

**AN EVALUATION OF THE ALKALINE WATERFLOODING
DEMONSTRATION PROJECT, RANGER ZONE
WILMINGTON FIELD, CALIFORNIA**

By
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May 1987

Performed Under Contract No. AC19-85BC10830

Keplinger Technology Consultants, Inc.
Tulsa, Oklahoma

**Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma**



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**Prepared for
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SUMMARY

An alkaline flood enhanced oil recovery project was conducted in the Ranger Zone of the Wilmington Field in California, the largest field in the state. Contained within a large anticlinal structure which lies partially offshore along the southern California coastline, the Ranger Zone is composed of unconsolidated sand and is characterized by moderately high permeability and porosity. The reservoir crude oil is variable in character but averages 23 cp in the project area. Alkaline flooding was considered for Wilmington since the crude oil is rich in organic acids and reacts with alkaline fluids to produce surfactants. Oil recovery can potentially be improved by increased displacement efficiency and by improved sweep.

The pilot project is comprised of two rows of injectors which enclose the Block 9 pattern area, and unconfined northern and southern areas. The injected fluids consisted of a 10.2 percent pore volume of a softened fresh water with 1 percent added salt, a 67 percent pore volume of an orthosilicate fluid, and a post-flush fluid of softened water with 0.75 percent added salt.

Oil recovery from the project has been poor. However, water production was reduced in some wells.

The key factors for the lower than expected oil recovery are attributed to high consumption of the alkaline fluids and to wellbore plugging problems. High consumption was due in part to the mixing of alkaline fluids with waters of high hardness and to reactions of the alkaline fluids with the reservoir rock. The plugging problems were due to the formation of calcium carbonate scale, magnesium silicate scale, and to silicate-containing precipitates. Workovers to remove the damage were only partially successful.

The performance may have been improved by several different procedures. However, these are considered to be of secondary importance since the consumption of the alkaline fluids appears to be the dominant factor affecting performance. These improvements include the use of a different preflush design and polymers for mobility control.

Interpretation of the pilot could have been improved by additional analyses of the produced waters. Such tests would have helped to define the mechanisms for the excessive consumption of the alkaline fluids.

It is recommended that future research be directed toward improving the tolerance of the alkaline fluids to hardness of formation waters. Such research may include work on the incorporation of co-surfactants and additional synthetic surfactants.

The project was well conducted and utilized the technology available at the time.

INTRODUCTION

The Wilmington Field is California's largest oil field and one of the major fields in the United States. The field is an anticlinal structure which lies partially offshore along the Southern California coastline (Figure 1). The field contains seven major zones, with the Ranger Zone containing most of the reserves. Oil recovery in the field is due to a combination of solution gas drive, reservoir compaction, edge water encroachment, and water injection. The reservoir crude oils are variable in character but are generally of relatively low gravity and high viscosity. Cumulative oil production from the field has been in excess of one billion barrels.

The Wilmington Field is generally separated into two areas. Primary development took place in the Old Wilmington area during the period of 1936 to 1950. The second area is East Wilmington, generally known as the Long Beach Unit. Development of East Wilmington was prevented by the City of Long Beach until water injection into Old Wilmington demonstrated the economic viability of the process and that subsidence could be prevented. THUMS Long Beach Company became the field contractor for the City of Long Beach in early 1965 to develop East Wilmington.

The major incentive for evaluating enhanced oil recovery (EOR) processes in Wilmington has been the relatively low recovery efficiency of waterflooding. The primary reasons for low recovery are an unfavorable mobility ratio and large permeability contrasts. Production performance is typically characterized by early breakthrough of water and low ultimate oil recovery.

