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AN EXPERIMENTAL INVESTIGATION ON THE USE OF A CAUSTIC-NITROGEN INJECTION PROCESS IN A WATERFLOODED OIL RESERVOIR

The University of Oklahoma PH.D. 1982

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AN EXPERIMENTAL INVESTIGATION ON THE USE OF A CAUSTIC-NITROGEN INJECTION PROCESS IN A WATERFLOODED OIL RESERVOIR

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY

TSAY, SIUH-CHUN

Norman, Oklahoma
1982

AN EXPERIMENTAL INVESTIGATION ON THE USE OF A CAUSTIC-NITROGEN INJECTION PROCESS IN A WATERFLOODED OIL RESERVOIR

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ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. D. E. Menzie, who served as advisor in this research, for his continued support, interest and guidance in the completion of this effort.

Appreciation is also expressed to Dr. R. M. Knapp, Director of The School of Petroleum and Geological Engineering, for his invaluable constructive criticisms regarding this research.

Acknowledgment is expressed to Dr. D. Tiab, Associate Professor of Petroleum and Geological Engineering, Dr. M. Townsend, Professor of Chemical Engineering, Dr. A. W. McCray, former professor of Petroleum and Geological Engineering, for their being members of the dissertation committee.

Invaluable assistance was provided by Mr. N. S. Knight for equipment repair, revision, and maintenance. His skill was always available when problems developed. Appreciation is also extended to Mr. Paul C. C. Chao, Engineer of Cities Service and an old friend of mine, for his help in aquisition of the crude oils used in this study.

Finally, I would like to express my appreciation to my wife Hsu-Ling (Julie), who handled all of the manuscript typing. Her encouragement and patience, along with that of my daughter Chin-Hsiun (Alice) and my son Chin-Hong (Henry), made this academic goal possible.

Tsay, Siuh-Chun

ABSTRACT

This study intends to investigate the recovery mechanisms involved in the use of the modified alkaline-nitrogen injection as one means to improve the oil recovery for a waterflooded oil reservoir.

In the specially designed experiments, consolidated Berea Sandstone cores were saturated with brine and flooded with a light oil and the waterfloods were conducted until the waterflood residual oil saturations were stabilized. Different improved oil recovery processes including alkaline injection, acidic oil slug injection, and intermittent nitrogen injection then followed.

To interpret the mechanisms encountered in recovering the residual oils, different combinations of the processes mentioned above were applied on each new core. The recovery mechanisms were then examined with the context of the effect of the pore size distributions, as indicated by relating the injection pressure gradient and the capillary number to the residual oil saturation.

A mathemetical expression, which relates the injection pressure gradient and the capillary number to the specific surface area per pore volume, was developed and used as a

theoretical basis for interpreting the recovery mechanisms encountered in removing the residual oil.

The experimental results indicated that the recovery of the residual oil is mainly dominated by the Jamin Effect, and the selective plugging of the flooded pore paths provides the necessary mechanism to overcome the Jamin Effect which prohibits the residual oil from moving. Results also showed that under proper conditions, the dispersed clay particles and the alkaline-oil emulsions formed in-situ can effectively plug the flow paths of smaller capillaries, while the nitrogen bubbles created from the nitrogen injections can sucessfully plug the flow paths of larger capillaries.

When the temperature increases from 78° F to 150° F, it was found that in the recovery processes we used, the recovery mechanisms for removing the waterflooded residual oil shifted from the capillary force domination to the viscous force domination. It was also found that even under such a different recovery condition, the alkaline-nitrogen injection process still yielded the optimal recovery.

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AN EXPERIMENTAL INVESTIGATION ON THE USE OF A CAUSTIC-NITROGEN INJECTION PROCESS IN A WATERFLOODED OIL RESERVOIR

CHAPTER I

INTRODUCTION

Waterflood has been in use since 1865, and by far the simplest of secondary recovery methods. Unfortunately, most waterfloods are inefficient in recovering oils, often leaving half or more of the original oil inplace unrecovered.

The low efficiency in waterflooding generally results from low sweep efficiency and low displacement efficiency; consequently, to increase oil recovery by waterflooding, sweep and displacement efficiencies should be improved.

Sweep efficiency is primarily affected by reservoir heterogeneities and mobility ratio, while displacement efficiency is affected by capillary forces between fluids and rock surfaces, expressed in terms of interfacial tension and wettability. A number of materials, such as cement, ground leather, and ground limestone, have been used in wellbore treatments to improve injection profiles in water-injection wells.[37] However, even if such treatments effect a better distribution of water in the formation at the wellbore, they are unlikely to be successful because of cross-formation flow near the wellbore. Silica gel, rubber latex, and asphalt have been tested as deeper-penetration plugging agents in attempts to decrease reservoir heterogeneity.[37]

One way to reduce capillary forces is to inject surfactants ahead of injection water into the reservoir. Yet, laboratory tests of this method showed no promise of its being an economical process. Another way to change capillary forces operating in a reservoir is to change the PH of the injected water. The change in PH may sometimes activate the surface-active materials natural to some crudes, and bring about gross wettability change.

The PH alteration can be obtained with cheap chemicals. Injection of an alkaline solution is one of the approaches which has been actively pursued by the oil industry to provide the useful mechanisms for the improved oil recovery. In a water-wet reservoir, there are two primary mechanisms available in alkaline floods, (1) the drastic reduction of oil-water interfacial tension by the caustic activation of potentially surface-active organic acids naturally occurring in the crude oil. The reduction of interfacial tension causes emulsification of crude oil in-situ that tends to lower injected water mobility, to dampen the tendency toward viscous fingering, to slow water channeling caused by reservoir heterogeneity, and to improve conformance or sweep efficiency, and (2) if the composition of crude oil is favorable, and under proper conditions of PH, salinity, and temperature, the wettability can be reversed. A discontinuous non-wetting residual oil is converted to a wetting phase, providing a flow path for what otherwise would be trapped oil. At the same time, lower interfacial tension induces the formation of an oil-external emulsion of water droplets in the continuous, wetting oil phase. These emulsion droplets tend to block the flow and induce a high pressure gradient in the region where they form. The high pressure gradient, in turn, is said to overcome the capillary forces already decreased by low interfacial tension, thus reducing oil saturation further.[13]

In a waterflooded oil reservoir, direct application of the mechanisms described above is unlikely to be possible since the oils in most of the waterflooded oil reservoirs do not provide enough surface-active organic acids to be active in the cautic solutions. And furthermore, the unrecovered oils are isolated in the pore paths so that the injected alkaline solution would bypass through the flow paths which have already been created by the waterflooding; therefore, to improve the oil recovery in the waterflooded oil reservoirs, modifications must be made so that the alkaline process can be applied.

One of the modifications, as described by McAuliffe,[37,38] is the injection of oil-in-water emulsion prepared externally. A field trial of emulsion injection was reported in 1973, and showed increased oil recovery and lower WOR's. Water tracer studies also showed that the sweep efficiency was significantly improved.

A simpler and more practical approach to the application of the emulsification-entrapment mechanism is the injection of an acidic oil slug followed by the injection of an alkaline solution of proper concentration.

If the oil slug contains enough surface-active organic acids, in-situ emulsification will occur. Similar improvement in sweep efficiency should be obtained in the porous media. However, it is obvious that the size of the injected oil slug must be so designed that it will yield the optimum sweep efficiency, and thus improvement in oil recovery can be economically justified.

As one can see that higher concentrations of caustic solution are required for the mechanism of wettability reversal (usually 0.5 wt. % to 15 wt. %, compared to 0.001 wt. % to 0.5 wt. % for emulsification and entrapment), and that the content of surface-active materials in the oil are limited even if an external oil slug is injected. It is very unlikely that the mechanism of wettability reversal can be utilized besides the emulsification-entrapment mechanism.

In addition to the mechanisms available in caustic floods, nitrogen injection could be one of the most favorable processes for improving the recovery of residual oil saturation. It has long been recognized that the waterflood residual oil can be reduced by the presence of a gas phase. Flooding with miscible gases, such as carbon dioxide and light hydrocarbons, is a proven enhanced oil recovery method. However, wide application may be limited by the availability and/or the cost of these materials. Carbon dioxide from natural deposits is in limited supply. Carbon dioxide from other source (e.g., coal gasification and power plant stack gas) is more expensive, and involves a long lead time. Natural gas and the hydrocarbons required to enrich it are expensive, at least in the United States. Above all, in most of the miscible processes, high pressure is generally required, which presents more problems for its applicability.

A universally available possible substitute for these fluids is nitrogen. Nitrogen does not develop miscibility with crude oils unless at very high pressures. However, at less than miscibility pressure, one would expect that some of the mechanisms in immiscible process would be operative. At still lower pressure, one would expect that at least the mechanism of immiscible displacement of oil by gas would be available.

It is the purpose of this study to investigate the interrelated effects of the nitrogen injection and the modified caustic injection in improving the oil recovery of a waterflooded oil reservoir. The results of this study should furnish information necessary for planning an effective economical alkaline process for a waterflooded oil reservoir.

CHAPTER II

LITERATURE REVIEW

The first patent on caustic flooding for improved oil recovery was issued in the United States in 1927. Since then, extensive published records of research and field testing have been accumulated.

In general, a waterflooded oil reservoir is usually considered not to be favorable for an ordinary alkaline flood because of the lack of sufficient surface-active organic acids content. However, understanding of the mechanisms available in the traditional alkaline processes may help design a useful economical alkaline process for waterflooded oil reservoirs.

There are now several proposed mechanisms by which caustic flooding may improve oil recovery. These include (1) emulsification and entrainment, (2) wettability reversal from oil-wet to water-wet, (3) wettability reversal from water-wet to oil-wet, and (4) emulsification and entrapment.

Each mechanism requires somewhat different initial conditions with respect to both oil and the injection water properties; each process is designed to improve the oil recovery in a somewhat different manner.

Application of The Mechanism of Emulsification and Entrainment

In 1942, Subkow[32] proposed an alkaline process to remove the bitumen from the bitumenous deposits. The proposed process involved the use of the caustic solution to activate the in-situ emulsification of the crude oil to produce the alkaline-oil emulsions; as a consequence, the emulsions were then entrained and produced by the continuously injected alkaline solution. He was also granted a United States patent for this process.

In 1956, Reisberg and Doscher,[54] in studying the interfacial behavior of the crude-oil-water system of the Ventura crude, suggested that, besides the mechanism of emulsification and entrainment in the alkaline flood process, the formation of the rigid film at the interface of both the alkaline solution and the oil plays an important role in improving the oil recovery by preventing the adhesion of the oil to the dry sand surface.

Application of The Mechanism of Wettability Reversal from Oil-Wet to Water-Wet

In 1959, Wagner and Leach[66] presented laboratory tests showing improved oil recovery through the gross change in preferential wettability in the reservoir rocks. They suggested that such wettability changes can be accomplished by injecting water which contains simple chemicals to alter the PH or salinity in the reservoir; such chemicals could include acids, base, and some salts. For the system they studied, cores initially oil-wet were flooded in such a way that they were made preferentially water-wet by the advancing flood water. This reversal in preferential wettability achieved greater oil displacement efficiency than that when either oil-wet or water-wet conditions were maintained throughout the flood. Using acid in their experiment as a wettability reversal chemical, they recognized that the improvement in oil recovery resulted largely from the favorable changes in relative oil and water permeabilities. This change in permeability provided a more favorable mobility ratio; the improved mobility can halt the gradual increase in producing WOR. As an example of their research, Figure 2.1, taken from Wagner and Leach, shows one of their experimental results, where this improvement in WOR and the corresponding increase in recovery were observed as the wettability was reversed by the injected acidic water.

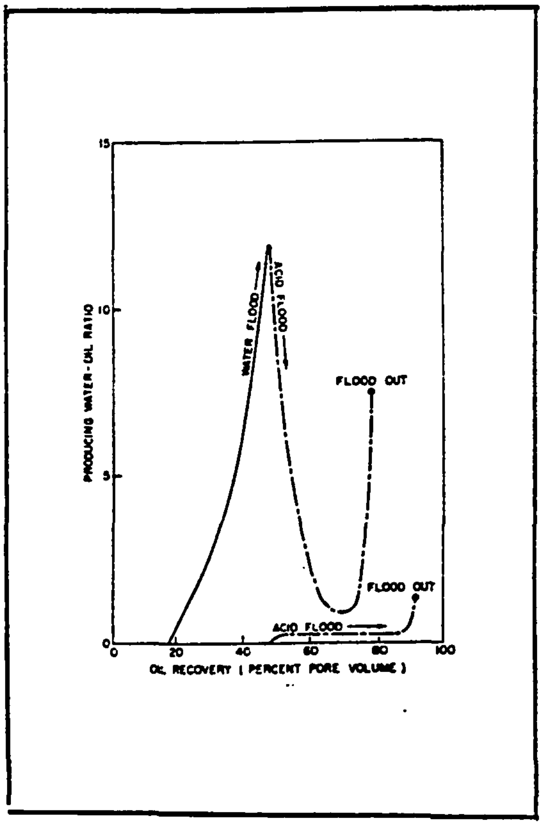

FIGURE 2.1- PRODUCTION PERFORMANCE OF NORMAL AND WETTABILITY REVERSAL WATER FLOODS OF UNCONSOLIDATED SANDSTONE CORES CONTAINING VISCOUS OIL. (Ref. 67)

In 1962, Leach and his colleagues conducted a field test in the Muddy "J" sand of the West Harrisburg Unit in Nebraska. Sodium hydroxide was injected as a slug of diluted caustic solution through a water injecting well. The field performance indicated that similar improvement in oil recovery was obtained because of the wettability reversal from oil-wet to water-wet in the reservoir rocks.[35]

In 1966, Mungan[44] published a laboratory work on wettability effects in caustic flooding. Restored oil-wet cores were used, and 0.5 N NaOH solutions were injected to recover the waterflood residual oil. The results indicated that at a reservoir temperature of 160° F, the formation can be reversed to water-wet rapidly and yield 11 to 15 percent PV of additional oil recovery. He also demonstrated that the water relative permeability was indeed lowered after the wettability was reversed from oil-wet to water-wet. As a result, this reversal yielded a more favorable water-oil mobility ratio even though the water saturation reached a higher value. Figure 2.2, taken from Mungan's paper, shows one of his experimental results in which the improvement in WOR responded with the increasing oil recovery due to the wettability reversal.

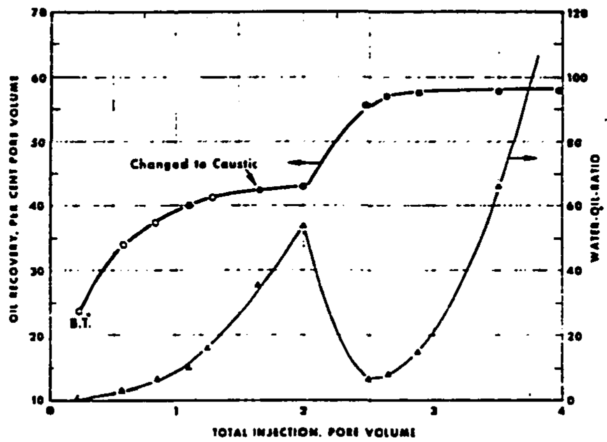

FIGURE 2.2- Wettability Reversal Flood in Watered-out Oil-Wet Core 7-1. (Ref. 44)

In the same year, Mungan ran more laboratory experiments on Teflon cores. In this research, he confirmed the benefits of wettability reversal of the reservoir rocks from oil-wet to water-wet. Figure 2.3 gives an example of the results obtained in this experiment.[45]

Ehrlich and his colleagues, in 1976,[23] described a laboratory evaluation of a potential field application of the alkaline-wettability reversal process for an oil-wet reservoir. They pointed out that all crude oils that they had tested showed a lower interfacial tension with

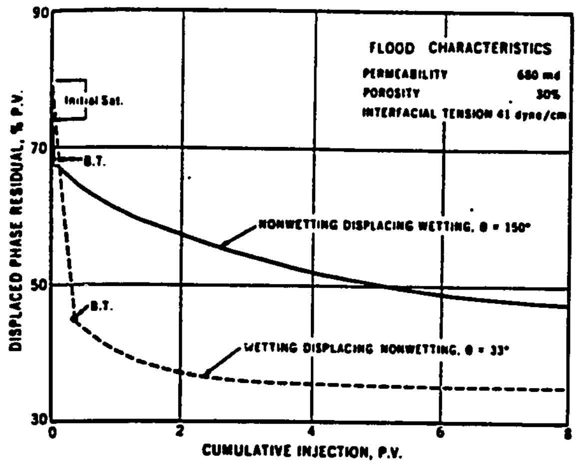

FIGURE 2.3-Effect of Wettability On Recovery Performance for Viscosity Ratio R=20. (Ref. 45)

an NaOH solution than they did with formation brine. If this interfacial tension were less than the critical value determined by reservoir properties, an NaOH waterflood would recover oil by an interfacial-tension lowering mechanism in addition to the recovery by the wettability-change mechanism.

Application of The Mechanism of Wettability Reversal from Water-Wet to Oil-Wet

In 1974, Cooke and his colleagues[13] reported a third mechanism with which caustic sodium hydroxide could improve waterflood oil recovery. The mechanisms, which are active at the front where alkaline water is displacing acidic crude oil, involve first the conversion of the water-wet rock to oil-wet. A discontinuous non-wetting residual oil is converted to a continuous wetting phase, providing a flowpath for what otherwise would be trapped oil. At the same time the low interfacial tension induces the formation of an oil-external emulsion of water droplets in the continuous wetting oil phase. These emulsion droplets tend to block flow and induce a high pressure gradient in the region where they form. The high pressure gradient, in turn, is said to overcome the capillary forces already decreased by low interfacial tension, thus further reducing the residual oil saturation.

Application of The Mechanism of Emulsification and Entrapment

Jennings and his colleagues, in 1974, proposed a fourth mechanism to improve the oil recovery by alkaline flood.[30] The mechanism involves the drastic reduction of oil-water interfacial tension by the caustic activation of potentially surface-active organic acids naturally occurring in the crude oil. The reduction of interfacial tension causes emulsification of crude oil in-situ that tends to lower injected water mobility, to dampen tendency toward viscous fingering, to slow water channeling caused by reservoir stratification, and to improve the volumetric conformance or sweep efficiency.

Fundamentally, the lowering of water mobility is mainly due to the entrapment of the oil emulsions by pore throats which are too small for the oil emulsion droplets to penetrate. According to Jennings' findings, caustic flooding at concentrations of about 0.05 to 0.5 wt. % NaOH can significantly improve the waterflood oil recovery of some low gravity viscous oils.

Success of this process also depends on the presence of sufficient concentration of naturally occurring surface-active organic acids in the crude to result in very low caustic-oil interfacial tension, below about 0.01 dyne/cm. McAuliffe[37,38] in 1973 proposed another approach to the application of the emulsification-entrapment mechanism, the injection of a diluted oil-in-water emulsion prepared externally. All of his laboratory experiments and field tests indicated that the injection of the emulsion could reduce the water channeling and improve the sweep efficiency; as a consequence, the oil recovery was improved significantly.

Dranchuk and his colleagues[20] in 1974 reported a laboratory caustic flood on Lloydminster crude oil. They found that during displacement tests, a very stable emulsion was produced, and there was evidence of reduced water mobility. They suggested that the mechanism of the improved oil recovery was due to in-situ emulsification of the crude oil and alkaline solutions. Scott and his colleagues[56] in 1965 also reported an improvement in oil recovery by using a low concentration NaOH solution, but they did not report the mechanism of emulsification and entrapment which obviously had occurred in their displacement tests.

Because no significant reduction in ultimate residual oil saturation results from the mechanism of emulsification and entrapment, it is directed primarily toward the viscous oil or oils in the heterogeneous reservoirs where sweep efficiency is poor. Under those circumstances, an improvement in vertical and areal sweep efficiencies through improved mobility ratio can be much more important economically than recovery of the residual oil from only the small volume of the reservoir normally swept.

Variation on Caustic Flooding

Numerous variations on the basic caustic flooding processes have been reported.[32] In 1962, Holbrook received a United States patent on caustic flooding after partially oxidizing the oil in a reservoir by injecting an oxygen-containing gas. Leach in 1965 obtained a patent on an injection of partially oxidized oil and alkaline solution. Bernard and Holbrook in 1965 patented the injection of an oil solution of petroleum acids followed by an alkaline solution. Sarem in 1974 published and obtained patents on a modified caustic flooding process in which a caustic sodium silicate solution is alternately injected with a calcium chloride solution to further improve the water-oil mobility ratio by precipitation of insoluble calcium silicate. There are many other proposed modification of alkaline floods. They mainly emphasized improving the content of the surface-active materials in the crude oils.

Introduction of The Gas Phase in a Waterflood Oil Reservoir

It has long been recognized that waterflood residual oil saturation can be reduced by the presence of a gas saturation. Craig[15] reviewed literatures on the effect of initial free gas saturation on waterflood residual oil. Residual oil saturation in water-wet consolidated rocks can be lowered up to 10 percent pore volume, depending on the magnitude of the gas saturation trapped by the waterflood.

In 1947, Pfister suggested a water drive process by intermittent air or gas injection, with estimates of increased production of about two percent above the waterflood recovery. In 1951, Saxon and his colleagues also proposed a gas-water injection process in the core displacement tests; the improvement in oil recovery similar to Pfister's results was obtained.

A recent study by Ehrlich and Black[58] indicated that mobilization of waterflood residual oil by simultaneous injection of water and nitrogen is possible in some cases even where nitrogen and oil are immiscible and no swelling, viscosity reduction, or vaporization of oil occurs. Residual oil saturation reduction is found to depend very strongly on three-phase relative permeability characteristics. For Berea sandstone, reductions of up to 18 percent pore volume were reported.

Summary of Contributions

All of the investigations discussed in this chapter have shown that a successful caustic flood performance is very dependent on the chemical and physical properties of the reservoir fluids and minerals. As a summary, the following items are believed to be important:

(1) Crude oil composition: All of the work on caustic flooding indicates that the composition of the crude oil is crucial to the caustic flooding process. Whether the mechanism involves a wetting change or emulsification, it is the nature of the polar compounds in the crude oil that determines if caustic can help and what concentration will be effective. Yen and his colleagues[71] provided a good review on the types of polar compounds which are effective in the alkaline process.

(2) Water composition: The chemical composition of the water used is also important. All agree that significant concentrations of multi-valent positive

ions, such as calcium in the water to make up the caustic solution, should be avoided. Sodium chloride, on the other hand, can be helpful in altering the effect of caustic on rock wettability, as well as in lowering the caustic concentration required to achieve minimum interfacial tension.

(3) Rock reactivity: Caustic reaction with rock may be responsible for favorable wettability changes. But reaction with rock also comsumes caustic. Nearly all reservoir rocks tend to react with sodium hydroxide to some extent; the reaction with the clay minerals of some reservoir rocks can be significant. In some reservoirs, it may be extensive enough to cast doubt on the ability of caustic flooding to be effective.

(4) Caustic concentration and slug size: Caustic concentration and volume injected appear to vary depending upon the recovery mechanism used. Concentrations are generally lowest for the emulsification mechanism, from about 0.001 to 0.5 weight percent. Higher concentrations ranging from 0.5 to 3.0 or even as high as 15.0 weight percent usually are

required for wettability reversal.

Most of the researchers agree that a slug of caustic solution can be nearly as effective as continuous injection,except for the mechanism of emulsification and entrainment, that requires a sufficient volume to insure continuous production of alkaline emulsion.

(5) Effect of gas saturation in alkaline flooding: Presence of gas phase in the waterflooding has been shown to be helpful in the improvement of residual oil recovery. From Craig's review, the reduction in residual oil saturation is dependent on the magnitude of the gas saturation trapped by the waterflood. It is without any doubt that the introduction of gas phase in the alkaline flooding will definetely improve the oil recovery further if both mechanisms were handled properly.

CHAPTER III

THEORETICAL CONSIDERATIONS

The trapping and the releasing of oil in natural petroleum reservoir occur under a wide variety of interrelated initial and applied conditions. Factors which determine microscopic displacement mechanisms are:

(1) Geometry of the pore network.

(2) Fluid-fluid properties.

(3) Fluid-rock properties.

(4) The applied pressure gradient and gravity.

When water displaces oil in a porous medium, in an ordinary waterflood process, the balance between capillary force and viscous force plays an important role in recovering the oil. In 1956 Moore and Slobod[42] proposed a "Viscap Concept," a theory of oil displacement based on competition between viscous and capillary forces in the pore paths. To illustrate the role of this competition, they suggested a capillary model a "doublet" as shown in Figure 3.1. The essential characteristic of the behavior of this system is that the oil-water interfaces in the two arms of the doublet generally will move with different velocities as the fluids respond to the combined effects of viscous and capillary forces. Thus one of the interfaces (see Figure 3.1(B)) will arrive at point B first, and will trap some oil in the other arm of the doublet. Moore and Slobod also described this phenomenon mathematically by:

$$\bar{v} = \frac{v_1}{v_2} = \frac{\dfrac{4Lqu}{\pi r_2^2} + r_2^2\left(\dfrac{1}{r_1} - \dfrac{1}{r_2}\right)\sigma \cos\theta}{\dfrac{4Lqu}{\pi r_1^2} - r_1^2\left(\dfrac{1}{r_1} - \dfrac{1}{r_2}\right)\sigma \cos\theta} \quad \ldots\ldots (3\text{-}1)$$

Where: r_1 and r_2 are radii of capillaries 1 and 2 respectively; u is the viscosity of fluids, assuming both have the same value; L is the distance cover which the capillary and viscous forces are competing, v_1 and v_2 are velocities in the capillaries, q is the total flow rate in the doublet system, and σ is the interfacial tension between oil and water.

