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A STUDY OF THE EFFECTS OF TEMPERATURE ON CAUSTIC DISPLACEMENT OF A VISCOUS CRUDE

By

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T-1291

A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering.

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CONTENTS

ABSTRACT

Investigations were made to determine the effect that temperature has on the efficiency of displacing a viscous crude oil with a weak solution of sodium hydroxide. Displacement tests in a berea sandstone core were made at 130, 160, and 190°F. At each temperature a test was made with both distilled water and a weak sodium hydroxide solution as the flooding agent.

Measurement of interfacial tensions between a Lloydminster crude oil and several weak solutions of sodium hydroxide indicated that a 0.20 weight per cent solution created the greatest reduction in interfacial tension. Interpretation of the test data showed that the sodium hydroxide in the injection water increased the recovery over that obtained by waterflooding. The data also indicated that the recovery was increased at 160°F

substantially more than at either 130 ^{o}F or 190 ^{o}F.

ACKNOWLEDGMENTS

The author expresses his gratitude to Mr. J. R. Bergeson, Thesis Advisor, for initiating the idea for the study and being most generous with his time. Appreciation is also extended to Professors D. M. Bass and G. H. Kennedy for serving on the thesis committee, and for their helpful suggestions throughout the investigation.

The assistance of Professor W. A. Wager in preparing the final draft is very much appreciated.

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The author is indebted to the National Science Foundation for the traineeship under which the investigation was completed.

INTRODUCTION

The improved production of oil by secondary recovery techniques is becoming more important due to the increasing cost of finding new oil reserves. The heavy viscous crude oil reservoirs exhibit very low recoveries and offer a great potential for new methods of secondary recovery.

One process that has been proposed is the addition of sodium hydroxide in small amounts to the water used in a waterflood. Researchers have studied the effects of rate, viscosity ratio and interfacial tension on sodium hydroxide or caustic waterflood recovery of viscous crude oil in an unconsolidated sand pack model. However, no work has been done to correlate the effect of temperature on recovery of a viscous crude. This investigation was conducted in order to determine if there is a temperature effect on the sodium hydroxide waterflood in a consolidated sandstone

core. The laboratory study utilizes a three foot long, two inch diameter linear berea sandstone model. Tests were conducted at various temperatures with both distilled water and a weak solution of sodium hydroxide as a waterflood agent. The oil recovery as a function of the amount of waterflood fluid injected is compared at each temperature. The effects of temperature on all factors besides the sodium hydroxide can be eliminated by the use of data obtained with distilled water. All tests were conducted with two pore volumes of waterflood agent being injected.

REVIEW OF LITERATURE

The poor performance of secondary recovery projects in high viscosity oil reservoirs has been discouraging to the oil industry. One process that may lead to increased secondary recovery from this type of reservoir is the addition of sodium hydroxide to the injection water. Emery, Mungan, and Nicholson (1969) have illustrated that in an actual field test additional oil was recovered as a result of the use of sodium hydroxide in the injection water. Approximately eight percent of a pore volume of a 0.5 N NaOH solution was injected into a single well. The pore volume was the 40-acre test area plus allowance for 25 percent migration outside of the test area. Therefore, all calculations were based on 50 acres. Production of one well adjacent to this injection well changed from all water to 23 barrels of oil per day

and 300 barrels of water per day. All of this oil was attributed to the injection of the caustic solution.

Laboratory work by Emery, Mungan and Nicholson (1969) showed that additional oil could be recovered from natural reservoir cores even after a water-oil ratio of 100 to 1. However, the greatest effect on recovery occurred when the NaOH injection was started immediately. A 0.5N NaOH solution waterflood increased recovery by approximately 5.5 percent of a pore volume. The tests were made using Singleton crude (viscosity=1.60 centipoise at 160 °F, 500 psi) at 160 °F in unconsolidated sand cores.

Scott, Collins and Flock (1965) have studied the effects of pH on interfacial tensions of several crude oil brine systems. They demonstrated that lowering the pH reduces the interfacial tension between the brine and crude oil. However, the greatest effect was demonstrated by increasing the pH of the brine solution. Several waterfloods were then conducted on sand pack models which indicated an improved recovery by use of weak sodium hydroxide solutions as the flooding agent. The increase in recovery was found to be 30 percent greater than the recovery obtained by brine waterflooding. These tests were all conducted at 80 °F using Lloydminster crude oil. The core was not cleaned between subsequent

tests using sodium hydroxide. This fact makes correlation of the results rather difficult.

The effect of temperature on caustic displacement of crude oil from the Lloydminster Field in Alberta, Canada is the subject matter for this thesis. All parameters except temperature are held as constant as possible during the tests. Analysis is accomplished at each temperature by reference to tests made with distilled water as the flooding agent. Interfacial tensions are measured for correlation of the test results.

EXPERIMENTAL PROCEDURE

The experimental procedure will be discussed with respect to model scaling, equipment design, investigation of model properties, and method of testing.

Model Scaling

End effects can be eliminated in a model if the waterflood is stabilized (Kyte, Rapoport, 1958). One criteria for stabilized waterfloods consists of having sufficient magnitude of the scaling coefficient which is described by the following equation (Rapoport, Leas, 1953).

$$\text{Scaling coefficient} = LV\mu_w$$

where

L = Length (centimeters)
V = Total flow rate per unit cross-sectional area (centimeters/second)
μ_w = Water viscosity (centipoise)

A scaling coefficient greater than approximately 1.5 signifies stability. Another criteria for stability is that a 50 psi pressure drop across the model insures stability (Kyte, Rapoport, 1958).

At all times during the tests at least one criteria was always met and therefore no end effects should be considered in the analysis of the data.

Equipment Design

The model consisted of a three foot long, two-inch diameter berea sandstone core. The core was fired at 825 ^{o}F to reduce the effect of clay swelling when fresh water is used. The core was coated with a chemically resistant paint and then sealed in a flanged stainless steel tube with a eutectic metal that expands on cooling. The ends of the core and the excess metal were then faced off to be flush with the flanges. Two pressure taps were then drilled into the tube so that they were 25.0 inches apart and centered on the core. The flanged ends were then bolted with O-ring seals to complete the installation of the core.

The oil used was a dead crude from the Lloydminster Field in Alberta, Canada.

A Ruska variable rate proportioning pump was used

to maintain the injection rate at 64.0 cubic centimeters per hour for the waterflood tests. A cylinder similar to the core holder was used to hold the fluid that was to be displaced into the core. The Ruska pump could then pump mercury into the bottom of this vessel and displace the fluid to the core. Two filters consisting of one-quarter-inch thick sections of the core were used to insure cleanliness of the injected fluid. One filter was used for the flooding agent and the other was used to filter the oil.

The temperature was controlled by an adjustable mercury thermostat connected to two 3500-watt heaters in an oil bath. The heating oil used for the bath was Texaco P-50 URSA oil. The oil was circulated by motor driven stirrers in order to maintain even temperature distribution throughout the bath.

The arrangement of the equipment can be best understood from the schematic diagram in Figure 1 and the photograph in Plate 1.

Investigation of Model Properties

The effective liquid permeability was obtained by flowing dry nitrogen at various flow rates and pressures through the core.

Porosity was obtained by weighing the core dry and then when completely saturated with water. The difference in weight is representative of the connected pore volume.

The relationship of the crude oil viscosity to temperature was obtained by the use of reverse-flow type viscometers in a constant temperature bath. The temperature was varied from 90 ^{o}F to 200 ^{o}F. Viscosity of the NaOH solution used for the waterflood experiments was measured with Ostwald viscometers. The range of investigation was 100 ^{o}F to 200 ^{o}F.

The method used to determine specific gravity was a hydrometer calibrated with liquids of known specific gravity. In order to determine the concentration of sodium hydroxide to be used, the upward interfacial tension between oil and several dilute solutions of sodium hydroxide was measured at room temperature. A direct reading DuNouy tensiometer was used to make the interfacial tension measurements. The solution that resulted in maximum reduction of interfacial tension was then chosen to be used as the caustic flooding agent.

The possibility of a film forming at the caustic-crude interface (Scott, Collins, and Flock, 1965) was considered as a potential factor in waterflood performance. Measurements of interfacial tension were

made at two-hour intervals up to twelve hours to determine if any changes in interfacial tension occurred during the period of the test.

In order to validate results from the equipment used, some tests were necessary to eliminate possible errors. Any reaction between the eutectic metal used to mount the core and the sodium hydroxide solution could cause erroneous recovery data. The metal was allowed to remain in contact with the sodium hydroxide solution at temperatures of 75 ^{o}F, 155 ^{o}F and 195 ^{o}F for various lengths of time up to 96 hours. Any loss in weight would indicate deterioration of the material and possible errors in the recovery data.

Method of Testing

The displacement test procedure for each waterflood experiment consisted of cleaning the core, obtaining initial saturations of oil and water, and waterflooding.

Cleaning the Core

The core was first cleaned with fifteen pore volumes of analytical grade toluene. Five pore volumes of analytical grade pentane were then forced through the core in order to return the core to the initial condition of

a water wet system (Clark, 1959). Dry nitrogen was passed through the core to displace the pentane and to dry the core. The core was then placed on a vacuum to complete the drying process. The core was clean and ready to be saturated for the next waterflood test.

Saturating the Core

The core, after being cleaned and dried, was first flooded with 2.5 pore volumes of distilled water or until the pH had returned to 7.0 indicating no presence of sodium hydroxide. The bath was then heated to approximately 140 ^{o}F so that the crude oil viscosity would be near 100 centipoise. Oil was then injected into the water saturated core until 1.2 pore volumes had been displaced. Considering a mobility ratio of 100, the core was at initial water saturation, and essentially no water would be produced from this saturation in the waterflooding tests.

Waterflooding

The waterflood tests were performed at 130, 160, and 190 ^{o}F. At each temperature two tests were made. One test was made using distilled water as the flooding agent and a comparative test was made using a 0.20 weight percent sodium hydroxide solution.

The injection was maintained at a constant rate of

64 cubic centimeters per hour. Two pore volumes of injected fluid constituted a test.