Various approaches have been considered in Wilmington for improving oil recovery. These include polymer flooding, alkaline injection¹⁻⁴, and micellar-polymer flooding. A micellar-polymer pilot was conducted and recovered a significant amount of oil. The pilot was not expanded based upon economic considerations.⁵

Alkaline flooding was considered at Wilmington because of reactions that occur between high pH fluids and the crude oil. The crude oil is rich in organic acids and forms surfactants upon contact with alkaline fluids such as sodium hydroxide. Oil recovery can potentially be improved when injecting low concentrations of alkaline solutions by two mechanisms. One of these is "entrapment" in which an in situ generated oil and water emulsion is formed. The emulsion acts to restrict movement in the zones contacted, thereby diverting flow into less permeable regions. Oil recovery is enhanced through sweep improvement. The second mechanism is "entrainment" in which the natural surfactants formed by the oil-water reactions reduce the oil-water interfacial tension. The result is a potentially improved displacement efficiency. Core tests demonstrated that substantial amounts of Wilmington crude oil could be displaced when injecting dilute concentrations of sodium hydroxide. Reference 6 discusses the status of the various field projects using alkaline fluids.

Based upon encouraging laboratory tests, a pilot alkaline flood project has been in progress since 1979. The major purposes of this report are to independently evaluate the performance of the project, to determine how the project could have been improved using advancements in technology, and finally to define critical areas of research that are needed to further develop the technology.

RESERVOIR DESCRIPTION

The Wilmington Field is located in the southwestern part of Los Angeles County, California (Figure 1). The field is an anticlinal structure underlying 13,000 surface acres. Production comes from several major zones. Depth to the top of the uppermost zone (Tar) is 2,000 feet; depth to the bottom of the lowest zone (237) is 6,500 feet.

The upper four zones (Tar, Ranger, Upper Terminal, and Lower Terminal) lie between the depths of 2,000 and 4,000 feet. They contain a low-gravity, high-viscosity crude oil. The structure is divided by several large transverse faults. Much of the early development was carried out in the old portion of the field in Fault Blocks I through VI (Figure 2). Oil recovery was through a combination of solution gas drive, sand compaction, and limited edge water encroachment. Waterflooding began in 1958 in the four upper zones.

In 1965, the Long Beach Unit was formed to develop the remaining fault blocks of the Wilmington Field, located in the eastern portion of the field (Figure 3). Water injection into Fault Block VI was conducted from a land based site. Expansion of waterflooding into the remaining fault blocks occurred by building injection facilities on four 10-acre earthfill islands. The wells were drilled directionally from those sites to each of the five reservoirs in the unit. The alkaline pilot was conducted in the Ranger Zone, which has by far the largest oil-in-place reserves. Figure 2 shows the location of the alkaline project, which was conducted in Fault Block VII.

The Ranger Reservoir lies at a depth of 2,225 to 2,800 feet, and is comprised of a gross thickness of 850 feet and a net sand thickness of 320 feet. The Ranger Zone consists of several subzones separated by impermeable shale barriers. Each interval is an interbedded sequence of shales and unconsolidated to semiconsolidated, poorly sorted, medium to fine grained sands. The sands are lenticular in character, but are

still traceable on well logs over large areas. Figure 3 shows a typical structural cross section of the Ranger Zone in Fault Block VII.

Waterflood operation began in the Ranger Zone of the Long Beach Unit in 1965. Figure 4 shows the performance of Ranger Economic Block 9 during the waterflood operations. The waterflood performance was considered to be poor. The low oil recovery was attributed to poor sweep efficiency, arising from an unfavorable mobility ratio and large permeability contrasts between the various Ranger subzones. In many instances, the water broke through prematurely to offset producers, indicating that a relatively small portion of the reservoir was contacted. The water appeared to be cycling through the uppermost subzone of the reservoir.

PROJECT DESIGN

PATTERN DESCRIPTION

Figure 5 shows the location and configuration of wells within the alkaline demonstration project. The pilot is divided into three distinct areas, as described below and also shown in Figure 5.