While capillary forces become large with respect to the viscous forces, as it is typical in water-wet reservoirs, the flow will be faster in the smaller capillary. Although this result is not obvious by inspection of Equation (3-1), calculations indicated that for most combinations of properties, the bypassed oil will be left in the larger capillaries in the water-wet system.[42]

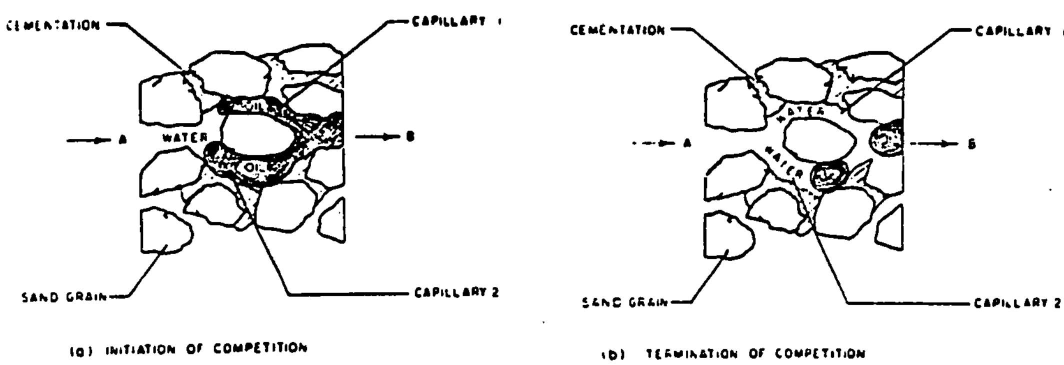

FIGURE 3.1

MODEL OF CAPILLARIES IN A POROUS MEDIUM TO ILLUSTRATE THE INTERPLAY OF CAPILLARY AND VISCOUS FORCES

If one considers the porous medium to be composed of numerous amounts of capillary doublets, the first flood-out region will include those doublets having larger average capillary diameters. The doublets of smaller capillary diameters will remain unflooded until a higher pressure gradient is applied. In an immiscible waterflood recovery process, when one of the capillaries in the doublet is flooded, trapped oil in the larger capillary will never be removed unless the flooded capillary is plugged by a foreign material, simply because the isolated oil drop is dominated by the Jamin Effect. Therefore, for any improvement in oil recovery by immiscible displacement after waterflood, some foreign materials must be introduced in order to interrupt the flow path which has already been created by the waterflood.

Mobilization of Residual Oils

In water-wet porous medium which has been waterflooded to a residual oil saturation, according to Darcy's Law, the flow of an aqueous phase through the porous medium containing immobile oil is:

$$V_w = \frac{K_{rw} K}{\mu_w} \frac{\Delta P}{L} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3\text{-}2)$$

where V_w is the apparent fluid velocity, K_{rw} is the relative permeability to the aqueous phase, K is the absolute permeability, μ_w is the viscosity for the aqueous phase, and L is the length of the linear system.

When more than one interface is present in a given flow path, conditions may be such that the resistance to flow is markedly increased or the resistance may become great enough to prohibit flow. This effect was discovered by Jamin, and is therefore called "Jamin Effect."

The phenomenon of the high pressures required to move the non-wetting globule is well described by Gardescu.[7] He found that the pressure drop required for onset of mobilization from A to B (refer to Figure 3.2) could be calculated by:

$$\Delta P_m = \left(\frac{4\sigma \cos\theta}{D}\right)_B - \left(\frac{4\sigma \cos\theta}{D}\right)_A \quad \text{..........(3-3)}$$

where ΔP_m is the pressure drop between the advancing end A and the receding end B, D is the capillary diameter at A or B, σ is the interfacial tension between oil and the aqueous phase, θ is the contact angle.

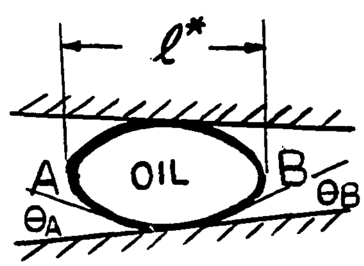

Figure 3.2

Idealized Pore Path

Mobilization of a globule of the non-wetting phase involves drainage and imbibition.[39] At the receding end of the globule (point B), oil displaces water (drainage); at the advancing end (point A), water displaces oil (imbibition). The pressure difference required to mobilize the oil globule is therefore proportional to the difference in drainage and imbibition capillary pressures.

For an oil globule of length ℓ^* trapped in a capillary tube of variation in diameter as shown in Figure 3.2, Equation (3-3) can further be expressed in:

$$\frac{\Delta P_m}{\ell^*} = \left(\frac{4\sigma \operatorname{Cos}\theta}{\ell^* D}\right)_B - \left(\frac{4\sigma \operatorname{Cos}\theta}{\ell^* D}\right)_A$$

$$= \frac{4}{\lambda}\left[(\sigma \operatorname{Cos}\theta)_B - \frac{(\sigma \operatorname{Cos}\theta)_A}{\beta}\right] \ldots (3\text{-}4)$$

where $\lambda = \ell^*/D_B$, and $\beta = D_A/D_B$. For the case of constant or nearly constant interfacial tension, Equation (3-4) becomes

$$\frac{\Delta P_m D_B^2}{\ell^* \sigma} = \frac{4}{\lambda}\left(\operatorname{Cos}\theta_B - \frac{\operatorname{Cos}\theta_A}{\beta}\right) \ldots\ldots (3\text{-}5)$$

Using cubic networks of capillary tubes of diameter D_B as a permeability model, the absolute permeability is given by:

$$K = \frac{\Phi D_B^{\,2}}{96} \quad \text{or} \quad D_B^{\,2} = \frac{96\ K}{\Phi} \quad \ldots\ldots(3\text{-}6)$$

Substitute $D_B^{\,2}$ into Equation (3-5) to obtain

$$\frac{K\,\Delta P_m}{\ell^{*}\sigma} = \frac{4\Phi}{96\lambda}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right) \ldots\ldots(3\text{-}7)$$

by approximating ($\Delta P_m / \ell^{*}$) = (ΔP/ L) we have:

$$\frac{K\,\Delta P}{L\,\sigma} = \frac{4\Phi}{96\lambda}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right)$$

or

$$\frac{\Delta P}{L\,\sigma} = \frac{4\ \Phi}{96\lambda K}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right) \ldots(3\text{-}8)$$

By combining Equation (3-1) and Equation (3-8), we have:

$$\frac{\Delta P}{L\sigma} = \frac{V_w\,\mu_w}{(k_{rw}K)\sigma}$$

$$= \frac{4\ \Phi}{96\lambda K}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right) \ldots\ldots(3\text{-}9)$$

From Kozeney's equation

$$K = \frac{\Phi}{K_z\ S_p^{\,2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3\text{-}10)$$

where K_z is Kozeney's constant, and S_p is specific area per pore volume. Substituting Equation (3-10) into Equation (3-9) we have

$$\frac{\Delta P}{L\,\sigma} = \frac{\mu_w V_w}{(K_{rw}K)\sigma} = \frac{K_z S_p^{\,2}}{24\lambda}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right) \quad ..(3\text{-}11)$$

Since K_z, λ, and β are very much dependent upon the rock type and the pore size distribution, they can be assumed constant for a specific value of liquid saturation. However, specific surface is the total area exposed within the pore space per unit volume. When the unit volume is the pore space, the specific area of N spherical grains of average radius $\bar{r}$ is given by:[50]

$$S_p = \frac{2}{\bar{r}} \quad ....(3\text{-}12)$$

By investigating Equation (3-12), one can see that the smaller the grain size, the larger the S_p and vice versa.

Equation (3-11) can further be expressed in:

$$\frac{\Delta P}{L\sigma} = \frac{K_z S_p^{\,2}}{24\lambda}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right) \quad ....(3\text{-}13a)$$

and also:

$$\frac{\mu_w V_w}{\sigma} = \frac{(K_{rw}K)\, K_z S_p^{\,2}}{24\lambda}\left(\cos\theta_B - \frac{\cos\theta_A}{\beta}\right) \quad ...(3\text{-}13b)$$

Under fixed saturation conditions, when the mobilization of residual oils occurs in the area of unflooded capillaries, the capillary number ($\mu_w V_w/\sigma$) required to remove the residual oil is proportional to S_p^2. As a consequence, when oil mobilization occurs in the area of finer sand grains, the capillary number will yield a larger value for a specific residual oil saturation than that in an area of coarser grain sands. Therefore, plots of the capillary numbers versus residual oil saturations can serve to explain qualitaively the mechanisms involved in the recovery of waterflood residual oil saturation.

Effect of Alkaline Injection

Unlike the ordinary alkaline flood for viscous oils, the waterflood non-acidic oil does not contain sufficient organic acids to produce in-situ emulsification. Therefore, any improvement in oil recovery must be attributed to the mechanisms other than in-situ emulsification.

It has long been recognized that clay minerals contained in oil reservoir formations may play an important role in the success or failure of enhanced oil recovery techniques. The reaction between the clay mineral and the injected chemical is usually undesirable. Mungan,[46] in his early work, indicated that formation damage, ie., reduction in permeability, has been generally attributed to clay minerals which expand or disperse upon contact with the alkaline water because of the change of PH in the injection fluid. It is suggested that the permeability reduction is due to the pore passages being blocked by particles, which may be dispersed clays, cementation materials or other fine particles.

Therefore, it is believed that if the clay dispersing could be controlled to some extent, the dispersed clay particles could be diverted to the flooded pore paths to block the flow passages. The effect of this selective plugging, together with lowering of the interfacial tension between oil and alkaline solution, will overcome the Jamin Effect which holds the oil droplets in the unflooded capillary of the doublet system.

Effect of Acidic Oil Slug Injection

When an acidic oil slug is injected into the porous media during the alkaline flood, if the interfacial tension is low enough, the acidic oil slug could be emulsified in-situ, could move downstream with the flowing caustic solution, and could be entrapped again by the pore throats too small for the emulsion droplets to penetrate. This mechanism of emulsification and entrapment results in a reduced water mobility that improves both vertical and areal sweep efficiencies.

Essentially, when the bypassed injected alkaline solution is interrupted by the selective plugging of the emulsion droplets, the chance for dislodging the isolated oil is then dominated by the Jamin Effect. If the Jamin Effect to retain the emulsion droplet or droplets is higher than that of the trapped oil, it is possible that the applied pressure will eventually displace the trapped oil. This condition can occur only when the emulsion droplets were lodged simultaneously as a chain in the flooded capillaries because the oil-in-water emulsions generally have lower viscosity and lower interfacial tension to the alkaline solution than the oil does.

As a result of the selective plugging of the oil-in-water emulsions, it can be expected that regardless whether the bypassed oil can be dislodged or not, the entrapment of the oil-in-water emulsion droplets, when occurring in the higher permeable region, will restrict flow, and water will begin to flow into the less permeable region, resulting in higher sweep efficiency. Or in other word, the doublets of smaller capillaries in the low permeable region of the porous medium would be flooded and would leave some isolated oils in the capillaries of larger diameters.

Effect of Intermittent Nitrogen Injection

It has long been recognized that waterflood residual oil saturation can be reduced by the presence of a gas phase. Residual oil saturation in water-wet consolidated rocks can be lowered by up to 10 percent pore volume depending upon the magnitude of the free gas saturation trapped by the waterflood.

The effect of nitrogen injection on waterflood residual oil saturations established with no gas present is essentially different from the effect of an initial gas saturation because of different saturation history. However, William and his colleagues[61] indicated in their recent study that with simultaneous injection of nitrogen and water in Berea sandstones, residual oil sturation reduction up to 18 percent pore volume was obtained.

Nitrogen will not develop miscibility with crude oil except at very high pressure or with very high API gravity oils; therefore, intermittent injection of nitrogen involves mechanisms of gas drive as well as the creation of gas saturations in the porous media. From a microscopic point of view, as the injected gas is trapped in the pore constrictions, it is further developed as chains of bubbles when the gas saturation is accumulated in the pore paths. As a result, such a bubble chain, when aligned in phase against the constriction, can withstand very appreciable pressure before breaking.[47] Therefore, the following injecting fluid will either displace the oil in the unflooded capillary of the flooded doublet or will be diverted to the unflooded regions of the core. This effect can be continued by the intermittent injection of nitrogen such that gas saturation can be propagated gradually following creation of more flow paths by the preceding continuous alkaline or waterflood.

Effect of the Injection Sequences

It is obvious from the discussion above that the Viscap Concept is the major mechanism dominating the displacement of oil in the waterflood, while selective plugging and Jamin Effect dominate the displacement of the residual oil left by the waterflood. Since the effective plugging particle or droplet size and the strength of resistance to the applied pressure gradients are different from one material to another, therefore the design of injecting sequences for different injection processes in the improved oil recovery methods is important.

CHAPTER IV

EXPERIMENTAL APPARATUS AND MATERIALS

The laboratory equipment was designed to study: (1) the basic physical properties of the petroleum fluids and the injected fluids encountered in the recovery processes, (2) the proper analytical procedures in order to interpret the displacement mechanisms which lead to improved oil recovery, and (3) the optimal process or processes which can economically improve the oil recovery.

Experimental Apparatus

(1) Core Displacement System: The core displacement system, as shown in Figure 4.1, can further be characterized by the following components:

(A) Core Holder Assembly (Figure 4.2): Typical clean Berea sandstone cores, 4.33 in. (11 cm) to 6.3 in. (16 cm) long and 1½ in. (3.7 cm) in diameter, were cast in fiber-glass resin with approximately 2.56 in. (6.5cm) in outside diameter. Both ends of the core unit were then cut and smoothed to the desired length and reinforced with four to six pieces of adjustable

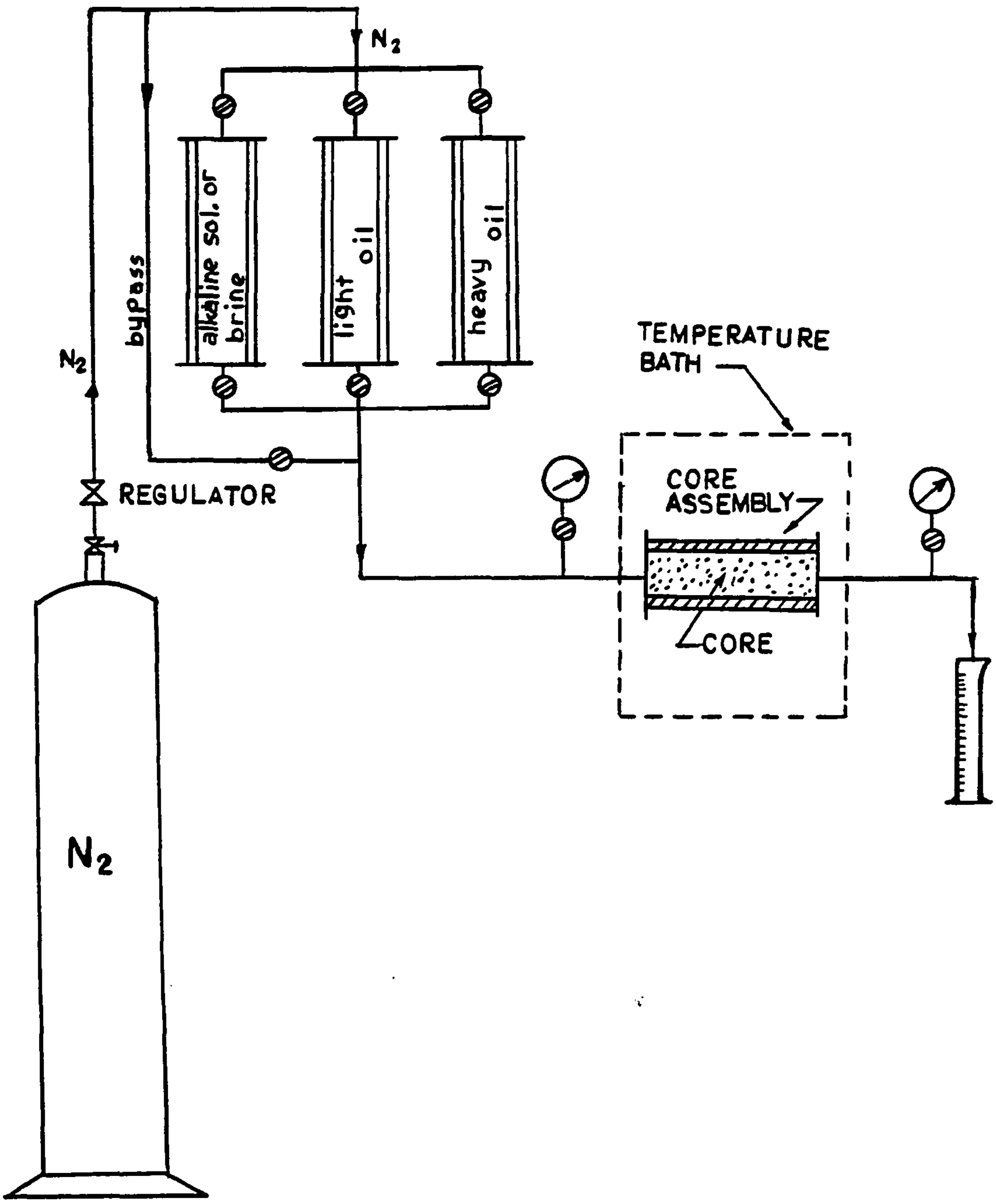

FIGURE 4.1

CORE DISPLACEMENT SYSTEM

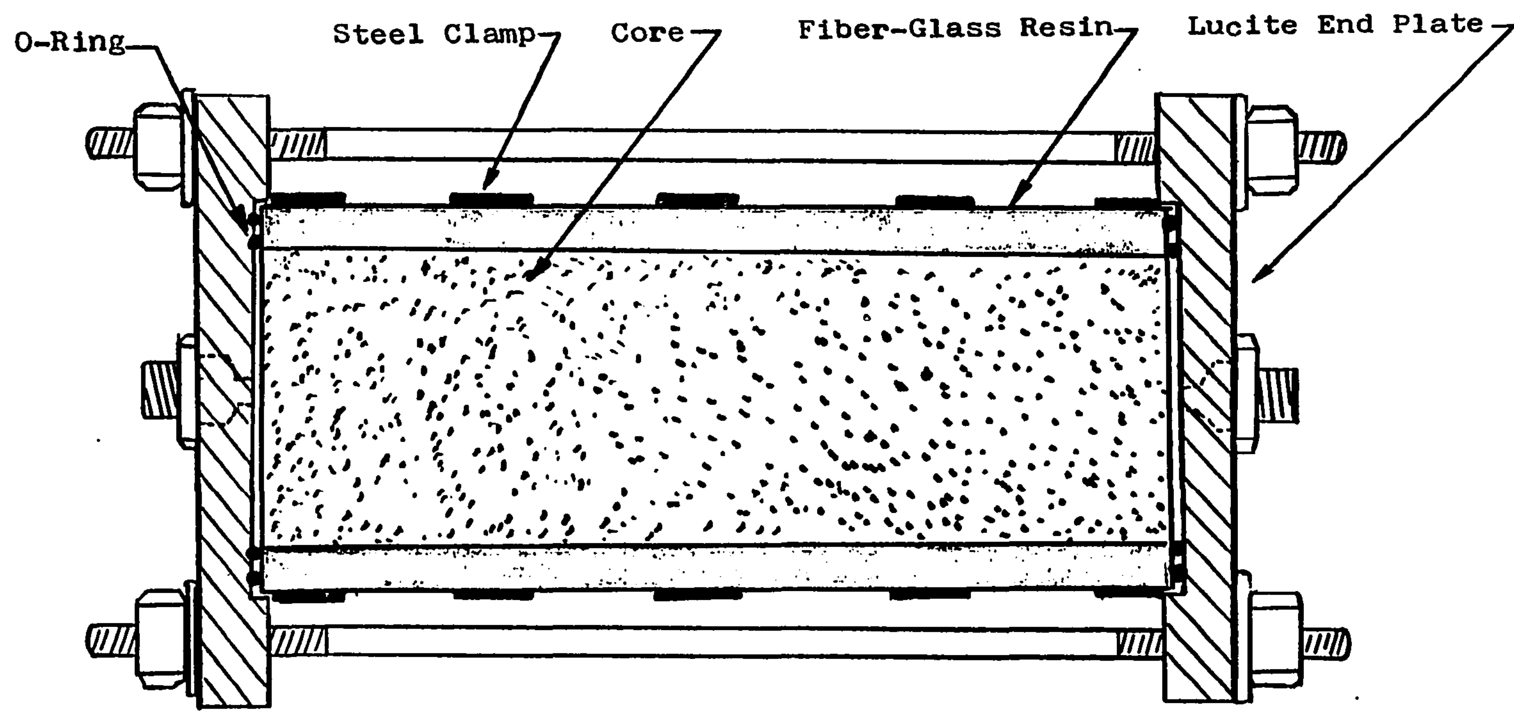

FIGURE 4.2 CORE HOLDER ASSEMBLY

stainless steel clamps, depending on the length of the core used. Two Lucite end plates were used to seal the ends of the cast core unit. To ensure the best pressure confinement, two oil resistent O-rings, 1 3/4 in. O.D. and 2 in. O.D. each, were fitted into two concentric machine-cut grooves on the surface of each end plate, leaving about 1/16 in. above the surface of the end plate. The O-rings provided the necessary pressure seal between the end plate and the cast core unit when both end plates were tightened by four 1/8 in. x 10 in. adjustable bolts and nuts. The end plates were so designed that a 1/4 in. hole was drilled through the center of each end plate and 26 radial grooves were also evenly cut from the center at radii of 1½ in. to permit even fluid entry and exit from the sand faces of the core unit. The entire system was then tested at 200 psig for at least 60 minutes to ensure that it was leak proof.

(B) Fluid Injection Assembly: High pressure nitrogen (2100 psig) cylinder was used to provide the pressure source for fluid injections. A pressure regulator was used in adjusting the upstream pressure. A bypass line of 1/8 in. tubing was also connected between the regulator and the core assembly to provide nitrogen injection when intermittent nitrogen injection was applied. Both alkaline and brine reservoirs were made of 2 in. stainless steel pipes which have maximum working pressure of 1000 psi. The light crude oil reservoir was made of 1½ in. cast plastic pipe and reinforced with steel clamps to withstand 100 psi, which is necessary for injecting the oil into the core. A glass chemical tiltration burret was modified for the purpose of acidic oil slug injections. It provided the the necessary volumetric accuracy to the reading of 0.1 cc.

(C) Heating Unit: Two heating apparatuses were used to supply heat to the injecting fluids as well as to the core assembly. A constant temperature water bath was used as a heat exchanger to pre-heat the injecting fluids at reservoir temperature, while a constant temperature electric oven was used to keep the core assembly at the same reservoir temperature.

(D) Pressure and Temperature Measuring Devices: All pressures were measured using ordinary Borden tube pressure gauges, which were calibrated by a mercury U tube with accuracy of $\pm$ 1 psi. Thermometers were used for temperature measurements.

(2) Fluid Property Measuring Devices:

(A) PH meter: Corning Model 125 PH meter was used to monitor the PH values of both injection and production fluids. The Model 125 uses a digital readout with resolution to 0.01 PH unit and 1 mV. It covers the range of 0 to 14 PH or 0 to $\pm$ 1800 mV. Temperature compensation can be made manually or by using Corning automatic temperature compensator. Both of the methods allow compensation over the 0° to 100° C. range. The power requirements are 50 to 60 HZ and 115 Volts ac.

(B) Interfacial Tensiometers: The Cenco-du Nouy tensiometer No 70545 was used to measure the interfacial tension between the brine and oil and between caustic solution and oil at room temperature. The interfacial tensiometer employs the ring method of measurement, which allows measurements to be made in 15 to 30 seconds. Measurement values are reproducible to within ± 0.05 dyne/cm and can be obtained by a direct scale reading. Because of the limitation of the du -Nouy tensiometer, Spinning Drop tensiometer was also used to measure the interfacial tensions below 0.5 dyne/cm as well as the interfacial tensions at temperatures of interest.

(C) Viscometers: Both Fann V-G meter and Stormer viscometers were used in measuring the viscosities of all the fluids. The Stormer viscometer consists of a spindle which is rotated in a test cup by a set of gears driven by a falling weight. The revolutions of the spindle are recorded by a revolution counter. By trial and error, weights are added to the line until a stabilized rotating speed of 600 rpm is obtained. The weight of driving force in grams is then used with a calibration chart to obtain the fluid viscosity. In principle, the Fann meter is like the Stormer, in that the basic measurement is the torque necessary to revolve an inner rotor in a stationary, fluid-filled test cup. The spindle is driven by a synchronous motor. Gear changes plus the two motor speeds allow six operating rmp's. Torque readings are obtained directly from a dial on the instrument.

(3) Miscellaneous: Christian Becker Model AR-2 analytical balance was used to weigh all of the chemicals. This balance gives weighing precision to 0.0001 grams, while the core assembly was measured by electrical balance, which gives the weighing precision to 0.01 grams. The specific gravities of the fluids were measured by the Westphal Balance which can yield accuracy to 0.0001 of SPG reading. Precision

electrical timer was used for time measurements which gives the time readings with the accuracy of 0.1 seconds.

Experimental Materials

(1) Porous Media: The porous media used in these experiments were Berea consolidated sandstones. The Berea cores, which had an average diameter of 1½ inches, and 4.3 to 6.3 inches in length, were measured to have 19 to 22 percent porosities and 260 to 509 md liquid permeabilities. The mineralogical contents of Berea sandstone were reported[61] as shown in Table I.

TABLE I

MINERALOGICAL PROPERTIES OF BEREA SANDSTONE

Composition, Percent by Weight				
Quartz	Feldspar	Carbonates	Clay	Fe-Ti Minerals
85	5	1	7	2

To understand the grain size distribution, sieve analysis of the ground Berea cores was made. The results given in Table II were plotted as shown in Figure 4.3. This analysis indicates that the Berea cores used were

TABLE II

SIEVE ANALYSIS FOR BEREA SANDSTONE

Total Weight 132.5 gr.