The data collected for each test consisted of the pressure drop along the core and the recovery by weight and volume. The water cut of the recovery was determined by use of a centrifuge. A check was also made using the weight and volumes of the fluid recovery when a discrepancy arose in the data.

RESULTS AND DISCUSSION

The results of this investigation will be discussed with respect to model properties, interfacial tension, waterflood performance, and reservoir model performance.

Model Properties

The effective liquid permeability obtained by the use of nitrogen is illustrated in Figure 2 and was found to be 549 millidarcies. The porosity (determined by weighing the core while wet and dry) was found to be 20.5 percent.

Viscosity relationships of the crude and caustic are illustrated in Figure 3 and 5 respectively. The gravity of the Lloydminster crude at various temperatures is illustrated in Figure 4.

Interfacial Tensions

The interfacial tension between Lloydminster crude oil and several weak solutions of NaOH is illustrated in Figure 6. It can be noticed that solutions between 0.10 and 0.30 weight percent NaOH reduce the interfacial tension below 0.1 dyne per centimeter. A 0.20 weight percent (0.05N) solution was therefore used for all subsequent tests.

The possibility of a film forming at the crude-water interface (Scott, Collins, and Flock, 1965) was then considered. By simply taking a drop of crude in a small beaker of caustic, the effects of reduction of surface tension along with the formation of a thin film could be noticed. The crude spread out very unevenly, and a thin light-brown film was formed almost instantly over the surface of the caustic solution. The characteristics of this film are not known and could effect the recovery performance of a reservoir.

Interfacial tension measurements were then made on the crude-caustic system after periods of setting time. The time was varied between two and twelve hours total at two-hour intervals. This procedure was conducted at 100 ^{o}F and 160 ^{o}F with no change in interfacial tension. This fact would discount any change in waterflood

performance due to changing characteristics of the film at the interface.

Waterflood Performance

The waterflood performances using distilled water as the flooding agent are illustrated in Figures 9, 10, 11, and 12. These curves are quite reasonable and the change in recovery with increasing temperature is due to the reduction in oil viscosity as shown in Figure 3. The water viscosity is also reducing with increasing temperature, but not with the magnitude demonstrated by the crude. The performances with distilled water serve as a basis for analysing the sodium hydroxide waterfloods.

The waterflood performances using 0.20 weight percent sodium hydroxide are illustrated in Figures 13, 14, and 15. It can be seen from these curves that an increase in recovery above that obtained with distilled water is realized at all three temperatures investigated. The increase in recovery for the 130 ^{o}F and 190 ^{o}F tests are nearly equal and account for a four percent increase in recovery. The test made at 160 ^{o}F resulted in an increase in recovery of 13 percent of the oil in place. The additional oil recoveries are a definite result of using the caustic solution as the flooding agent.

A summary of the waterflood test results is illustrated in Figure 16. Comparison of the results is simplified by use of this illustration.

The reduction in interfacial tension is related to the additional oil recovery in the caustic waterfloods, but the anamoly at 160 °F is difficult to understand. The test at 160 °F was repeated with the same results. A water-in-oil emulsion did exist but was eliminated by using toluene to cut the sample before determining the water-oil ratio with the use of the centrifuge.

Another possible explanation for the recovery at 160 °F would be a drastic change in the viscosity of the sodium hydroxide solution. This possibility was eliminated by the data illustrated in Figure 5 which indicated a normal reduction in viscosity with increasing temperature. Figure 5 also illustrates several viscosity measurements of distilled water (Amyx, Bass, and Whiting, 1960) which illustrate that the caustic behaves very much like distilled water.

The possibility of a change in crude-caustic interfacial tension causing the recovery change at 160 °F was considered. The possibility of the film causing the change was eliminated on the basis of the tests discussed in the previous section.

One possible explanation for the performance of the caustic waterflood at 160 ^{o}F is the change between the sandstone core and the caustic with respect to temperature. It was noticed that in cleaning the core after a caustic waterflood, the pH of the effluent remained above that of distilled water until at least ten pore volumes of distilled water was passed through the model. This fact suggests that the NaOH is being absorbed into the system. Monitoring of the pH of the effluent during a caustic test showed that approximately 0.1 pore volume of water was produced before the pH changed significantly enough to consider that the caustic was the produced water. This delay in pH increase strengthens the idea of the NaOH being absorbed into the system and suggests that a higher concentration of NaOH should possibly be injected first to offset the loss. The properties of sandstone-caustic interfacial tension or chemical reactions were not within the scope of this investigation but may be of importance in the explanation of results obtained.

Relative permeability curves for the tests were then constructed. These curves are illustrated in Figures 7 and 8. The curves for the distilled water tests almost coincide and indicate that a change in recovery is due

entirely to the viscosity changing with increasing temperature.

The relative permeability curves for the caustic tests as illustrated in Figure 8 are separated by a significant amount. This separation would indicate that some mechanism besides a change of viscosity is present. The mechanism causing this shift is the reduction in crude-caustic interfacial tension.

The relative permeability for the 160 ^{o}F crude-caustic test is not a linear relation as plotted on Figure 8. The changing slopes indicate a favorable permeability to oil at low values of water saturation. The curve then increases in slope which indicates a permeability less favorable to oil than any other test at high water saturations. The two tests at 160 ^{o}F yield consistent results. The discrepancy in the higher water saturation part of the curve is due to a problem with emulsions forming during the first test. This curved relative permeability plot indicates that some new factor has been introduced. The possibility of a change in crude-caustic interfacial properties has been eliminated and the author feels that the sandstone-caustic interfacial properties are the mechanism causing the change in relative permeability.

The explanation for the drastic change in waterflood performance at 160 °F using the caustic is not apparent at this time. However, the indication of NaOH being absorbed and the curved relative permeability plot of the 160 °F caustic test indicate that a study of reservoir rock-caustic properties would be beneficial in understanding the mechanism involved for the increased oil production.

Reservoir Model Performance

The model performed quite well until the 100 °F caustic waterflood was attempted. Very low recovery indicated that some type of channeling had developed. The eutectic metal was checked for 76 hours at 195 °F, 160 °F, and 74 °F. The most severe corrosion occurred at 195 °F and resulted in a loss in weight of 0.09 percent of the sample tested. The possibility of a channel forming in the metal was therefore eliminated.

The possibility of the core fracturing was also investigated. Based on a pressure of 1500 psig on the core, the core holder could expand a maximum of 0.0005 inch. This calculation was based on a tube with no supports. The core holder used had flanges at each end with reinforcing brackets spaced between the ends. These

additional braces would essentially eliminate any expansion. The author feels there was no chance of the core fracturing without the brackets and therefore no consideration should be given this possible explanation of the apparent channeling.

The sodium hydroxide may have formed a channel in the core as the NaOH will react with silica. After the apparent breakdown of the model, a white cloudy substance was noticed in the effluent. This cloudiness may be due to silica content of the effluent being increased due to reaction of the NaOH with the core. Emery, Mungan, and Nicholson (1969) noted silica in the effluent of their core tests and in the produced water of the field test. The sodium hydroxide reacting with the sandstone core is felt to be the explanation for the breakdown of the model.

The tests that were used are not considered by the author to represent changes due to the NaOH reacting with the sandstone. All tests used for the analysis were obtained in random order. The increased oil recovery could not be a result of the model operating incorrectly because this change would create a significant decrease in waterflood performances. As soon as a discrepancy in the recovery was noted, the subsequent tests were

eliminated from any correlation of waterflood performance.

CONCLUSIONS

The purpose of this thesis was to examine the effect that temperature has on waterflood recovery when a weak sodium hydroxide solution is used as the flooding agent. The following conclusions may be drawn as a result of this investigation.

1. Sodium hydroxide reduces the crude-water interfacial tension. There was a definite range of 0.10 to 0.30 weight percent NaOH that reduces the interfacial tension below 0.1 dyne per centimeter for Lloydminster crude oil.

2. Use of a weak sodium hydroxide solution increased oil recovery at all temperatures investigated.

3. The investigation at 160 ^{o}F indicated an increase in recovery over three times that of the tests made at 130 ^{o}F and 190 ^{o}F.

4. The explanation for the largest change in recovery at 160 °F is not crude-caustic interfacial tension. Sandstone-caustic interfacial properties are indicated to be the explanation for the waterflood performance at 160 °F.