1. Pattern Area. This area encompasses 93 acres, and includes eight injection wells and eleven producing wells. This area, also known as Block 9, is covered by the cost-shared contract between DOE and the City of Long Beach. This area provides the major basis for evaluation of the project.
2. Northern Area. This area encompasses 50 acres, and is located downstructure and extends to the aquifer. It contains six producing wells.
3. Southern Area. This area encompasses 41 acres, and is located upstructure of the pattern area. This area also contains six producing wells.

Reservoir properties of the pilot area are listed in Tables 1 and 2.

LABORATORY STUDIES

Laboratory studies were performed using core material from the Ranger Zone as a support for this alkaline demonstration project.^{1-4,}

⁷⁻¹¹ These tests included routine core analysis, special core analysis, including relative permeability measurements, alkaline waterflood tests, and water analysis tests. Each of these groups of tests are described in this section of the report.

In order to perform laboratory tests, two cores were obtained from the Ranger Zone. These cores were obtained during re-drilling of Wells B-827-A and B-110-IA. The core samples were recovered in plastic pipe and were frozen after being cut into three-foot lengths and sealed. Core plug samples used in this study were cut parallel to the core axis.

Routine Core Analysis

Routine core analysis tests were performed on core plug samples from Well B-827. Air permeability, helium porosity, grain density, and liquid saturation measurements were obtained from these samples. Initial routine core measurements were made to determine permeability and porosity with low overburden pressures. Due to the unconsolidated nature of the Wilmington Sand, routine air permeability and helium porosity measurements were repeated using a 1,600 psi net confining pressure. As expected, a significant change in air permeability and helium porosity was observed under the higher levels of overburden pressure. Results of routine core analysis are presented in Table 3.

Special Core Analysis Tests

Special core analysis tests were performed using core plug samples from Well B-827-A and Well B-110-IA. These tests include unsteady-state water-oil relative permeability tests, waterflood susceptibility tests, cation exchange capacity measurements and electrical resistivity (formation factor) measurements.

The unsteady-state water-oil relative permeability tests were performed at a constant rate of one foot per day. These tests were performed in conjunction with alkaline flood tests and are discussed in a later section of this report.

The results of waterflood susceptibility tests are presented in Table 4. The conditions under which these tests were performed was not specified. The average displacement efficiency is 49.4 percent of the oil-in-place which is considered to be an average displacement efficiency.

The results of cation exchange capacity tests are presented in Table 5. The test method for determining cation exchange capacity of this reservoir sand was not described. However, these tests were performed along with electrical resistivity tests (formation factor tests) for well logging purposes. The cation exchange capacity varies from 2.6 to 11.5 milliequivalents per 100 grams, and averages 4.8 milliequivalents per 100 grams. Appendix I discusses the general procedures for cation exchange capacity measurements.

Alkaline Waterflood Tests

Tests performed to evaluate the alkaline waterflood process included measurement of interfacial tension, crude oil acid number tests, caustic consumption tests, and comparative flow tests. The measurements of interfacial tension by the pendant drop method and spinning drop method were performed with sodium hydroxide and sodium orthosilicate. The results of these tests indicated that when alkaline chemicals were added to injection water the interfacial tension between oil and water was reduced enough to mobilize residual oil. These tests also indicated that sodium orthosilicate performed better than sodium hydroxide in reducing the interfacial tension.

The crude oil acid number of the Ranger Zone oil used in laboratory testing was also measured. The crude oil acid number is expressed as potassium hydroxide uptake in milligrams per gram of crude oil. If the acid number is high, the crude oil tends to have a higher quantity of organic acids to react with the alkali solutions and, therefore, more surfactant is generated by the reaction. Typically, crude oils with a minimum acid number of 0.5 are considered suitable for alkaline flooding. The acid number of Ranger Zone crude oil varies from 0.86 to 2.5 milligrams of KOH per gram of oil.