Sieve Size (in.)	Cumulative Weight (gr.)	Percent of Cumulative Weight (%)	Sand Caught on Sieve (wt. gr.)	Percent Coarser Than (%)
0.0232	0.162	0.124	0.162	0.124
0.0177	6.975	5.201	6.813	5.324
0.0083	17.749	8.224	10.774	13.549
0.0041	102.100	64.390	84.351	77.939
0.0025	119.800	13.511	17.700	91.450
0.0015	124.000	3.206	4.200	94.656
0.0015	131.000	5.344	7.000	

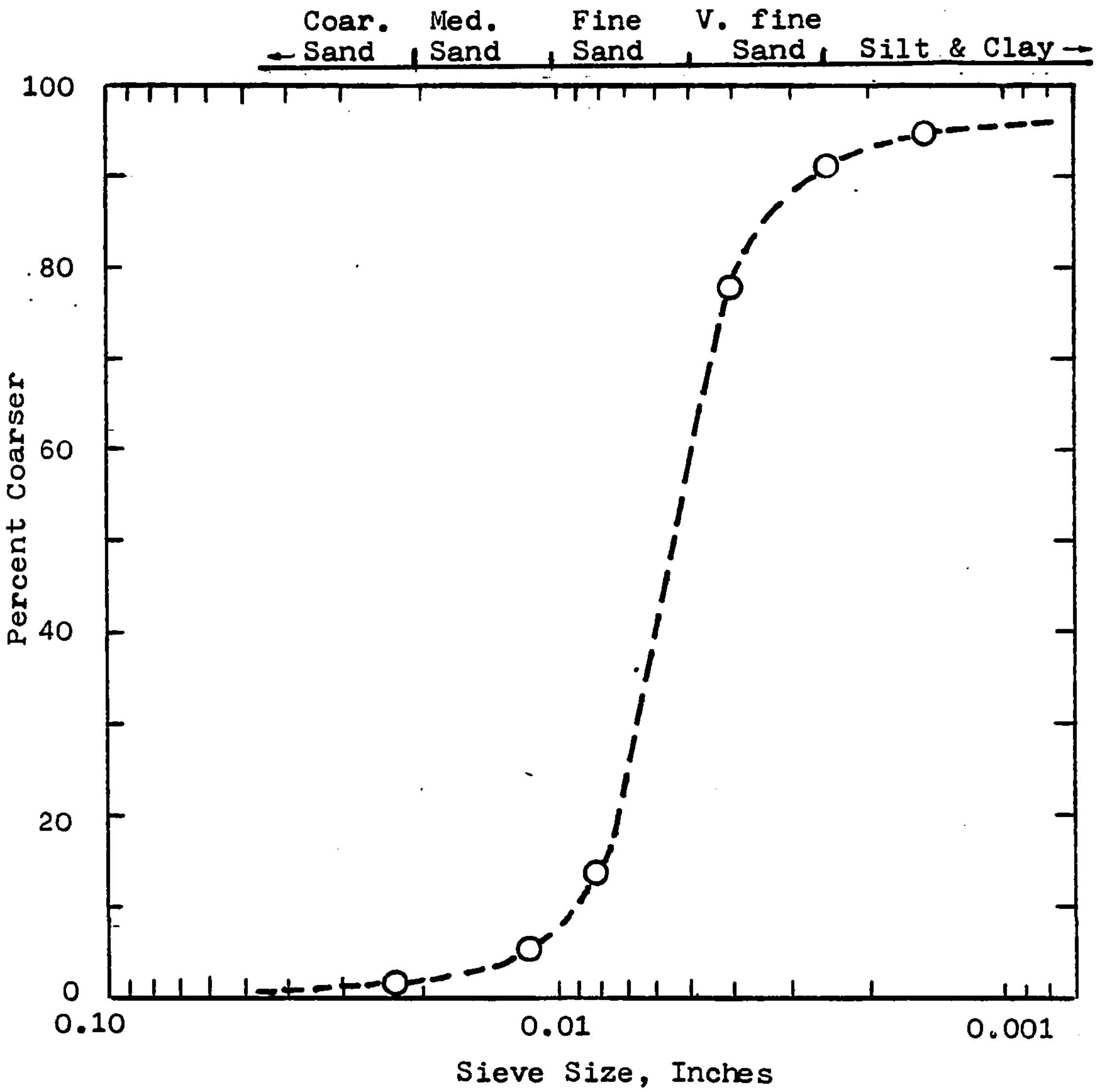

FIGURE 4.3

CUMULATIVE GRAIN-SIZE DISTRIBUTIONS
OF BEREA CORES

well sorted and were composed of 83 percent fine to very fine sand, 9 percent silt and clay minerals, 6 percent medium sand, and 2 percent coarse sand.

(2) Crude Oils: The oil samples selected for this study were light crude from N. E. Purdy, Springer A Sand, Lindsay, Oklahoma of Cities Service, and heavy crude from LOCO Field, Ardmore, Oklahoma of Conoco. The former was used to simulate the reservoir oil for saturating the Berea Sand, while the latter was used to mix with the light crude for slug injections. Dead oils were used in the entire laboratory experiments. To avoid the plugging by the impurities in the oil samples, the oil samples were filtered before use. The manner in which each oil's viscosity responds to temperature was measured as shown in Figure 4.4. The specific gravity of the light crude and the heavy crude at room temperature (78° F) was measured to be 36° API and 21° API respectively.

(3) Chemicals: The basic chemicals used in this study included Reagent grade sodium hydroxide ($NaOH$) and Reagent grade sodium chloride ($NaCl$). Sodium hydroxide was used in preparing the alkaline solutions while $NaCl$ was used for the brine.

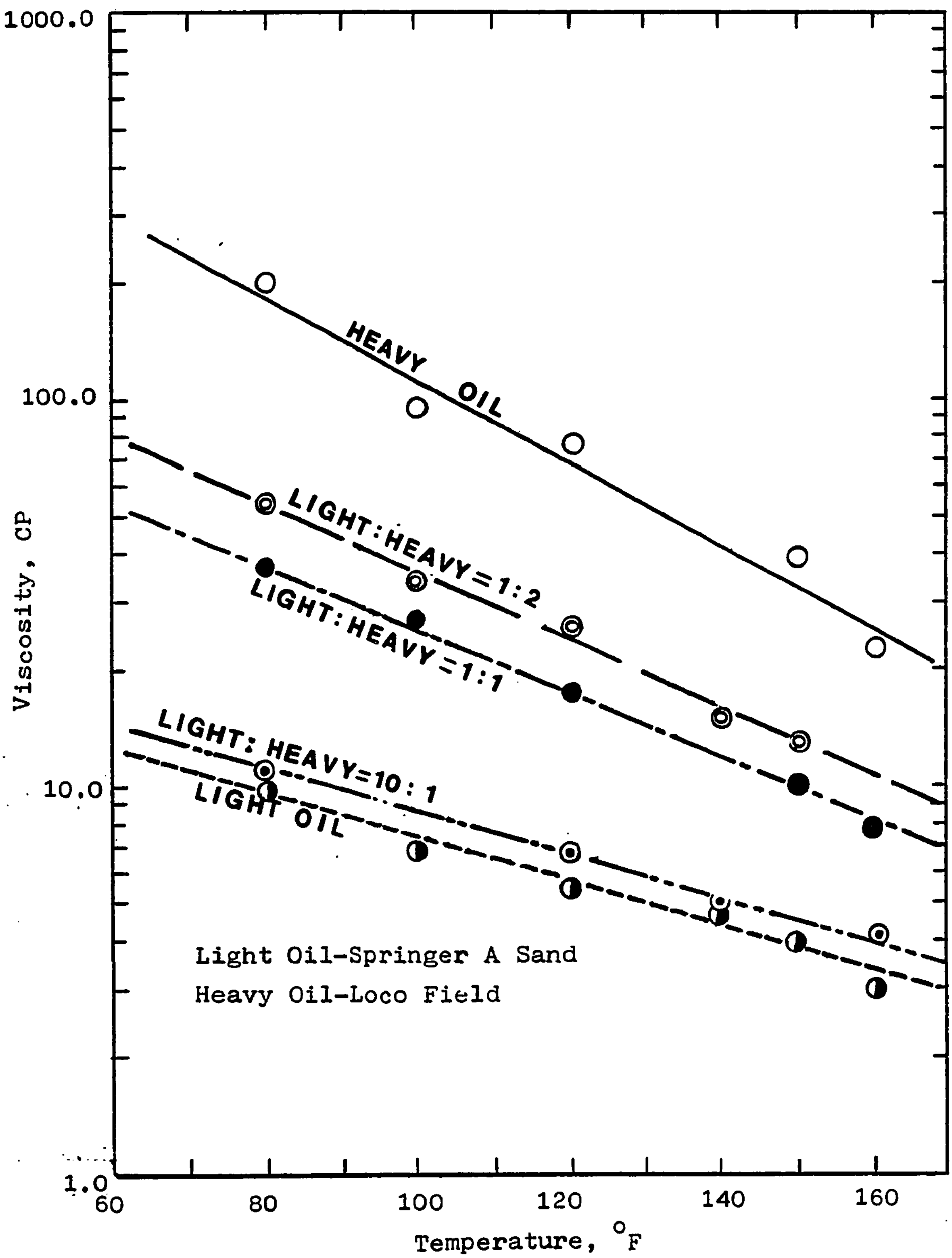

FIGURE 4.4 OIL VISCOSITY VS TEMPERATURE

CHAPTER V

EXPERIMENTAL PROCEDURE

Preparation of The Core Assembly

The clean Berea core was placed in the oven and dried at 300^{o} F for at least 72 hours, and was cooled in the drier for several hours. To minimize the penetration of fiber-glass resin, the core was first coated with a thin layer of fiber-glass resin and dried; the coating process was then repeated for two more times. The dried coated Berea core was then placed in the center of a cylindrical module and cast in the fiber-glass resin. The cast core had an outside diameter of approximately 2.56 in., and length ranged from 4.33 in. to 6 in. The core unit was then cut at both ends to the desired length, and the peripheral fiber-glass resin on each end was finished with fine sanpaper to provide good sealing with the end plates by O-rings. The complete core assembly was then tested at 200 psi for at least 60 minutes to ensure leak proof.

Initial Saturation

In a typical experimental run with the Berea core, the core was evacuated by a vacuum pump to a pressure of about 0.3 Kpa for at least 4 hours. The evacuated core was then saturated with air-free simulated brine at 20 psi, and stayed undisturbed for at least 12 hours to allow equillibrium between clay minerals and brine. In saturating the core, the aqueous phase used was 10,000 ppm NaCl brine. After saturation, about five more pore volumes of brine were put through the core at escalated pressure to ensure complete saturation, and also the specific liquid permeability was obtained. The saturated core was then removed and weighed to determine the pore volume and porosity. During the removal of the core from the core assembly, care was taken to avoid any brine evaporation before and after weighing. Reassembly was made immediately after the core was weighed, and the light oil was then introduced to flow through the core until residual water saturation was obtained, and the core was allowed to stand a day. Before starting the waterflood, 1 to 2 pore volumes of oil were flowed through the core to determine the effective permeability to oil at residual water saturation. And the initial oil saturation was then determined by weight as well as volumetric balance.

Improved Oil Recovery

A control waterflood was run on the oil-flooded core before any improved oil recovery process, and the residual oil saturation after waterflooding was determined by weight and volumetric balances.

To understand the interactions among different processes, combinations of the following five processes were conducted in each core.

(1) Continuous Waterflood with Intermittent Nitrogen Injection: Continuous waterflooding was performed at escalated pressure as an ordinary waterflood, except that nitrogen was introduced intermittently until gas breakthrough during each pressure step. Intermittent injection of nitrogen was repeated several times at each pressure step until no more oil was produced because of the waterflood. The effective water permeability and residual oil saturation were calculated at the end of each pressure step.

(2) Continuous Alkaline Injection: To understand the effect of alkaline solution on the

improvement of the oil recovery, alkaline solution was introduced to flow through the core at escalated pressures. At least 2 pore volumes of alkaline solution were injected at each pressure step until no more oil was produced. The cumulative fluid productions, the pressures, the temperatures and times were all recorded.

(3) Alkaline-Oil Slug Injection: An oil slug containing sufficient surface-active materials was injected into the core prior to the continuous injection of alkaline solution. The volume of oil slug injected was measured by using a modified titration burette. The alkaline solution was then injected continuously through the core at escalated pressures. At least two pore volumes of alkaline solution were injected at each pressure step or until no more significant oil was produced. Effective water permeability and residual oil saturation was calculated at the end of each pressure step.

(4) Continuous Alkaline Flood with Intermittent Nitrogen Injection: Alkaline solution was injected continuously at escalated pressures, while nitrogen was introduced intermittently until gas breakthrough.

Intermittent nitrogen injections were repeated several times in each pressure step until no more significant oil was produced. Effective permeability of water and residual oil saturation were calculated at the end of each pressure interval.

(5) Continuous Alkaline Flooding with Oil Slug and Intermittent Nitrogen Injections: The procedures were the same as alkaline-nitrogen process as described in process (4), except an acidic oil slug was injected prior to the injection of the alkaline solution.

CHAPTER VI

SUPPLEMENTARY EXPERIMENTS AND OBSERVATIONS

Measurement of The Interfacial Tensions

The effect of NaOH on the interfacial tensions(IFT) of N.E. Purdy Unit, Springer A oil was minimal, on the other hand NaOH could significantly reduce the IFT of the heavy oil (LOCO Field, Ardmore, CONOCO) between 0.15 to 0.20 weight percent of NaOH. Because of the narrowness in effective NaOH concentrations on the heavy crude, direct use of LOCO Field heavy crude as an injecting oil slug is limited. Studies have shown that oil slugs with wider effective NaOH concentrations can be obtained by simply mixing the above two crudes in appropriate proportions. Figure 6.1 gives the details of these studies.

Because of the limitations of the Du-Nouy interfacial tensiometer, all interfacial tensions were measured at 78° F and the minimum readable readings were made at 0.5 dyne/cm. Interfacial tensions below 0.5 dyne/cm were measured by Spinning Drop interfacial

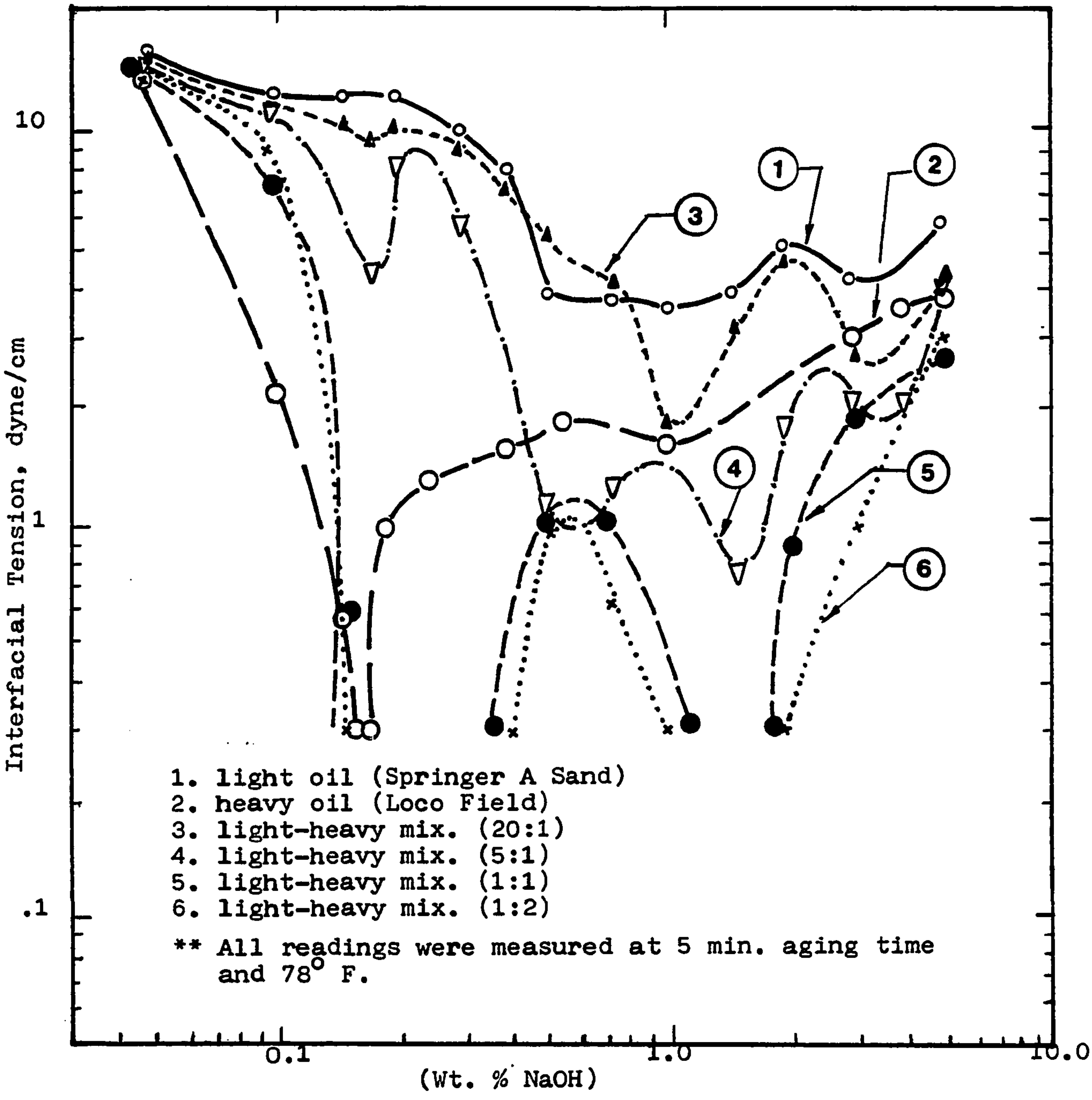

FIGURE 6.1
EFFECT OF NaOH ON THE INTERFACIAL TENSIONS OF OILS

tensiometer. Spinning Drop interfacial tensiometer was also used to measure interfacial tensions of the crude-alkaline system at temperatures of interest. (Table B-2)

Reactivities of Alkaline Solutions to Berea Sandstones

Reactivities of the alkaline solutions to the saturated Berea cores were determined by measuring the permeability reductions and PH changes. Studies indicated that the permeability reduction in the injection of 0.175 wt. percent NaOH solution were less severe than that in the injection of 1.00 wt. percent NaOH solution. The results as shown in Figure 6.2 indicate that a maximum permeability reduction of 25 percent of the initial liquid permeability was stabilized after the injection of approximately 12 pore volumes of 0.175 wt. percent NaOH solution. On the other hand, approximately 55 percent reduction in original liquid permeability was observed after 7 pore volumes of 1.00 wt. percent NaOH solution had been injected. Measurement of the permeability reductions in the injection of 1.00 wt. percent NaOH solution also showed that partial permeability restoration occurred after 7 pore volumes of the alkaline

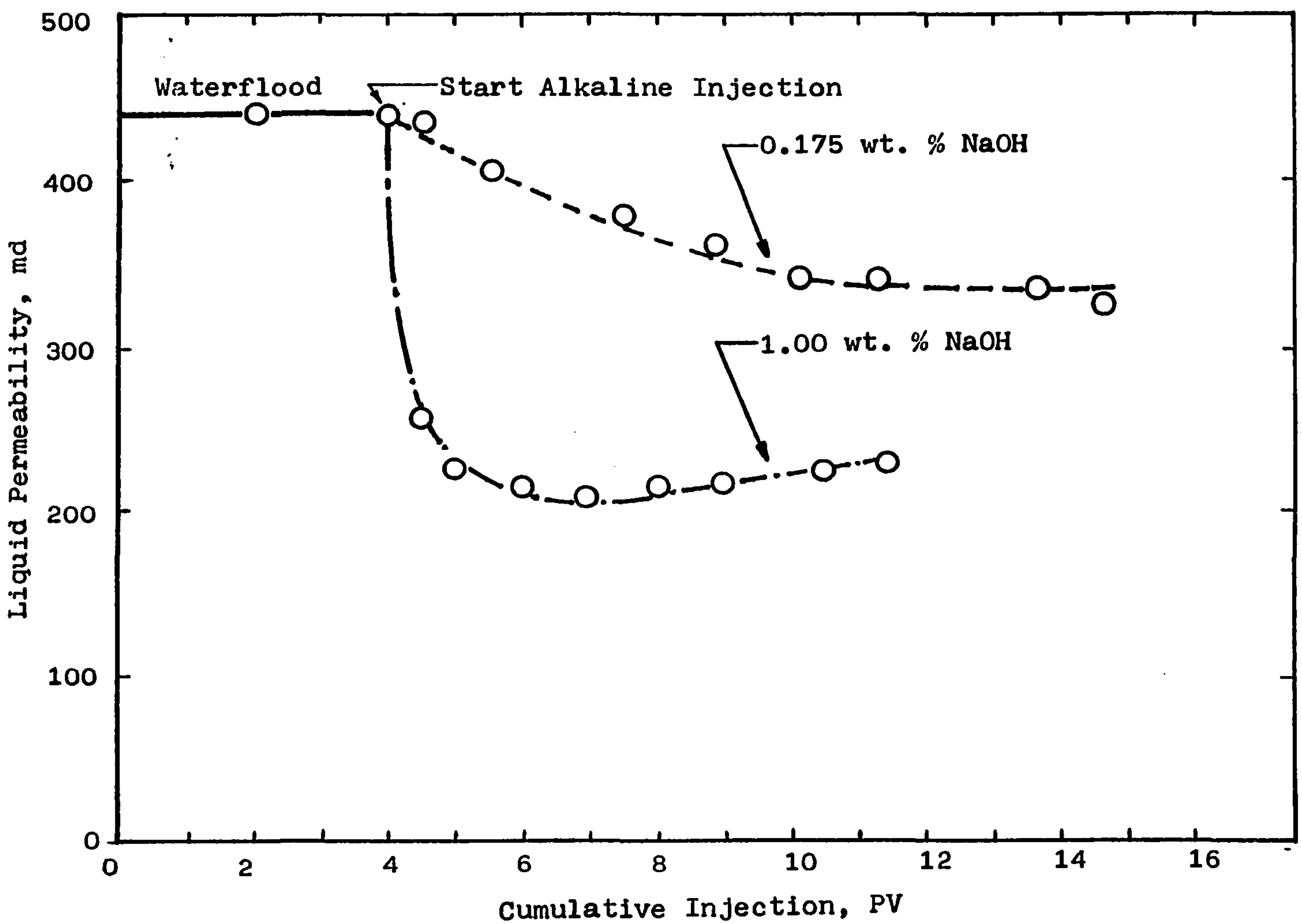

FIGURE 6.2-EFFECT OF NaOH CONCENTRATIONS
ON PERMEABILITY

solution had been injected. This indicates that continuous injection of the high concentration NaOH solution initiated the disolution of the silicate minerals. They are predominately clay and large-surface-area silica minerals.[63]

In the meantime, monitoring of the PH values of the producing liquid indicated that the alkaline consumption reached a constant rate after 6 pore volumes of 1.00 wt. percent NaOH solution had been injected; however, the consumption rate did not stabilized even after the injection of 14 pore volumes of 0.175 wt. percent NaOH solution.

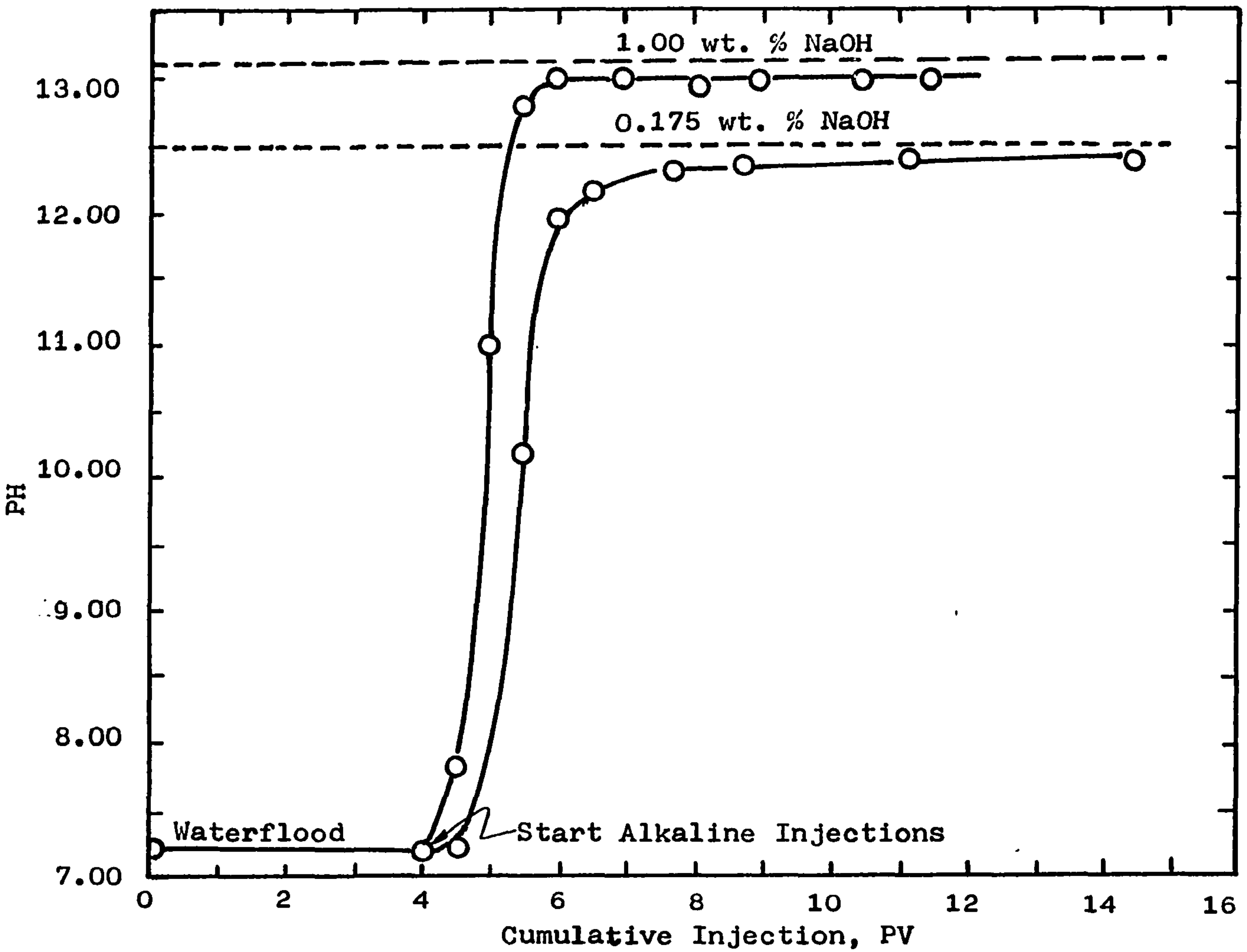

FIGURE 6.3- CAUSTIC CONSUMPTION FOR BEREA CORES

CHAPTER VII

PRESENTATION AND DISCUSSION OF THE RESULTS

In order to understand the mechanisms encountered in the alkaline flood process, five different injection processes were used in the core displacement tests. To make the utmost use of the core samples and to assess the interactions among different displacement processes, different combinations of the five processes were conducted in each core. They were then further classified into three different categories, namely, (1) waterflood followed by continuous waterflood with intermittent nitrogen injections, (2) waterflood followed by continuous alkaline flood with intermittent nitrogen injection, and (3) waterflood followed by oil slug injection and continuous alkaline flood with intermittent nitrogen injections.