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APPENDIX

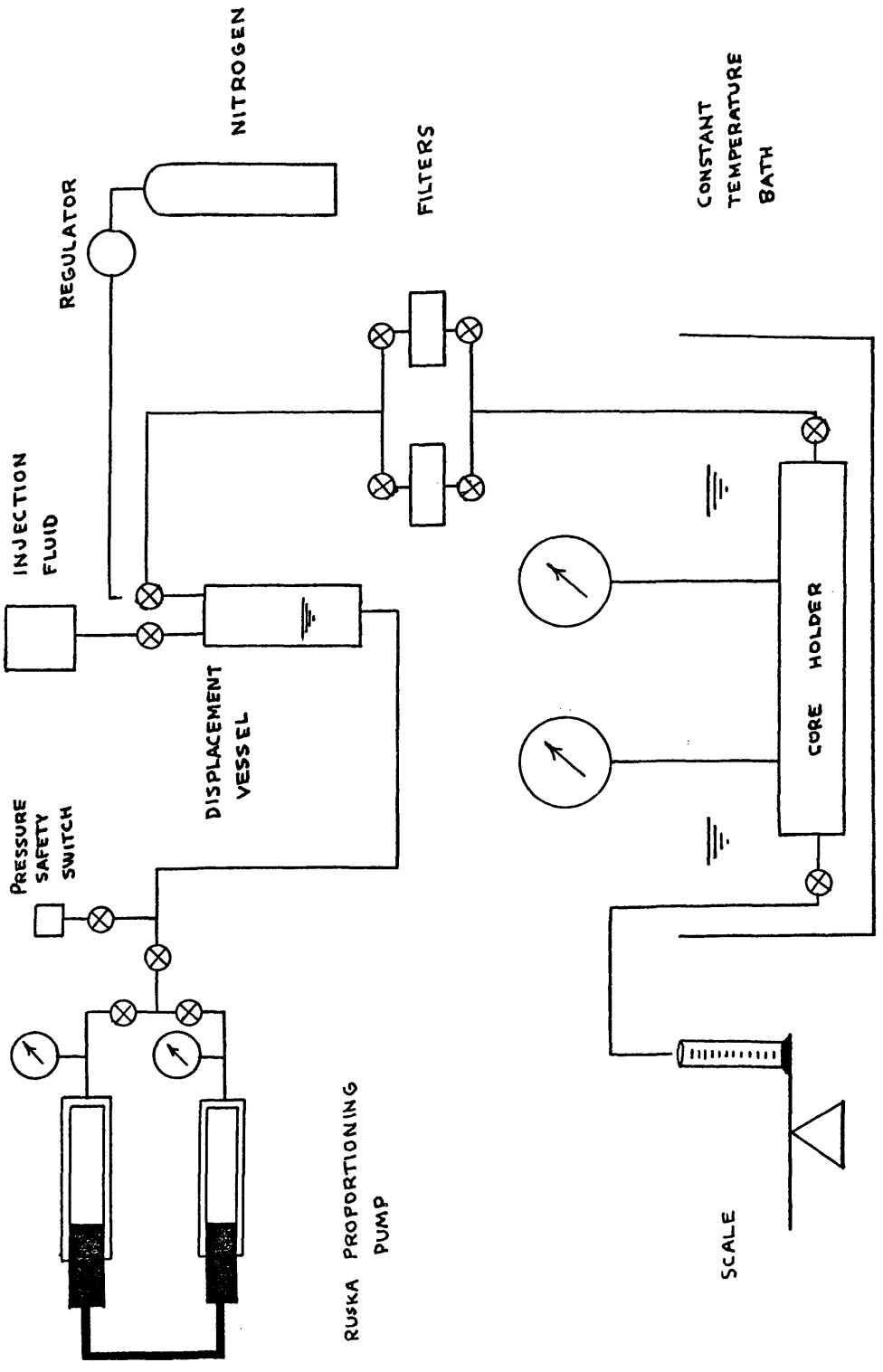


Figure 1 SCHEMATIC DIAGRAM OF EQUIPMENT

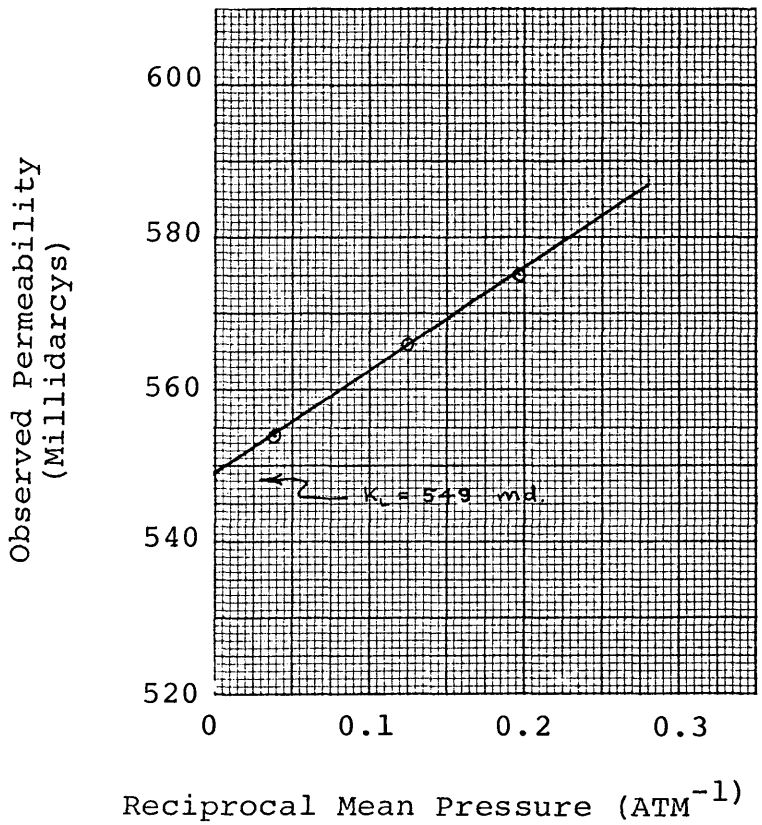


Figure 2 PERMEABILITY OF CORE TO NITROGEN
EFFECTIVE LIQUID PERMEABILITY,
549 MILLIDARCYS

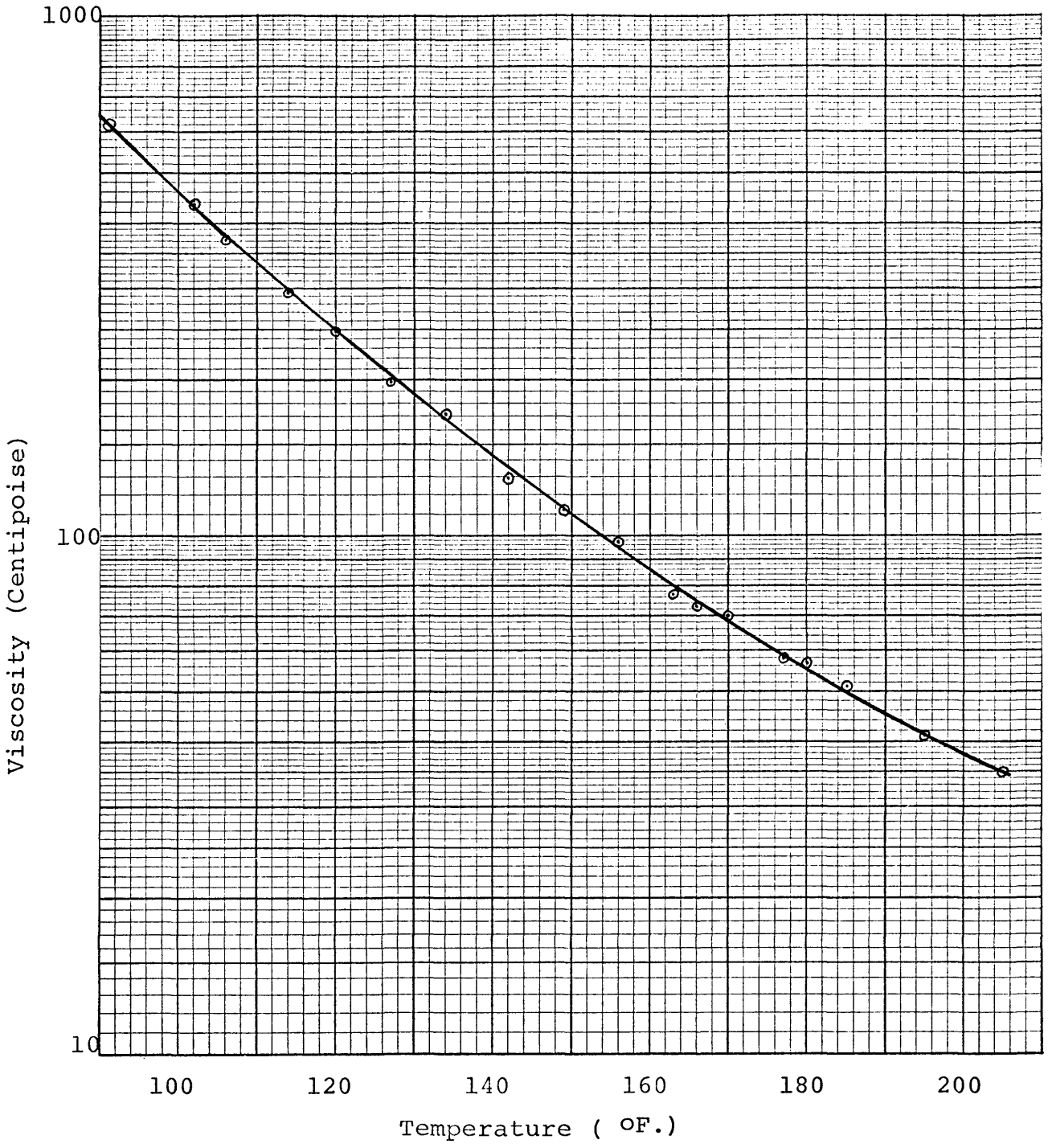


