that greater recoveries are predicted for the mixed sand than for the 20/30 sand. When the permeability ratios found for 10°C are used to predict oil

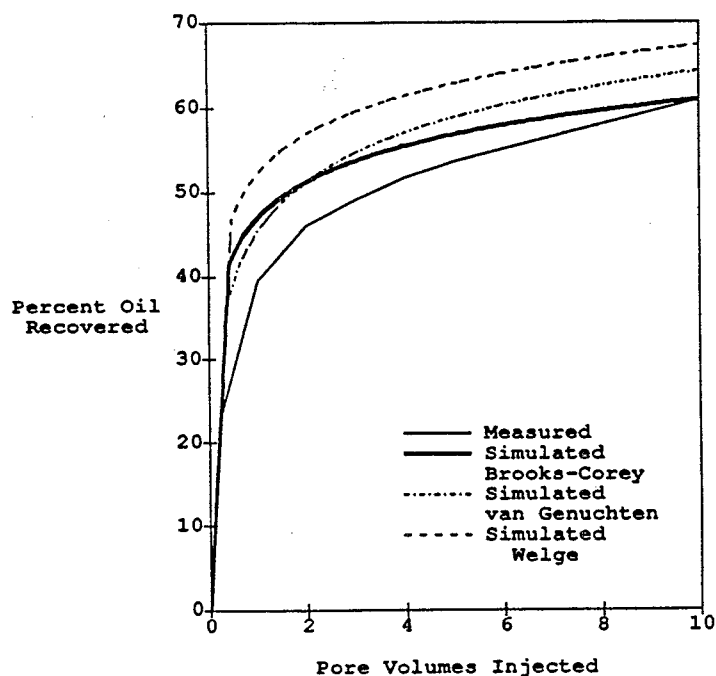


Figure 34. Measured oil recovery curve versus water injected for the 20/30 sand at 10°C and the simulated oil recovery curves using permeability ratios generated by the Brooks and Corey (1964) and van Genuchten (1980) equations and the Welge (1952) method.

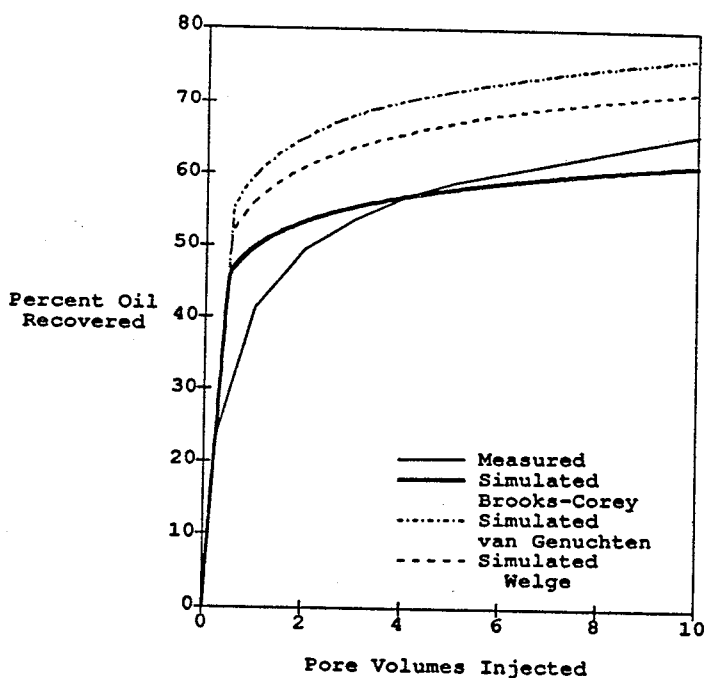


Figure 35. Measured oil recovery curve versus water injected for the mixed sand at 10°C and the simulated oil recovery curves using permeability ratios generated by the Brooks and Corey (1964) and van Genuchten (1980) equations and the Welge (1952) method.

recovery at higher temperatures by adjusting the viscosity ratio, the degree of additional oil recovery that is predicted is not as great as that found in the laboratory experiments. When these equations for the permeability ratios were used in an attempt to actually simulate the laboratory experiments by taking into account the initial water saturations at the start of the displacements, the predicted increases in oil recovery with temperature are significantly lower than was found in the laboratory displacements. Therefore, there appears to be something besides the more favorable viscosity ratios contributing to the greater oil recoveries at higher temperatures.