The experimental results obtained are based on the following primary conditions and are brought to focus on the discussion of the mechanisms involved in the improved oil recovery processes.

1. The brine containing 10,000 ppm NaCl was used as a connate water saturation as well as a

waterflooding liquid because it provided a stable reaction with the clay contents.

2. The alkaline solution containing 0.175 weight percent of NaOH was used for the purpose of alkaline injections in all of the improved oil recovery processes because it provided the useful dispersed clay particles and also provided the low interfacial tension with the injected acidic oil slug to produce the in-situ emulsifications. The interfacial tensions between the alkaline solution and the oil slug as low as 0.04 dyne/cm at 78° F and 0.03 dyne/cm at 150° F were observed using Spinning Drop Tensiometer and the formation of alkaline oil emulsions were also observed in the test tubes.

3. A light-heavy oil mixture of ratio 1:1 was chosen as an injected acidic oil slug because it provided both a useful effective ranges in low caustic concentrations and a reasonable low oil viscosity at room temperature and at 150° F respectively.

4. The Berea sandstone cores used provided the grain size distributions ranging from clay to coarse sand; therefore, it is assumed to be sufficient to supply the necessary pore size distributions for the observations of the effect of the selective plugging by different recovery processes.

Presentation of The Results

(1) Waterflood Followed by Continuous Waterflood with Intermittent Nitrogen Injections: The experiments were done using two cores having the characteristics as shown in Table III. Core #1 was saturated with oil to an initial oil saturation of 64.04 percent and waterflooded at constant pressure gradient of 189 psi/ft to a waterflooded residual oil saturation of 43.78 percent. Nitrogen was then introduced intermittently at the same constant pressure gradient until no more oil production could be obtained. Figure 7.1 gives the details of the injection history. It indicates that the final residual oil saturation of 28.55 percent was obtained after approximately 7.0 PV of water had been injected.

Core #2 was first saturated with oil to an initial oil saturation S_{oi} of 69.47 percent and waterflooded at escalated pressure gradients from 59 psi/ft to 724 psi/ft until a waterflood residual oil saturation of 35.48 percent was obtained. Nitrogen was then introduced intermittently at escalated pressure gradients from 146 psi/ft to 645 psi/ft until no more oil was produced.

The injection history as shown in Figure 7.2 indicates that a final residual oil saturation of 31.40

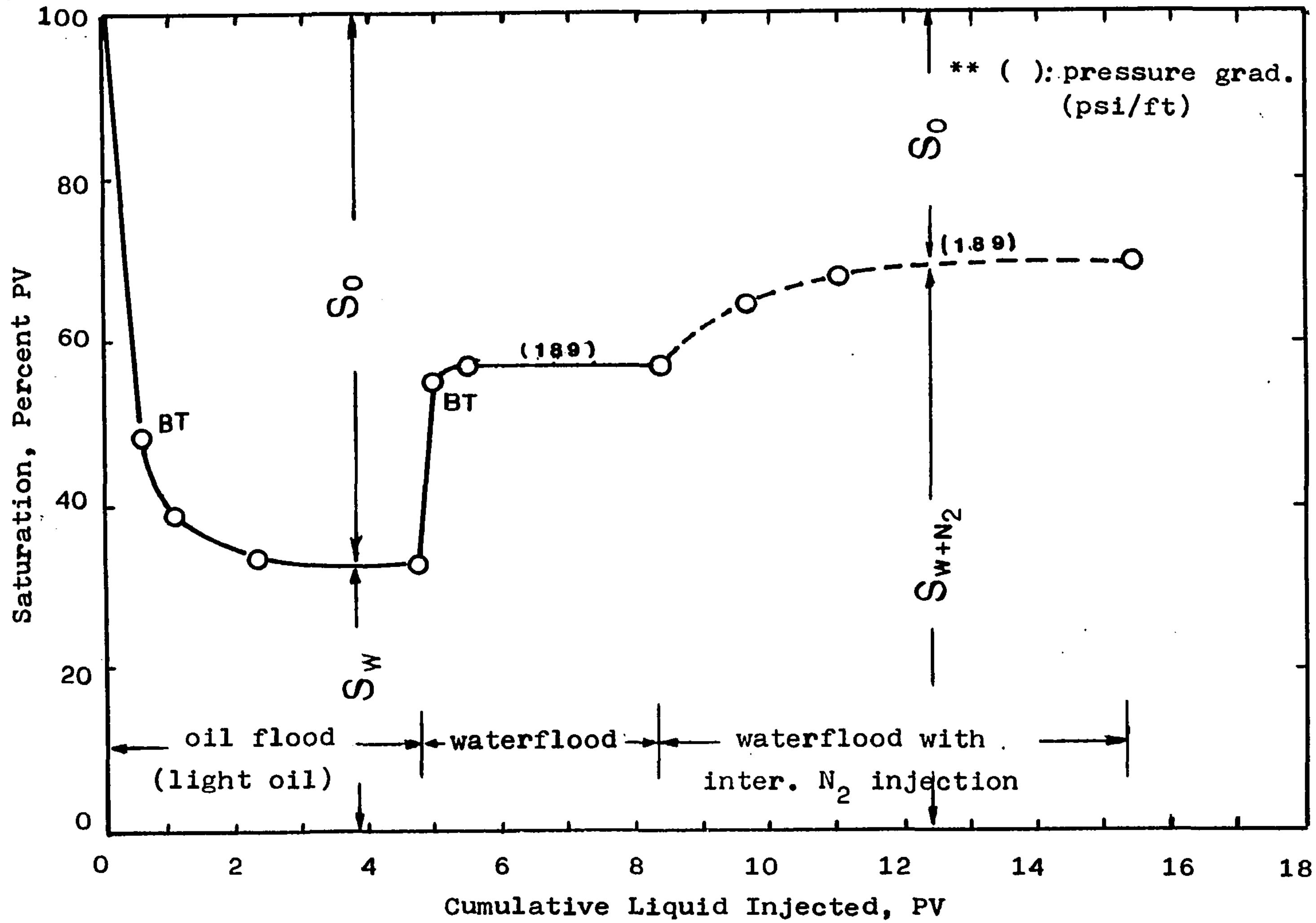

FIGURE 7.1- DISPLACEMENT TEST FOR CORE # 1 AT 78° F
(Berea Sand, Linear Flood)

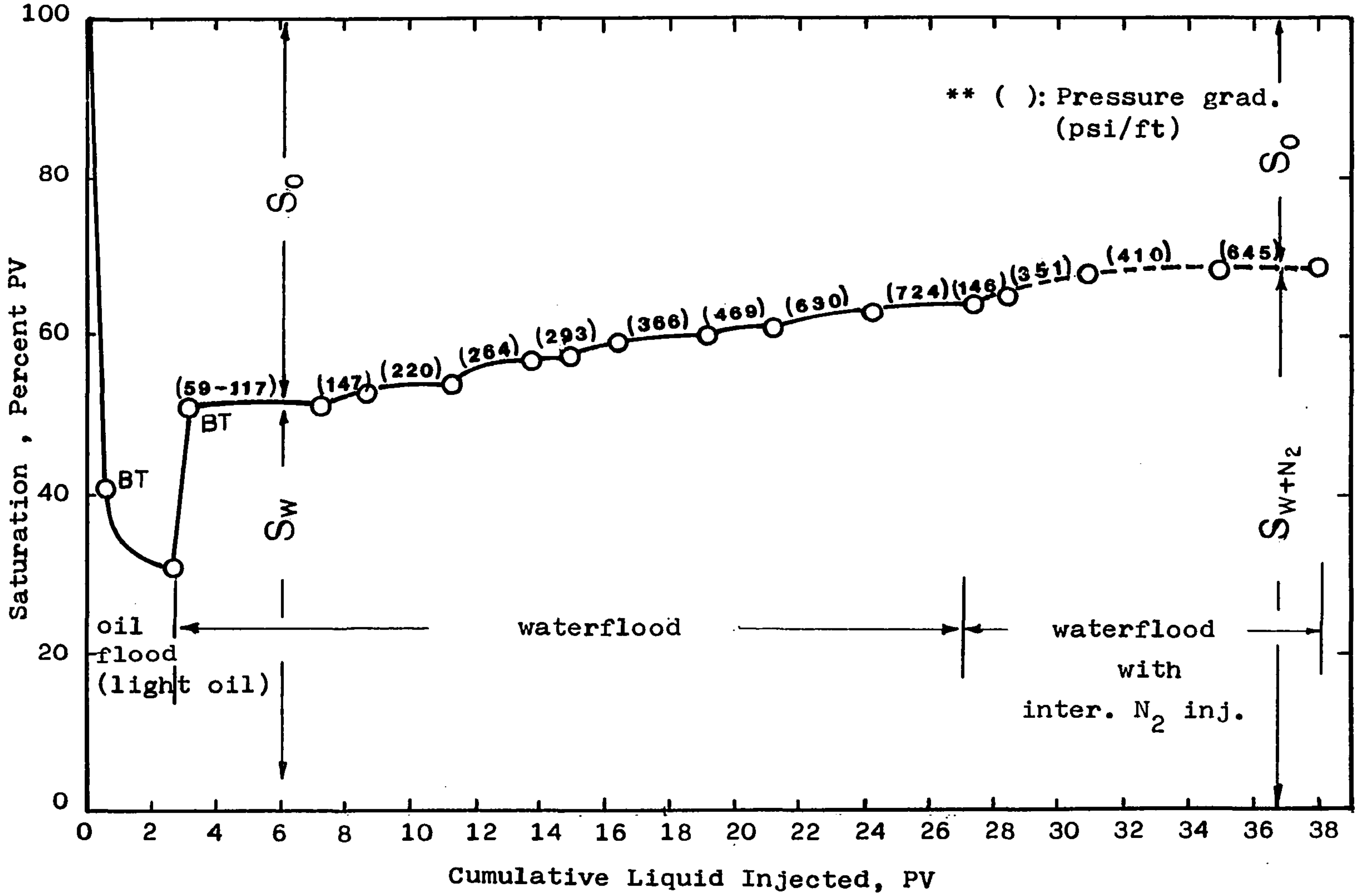

FIGURE 7.2- DISPLACEMENT TEST FOR CORE # 2 AT 78° F
(Berea Sand, Linear Flood)

percent was obtained.

TABLE III

PROPERTIES OF CORES USED IN CATEGORY 1

Core No.	Size Length x Diameter (cm x cm)	Liquid Permeability (md)	Porosity (%)
#1	10.0x3.7	278	21.08
#2	10.4x3.7	408.5	21.88

(2) Waterflood Followed by Continuous Alkaline Flood with Intermittent Nitrogen Injection: The experiments were done by using four different cores as characterized in Table IV. As can be seen from Figure 7.3, core #3 was saturated with oil to an initial oil saturation S_{oi} of 69.24 percent, and waterflooded with approximately 4 pore volumes of 10,000 ppm NaCl brine at 152 psi/ft to a waterflood residual oil saturation of 44.28 percent. Nitrogen was introduced intermittently while continuous alkaline solution was injected at 287 psi/ft. The results indicated that a final residual oil saturation of 25.00 percent was obtained.

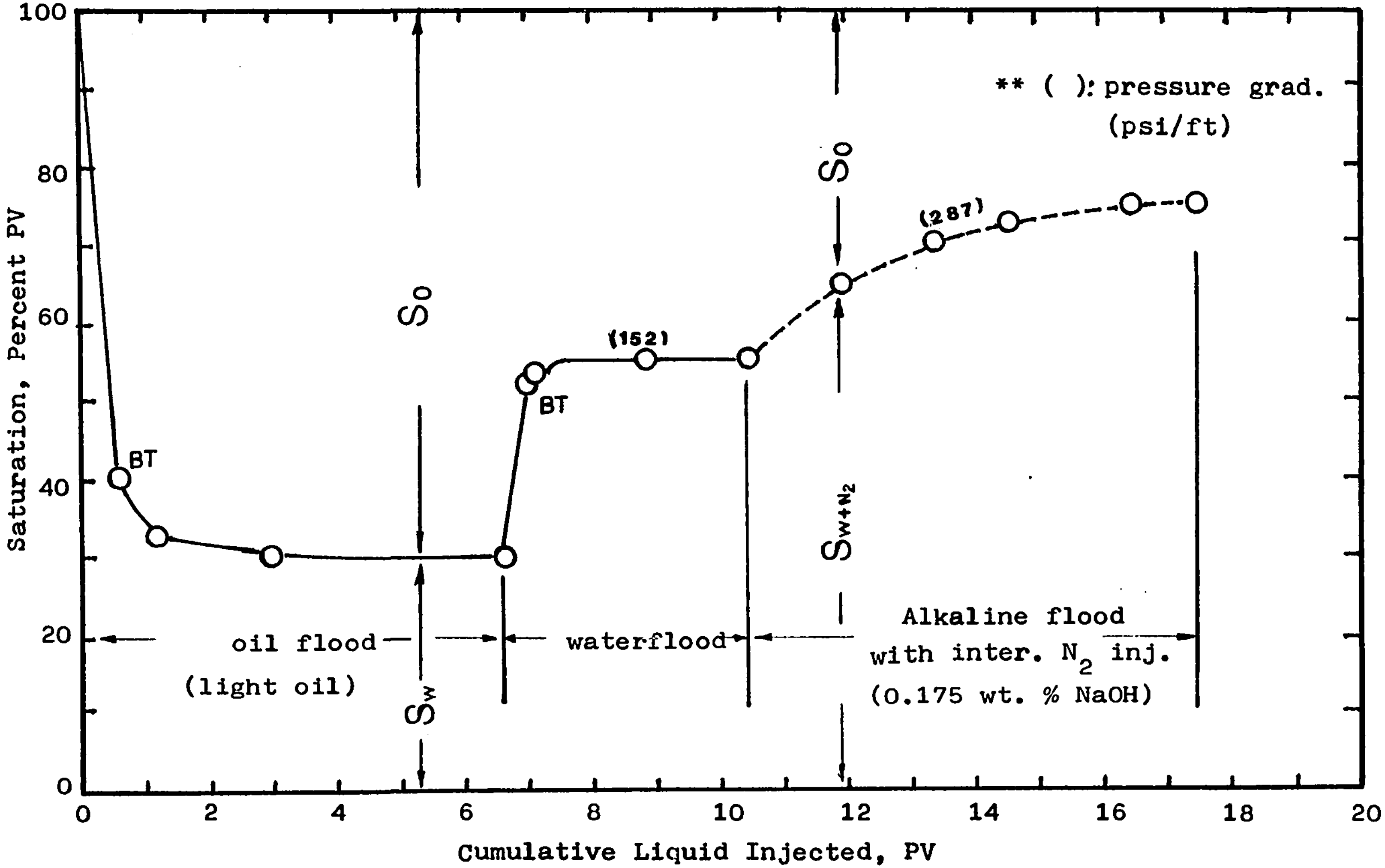

FIGURE 7.3- DISPLACEMENT TEST FOR CORE # 3 AT 78° F

(Berea Sand, Linear Flood)

TABLE IV

PROPERTIES OF CORES USED IN CATEGORY 2

Core No.	Size Length x Diameter (cm x cm)	Liquid Permeability (md)	Porosity (%)
#3	10.0x3.7	260.0	21.23
#4	15.1x3.7	274.0	19.40
#5	9.9x3.7	484.0	21.20
#6	10.0x3.5	411.0	22.30

The waterflood in core #4 was started at S_{oi} of 68.33 percent and was flooded at 141 psi/ft for about 7.5 pore volumes of 10,000 ppm NaCl brine until a waterflood residual oil saturation of 43.11 percent was achieved. Approximately 3.5 pore volumes of alkaline solution (0.175 wt. %) was then injected continuously at 202 psi/ft. The result indicated that no additional oil was produced during this alkaline injection. Nitrogen was then introduced intermittently while alkaline solution was injected continuously at 182 psi/ft. During the injection of 6.5 pore volumes alkaline solution, significant improvement in oil recovery was observed. The results in Figure 7.4 indicate that a final residual oil saturation of 24.90 percent pore volume was achieved.

To assess the influence of the production history on the alkaline-nitrogen process, core #5 was saturated with oil to S_{oi} of 68.05 percent and waterflooded at escalated pressure gradients from 185 psi/ft to 431 psi/ft until a waterflood residual oil saturation of 31.28 percent pore volume was obtained. Continuous alkaline solution was then introduced at 308 psi/ft and no significant improvement in oil recovery was observed after 4.5 pore volumes of alkaline solution had been injected. Nitrogen was then injected intermittently. As can be seen in Figure 7.5, the final results indicate that a residual oil saturation of 24.05 percent was achieved.

Waterflood was started in core #6 at initial oil saturation of 66.63 percent. A pressure gradient of 61 psi/ft was used in waterflooding until water breakthrough. The pressure gradient was then increased to 122 psi/ft but there was no increment in oil recovery obtained, leaving waterflood residual oil saturation

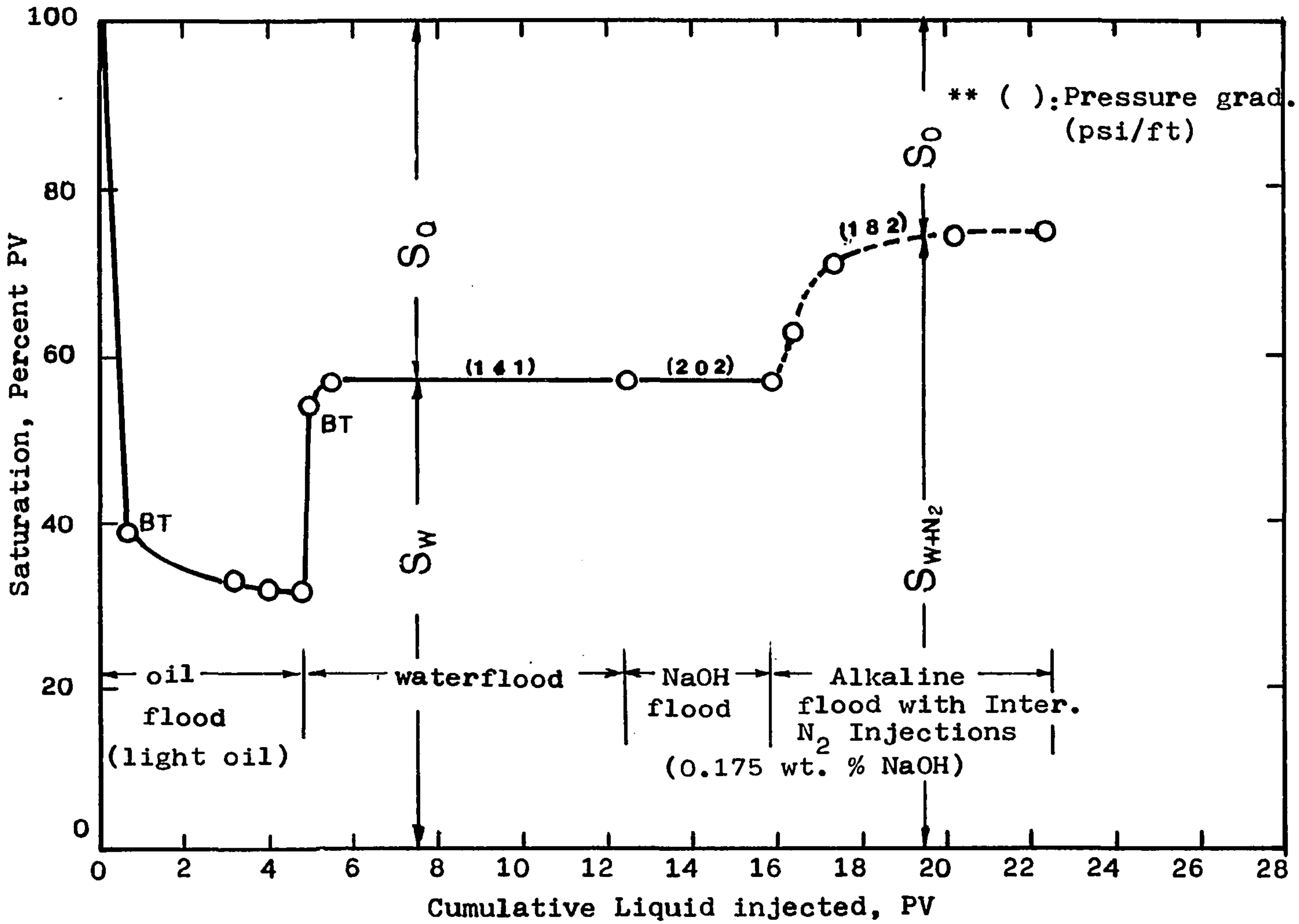

FIGURE 7.4- DISPLACEMENT TEST FOR CORE # 4 AT 78° F
(Berea Sand, Linear Flood)

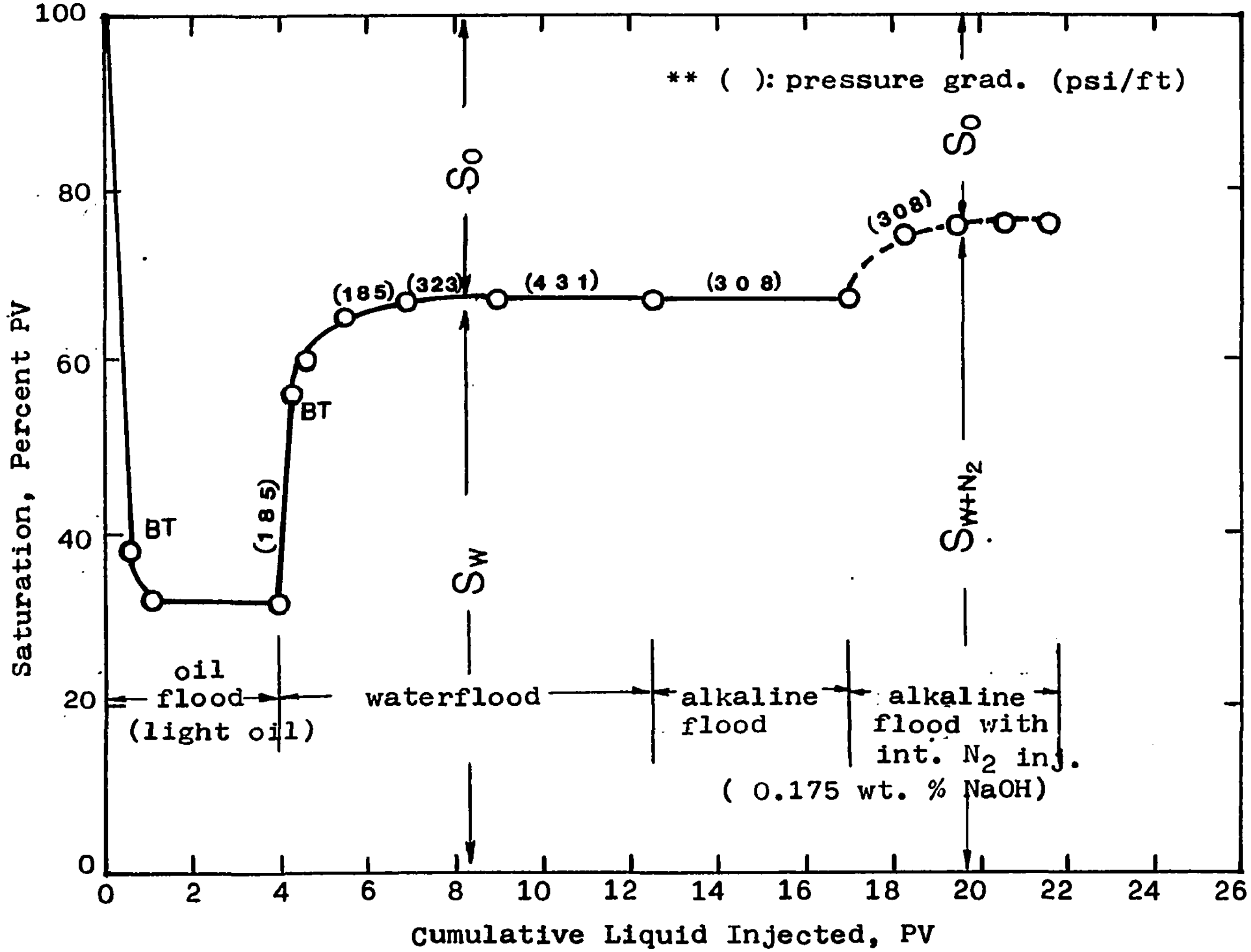

FIGURE 7.5- DISPLACEMENT TEST FOR CORE # 5 AT 78° F
(Berea Sand, Linear Flood)

stabilized at 46.56 percent. Alkaline solution was then injected continuously at escalated pressure gradients from 91 psi/ft to 594 psi/ft, and significant improvement in oil recovery was observed. The final residual oil saturation due to alkaline injection was 36.15 percent. Nitrogen was then introduced intermittently and in the meantime the injection pressure gradients were escalated gradually from 91 psi/ft to 400 psi/ft. The results as shown in Figure 7.6 indicate that a final residual oil saturation of 25.56 percent was obtained.