Figure 3 EFFECT OF TEMPERATURE ON
VISCOSITY OF LLOYDMINSTER CRUDE OIL

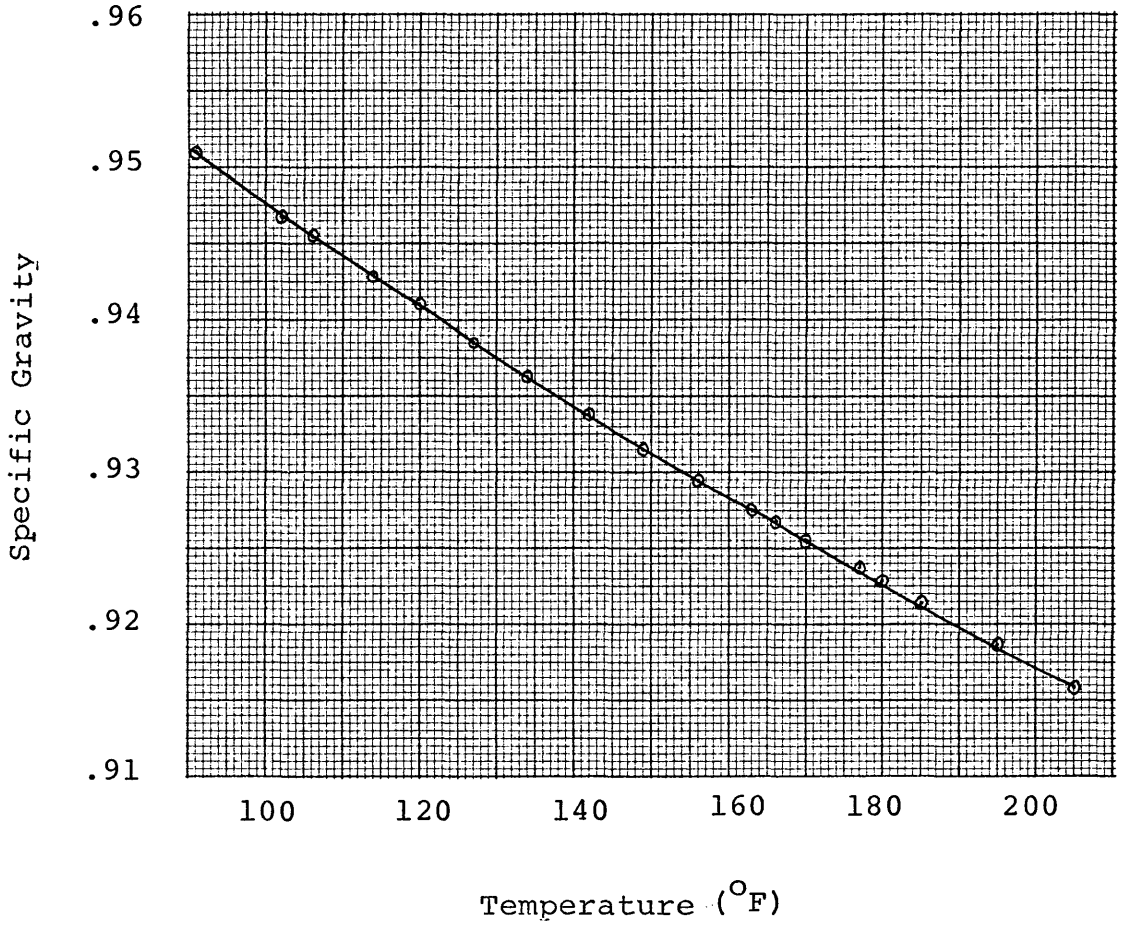


Figure 4 SPECIFIC GRAVITY OF LLOYDMINSTER CRUDE OIL

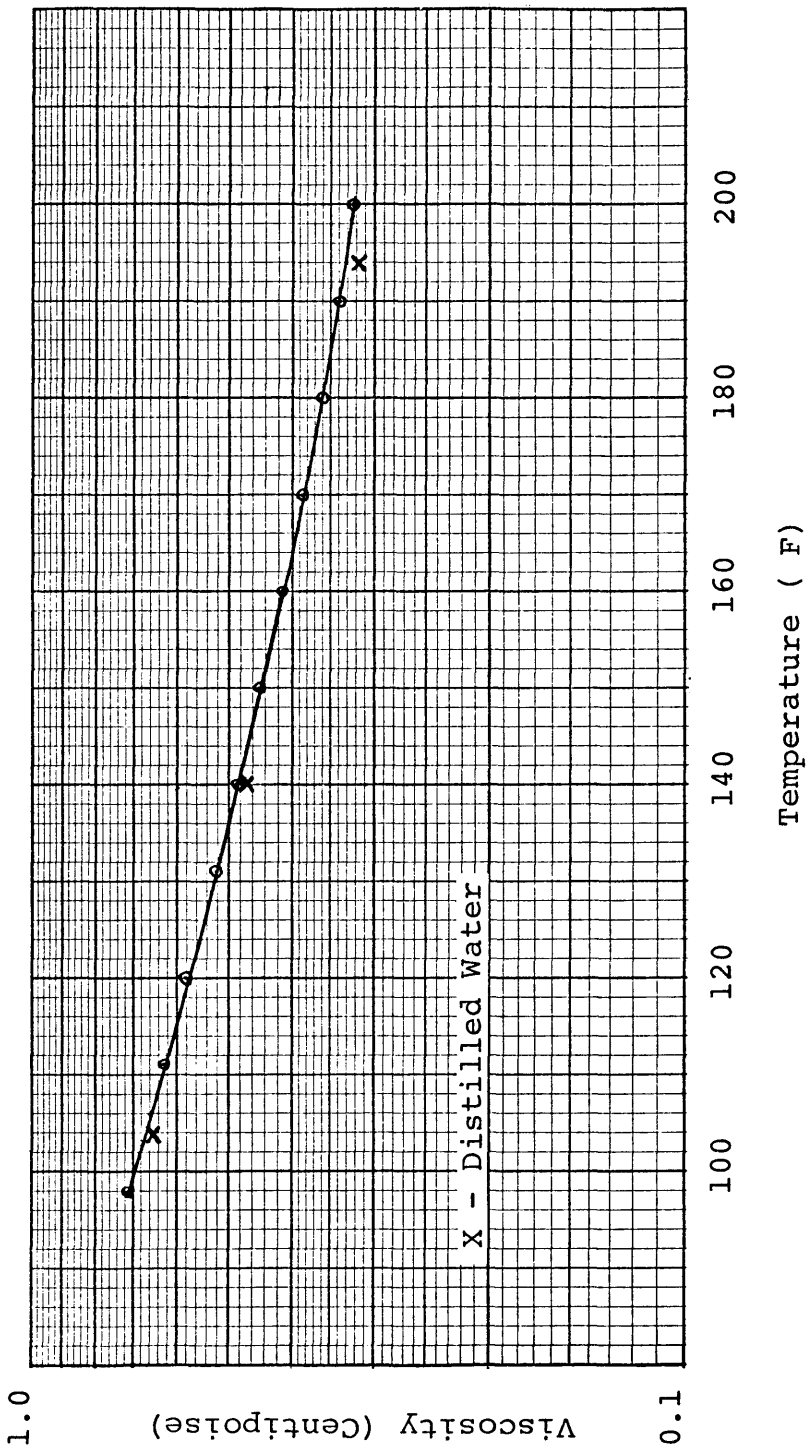


Figure 5 VISCOSITY OF 0.20 WEIGHT PERCENT NaOH SOLUTION

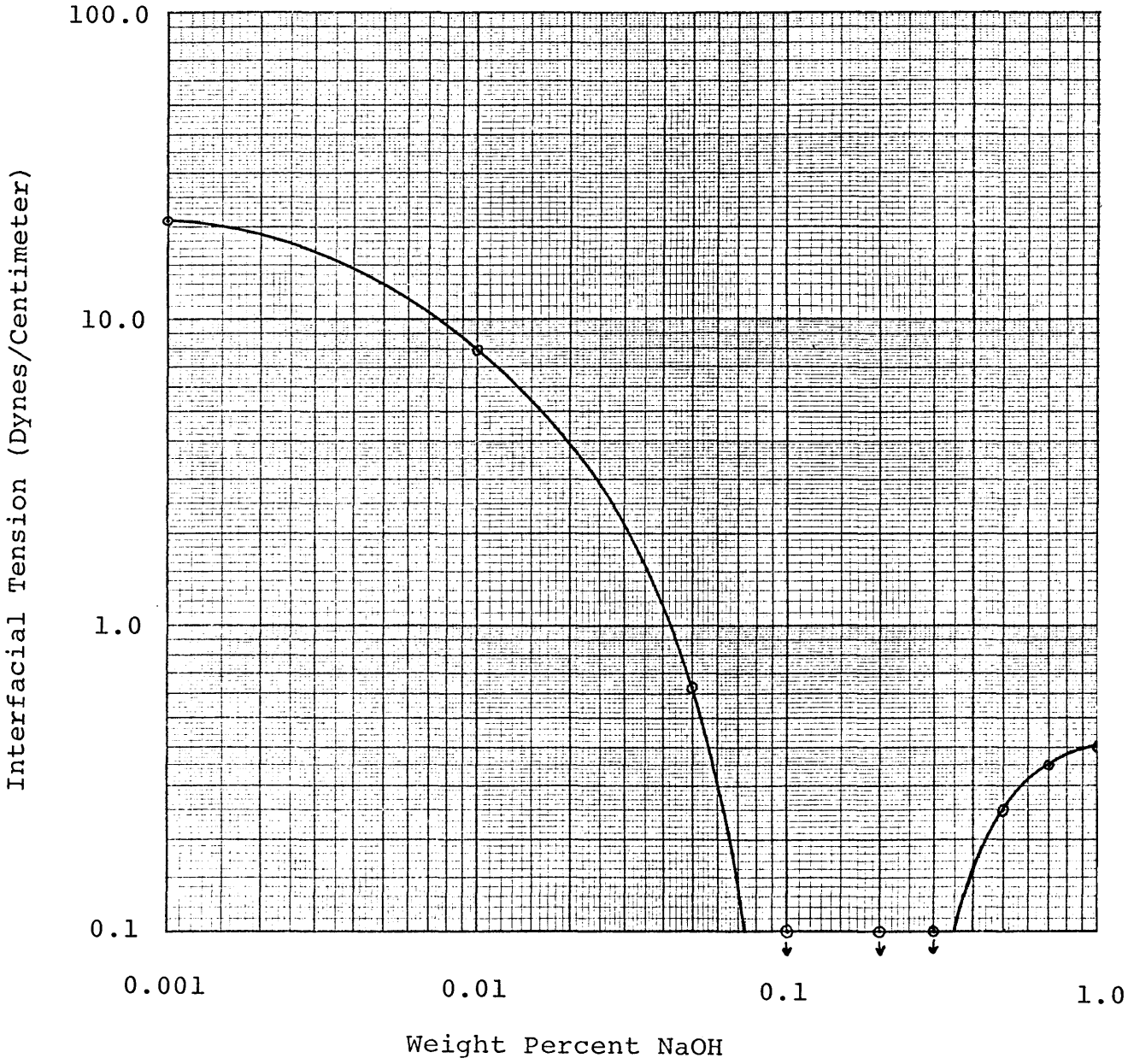