A few simulations were performed using the permeability ratios determined by the Welge method for the 20/30 sand at the higher temperatures. These simulations showed that the higher permeability ratios for low water saturations found at higher temperatures predict greater oil recoveries at a given viscosity ratio than are predicted by the permeability ratios found at 10°C. Thus, it appears that the higher permeability ratios can contribute to an increase in oil recovery at higher temperatures.

SECTION 7

CONCLUSIONS

These experiments have shown that the use of hot water will increase the recovery of oils from sands over that which can be recovered using a waterflood at ambient temperatures. The increase in oil recovery found over the moderate temperature range studied here was approximately 17 to 22 percent for both a very uniform silica sand and a second silica sand with a somewhat larger range of grain sizes. This reduced the residual oil saturation remaining in these sands after 10 pore volumes of water throughput from 0.39 to 0.30 for the 20/30 sand, and from 0.33 to 0.23 for the mixed sand. These are approximately 25 to 30 percent reductions in the residual oil saturations. However, even the residuals of 23 to 30 percent of the pore space found in 50°C constant temperature displacements would probably require additional treatment, such as bioremediation.

The transient temperature experiments showed that the benefits of hot water injection in terms of the amount of oil recovered can be achieved under conditions more closely resembling those found in the field. This increase in recovery occurs even though the temperature data from these displacements show that very little heat is transferred in front of the hot water bank. The maximum pressure reached in the transient temperature experiments, which occurred just before water breakthrough, was approximately the same as that measured in the ambient temperature experiments, however, the pressure drop during the subordinate phase of the displacement is significantly smaller than in the ambient temperature displacements. Therefore, the benefits of hot water on the pressure needed to drive the displacement are not realized until the latter part of the displacement.

Permeability ratios were estimated from both the capillary pressure-saturation relationship and the displacement data. Although permeability ratios calculated by the method of Jones and Roszelle (1978) show essentially no effect of temperature, the ratios calculated based on the capillary pressure-saturation curves and from the displacement data based on the method of Welge (1952) show a shift to higher ratios (in terms of k_r/k_w), at least at low water saturations. These results are consistent with those of Davidson (1969) and Sinnokrot et al. (1971). These permeability ratios were used in an attempt to simulate the experimental results for the constant temperature displacements, but simulations using the Buckley-Leverett equation with the assumption that capillary pressure effects are not significant in the column were not successful in predicting the laboratory results. However, qualitative observation of the results of the simulations shows that the predicted increase in oil recovery as the temperature is increased based just on changes in the viscosity ratio does not appear to account for all of the increase in oil recovery that was observed in the displacement experiments. The permeability ratio shifts that were observed at higher temperatures will contribute to increased recoveries. However, until better predictions of oil recovery can be made, the total cause of the increased recoveries cannot be determined.

This one-year laboratory research project, even when combined with the knowledge gained from previous research, still leaves many areas where further research is needed in order to fully understand the effects of heat on the displacement process and how the process will work in the field. This research involved the use of ideal soil conditions, i.e., homogeneous sands which contained no clays or organic matter, and which had very little variation in grain sizes. Thus, the wettability of the media was uniform. Additional laboratory research is needed with other oils and porous medium to get a better understanding of how much might be gained from the addition of heat to the displacement process and to determine under what conditions of oil properties and porous media properties these gains can be made. The effects of heterogeneity, the presence of clays and organic matter, and nonuniform wetting properties of the soils need to be assessed. Additional effort should be made also in simulating the displacement process, both in terms of describing the multiphase displacement process and in describing heat flow in the system. A closely related area deserving of additional research is the addition of inorganic chemicals such as salts, acids or bases, in the hot

water, which in some cases can alter the wettability of the system and/or its interfacial tension and may further enhance the displacement process.

The use of hot water displacements can be extended to field demonstration trials or, as an intermediate step, to the testing of contaminated field cores in the laboratory. A couple of potential problems in extending the technique to the field are soil heterogeneity, which would limit the contact between the displacing fluid and the oil, and the heat losses that occur as the water is injected into the subsurface and moves through it. These concerns can only be addressed by testing actual field cores and under actual field conditions.