(3) Waterflood Followed by Oil Slug Injection And Continuous Alkaline Flood with Intermittent Nitrogen Injection: Four cores, as described in Table V were used for the purpose of studying the influence of acidic oil slug injection during alkaline flood.

To begin with, core #7 was saturated with oil to an initial saturation of 62.20 percent and waterflooded to a residual oil saturation of 44.20 percent at 70 psi/ft. An acidic oil slug of 1.3 cc (or approximately 4.25 % PV) was injected into the core and was followed by continuous injection of 0.175 percent by weight oaustic solution at constant pressure gradient of 70 psi/ft. Significant

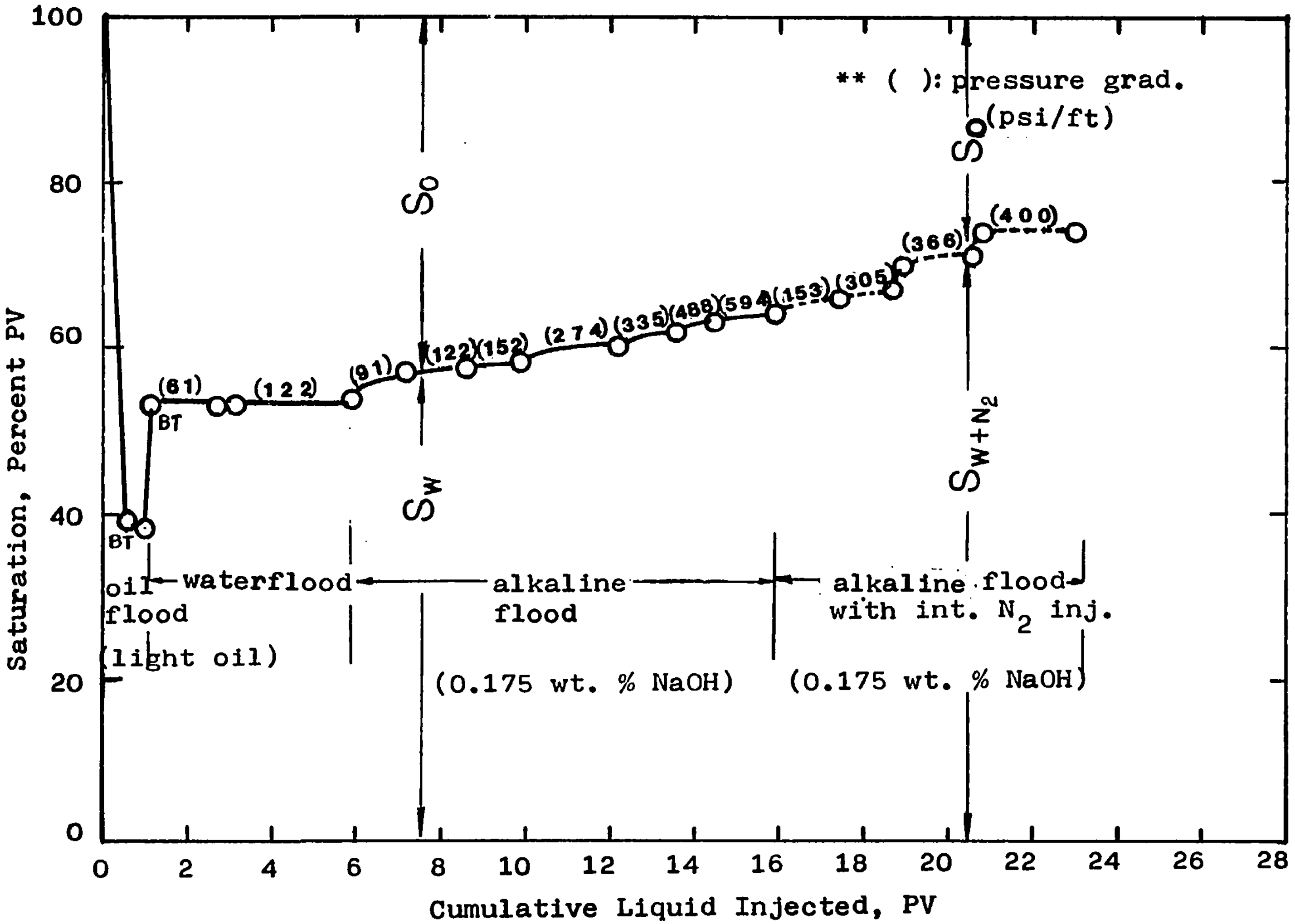

FIGURE 7.6- DISPLACEMENT TEST FOR CORE # 6 AT 78^{o} F
(Berea Sand, Linear Flood)

improvement in oil recovery was observed. The results as shown in Figure 7.7 indicate that a final residual oil saturation of 38.65 percent was obtained after the injection of 7.5 pore volumes of alkaline solution.

TABLE V

PROPERTIES OF CORES USED IN CATEGORY 3

Core No.	Size Length x Diameter (cm x cm)	Liquid Permeability (md)	Porosity (%)
#7	15.3x3.7	262.0	18.60
#8	15.1x3.7	282.0	19.60
#9	15.5x3.7	419.0	21.12
#10	15.0x3.7	509.0	20.34

A similar process was conducted in core #8 except a second acidic oil slug was injected at the end of the first continuous alkaline injection. It was followed by injection of approximately 1 pore volume of alkaline solution at 166 psi/ft. No significant improvement im oil recovery was observed. Nitrogen was then introduced intermittently at 166 psi/ft. Significant improvement in oil recovery was immediately observed, and the final residual oil saturation as shown in Figure 7.8 was 34.62 percent pore volume.

In core #9, the core was first saturated with oil to a S_{oi} of 68.03 percent, and waterflooded at escalated pressure gradients from 149 psi/ft to 482 psi/ft until a waterflooded residual oil saturation of 38.07 percent was obtained. An acidic oil slug of 1.3 cc (approximately 3.6 % PV) was then introduced into the core and followed by continuous injection of 0.175 percent by weight NaOH solution at escalated pressure gradients from 216 psi/ft to 590 psi/ft. After 5 pore volumes of alkaline solution had been injected, the results indicated that a residual oil saturation of 38.04 percent was obtained. When compared to the oil saturation prior to the injection of the second slug, no improvement in oil recovery can be observed. Nitrogen was then introduced intermittently, and the pressure gradients were increased gradually from 118 psi/ft to 590 psi/ft. Significant increases in oil recovery were observed during the injection of 4 pore volumes alkaline solution. The results in Figure 7.9 indicate that a final residual oil

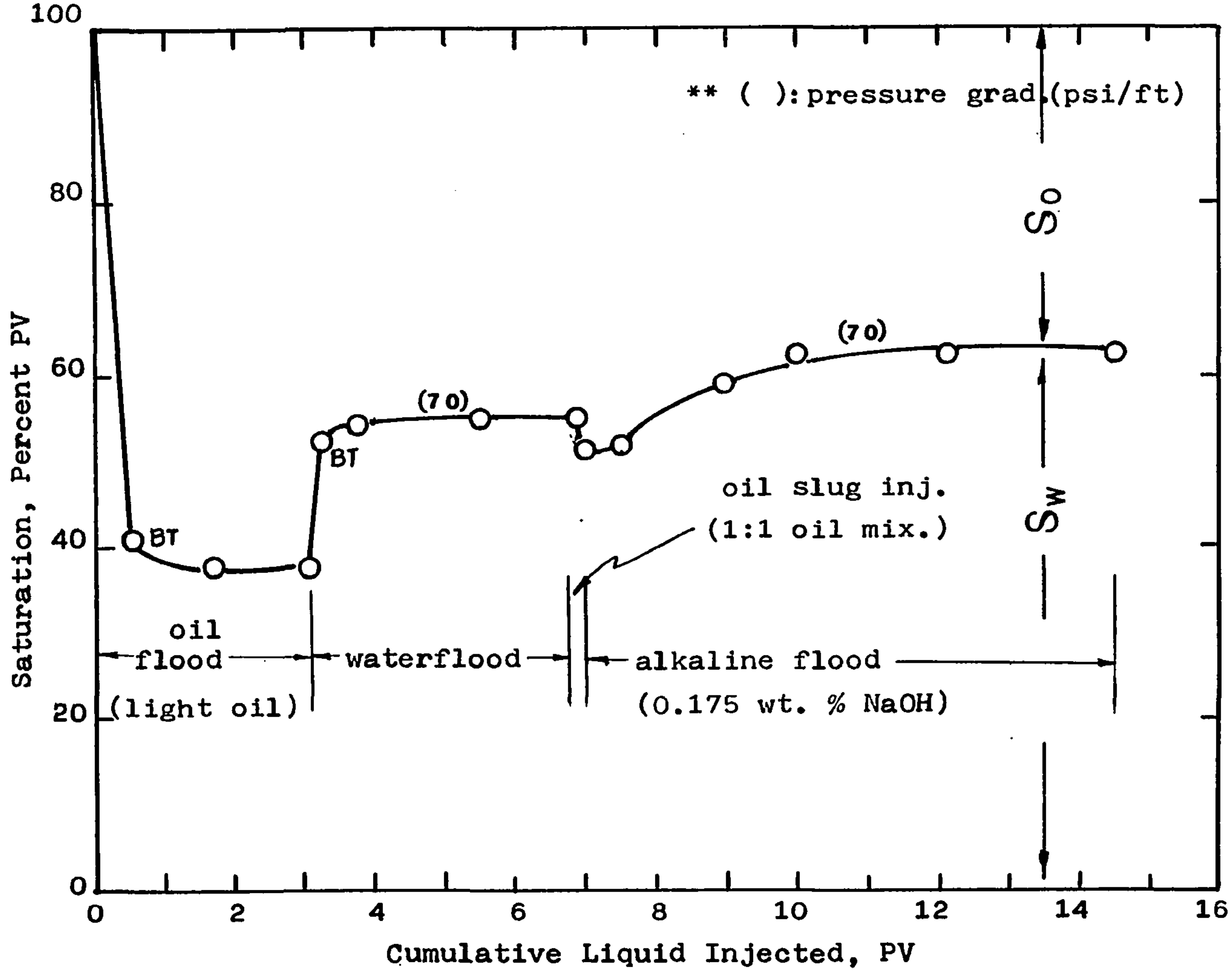

FIGURE 7.7- DISPLACEMENT TEST FOR CORE #7 AT 78° F

(Berea Sand, Linear Flood)

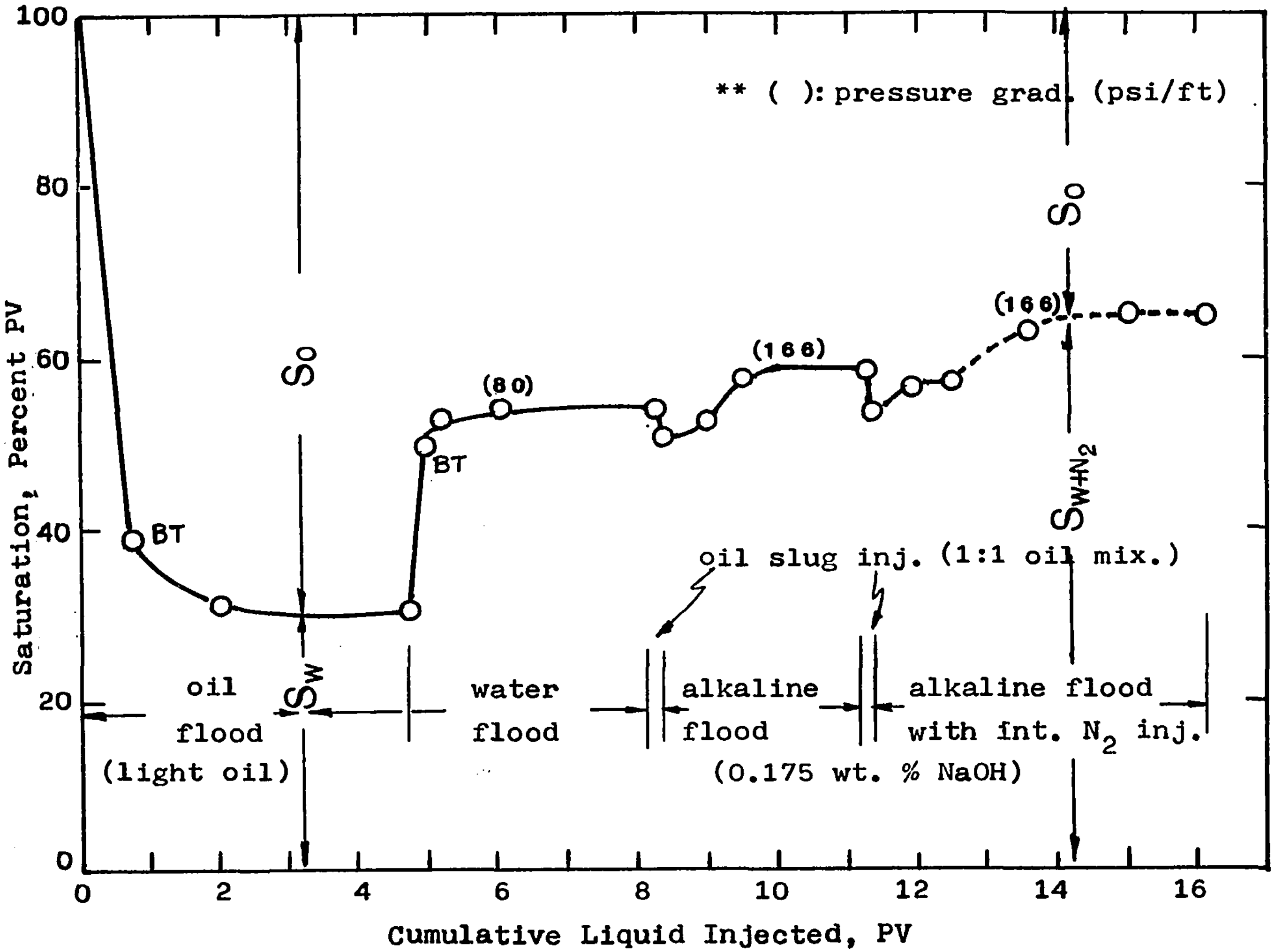

FIGURE 7.8- DISPLACEMENT TEST FOR CORE # 8 AT 78° F
(Berea Sand, Linear Flood)

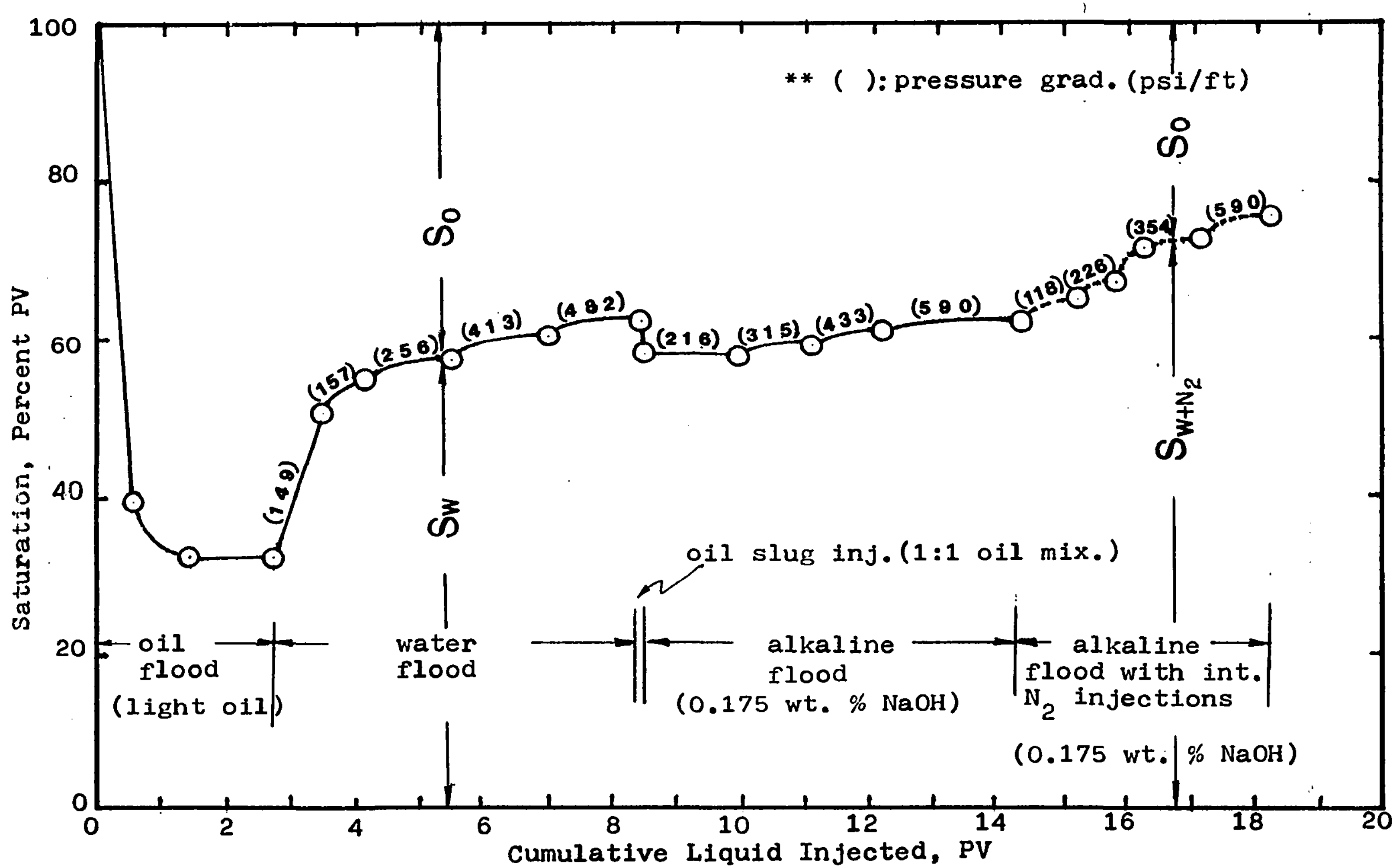

FIGURE 7 .9- DISPLACEMENT TEST FOR CORE # 9 AT 78° F
(Berea Sand, Linear Flood)

saturation of 24.20 percent was obtained.

To further investigate the effect of the second acidic oil slug, core #10 was saturated to S_{oi} of 65.74 percent and waterflooded at 61 psi/ft to a residual oil saturation of 38.07 percent. It was then followed by injection of 1.00 cc (3.5 % PV) of acidic oil slug. Injection of 0.175 percent NaOH solution was carried out continuously at escalated pressure gradients from 134 psi/ft to 224 psi/ft. A slight increase in oil recovery was observed after 6.5 pore volumes of alkaline solution had been injected, thus leaving the residual oil saturation at 34.65 percent. Injection of 1 cc of second acidic oil slug was then started and followed by continuous injection of alkaline solution with intermittent nitrogen injections, while the injection pressure gradients were escalated from 171 psi/ft to 224 psi/ft. As can be seen from Figure 7.10, significant improvement in oil recovery was observed, leaving the final residual oil saturation at 24.90 percent.

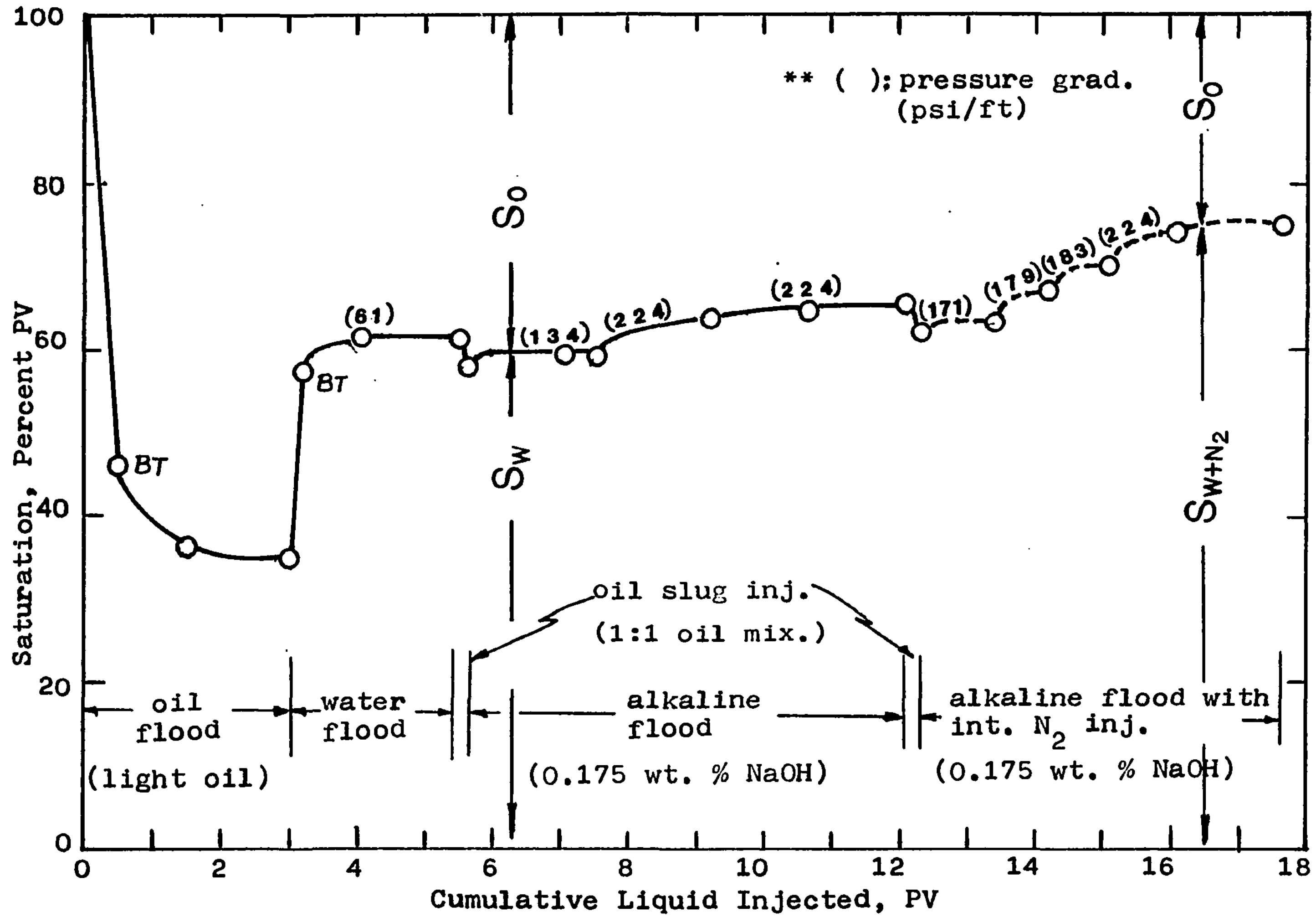

FIGURE 7 .10- DISPLACEMENT TEST FOR CORE # 10 AT 78° F

(Berea Sand, Linear Flood)

Discussion of The Results

According to the theoretical analyses described in Chapter IV, the mobilization of the residual oil in the waterflooded porous media is mainly dominated by the Jamin Effect. An examination of Equations 3-13a and 3-13b indicates that the capillary number curve relating ($\Delta P/L$) or ($\mu_w V_w/\sigma$) to the reduced residual oil saturations is directly proportional to S_p^2, which is very much dependent upon the grain size distribution of a consolidated porous medium. Therefore, the pressure gradient and the capillary number curves will be unique for geometrically similar systems if the improvement in oil recovery is mainly due to the reduction of the interfacial tension or the increase in pressure gradients. Any variations from this condition should be attributed to the change in rock properties or the change in pore size distributions.

To examine this phenomenon, the injection pressure gradients in different recovery processes were plotted with respect to the residual oil saturations using the data obtained in the ten displacement tests. As one can see from the results indicated in Figures 7.11 to 7.16, a general decreasing trend in the residual oil saturation with respect to the increasing injection pressure gradients was observed, although they were not well correlated.

A further comparison was made by plotting the six different processes in Figure 7.17. The results indicated that different levels of injection pressure gradients were required for different recovery processes at a specific residual oil saturation.

Similar experimental results from Dullien and his colleagues,[21] in a tertiary surfactant flood, were found that the residual oil saturations in cores of different properties can be correlated with the Structural Difficulty Index D, which is a function of the pore size distributions. In general, they found that lower pressure gradient is required for porous medium of larger mean pore neck diameter to reach a specific residual oil saturation. Among the porous media they used, the results indicated that a unique curve was found for a specific type of porous medium when the pressure gradients ($\Delta P/L$) were plotted with respect to the residual oil saturation in the surfactant floods they ran.