Figure 6 INTERFACIAL TENSION OF CRUDE OIL-SODIUM HYDROXIDE SOLUTIONS

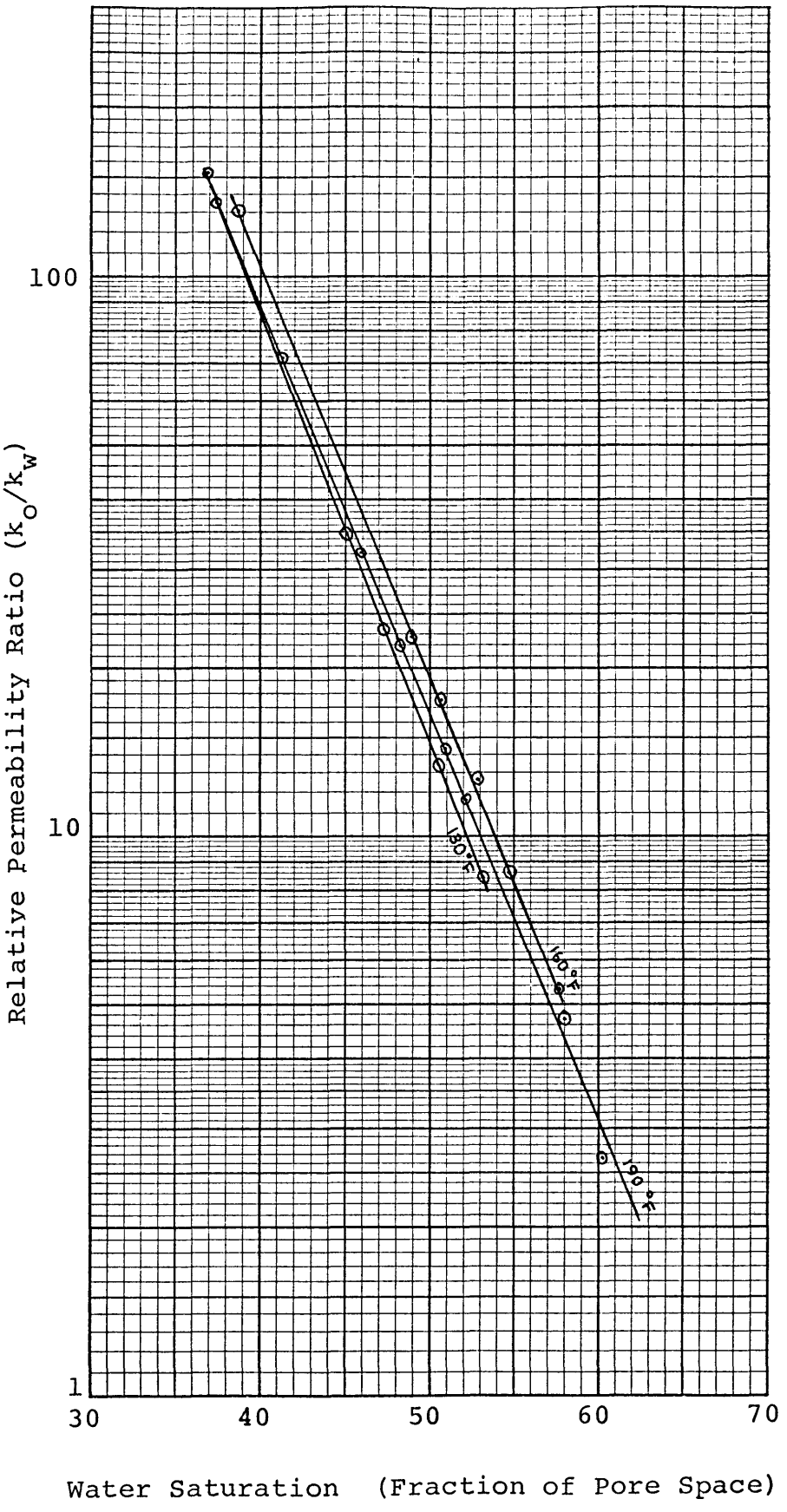


Figure 7 RELATIVE PERMEABILITY FOR OIL-WATER TESTS

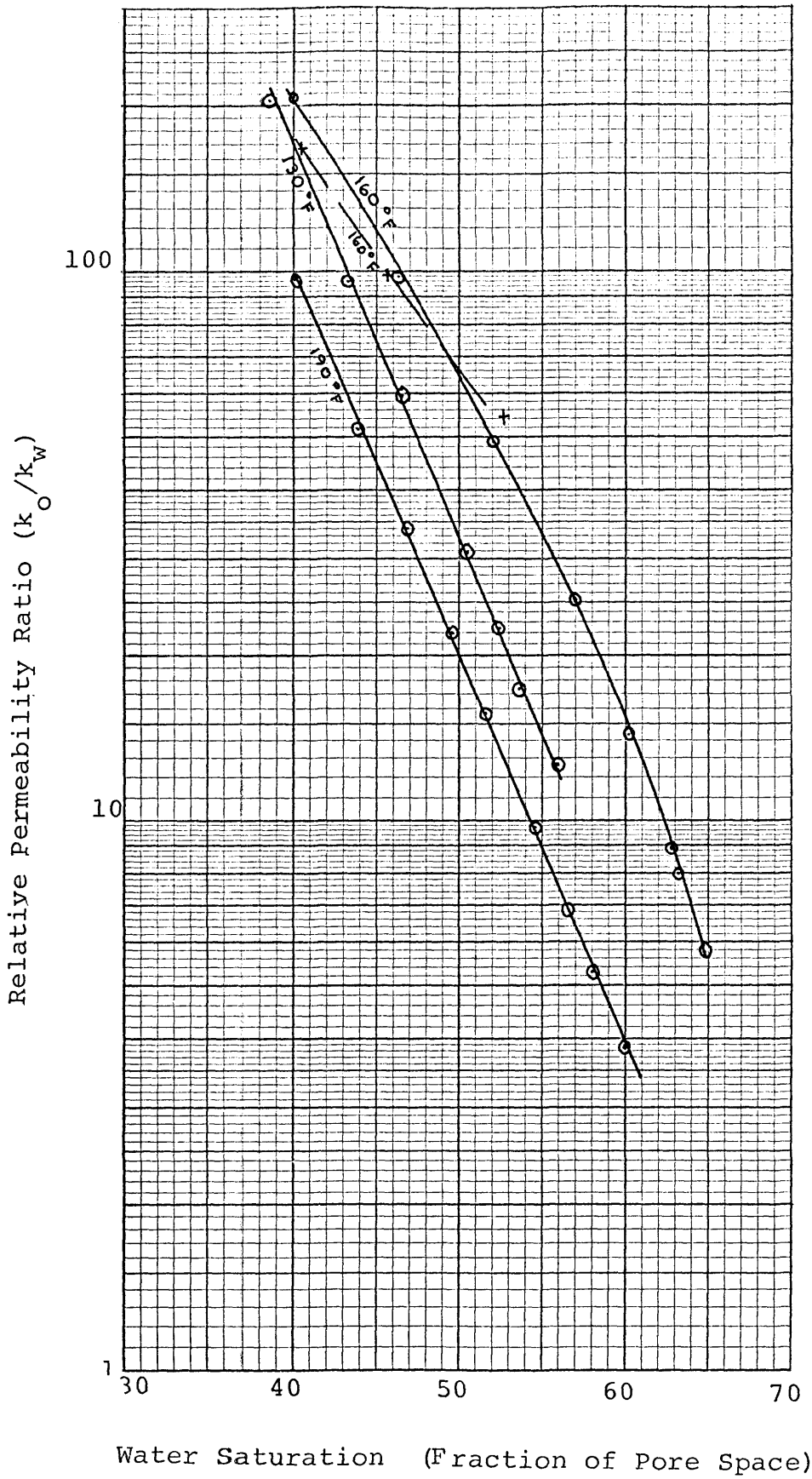


Figure 8 RELATIVE PERMEABILITY FOR OIL-CAUSTIC TESTS

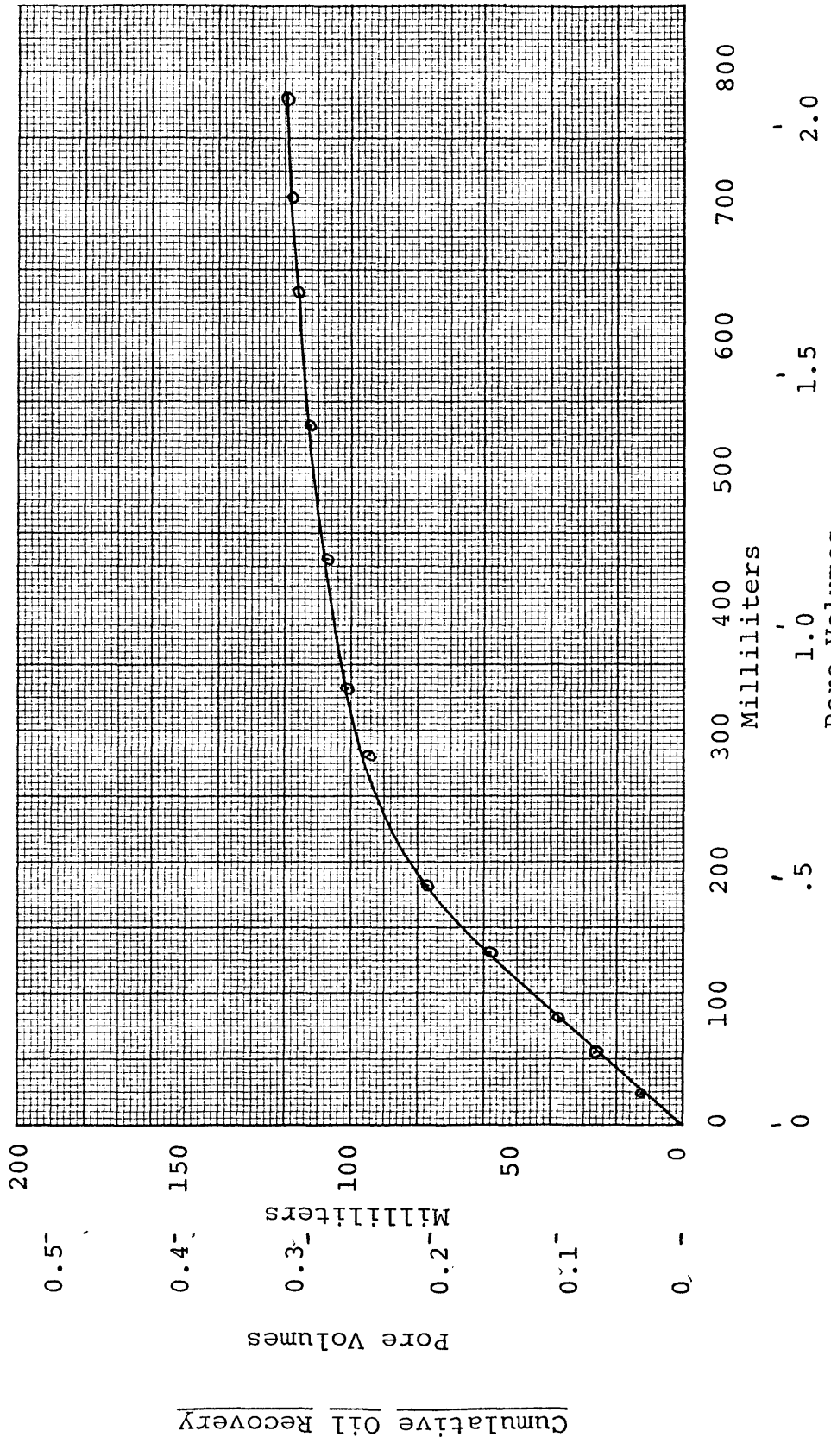


Figure 9 WATERFLOOD PERFORMANCE (DISTILLED WATER AT 100° F)