The wide range of contamination problems facing those involved in subsurface restoration will require a variety of remediation techniques in order to deal with the problems effectively and efficiently. Thermal methods such as hot water displacements of oily contaminants is one technique which should be useful in some situations. Hot water displacements should be considered where there is a free immiscible phase present that is viscous and essentially nonvolatile. Highly viscous oils are likely to show a significant decrease in viscosity with increasing temperature, thus a greater increase in recovery can be expected when hot water is used. Volatile organics are likely to be recovered more readily in the gaseous phase than the liquid phase, thus another type of heat process may be of greater benefit when highly volatile organics are to be recovered. Hot water and steam displacements have significant advantages over some other remediation techniques which are being researched currently in that they do not require the addition of new potential contaminants to the subsurface, as is required when surfactants or cosolvents are used. Also, hot water when used with light oily wastes should be able to direct the displacing water and any chemicals it may contain to the oil that is to be recovered due to buoyancy effects. Additional recovery from fine materials may be possible by using hydrofracturing in conjunction with the application of hot water. Although hot water displacements cannot remove all the oily contaminant and the residual oil left behind will often require additional treatment, using hot water displacement as a first step in remediation can greatly reduce the contamination level, leaving behind a residual oil that may be amenable to processes such as bioremediation.

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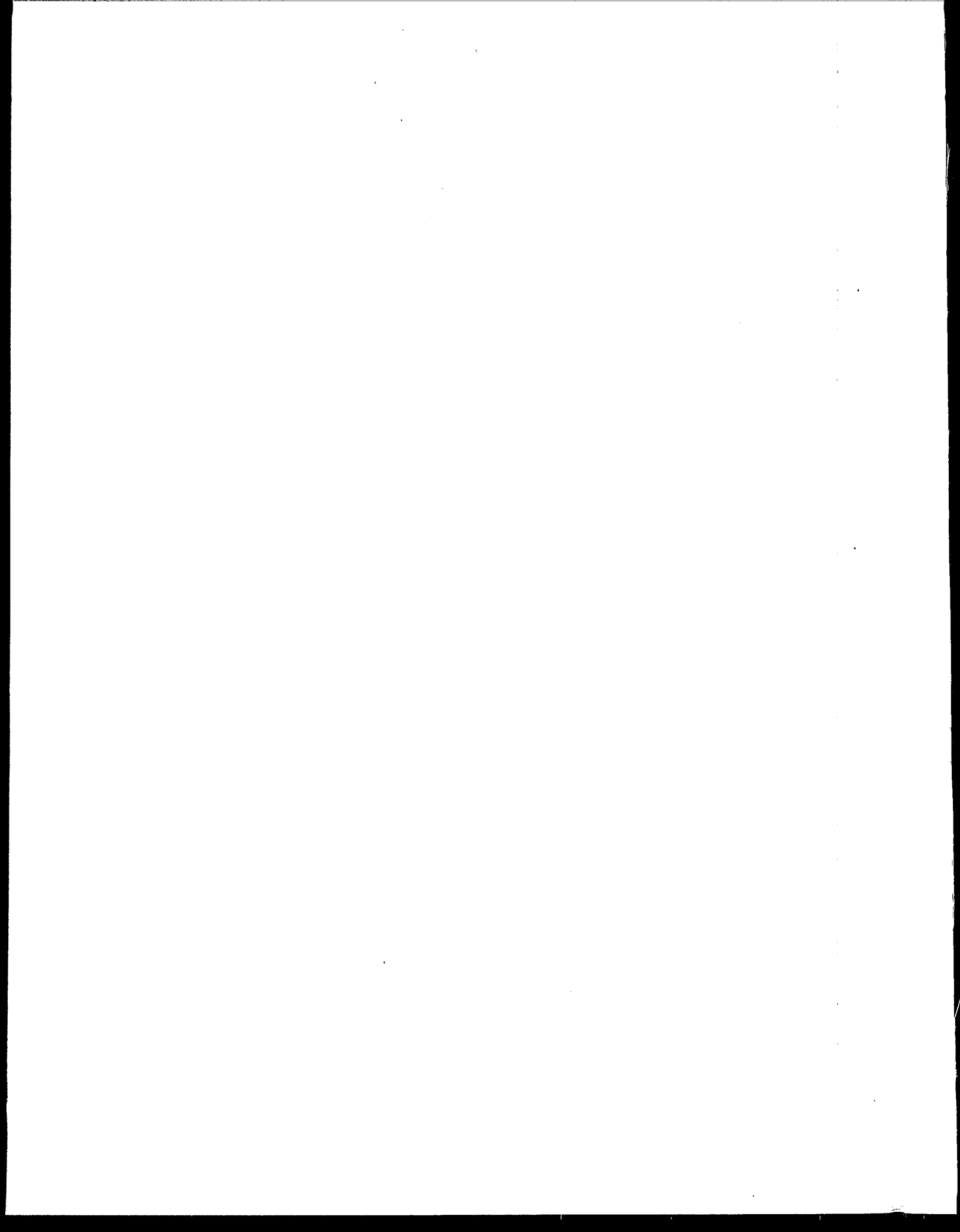
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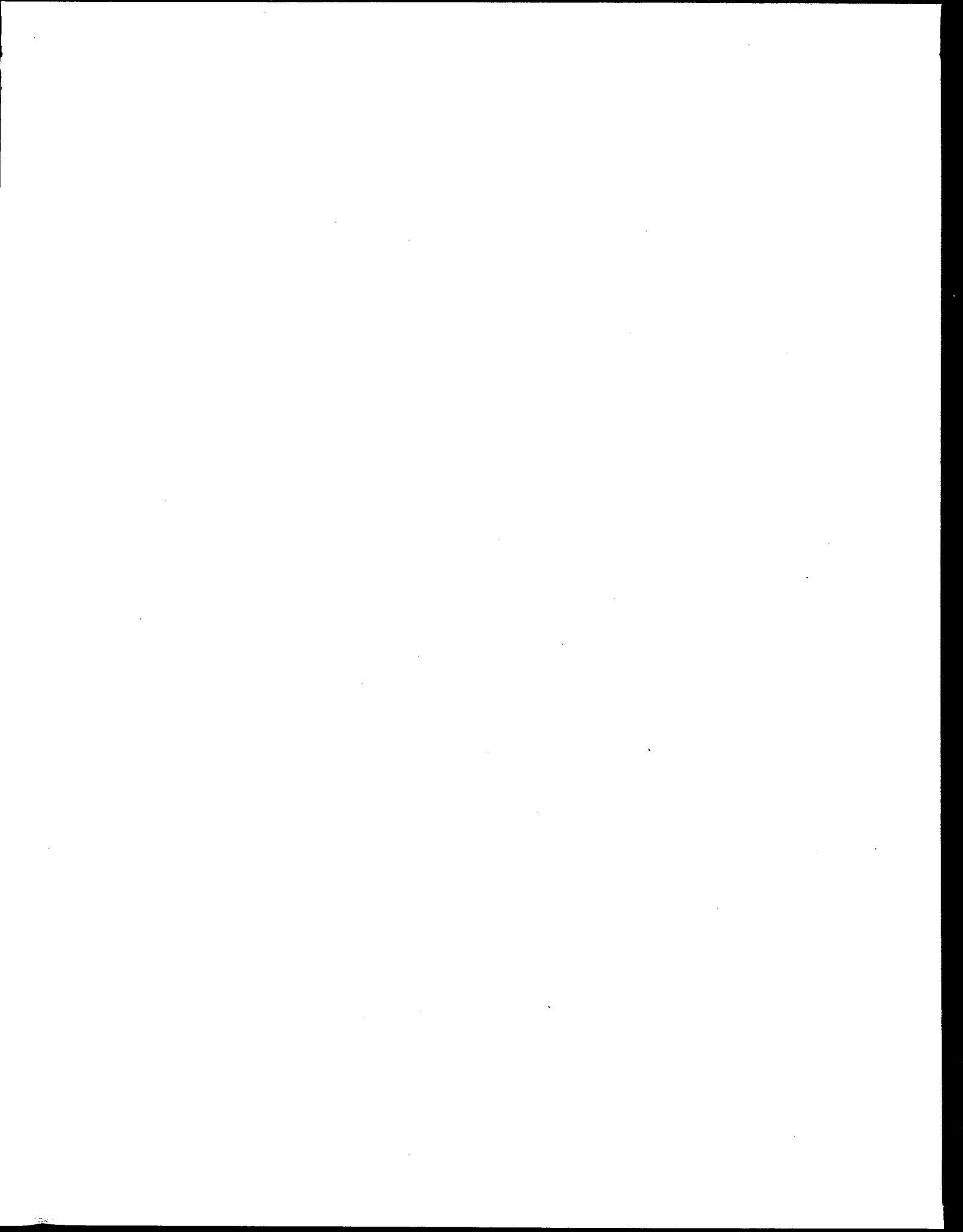
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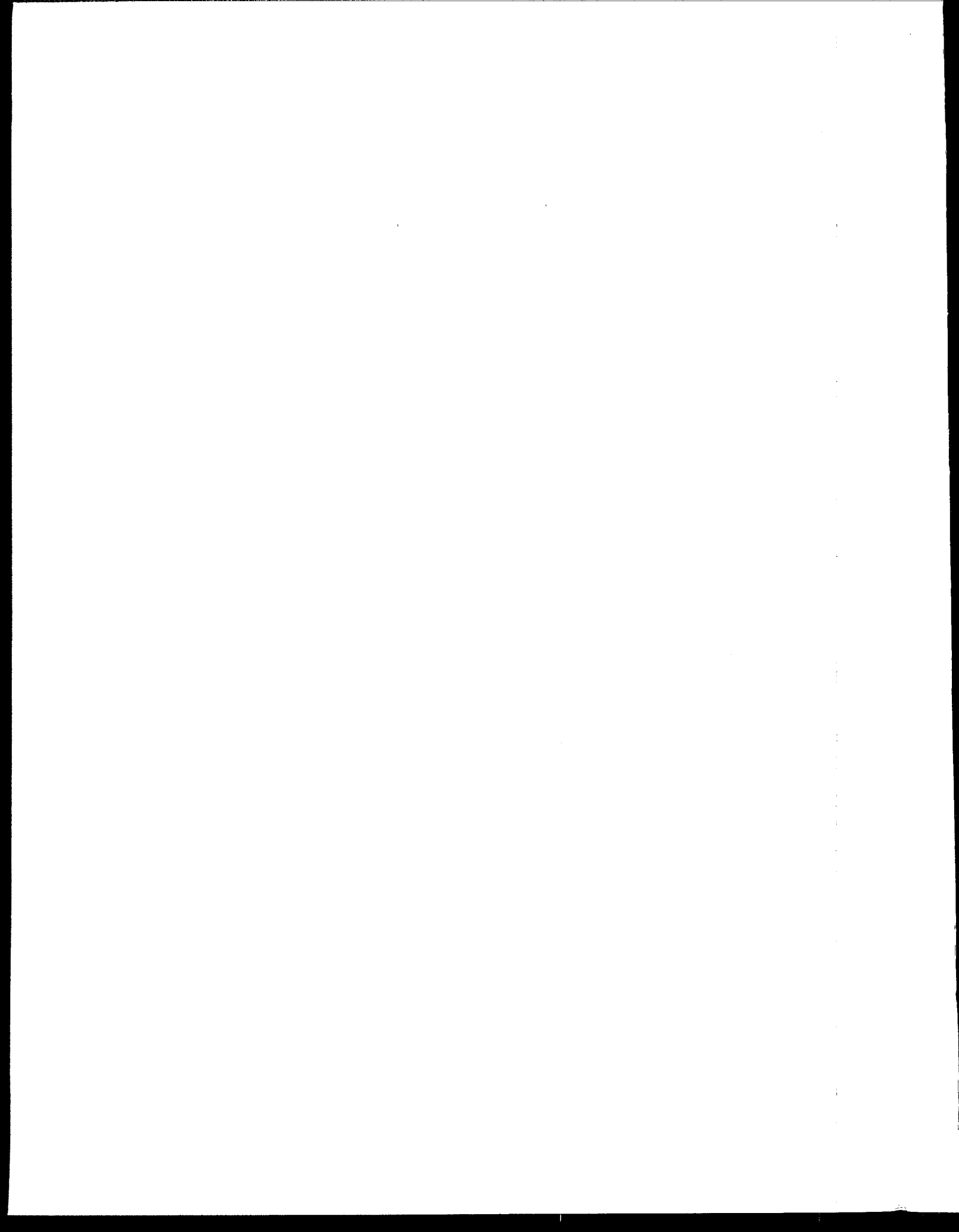
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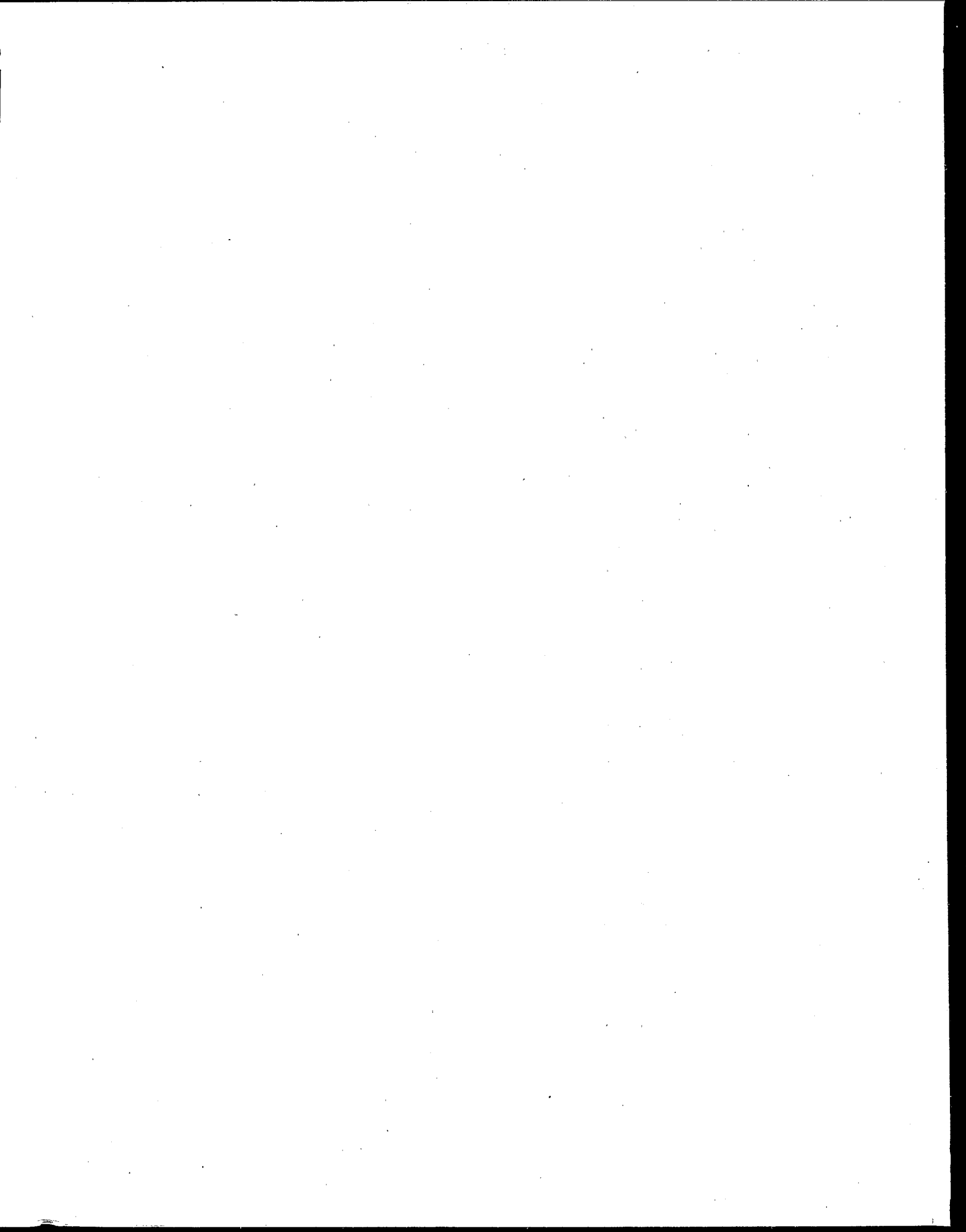
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