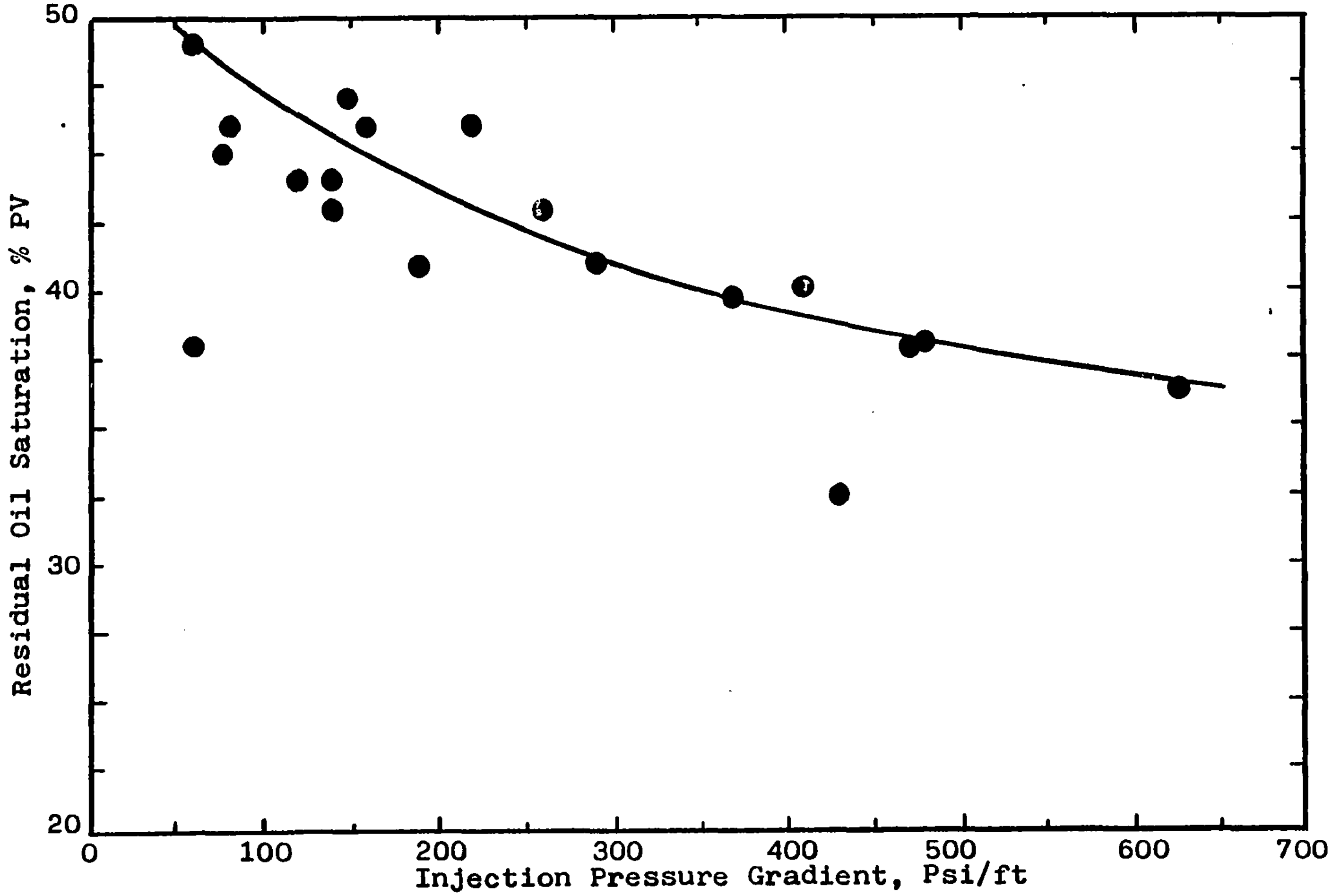

FIGURE 7.11- INJECTION PRESSURE GRADIENT VS S_{or}
FOR WATERFLOOD PROCESS AT 78^{o} F

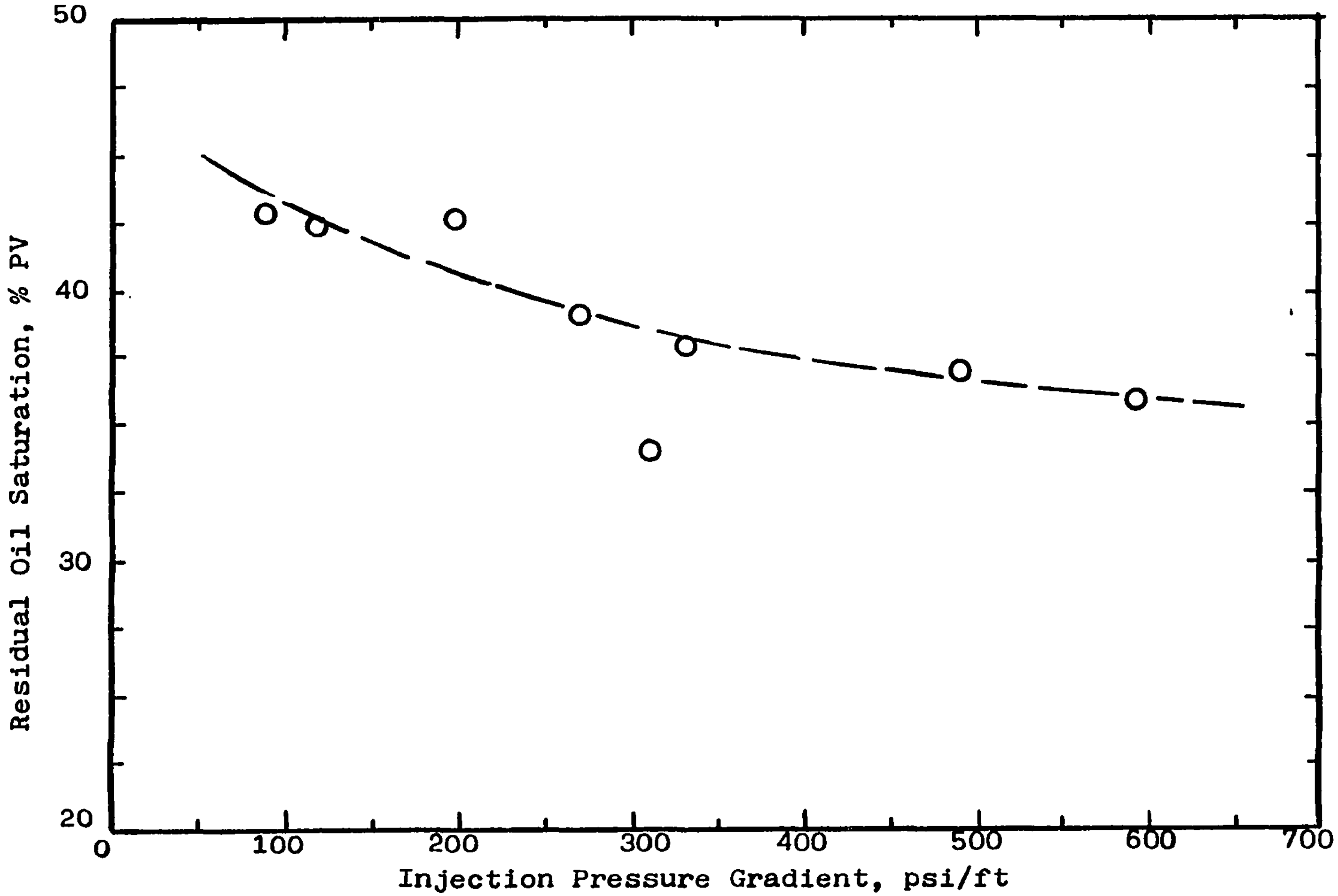

FIGURE 7.12- INJECTION PRESSURE GRADIENT VS S_{or}
FOR ALKALINE INJECTION PROCESS AT 78° F

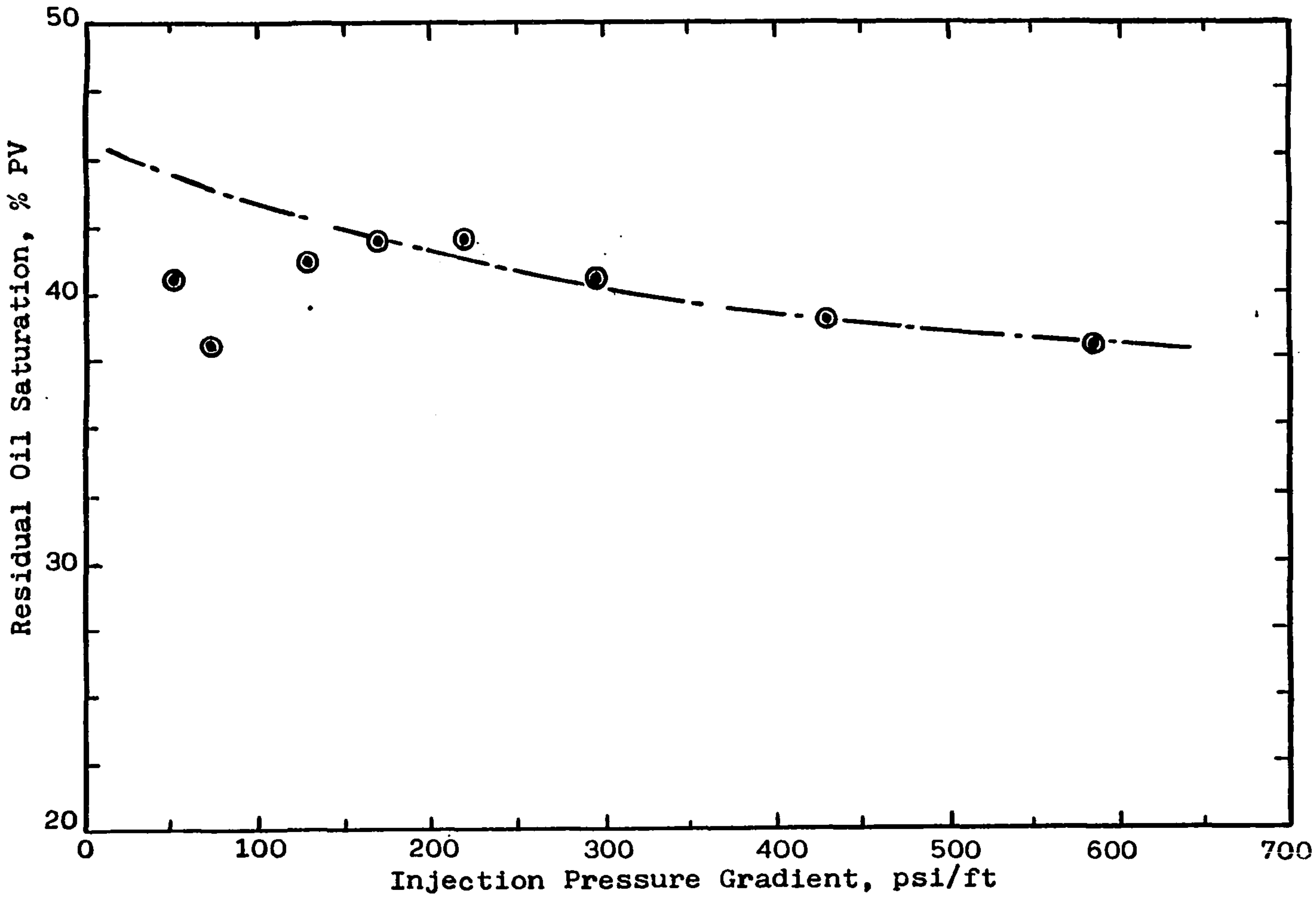

FIGURE 7.13- INJECTION PRESSURE GRADIENT VS S_{or} FOR ALKALINE-OIL SLUG INJECTION PROCESS AT 78° F

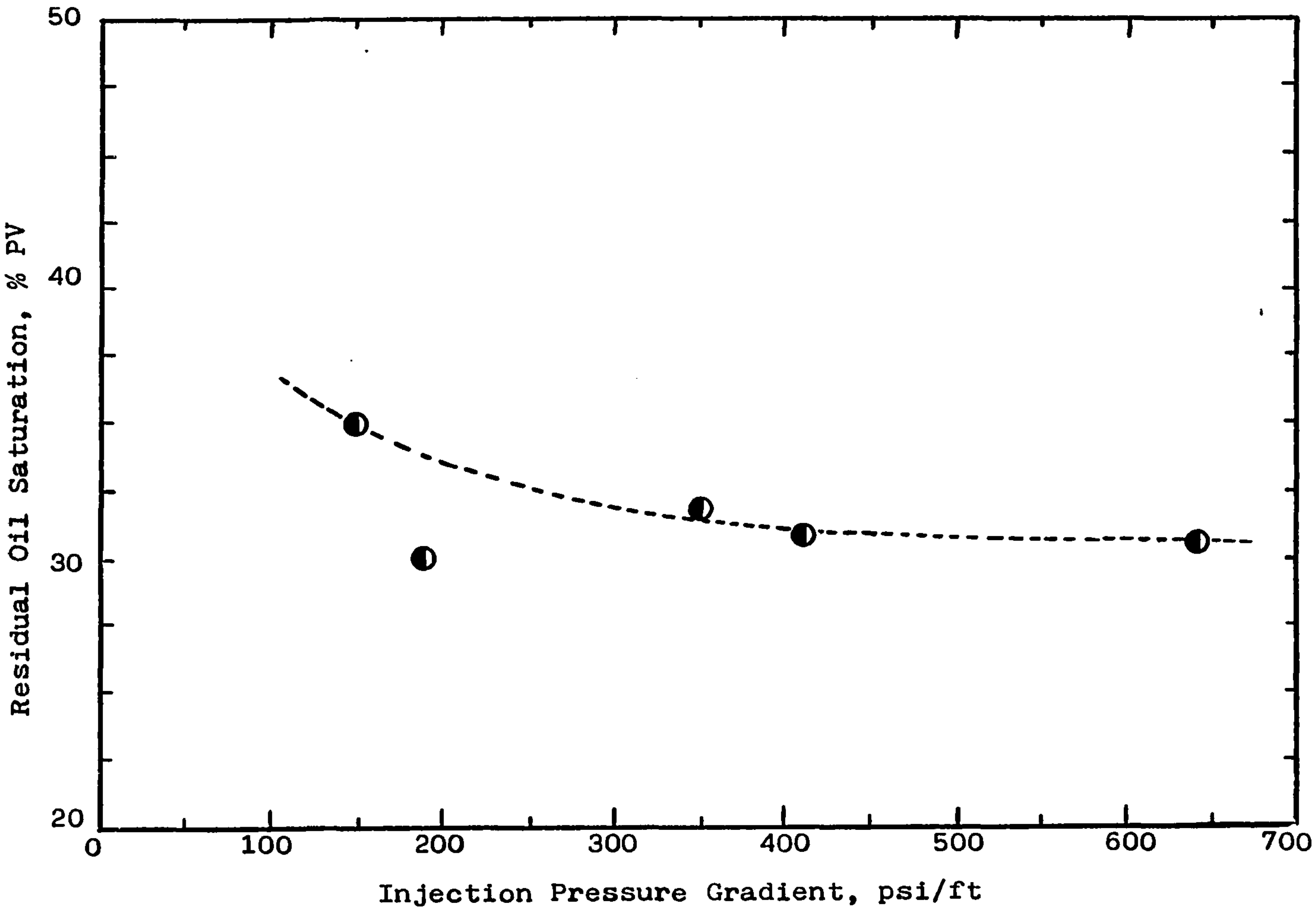

FIGURE 7. 14- INJECTION PRESSURE GRADIENT VS S_{or} FOR WATERFLOOD-NITROGEN INJECTION PROCESS AT 78° F

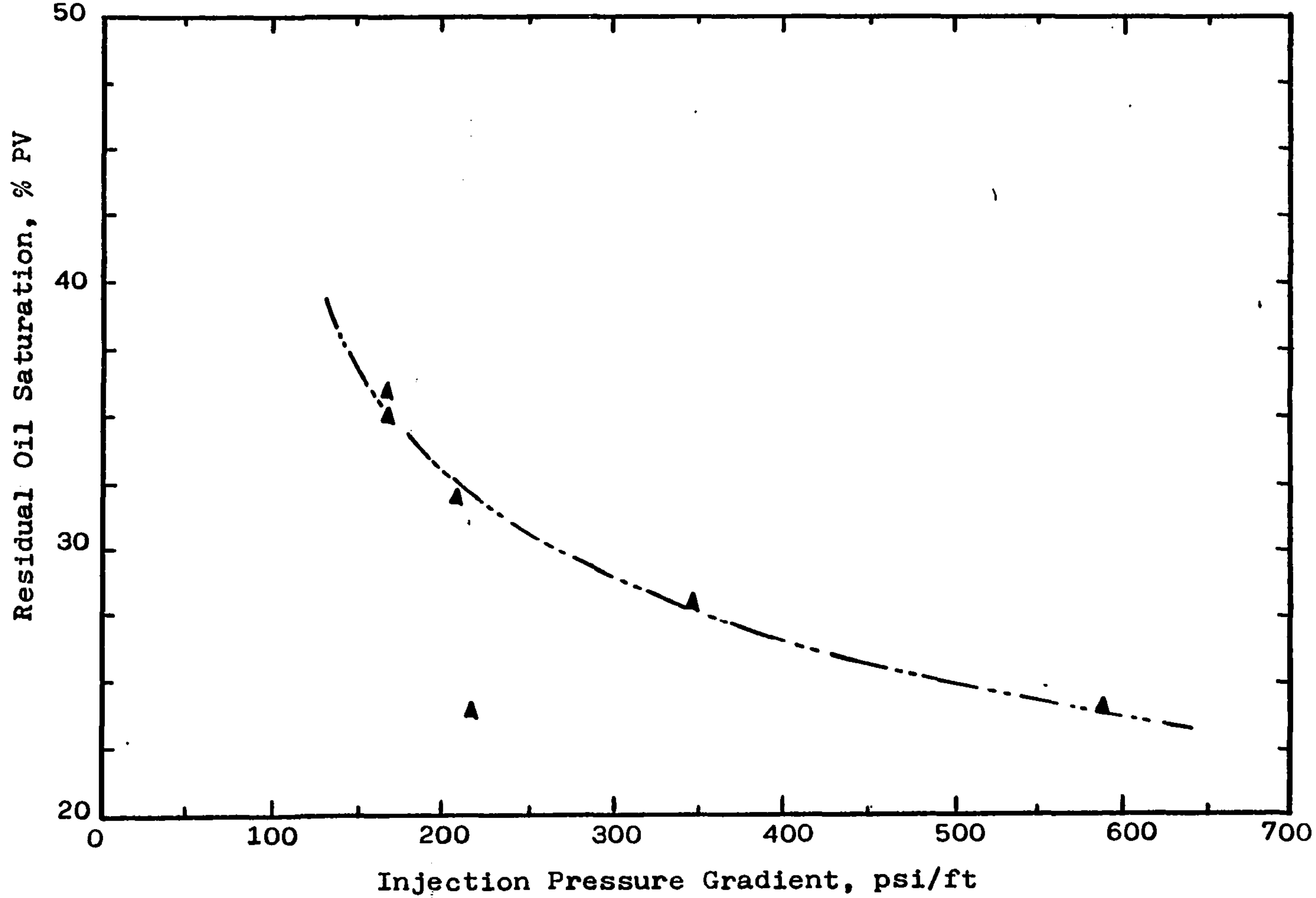

FIGURE 7. 15- INJECTION PRESSURE GRADIENT VS S_{or} FOR ALKALINE-OIL SLUG- NITROGEN INJECTION PROCESS AT 78^{o} F

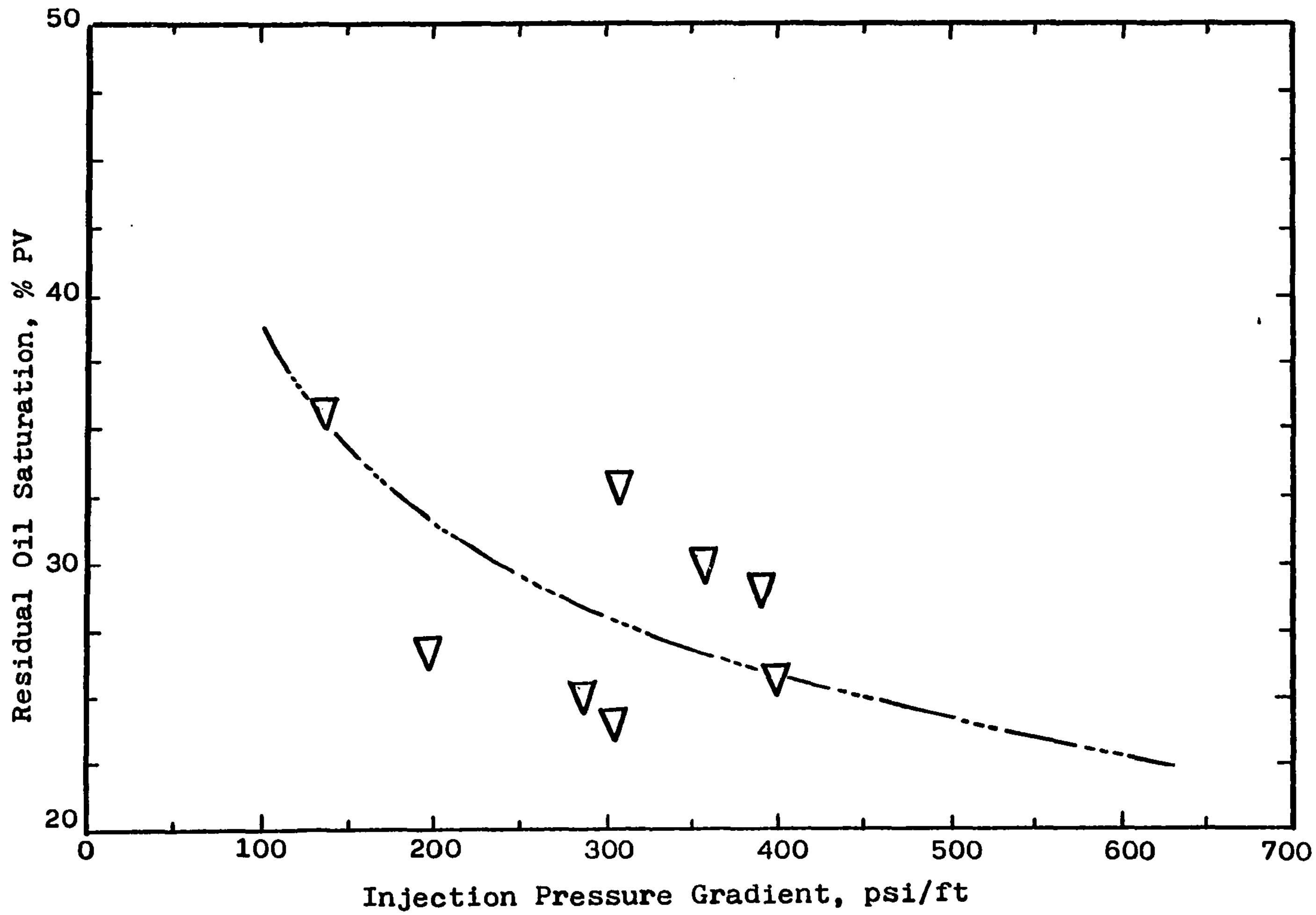

FIGURE 7.16- INJECTION PRESSURE GRADIENT VS S_{or} FOR ALKALINE-NITROGEN PROCESS AT 78° F

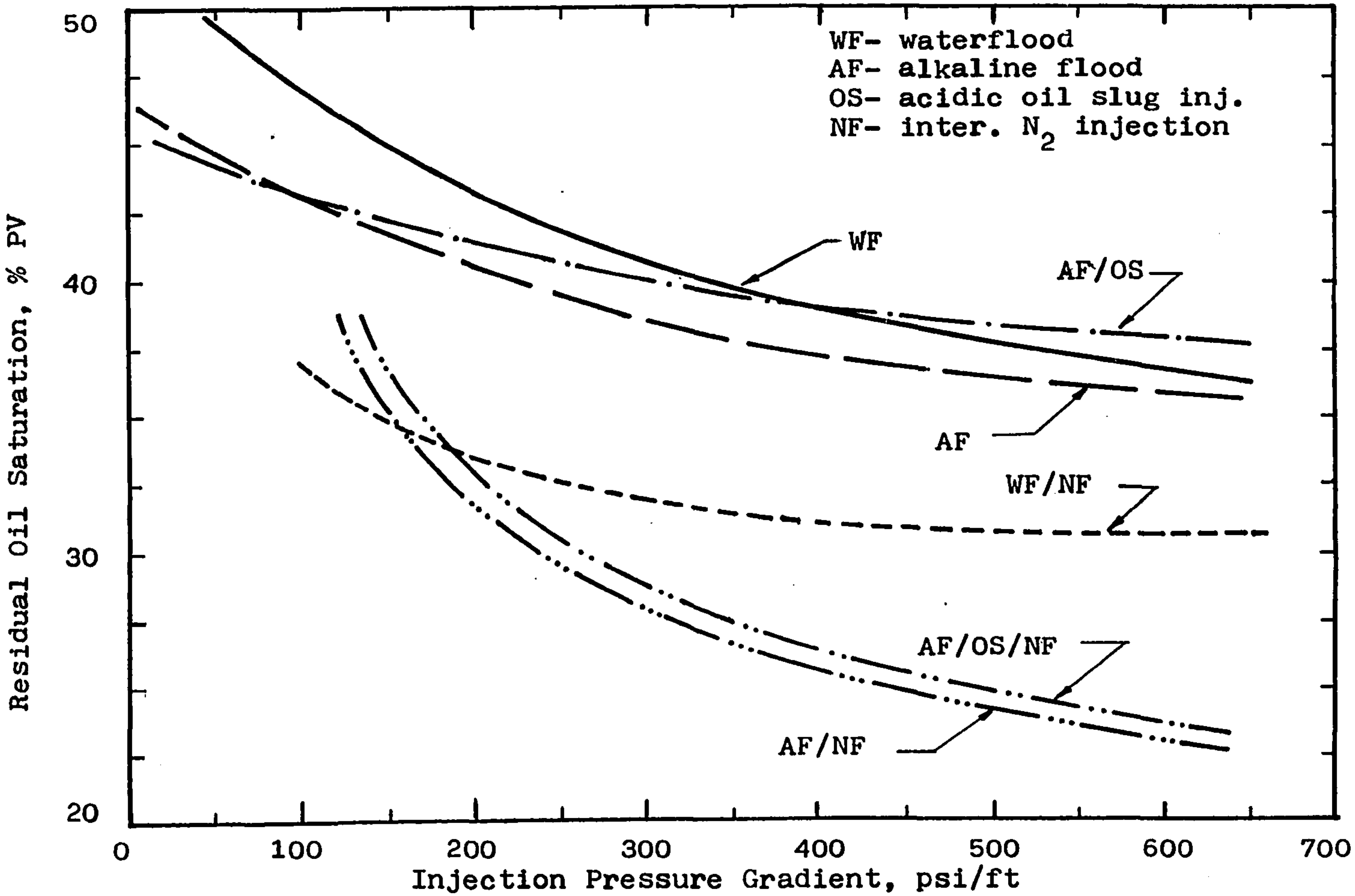

FIGURE 7.17- INJECTION PRESSURE GRADIENT VS S_{or}
FOR DIFFERENT PROCESSES AT 78^oF

By the same token, the results observed in Figure 7.17 suggest that the recovery mechanisms by different processes in porous media of basically similar rock properties (all Berea Sandstones) yield similar recovery behaviors to that which occurs in porous media of different rock properties. The explanation of this phenomenon could be (1) chemical reactions between the injection fluid and the rock body, which change the pore structure of the rock samples, and (2) selective plugging of pore spaces by foreign materials such as emulsion droplets or dispersed clay particles.