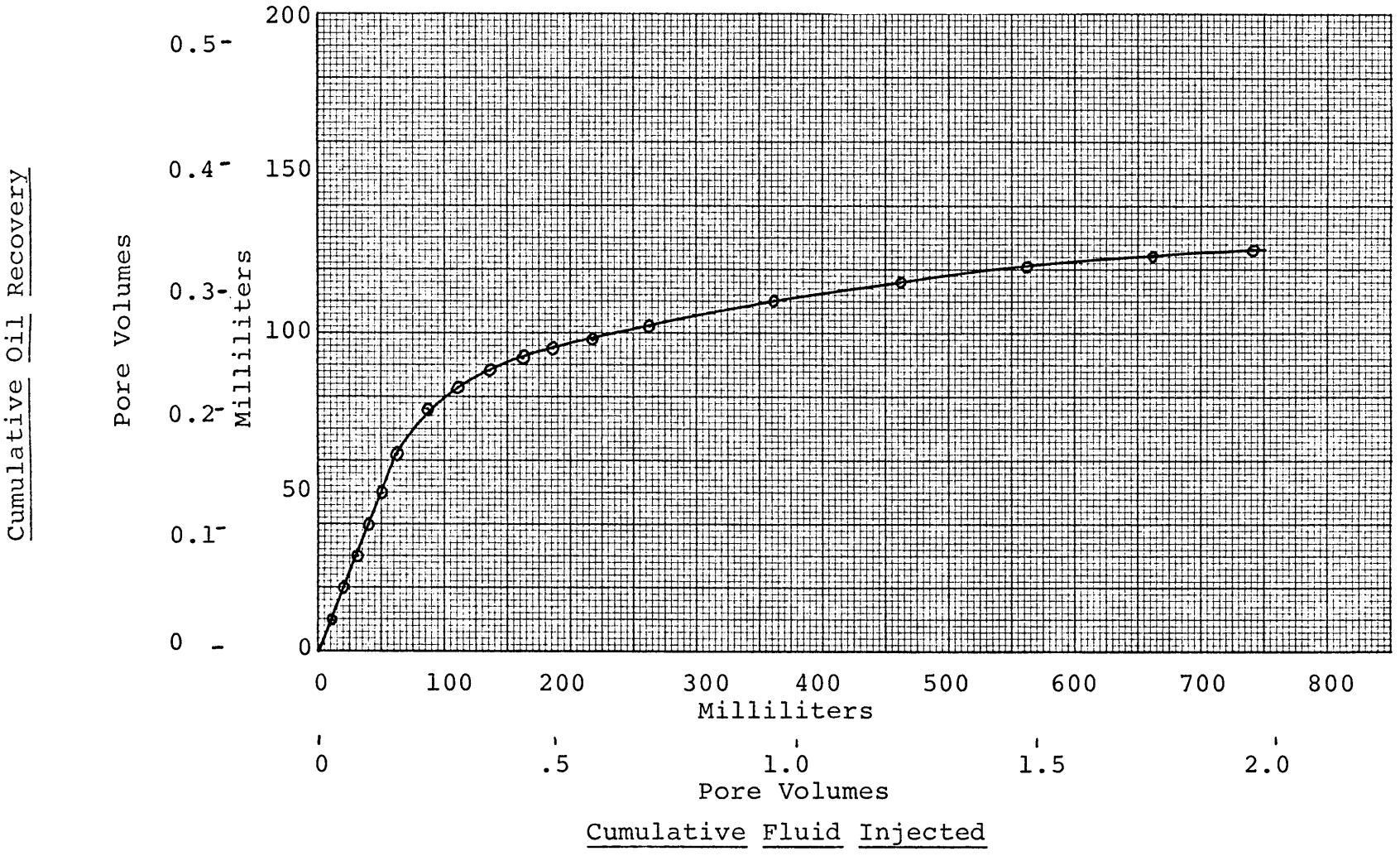


Figure 10 WATERFLOOD PERFORMANCE (DISTILLED WATER AT 130° F)

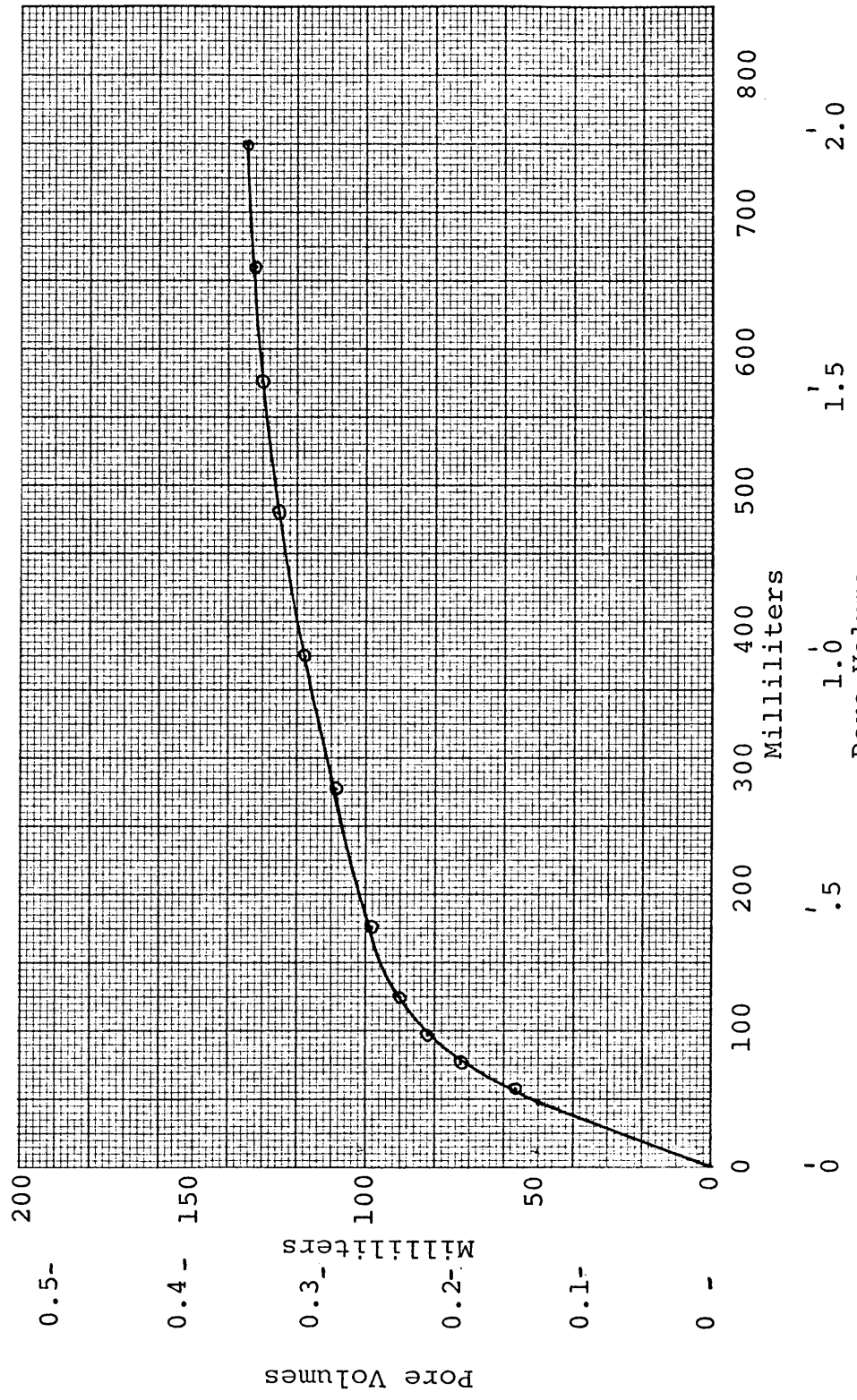


Figure 11 WATERFLOOD PERFORMANCE (DISTILLED WATER AT 160° F)