Caustic consumption tests were performed using core material from the Ranger Zone. These tests included static equilibrium tests (sometimes referred to as "bottle tests"), reversible adsorption tests, and chemical consumption tests. The reversible adsorption and chemical

consumption tests were dynamic tests at room and reservoir temperature. Chemical consumption tests were performed to obtain short-term and long-term alkaline consumption data. Testing was performed by Petroleum Testing Service, Inc., and by California State University at Long Beach. Results of consumption tests performed by California State University are given in Table 8. Alkali consumption ranged from 8.6 to 16.9 milliequivalents of alkali per 100 grams of rock at a reservoir temperature of 125°F over a test period of 36 days.

Sixty-two comparative flow tests were performed by Petroleum Testing Service to compare the recovery of oil by conventional waterflooding and the recovery by alkaline waterflooding. The tests were also performed to evaluate two proposed mechanisms of oil recovery by alkaline waterflooding, the entrapment process and the entrainment process.

As discussed in Appendix I, the entrapment process occurs by the emulsification of oil into a water phase and the subsequent lodging of the oil globules at the pore throats. The droplets are large, since the interfacial tension is relatively high. The concept is that the lodged globules will reduce permeability in the contacted areas and divert flow into other areas.

The entrainment process occurs by the formation of a stable oil-in-water emulsion. The oil is dispersed into very small droplets due to the low interfacial tension. The oil is carried through the formation and is eventually produced. It is anticipated that the entrainment process will prevail when the salinity is properly adjusted, and the entrapment process will prevail when the salinity is lower or higher than optimum.

The results of the laboratory displacement tests are presented in Table 6. These tests were conducted to evaluate both the entrapment and entrainment mechanisms. Tests 1 through 6, 13, 28, and 29 evaluated the entrapment process, and the remainder of the tests evaluated the entrainment process. As noted in Table 6, the entrapment tests are characterized by the lack of sodium chloride in the alkaline slug. The general procedure was to initially waterflood a core to establish a

baseline oil recovery from water injection. The core was then resaturated in preparation for the alkaline fluid displacement test. The alkaline flood was initiated by first injecting water until a predetermined point was reached (water breakthrough or a WOR = 5, as noted in Table 6). Alkaline fluids were next injected. Table 6 shows the total oil recovery with the alkaline fluids and the incremental oil recovery over waterflooding. Definitive comparisons between the entrapment and entrainment tests were not possible since test conditions were not sufficiently controlled. However, the entrapment process was generally less efficient.

Table 7 shows additional data on the displacement tests conducted on Sample Nos. 39 through 62. The results denoted as "A" represent the waterflood, and the results denoted as "B" represent the alkaline flood. Oil recoveries ranges from 46.8 to 78.7 percent original oil-in-place (OOIP) for the alkaline flood, with an average of 60.5 percent OOIP. The incremental recovery over waterflooding averaged about 6 percent OOIP.

During alkaline waterflooding, the concentration of nine ions in the produced water were measured. These ions were calcium, magnesium, potassium, aluminum, hydroxide, bicarbonate, carbonate, sulfate, and silica. The pH of the produced water was also measured along with the volumes of produced oil and water. These data indicate a decrease in calcium, magnesium, and bicarbonate ions and an increase in potassium, aluminum, hydroxide, carbonate, sulfate, and silica ions, in addition to a rise in pH as the alkaline flood progressed. These data indicate the core material is undergoing dissolution when contacted with strong alkaline solutions.

The measurement of pH during these tests suggests the consumption of alkali during these tests but is not sufficient to quantify the alkali loss during the alkaline flood.

Chemical Consumption Tests

Table 8 shows the results of consumption tests conducted with sodium hydroxide and sodium orthosilicate in sand from the Ranger Zone. Such data are needed as input for the simulation studies to help in the design of the project and in the prediction of performance. The results show that the adsorption is continuously increasing with time. Such data suggest that a kinetics-based adsorption loss term should be used in any model to simulate performance of the project.