It is very unlikely that dissolution of the rock structure due to chemical reactions between the injected fluids and the rock body occur because the fluids used are either inert in chemical reactions, such as nitrogen, or very weak in chemical reactions because the alkaline solution used is only 0.175 wt. percent in concentration. This is not chemically active enough to cause dissolution of the rock body to any extent. Therefore the only explaination left for the non-unique curves obtained in different processes is the selective plugging of the porous medium.

The results indicated in Figure 7.17 also suggest that there are basically three distinct levels of selective plugging effects existing in the improved oil recovery processes. First, selective plugging effect from in-situ emulsion droplets and dispersed clay particle which is basically minor. It is believed that the selective plugging has occurred in the flow passages of the smaller doublet systems. Second, the bubbles created from intermittent nitrogen injection provide the residual oil recovery by plugging the flow paths of the larger doublet systems. Third, the combination of emulsion and nitrogen bubbles, as well as the combination of dispersed clay particles and the nitrogen bubbles, provides wider ranges of selective plugging in the porous media; consequently, higher pressure gradients were built up in the region of larger doublet systems and yielded more recovery in residual oil left by waterflood.

The hypothesis described above can further be justified by the results indicated in Figure 7.18, which is obtained by plotting the logarithm of capillary number ($V_w \mu_w / \sigma$) with respect to the reduced residual oil saturations. This plot indicates a phenomenon similar to the one observed in Figure 7.17. As having been well described in Equation 3.13b, the alkaline-oil slug-nitrogen process reveals that the best selective plugging occurred in such a manner that the residual oils in most of the medium to large doublet systems had been effectively swept.

It should be noticed that all the analyses made above were based upon the assumption and the facts that all of or at least the majority of the doublet systems in the porous media had been completely swept during the ordinary waterflood process, and as a result, residual oils were left behind in the larger arms of the flooded doublet systems. Therefore, the improvement in residual oil recovery during the enhanced oil recovery processes mentioned above was essentially dominated by the Jamin Effect.

The understanding of the properties of the dispersed clay particles, the emulsion droplets and the nitrogen bubbles mentioned above can further serve to explain the recovery mechanisms in different injection processes. Clay contents are generally believed to be

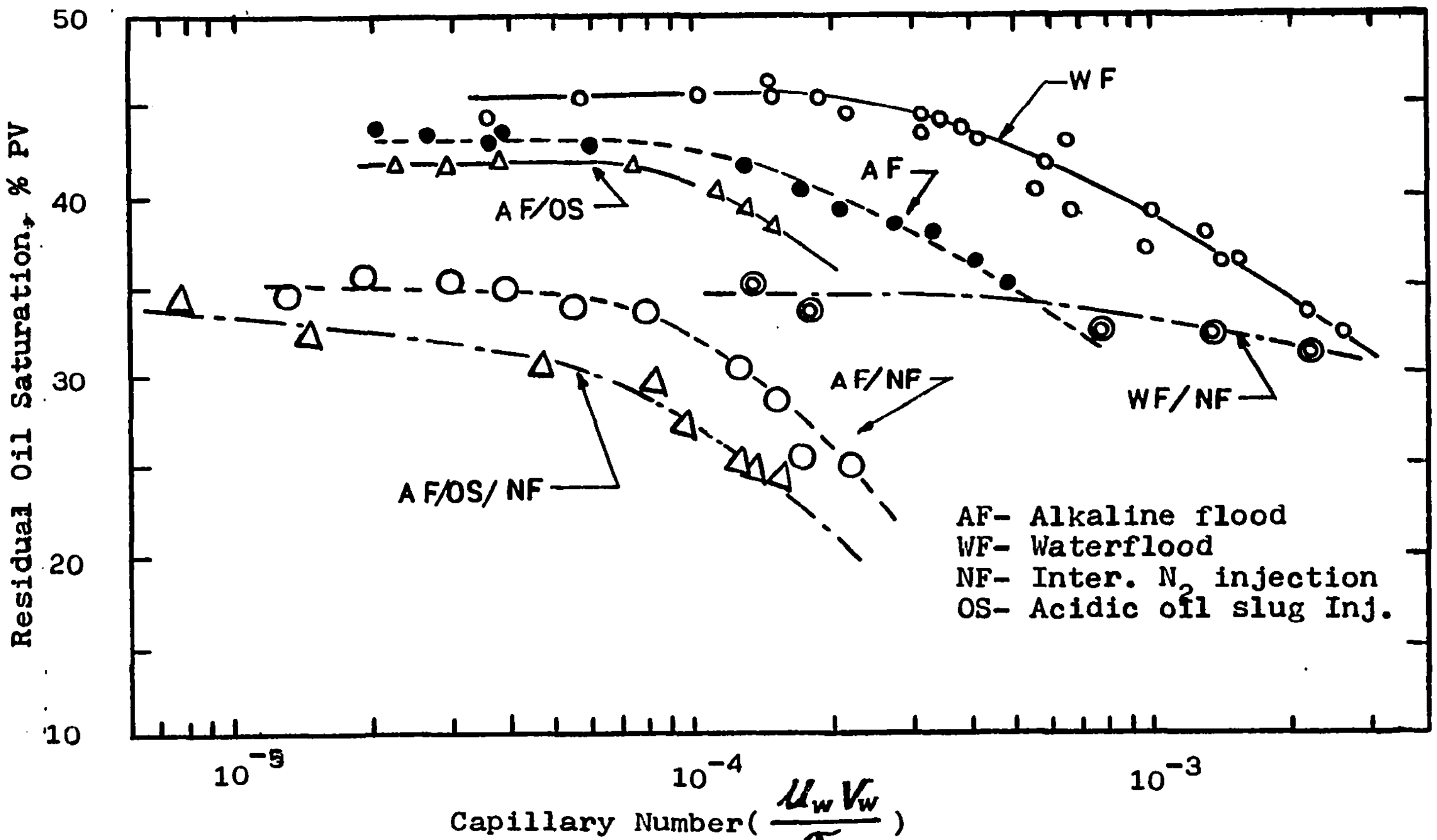

FIGURE 7.18- CAPILLARY NUMBERS VS S_{or} FOR DIFFERENT RECOVERY PROCESSES AT 78° F

harmful to the improved oil recovery processes. Clay may adsorb many substances which may be injected into the reservoir to improve oil recovery. Particularly in the alkaline flooding process, hydroxyl effect will promote clay cleavage, disperse the clay particles, and block the pore passages. However, in case of sandstone formations of relatively clean or low clay content, clay swelling can be controlled to a certain extent that the flow path-blocking effect can be used as a mechanism for improving the oil recovery.

To demonstrate this idea, two Berea cores were saturated with brine and flooded with alkaline solutions of 0.175 wt. percent NaOH and 1.0 wt. percent NaOH respectively. The results as shown in Figure 6.2 indicate that after 15 pore volumes of 0.175 wt. percent NaOH solution had been injected, the permeability reduction was well controlled within 25 percent of its initial value. On the other hand, 55 percent reduction in permeability was observed after 6 pore volumes of 1.0 wt. percent NaOH solution had been injected.

More specifically, a Berea sandstone of 400 md, for example, will have equivalent capillary tubes of 8 microns in diameter. The particle sizes for clay minerals are generally between 0.2 to 4 microns in diameter, it is therefore reasonable to assume that some dispersed clay particles will successfully block the flow passages of smaller diameters and the rest will flow through the flow passages of larger diameters if the clay swelling is controlled to a certain extent.

The droplet size of the oil-in-water emulsions varies in a much wider range, depending upon the type and the content of surface active materials in the crudes. McAuliffe and his colleagues[37,38] found that for most of the acidic oils, emulsion droplet size ranges from 0.1 to 12 microns in diameter. Inspecting the results indicated in Figure 7.17 and 7.18, one may reasonably assume that the average droplet size for the acidic oil slugs used in this study is similar to the particle size of the clay particles except that the droplet size distribution is more uniform. Furthermore, because of the fact that alkaline-nitrogen process yields better recovery than brine-nitrogen process and that brine-nitrogen process yields better recovery than alkaline-oil slug process, therefore, it is reasonable to assume that nitrogen bubbles provide the selective plugging effect in most of the medium to large doublet systems.

More experimental observations of the selective plugging effects in different processes were made by monitoring the PH changes in the producing liquids. Figure 7.19 indicates the PH variations of the producing liquids in the alkaline-nitrogen process. As one can see that the PH values stabilized at 12.4 after the injection of 1 pore volume of 0.175 percent (by weight) NaOH solution. However, periodic reductions in PH responded to the intermittent nitrogen injections were observed until no more oil is producible. This reveals the occurrence of the continuous selective plugging effects by the increasing gas saturation from the successive intermittent nitrogen injections. The PH reduction in each production period is believed to be due to the dilution of the alkaline solution with the brine water which had been left behind the trapped oil during the waterflooding. The variations in PH values of the producing liquid of the alkaline-oil slug-nitrogen process was also plotted as shown in Figure 7.20. Drastic reduction in PH value was observed with each oil slug injection. It is particularly obvious

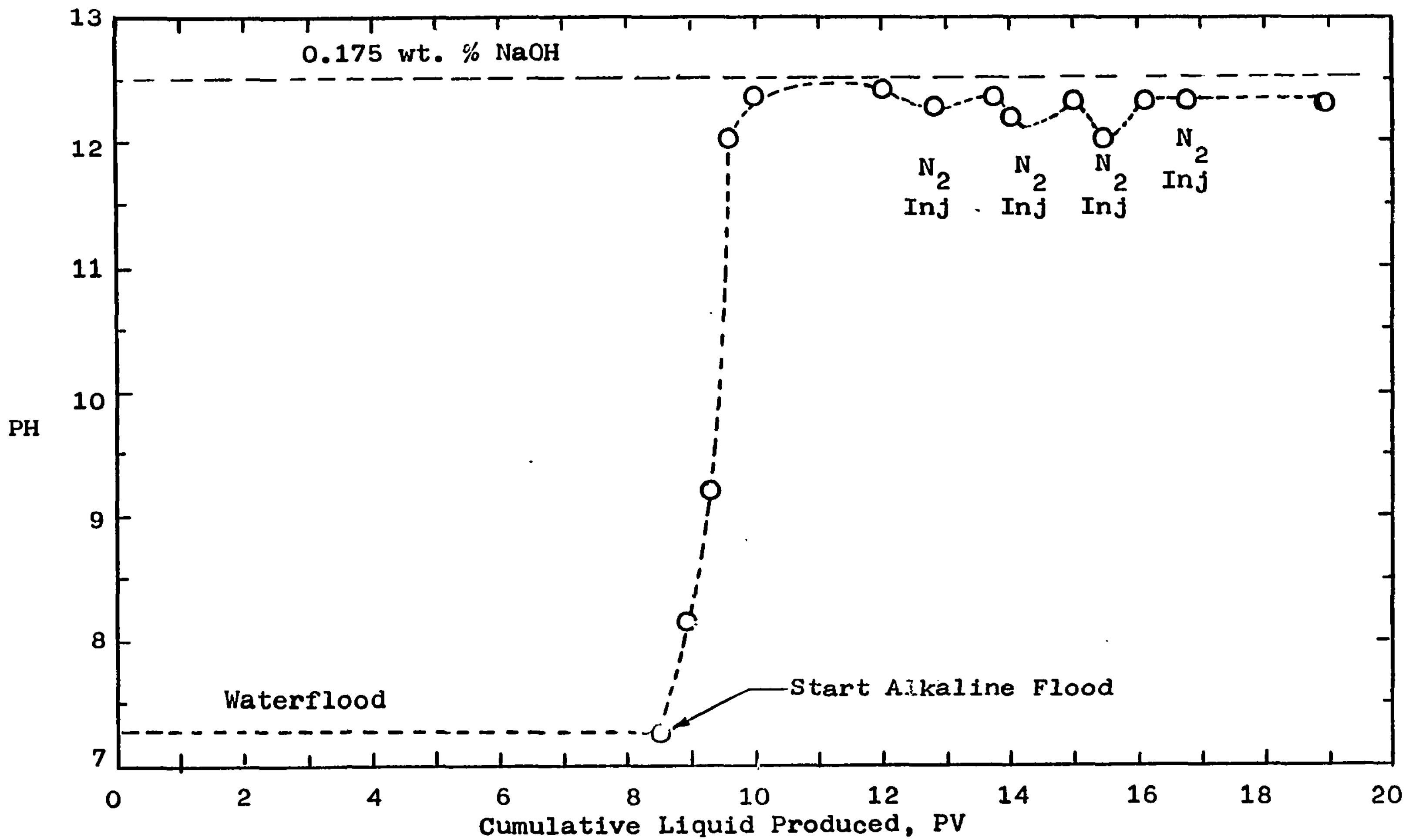

FIGURE 7.19 - PH VARIATION OF PRODUCING WATER FOR ALKALINE- NITROGEN PROCESS

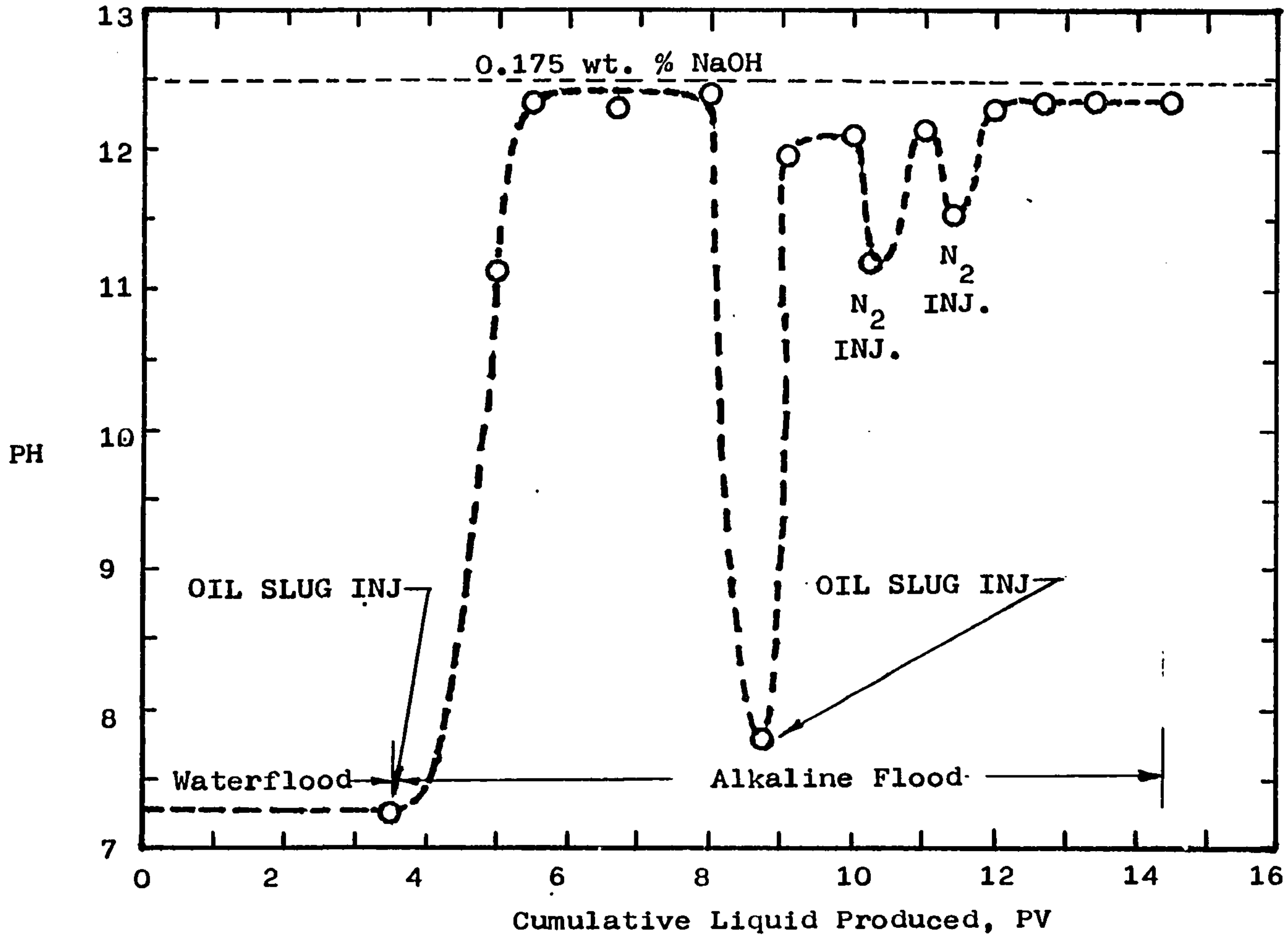

FIGURE 7.20- PH VARIATION OF PRODUCING WATER FOR ALKALINE-OIL SLUG-N_2 PROCESS

in the injection of the second oil slug. The PH reduction was mainly due to the alkaline consumption by in-situ emulsification of the acidic oil and partially due to the dilution of the injected alkaline solution by the produced connate water. Similar but more severe PH reductions to that of alkaline-nitrogen process were observed during the intermittent injections of nitrogen. This suggests that a better plugging effect was obtained by the combined effects of the nitrogen bubbles and emulsion droplets. Figure 7.21 also gives an example of the effect of slective plugging by clay particles and the continuous effect of nitrogen injections in the alkaline-nitrogen injection process. The manner that the PH reductions responded to the oil recovery in the intermittent nitrogen injections after continuous alkaline injection suggests that nitrogen bubbles provide a better plugging effect in the pore passages of larger diameters.

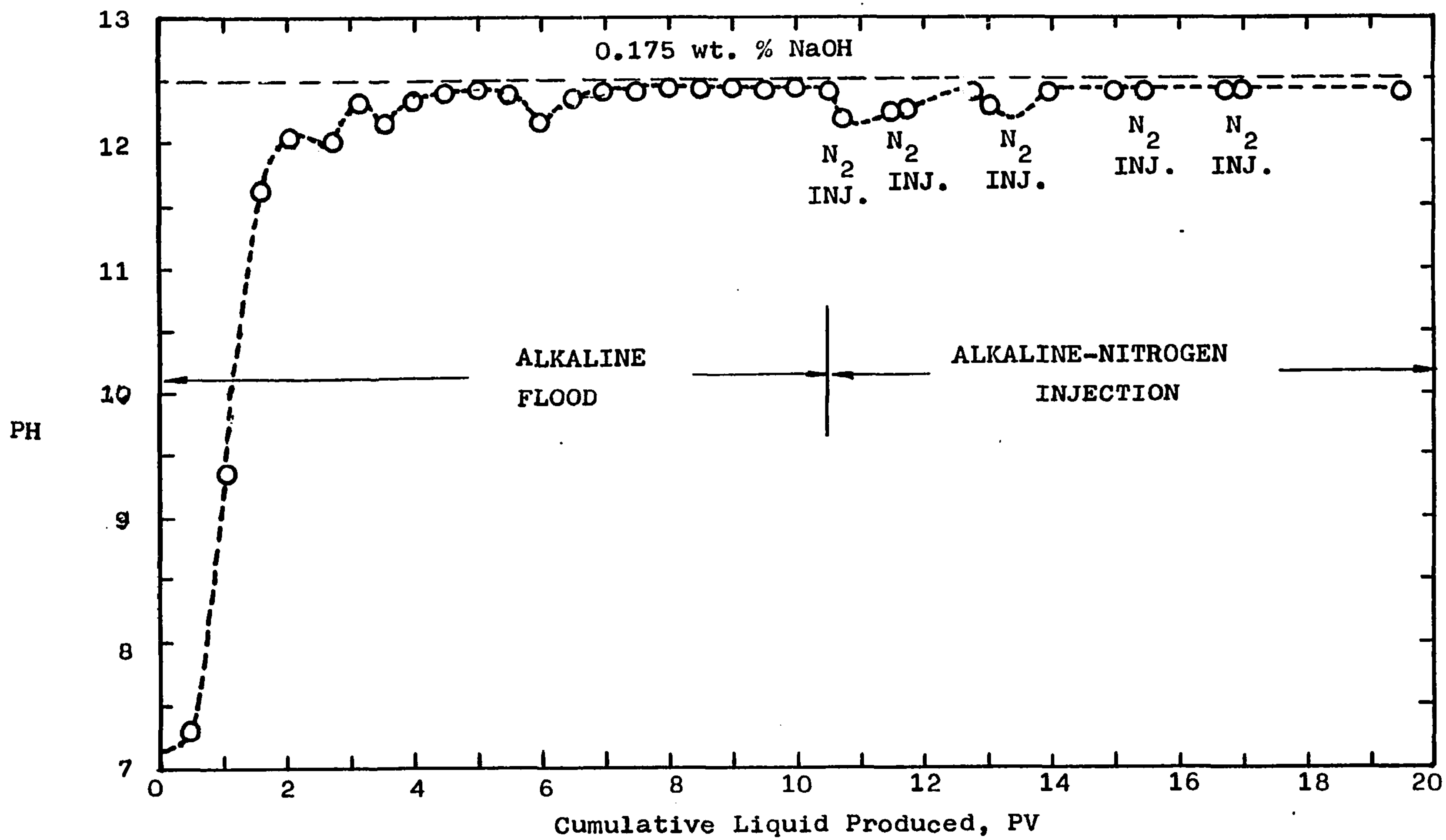

FIGURE 7.21- PH VARIATION OF PRODUCING WATER FOR ALKALINE-NITROGEN PROCESS

Effect of Temperature

In view of the previous discussions, it is clear that the recovery processes including various combinations of alkaline injection, acidic oil slug injection, and nitrogen injection can improve the recovery of the waterflood residual oil saturation to various extents. Therefore, further investigations on the effect of temperature to three of the most favorable recovery processes were made. The processes of waterflood-nitrogen injection, alkaline-nitrogen injection, and alkaline-oil slug-nitrogen injection were conducted at 150° F using three different cores.