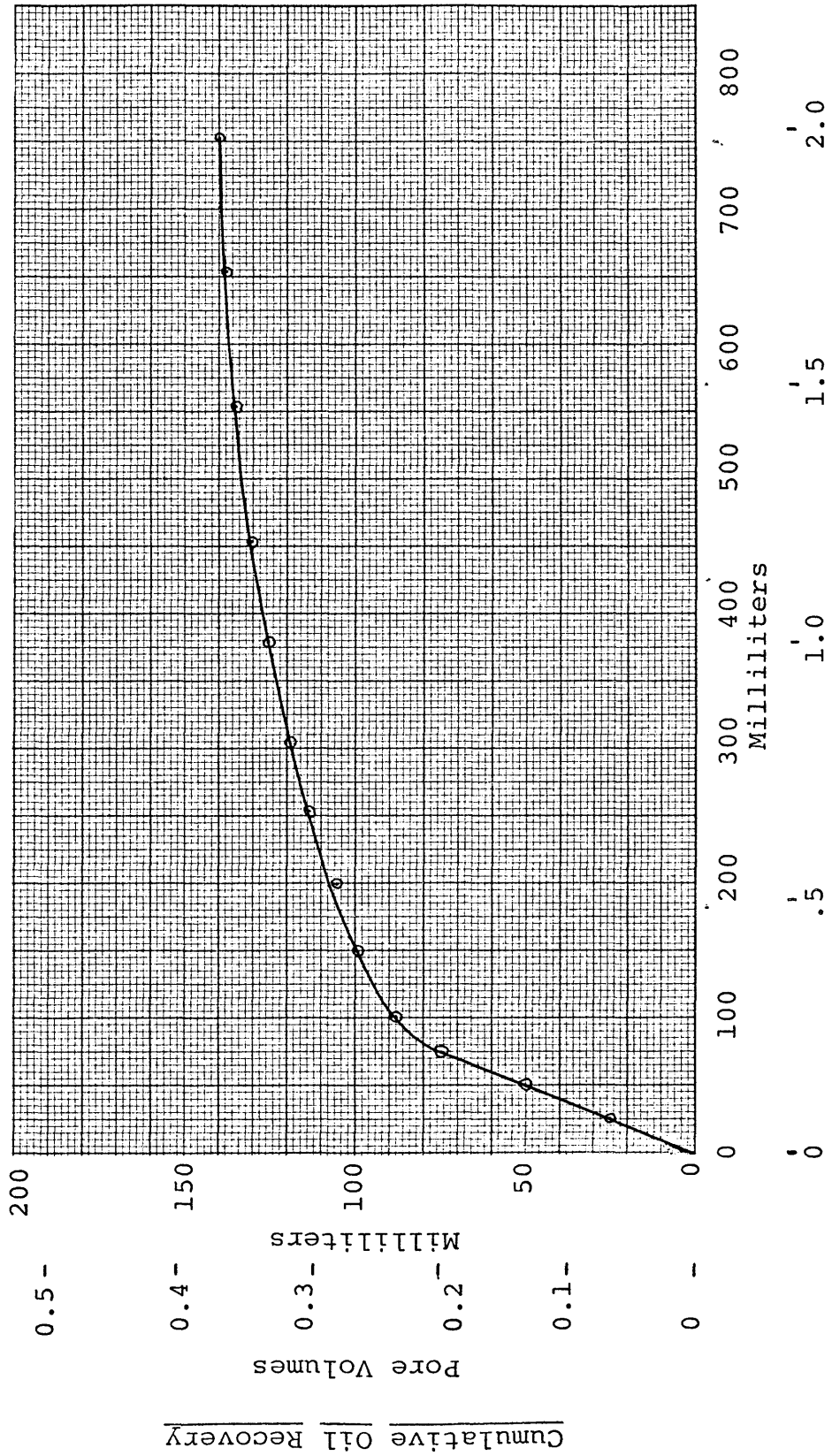


Figure 12 WATERFLOOD PERFORMANCE (DISTILLED WATER AT 190° F)

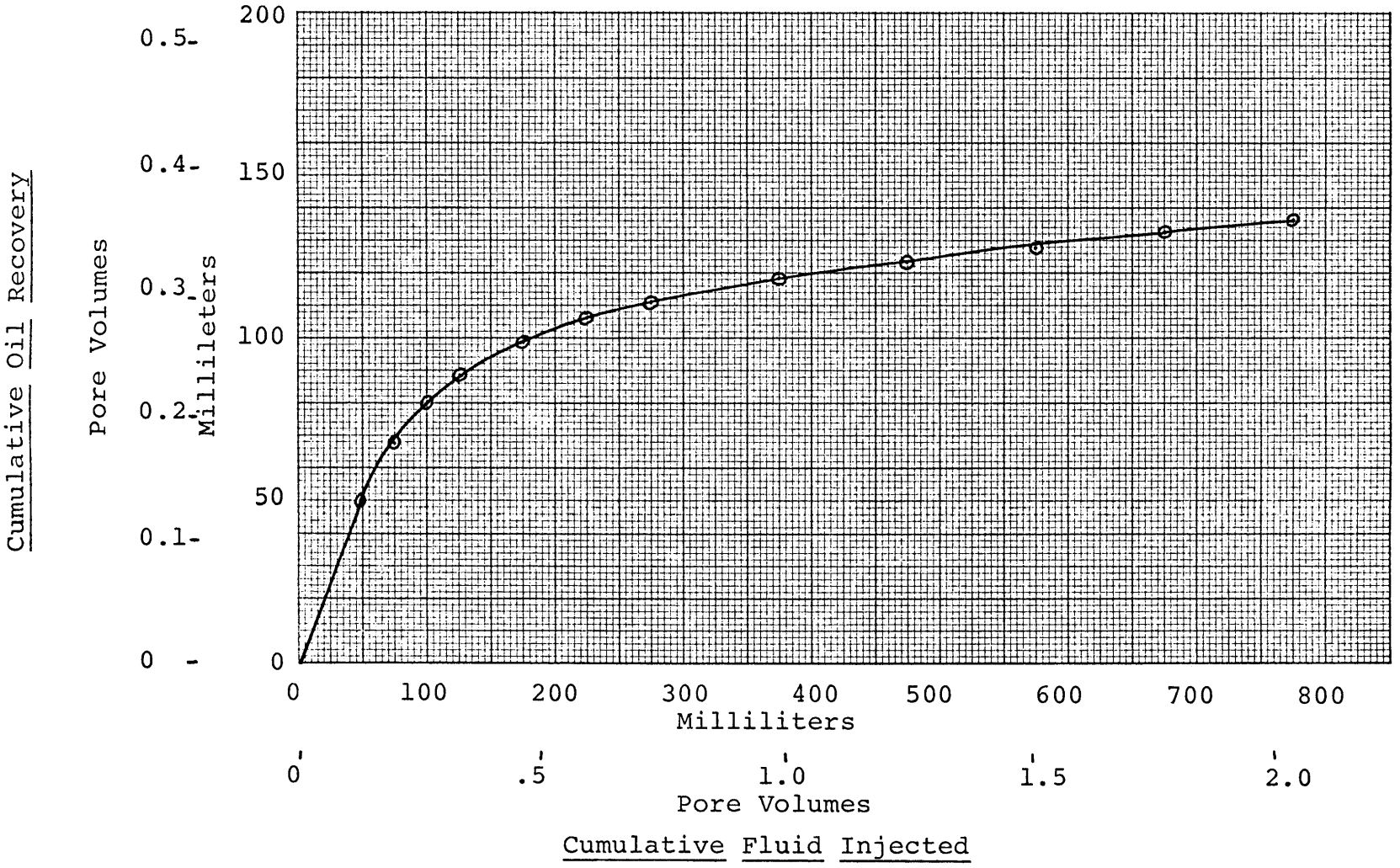


Figure 13 WATERFLOOD PERFORMANCE (0.20 WEIGHT PERCENT NaOH at 130° F)

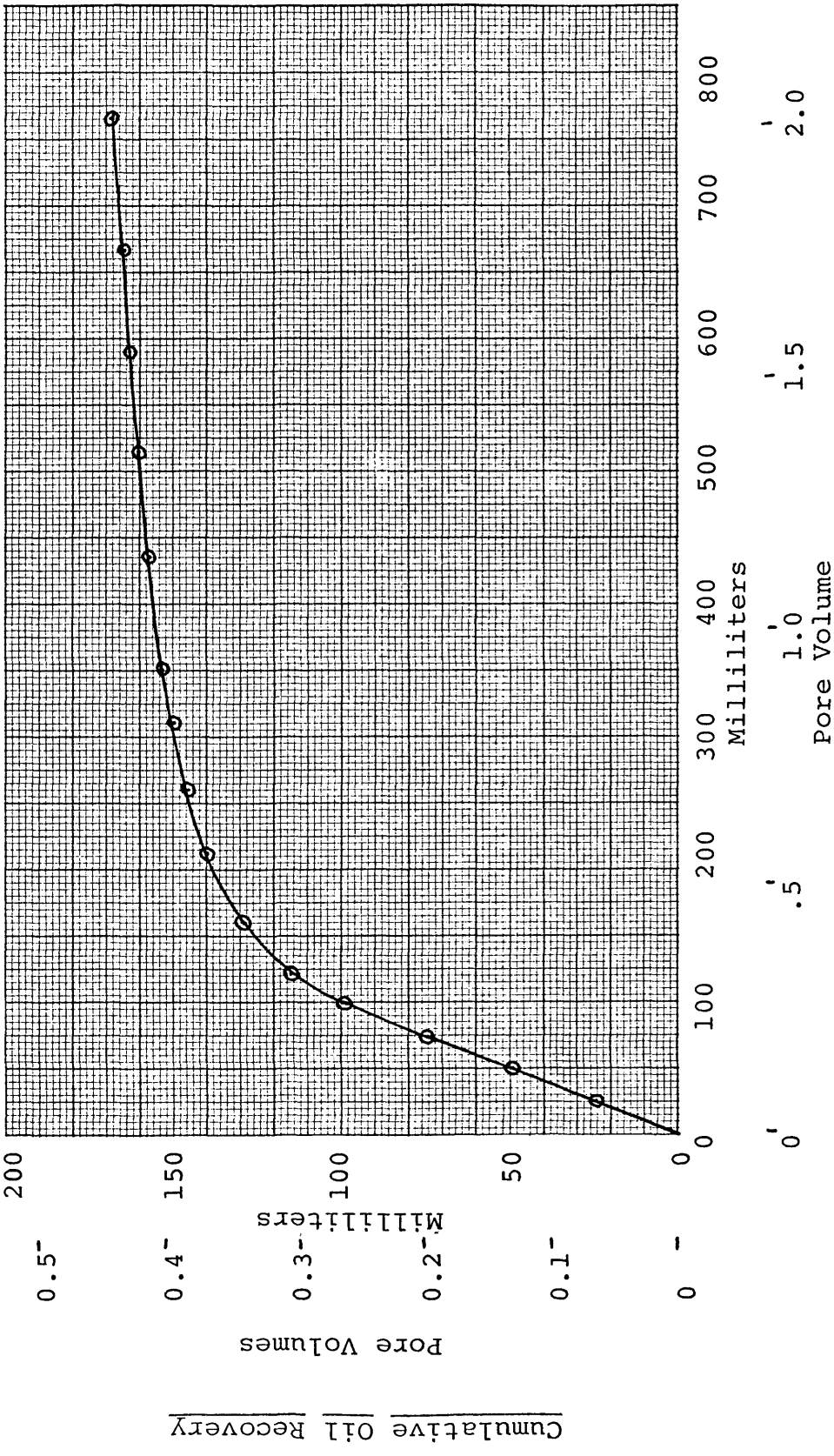


Figure 14 WATERFLOOD PERFORMANCE (0.20 WEIGHT PER CENT NaOH AT 160° F)