For the purpose of comparisons between the results of 150° F and 78° F, Curves of $\Delta P/L$ .vs. S_{or}, and ($\mu_w V_w / \sigma$) .vs. S_{or} at 150° F were plotted against those of 78° F. Inspecting the results indicated in Figure 7.22, one can see that both the alkaline-nitrogen injection process and the alkaline-oil slug-nitrogen injection process yielded lower pressure gradients required at 150° F than those required at 78° F to remove the residual oil saturation in the region of pressure gradients less than 300 psi/ft. While in the waterflood-nitrogen injection process, no

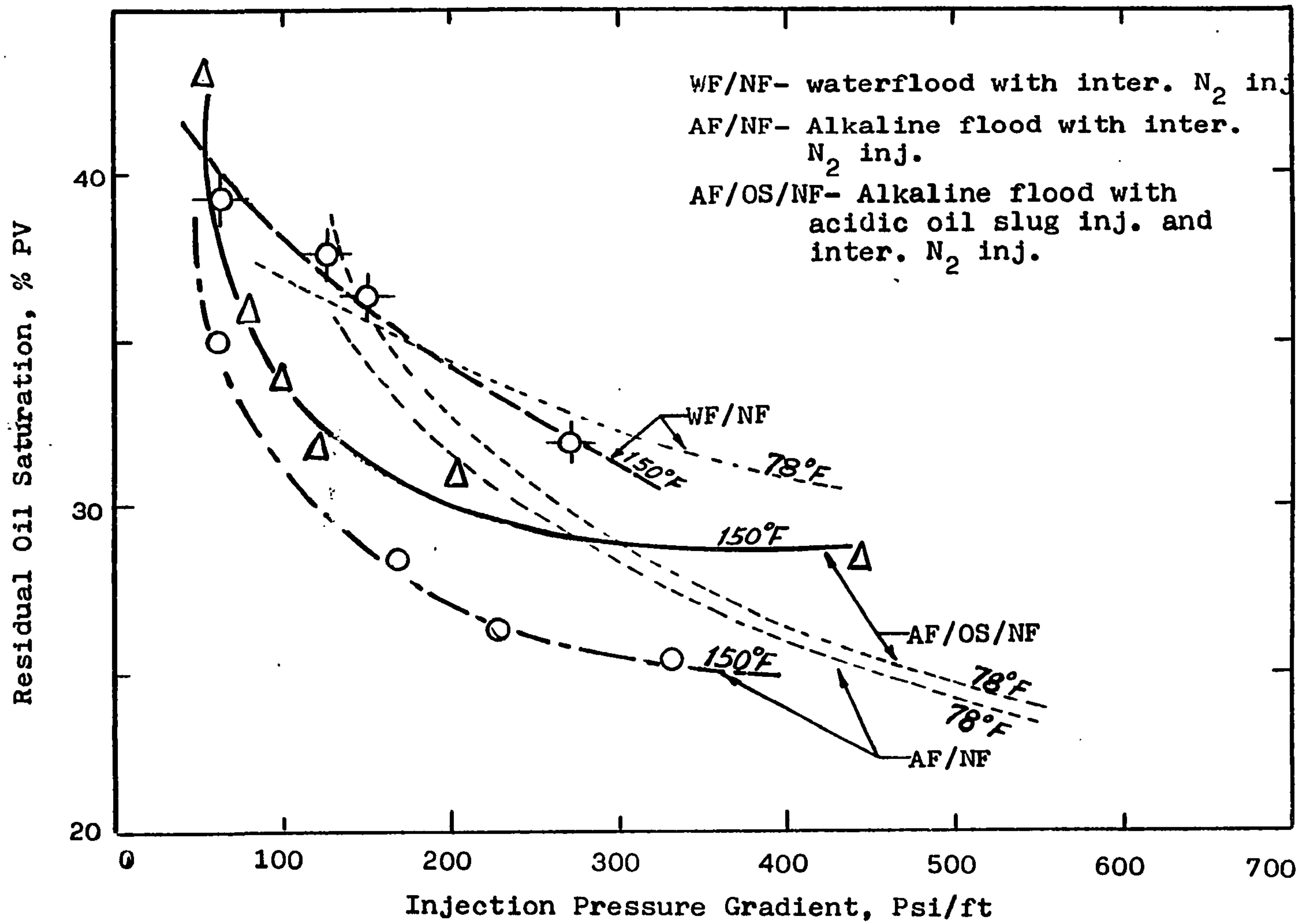

FIGURE 7.22- INJECTION PRESSURE GRADIENT VS S_{OR} FOR DIFFERENT PROCESSES AT 150° F & 78° F

improvement in recovery pressure gradient was available as compared to that of 78° F. The possible explanation of this phenomenon is that the effective plugging for nitrogen bubbles generally occurs in the flow paths of larger doublet system in which capillary force domination is minor compared to the viscous force domination. However, in capillaries of smaller doublet systems, the removal of residual oil by the capillary force domination is significant. Therefore, while the temperature increasing, the reductions in fluid viscosities provide a higher flow velocity in the flow path to such an extent that the removal of the residual oil shifts from the capillary force domination to the viscous force domination, and finally yields a lower pressure gradient for residual oil removal. This is true as indicated in Figure 7.22, when alkaline solution and oil slug were used in the improved oil recovery processes. In which the oil emulsion droplets and dispersed clay particles are supposed to be effective in plugging the flow paths of smaller doublet systems.

This explanation can further be justified by the results as shown in Figure 7.23, where constant

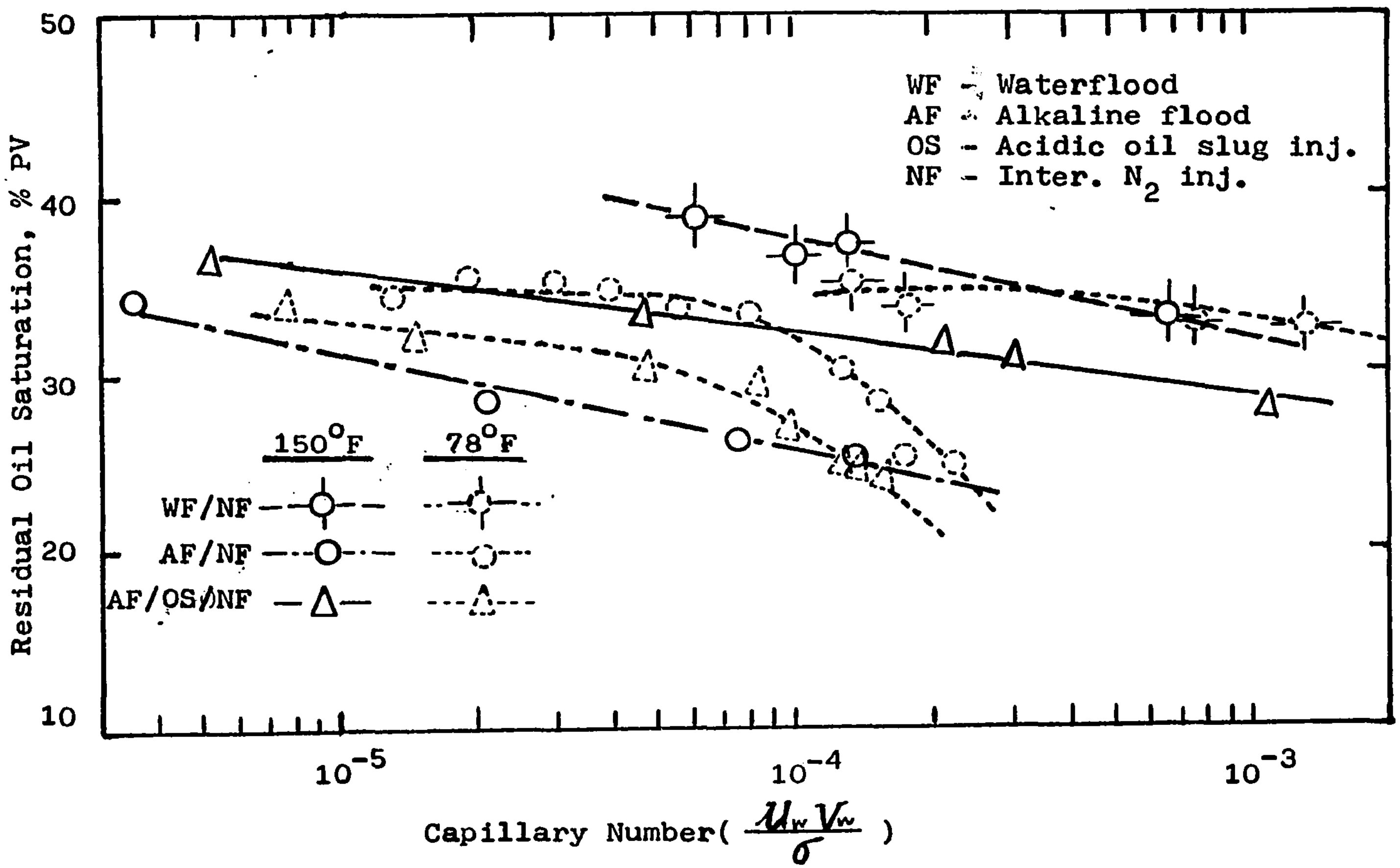

FIGURE 7.23- CAPILLARY NUMBER VS S_{or} FOR DIFFERENT RECOVERY PROCESSES AT 150° F & 78°F

slopes were found in all three curves at 150° F when the residual oil saturations were plotted against the capillary numbers. According to Abrams' study[1], the constant slope in capillary number-residual oil saturation plot indicates a gradual shift from the capillary force domination to the viscous force domination in the residual oil removal.

Inspecting the pair of curves for waterflood-nitrogen injection process for both temperatures, one can find that both curves indicate relatively similar constant slopes, which once again reveal that nitrogen is mainly effective in plugging the flow paths of larger doublet systems. On the other hand, the curve pairs of the alkaline-nitrogen process and the alkaline-oil slug-nitrogen injection process indicated that removal of residual oil was mainly dominated by capillary forces at 78° F and shifted to the viscous force domination when the temperature was increased to 150° F. As a result, this once again confirms that the dispersed clay particles and emulsion droplets are effective mainly in the flow paths of smaller doublet systems.

At 150° F, the alkaline-oil slug-nitrogen process required higher capillary numbers than those of the alkaline-nitrogen process in order to reduce residual oil saturations. This manner suggests that the combination of clay particles and emulsion droplets at higher temperature provides the plugging effect in smaller doublet systems than those of clay partioles if one assumes that the selective plugging of the nitrogen is an independent event. The reason for this effect is not clear, however, it may serve as an indication of the temperature effect.

CHAPTER VIII

CONCLUSIONS

This study made a useful contribution to the knowledge of the recovery mechanisms available in the possible use of the alkaline and nitrogen injections as an effective economical improved oil recovery method in a waterflood reservoir. As a result of this study, the following conclusions were made for the subject experimental conditions.

1. In a water-wet oil reservoir, the " Viscap" concept dominates the waterflood oil recovery in such a manner that the residual oil is left in the larger capillaries of the entire flooded doublet systems in the porous medium. This phenomenon contributes one of the reasons for the low efficiency in recovering the oil from the reservoir. The trapped oil left in the porous medium is then controlled by both the Jamin Effect and the nature of the doublet system. The isolated oil will not be recovered unless

sufficient pressure gradient is applied across the oil drop to overcome the Jamin Effect which restricts the oil drop from moving. In a sense of practical application, this condition may not be able to achieve because the flooded arm of the doublet will be served as a flow path and thus reduced the pressure gradient across the oil droplet.

2. Besides the application of interfacial tension reduction chemicals, one of the ecomomical approaches to remove the waterflood residual oil is the use of the deep penetrating plugging agents to block the flow paths of the doublet systems. As a result, a local pressure gradient can be built up to remove the isolated oils.

3. In a relatively clean sandstone, the clay swelling can be controlled to a certain extent by injecting alkaline solution of proper concentration such that the dispersed clay particles can be used as an effective selective plugging material to improve the oil recovery in a waterflood reservoir.

4. The injection of an acidic oil slug of

proper size and surface-active material contents which can produce in-situ emulsifications when followed by injecting a proper alkaline solution. The alkaline-oil emulsions formed in the porous medium can therefore be used as a deep penetrating plugging material to improve the sweep efficiency in a waterflood oil reservoir.

5. The injection of nitrogen has been proved to be the most effective selective plugging process in this study. The selective plugging effect can further be promoted by introduction of nitrogen intermittently into the porous medium.

6. It was found in this study that both the dispersed clay particles and the emulsion droplets created in-situ were mainly effective in plugging the flow paths of smaller capillaries, while the nitrogen bubbles were most effective in the flow paths of larger capillaries.

7. Among the favorable combinations of the alkaline injection, the acidic oil injection, and the nitrogen injection as the improved oil recovery processes, it is found that an optimal

recovery process, including the injection of 0.175 weight percent NaOH solution with approximately three cycles of nitrogen injections, will yield the optimum ultimate residual oil saturation. In the fluid system and porous medium used in the displacement tests, all cases indicated a ultimate residual oil saturation as low as about 25 percent pore volume was achieved. And it was also foumd that the ultimate residual oil saturation in this process is independent of the production history.

8. During the alkaline-nitrogen injections, external injection of acidic oil slug did not yield the expected results at least equivalent to that of the alkaline-nitrogen injection. This may be due to the properties of the Berea sandstone which is relatively homogeneous, and may also be due to the property of the acdic oil slug which did not produce the favorable emulsion droplet size distributions.

9. When temperature increases from 78^{o} F to 150^{o} F, it was found that in the recovery

processes we used, the recovery mechanisms for removing the waterflood residual oil shifted from the capillary force domination to the viscous force domination. It has also been found that even in such a different recovery condition, the alkaline-nitrogen injection process still yielded the optimum oil recovery.

10. It is concluded that the successful application of the alkaline-nitrogen injection process is very much dependent upon the characteristics of the porous media, the type of the heavy crudes as an oil slug, as well as the reservoir temperature and the injection pressure gradients. It is therefore suggested that investigations must be made based on the individual reservoir conditions, should one desire to apply the suggested process as a practical EOR method.

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APPENDICES

APPENDIX A

NOMENCLATURE

AF = Alkaline flood

B.T. = Breakthrough

D = Capillary diameter, cm

IFT = Interfacial tension

K = Absolute permeability, darcy

K_{rw} = Relative permeability to aqueous phase

K_z = Kozeny's constant

L = Length, cm

NF = Intermittent nitrogen injection

OS = Acidic oil slug injection

PV = Pore volume

q = Total flow rate, cc/sec

R = Viscosity ratio

r = Radius of capillary, cm

$\bar{r}$ = Average spherical grain radius, cm

S_{oi} = Initial oil saturation, percent

S_{or} = Residual oil saturation, percent

S_p = Specific surface per pore volume, cm^{-1}

V	=	Velocity, cm/sec
WF	=	Waterflood
β	=	D_A/D_B, ratio of capillary diameters between advancing end and receding end.
ϕ	=	Porosity, fraction
ΔP	=	Pressure drop, atm
ΔP_m	=	Pressure drop between advancing end and receding end of an oil drop in the capillary. atm
λ	=	ℓ^*/D_B, ratio between length of oil droplet and capillary diameter at receding end.
μ	=	Visicosity, cp
σ	=	Interfacial tension, dyne/cm

APPENDIX B

SUMMARY OF EXPERIMENTAL RESULTS

TABLE B-1

MEASUREMENT OF VISCOSITIES

Temp. $^{\circ}F$	Viscosity, cp				
	Light Oil	Heavy Oil	Light-Heavy Oil Mixtures		
			1:2	1:1	10:1
78	9.5	203	54	37	11
100	6.6	95	32	28	10
120	5.2	74	27	18	7
140	4.5	-	15	-	4.8
150	4.0	31	12	10	-
160	2.8	23	-	8.5	4.2

** Viscosity of 10,000 ppm NaCl Brine= 0.92 cp @ 78° F

** Viscosity of 10,000 ppm NaCl Brine= 0.45 cp @ 150° F.

** Viscosity of 0.175 wt. % NaOH solution = 0.88 cp @ 78° F.

** Viscosity of 0.175 wt. % NaOH solution = 0.43 cp @ 150°F.

TABLE B-2

MEASUREMENT OF INTERFACIAL TENSIONS

NaOH Conc. Wt. % and PH	Interfacial Tension, dyne/cm (78° F)							
	Light Oil	Heavy Oil	Light-Heavy Oil Mixtures					
			20:1	10:1	5:1	2:1	1:1	1:2
0.05% (PH=12.04)	15.78	12.50	-	-	-	-	-	-
0.10% (PH=12.32)	12.20	1.87	11.14	11.93	11.65	6.8	vl	9.27
0.15% (PH=12.48)	12.10	0.65	10.06	9.24	7.91	0.58	vl	vl
0.175%(PH=12.50)	-	vl	8.54	6.01	4.51	vl	vl	vl
0.20% (PH=12.58)	12.22	1.01	10.05	9.86	8.14	vl	vl	vl
0.30% (PH=12.74)	9.84	1.35	9.06	7.76	6.01	0.60	vl	vl
0.40% (PH=12.76)	7.92	1.51	8.15	6.44	1.94	vl	0.81	vl
0.50% (PH=12.83)	3.85	1.82	5.25	1.19	0.93	1.13	0.98	0.99
0.75% (PH=13.06)	3.69	1.51	4.18	1.53	1.28	1.69	0.88	-
1.00% (PH=13.19)	3.53	1.87	1.78	1.29	1.48	1.08	vl	vl
1.50% (PH=13.28)	3.96	2.98	-	1.74	0.78	vl	vl	-
2.00% (PH=13.40)	5.01	1.92	5.12	2.18	1.83	1.38	0.88	vl
3.00% (PH=13.53)	4.19	1.41	2.91	1.69	2.28	0.98	1.18	0.98
5.00% (PH=13.68)	5.85	4.02	3.93	3.61	3.91	2.85	2.60	2.91

* IFT of Brine-Light Oil = 21.70 dyne/cm @ 78° F.
* IFT of Brine-Light Oil = 20.06 dyne/cm @ 150° F.
* IFT of 0.175 wt. % NaOH-Light Oil = 12.08 @ 150° F.
* IFT of 0.175 wt. % NaOH-1:1 Oil slug = 0.04 dyne/cm @ 78° F.
* IFT of 0.175 wt. % NaOH-1:1 Oil Slug = 0.03 dyne/cm @ 150° F.

** vl = IFT less than 0.5 dyne/cm

TABLE B-3

EXPERIMENTAL RESULTS OF CORE DISPLACEMENT TESTS FOR CATEGORY I

Core#	Satn. Before EOR	Proc	Cum. PV Inj	$\Delta P/L$ Psi/ft	S_{or} %	WOR	K_w @S_{or}	Cap. No	PH
1	S_{oi}=64.04% S_{orwf}=43.78%	1	1.3	189	-	-	-	-	-
		1	2.7	189	-	-	-	-	-
		1	7.0	189	28.55	45	14.5	2.84×10^{-4}	-
2	S_{oi}=69.47% S_{orwf}=35.48%	1	1.2	146	35.02	27	35.0	1.37×10^{-4}	-
		1	3.5	351	32.00	30	24.0	9.68×10^{-4}	-
		1	7.5	410	32.00	-	31.5	1.33×10^{-3}	-
		1	10.7	645	31.4	73	33.0	2.19×10^{-3}	-

** Process 1: Waterflood with Intermittent Nitrogen Injection

TABLE B-4

EXPERIMENTAL RESULTS OF CORE DISPLACEMENT TESTS FOR CATEGORY II

Core#	Sat. Before EOR	Proc	Cum. PV Inj	Δ P/L Psi/ft	S_{or} %	WOR	K_w md	Cap. No	PH
3	S_{oi}=69.24% S_{owf}=44.28%	4	1.36	287	34.9	16	-	-	-
		4	3.00	287	29.9	40	-	-	-
		4	4.20	287	27.6	198	-	-	-
		4	7.10	287	25.0	450	4.1	2.23×10^{-4}	-
4	S_{oi}=68.33% S_{orwf}=43.11%	2	3.50	202	43.1	-	1.5	4.75×10^{-5}	-
		4	4.10	182	36.72	10	-	-	-
		4	5.80	182	29.00	14	-	-	-
		4	7.60	182	24.90	17	-	-	-
		4	10.00	182	24.90	70	4.3	1.44×10^{-5}	-
5	S_{oi}=68.05% S_{orwf}=31.28%	2	0.50	308	31.28	-	46.0	2.47×10^{-3}	8.13
		2	1.00	308	31.28	-	31.0	1.64×10^{-3}	9.20
		2	1.50	308	31.28	-	22.0	1.17×10^{-3}	12.00
		2	2.00	308	31.28	-	15.0	8.22×10^{-4}	12.27
		2	3.00	308	31.28	-	12.0	6.72×10^{-4}	12.39
		2	4.20	308	31.28	-	12.0	6.31×10^{-4}	12.41
		2	4.50	308	31.28	-	11.0	5.90×10^{-4}	12.42

** Process 2 : Alkaline Flood.

** Process 4 : Alkaline Flood with Intermittent Nitrogen Injection.

TABLE B-4 (Cont.)

EXPERIMENTAL RESULTS OF CORE DISPLACEMENT TESTS FOR CATEGORY II

Core#	Sat. Before EOR	Proc	Cum. PV Inj	ΔP/L	S_{or}	WOR	K_w md	Cap. No	PH
5		4	5.70	308	25.5	25	4.6	2.51×10^{-4}	12.38
		4	7.00	308	24.9	58	3.3	1.58×10^{-4}	12.23
		4	8.20	308	24.0	180	5.5	2.60×10^{-4}	12.30
		4	9.50	308	24.0	420	3.3	1.76×10^{-4}	12.35
6	S_{oi}=66.63% S_{orwf}=46.56%	2	1.70	91	43.5	16	0.6	2.01×10^{-5}	11.61
		2	2.80	122	43.1	100	0.8	3.87×10^{-5}	12.01
		2	3.90	152	42.5	70	0.9	6.32×10^{-5}	12.17
		2	6.30	274	38.83	100	2.1	1.69×10^{-4}	12.36
		2	7.70	335	37.91	155	2.0	2.66×10^{-4}	12.43
		2	8.60	488	36.28	200	2.10	4.10×10^{-4}	12.43
		2	10.10	594	36.15	200	2.00	4.76×10^{-4}	12.47
		4	11.40	153	34.50	40	0.46	1.30×10^{-5}	12.34
		4	12.90	305	34.00	110	1.40	7.81×10^{-5}	12.39
		4	14.80	366	29.40	30	1.80	1.22×10^{-4}	12.44
		4	17.10	400	25.50	30	1.50	1.48×10^{-4}	12.41

TABLE B-5

EXPERIMENTAL RESULTS OF CORE DISPLACEMENT TESTS FOR CATEGORY III

Core#	Sat. Before EOR	Proc	Cum. PV Inj.	$\Delta P/L$ Psi/ft	S_{or} %	WOR	K_w md	Cap. No.	PH
7	S_{oi}=62.20% S_{orwf}=44.20%	3	0.60	70	47.80	20	-	-	-
		3	2.00	70	40.50	60	-	-	-
		3	3.20	70	38.65	60	-	-	-
		3	6.30	70	38.65	-	-	-	-
		3	7.60	70	38.65	-	3.2	1.22×10^{-3}	-
8	S_{oi}=69.25% S_{orwf}=45.60%	3	0.60	166	47.50	40	-	-	-
		3	1.60	166	42.00	30	-	-	-
		3	3.00	166	40.92	18	4.2	-	-
		5	4.30	166	43.20	20	-	-	-
		5	5.40	166	37.00	29	-	-	-
		5	6.80	166	34.62	45	-	-	-
		5	7.90	166	34.62	63	-	1.35×10^{-4}	-
9	S_{oi}=68.03% S_{orwf}=38.07%	3	0.60	138	41.69	-	2.0	2.83×10^{-5}	12.22
		3	1.60	216	41.69	-	1.4	3.90×10^{-5}	12.22
		3	2.80	315	41.69	-	1.8	7.30×10^{-5}	12.35
		3	3.80	433	39.29	25	1.9	1.29×10^{-4}	12.18

TABLE B-5 (cont.)

EXPERIMENTAL RESULTS OF CORE DISPLACEMENT TESTS FOR CATEGORY III

Core#	Sat. Before EOR	Proc	Cum. PV Inj.	$\Delta P/L$ Psi/ft	S_{or} %	WOR	K_w md	Cap. No.	PH
9		3	6.00	590	38.00	53	2.6	1.45×10^{-4}	12.42
		5	6.50	118	34.70	33	0.4	7.80×10^{-6}	12.33
		5	7.70	206	33.50	40	0.4	1.45×10^{-5}	12.45
		5	8.70	354	26.85	10	1.40	8.20×10^{-5}	12.41
		5	9.80	590	24.20	12	1.84	1.61×10^{-4}	12.46
10	S_{oi}=65.74% Sonwf=38.07%	3	2.00	134	41.06	500	29.0	6.34×10^{-4}	11.17
		3	3.60	224	36.10	66	-	-	12.38
		3	5.10	224	35.72	50	-	-	12.40
		3	6.50	224	34.65	95	36.0	1.25×10^{-3}	12.40
		5	7.80	171	36.20	20	3.2	1.03×10^{-4}	7.80
		5	8.60	179	33.50	24	3.7	1.06×10^{-4}	12.17
		5	9.40	183	29.20	31	3.5	3.88×10^{-4}	11.18
		5	10.40	224	25.50	40	-	-	11.60
		5	12.00	224	24.92	50	6.6	2.38×10^{-4}	12.33

** Process 3: Alkaline Flood with Acidic Oil Slug Injection.

** Process 5: Alkaline-Acidic Oil Slug-Nitrogen Injection.

TABLE B-6

EXPERIMENTAL RESULTS OF CORE DISPLACEMENT TESTS FOR TEMP.=150° F

Core#	Sat. Before EOR	Proc	Cum. PV Inj.	$\Delta P/L$ Psi/ft	S_{or} %	WOR	K_w md	Cap. No	PH
11	S_{oi}=68.77% S_{orwf}=50.96%	1	2.10	61	38.75	33	18.0	5.99×10^{-5}	-
		1	4.40	122	37.34	33	22.0	1.33×10^{-4}	-
		1	6.22	153	36.60	67	28.0	1.02×10^{-4}	-
		1	9.50	275	32.00	37	48.0	6.48×10^{-4}	-
12	S_{oi}=70.87% S_{orwf}=42.07%	5	1.10	48	43.20	27	0.35	4.83×10^{-6}	9.92
		5	2.80	73	35.99	34	0.37	5.16×10^{-6}	11.64
		5	5.40	101	33.52	40	.46	4.60×10^{-5}	12.32
		5	7.20	121	32.00	50	9.20	2.15×10^{-4}	12.32
		5	8.00	193	31.05	50	8.77	3.28×10^{-4}	12.38
		5	9.80	435	28.39	57	12.9	1.08×10^{-3}	12.38
13	S_{oi}=68.10% S_{orwf}=40.46%	2	1.30	55	40.46	-	1.5	1.49×10^{-5}	10.46
		2	2.60	110	38.48	22	2.5	4.97×10^{-5}	12.20
		2	4.10	138	38.00	250	2.8	6.99×10^{-5}	12.15
		2	6.00	221	37.60	50	1.8	7.04×10^{-5}	12.18
		4	6.50	55	34.18	12	0.36	3.56×10^{-6}	12.00
		4	8.30	165	28.42	33	0.69	2.08×10^{-5}	12.34
		4	10.00	225	26.30	42	1.84	7.305×10^{-5}	12.28
		4	12.50	338	25.40	80	2.27	1.36×10^{-4}	12.31

** Process 1: WF/NF Process 2: AF Process 4: AF/NF
Process 5: AF/OS/NF