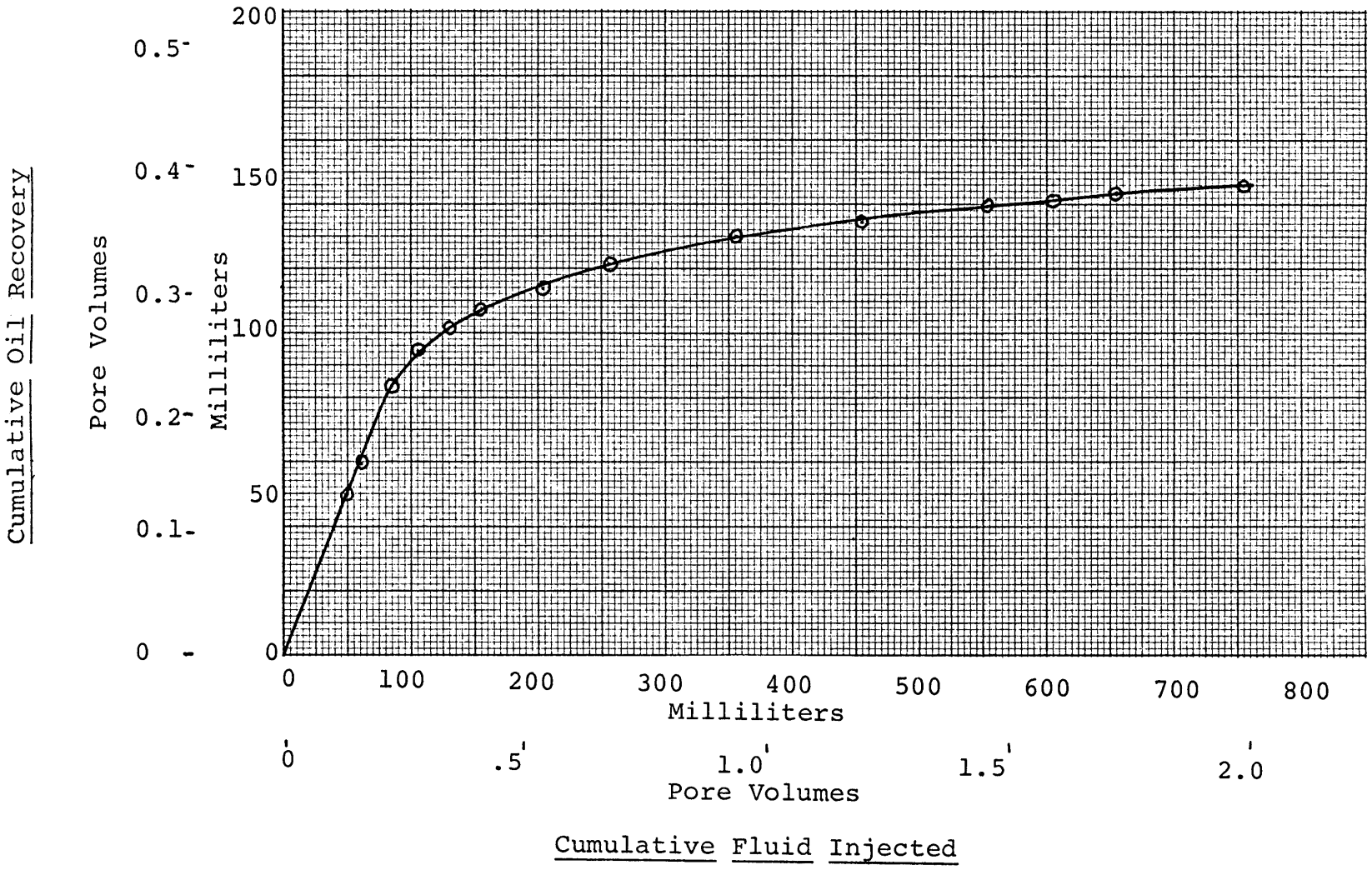


Figure 15 WATERFLOOD PERFORMANCE (0.20 WEIGHT PER CENT NaOH AT 190° F)

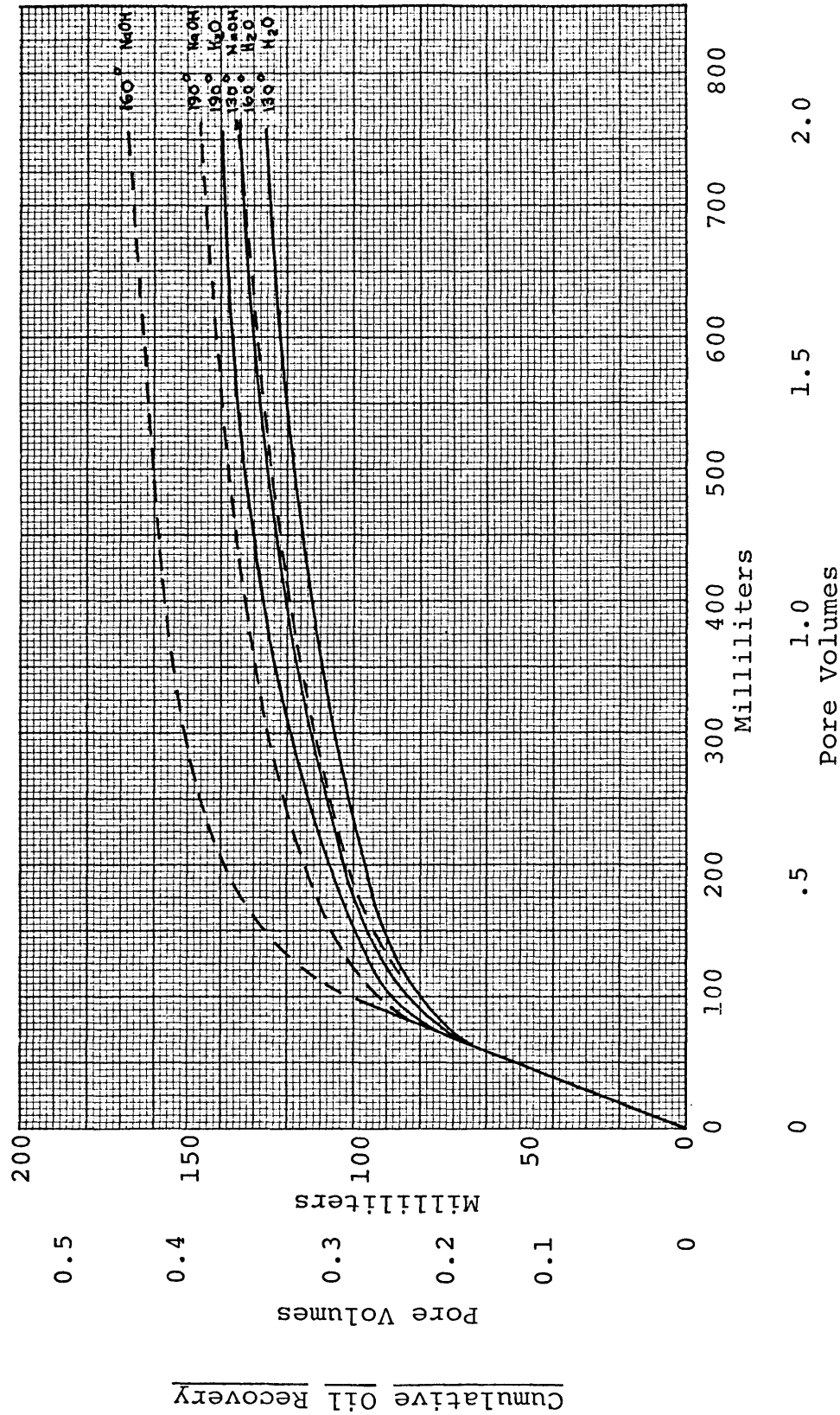
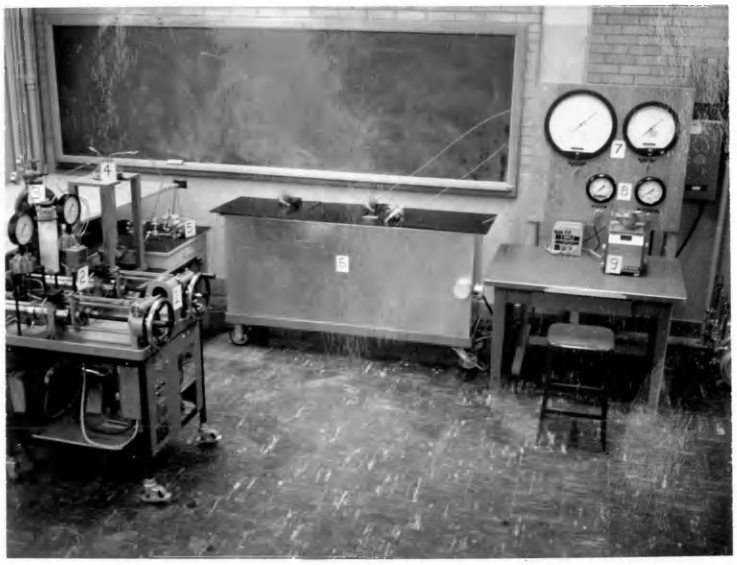


Figure 16 SUMMARY OF WATERFLOOD PERFORMANCES



1. Ruska Proportioning Pump
2. Pressure Safety Switch
3. Nitrogen Supply
4. Displacement Vessel
5. Filters
6. Constant Temperature Bath
7. Core Pressure Gauges
8. Pump Pressure Gauges
9. Scale

Plate 1 EQUIPMENT