Water Analysis and Additional Laboratory Testing

A number of water analyses were performed before, during, and after alkali injection. The tests were performed to provide data for other laboratory testing, as a means of quality control of the injection fluids, and as a means of monitoring the progress of the waterflood.

Additional testing was performed on the produced oil and water to determine the extent of produced emulsions that may occur during the alkaline flood project. Initial testing was performed by the Tretolite Division of the Petrolite Corporation and by Petroleum Testing Service. The produced emulsions were found to be treatable by available emulsion breakers.

SIMULATION STUDIES

Simulation studies were conducted by Scientific Software Corporation to assist in the design of the project and to predict the performance of the pilot.^{3,13} This discussion summarizes the results of the simulations that were conducted in support of the project.

Simulator

The simulator used in these studies was derived from a three-phase, three-dimensional black oil reservoir simulator. It has the ability to account for up to six different active agents in the aqueous phase. Any or all of the six agents may be alkaline or polymer-containing fluids.

The effects of the alkaline fluids are represented by changes in the relative permeabilities. This simplified approach was chosen to represent the many complex mechanisms and reactions that occur in the alkaline process. The model contains the following capabilities:

1. Six different water-phase solutions or agents, with a material balance made on each of the fluids.
2. Miscible mixing parameters, based upon the techniques of Todd and Longstaff.
3. Loss of active species of alkaline fluids (e.g., OH^{-1}) by an equilibrium, chemical reaction (e.g., Ca^{+2}).
4. Loss of active species through chemical adsorption, assumed to occur instantaneously upon contact.
5. Linear weighting of relative permeability curves, ranging from normal water/oil relative permeability relationships to the comparable water/oil relationships when 100 percent of the active alkaline agent is being used.
6. Permeability reductions, based upon the conditions of points 4 and 5.

Following the laboratory work conducted during 1978 to 1980, the simulator was expanded to include two more capabilities:

1. Consumption of an active species through a nonequilibrium, kinetically controlled reaction between the species and the rock matrix. This mechanism, referred to as long-term consumption, was based upon laboratory tests of Bunge and Radke⁷ and Lieu.⁹
2. Linear weighting of relative permeability curves up to minimum threshold concentration of alkaline fluids, above which an optimum alkali/oil relative permeability relationship was used. This

threshold concentration corresponds to the point where very low interfacial tensions occur.

The computational algorithm used in the simulator is by an implicit-pressure/explicit-saturation (IMPES) formulation. The model was used in a one-dimensional form to simulate laboratory tests, in two-dimensional form to represent a limited area of the field, and finally in a three-dimensional form to represent the entire pilot project.

Laboratory Simulations

Sixty-two sets of laboratory floods were conducted to determine the optimum combination of alkali and salt concentrations to maximize oil recovery. The floods were conducted on cores which had been collected in plastic-lined pipe and preserved by freezing. Cores were cut parallel to the axis. All tests included a baseline waterflood to determine the oil recovery and to determine oil/water relative permeability relationships. Thereafter, alkaline fluids were injected to determine the incremental oil recovery and to determine the corresponding relative permeability relationships.

Figure 6 shows the results of tests conducted on core Sample No. 21 and the predicted performance from simulation studies. An instantaneous consumption calculated for this core flood was 0.4 meq/100 gm of rock, compared to an average value of 1.0 meq/100 gm for all tests. The match of performance for this core test was achieved with very little adjustment of oil-alkaline relative permeability curves. The water/oil and alkali/oil relative permeability relationships from this test were normalized to match typical laboratory displacement performance. These curves were later used in the two-dimensional slug optimization study and the three-dimensional alkaline prediction cases. The laboratory simulations assumed that consumption losses were instantaneous with no exposure-time dependency. The two- and three-dimensional simulation studies incorporated a time-dependent adsorption loss.

The long-term consumption work of Lieu⁹ indicates that the amount of alkaline adsorption is related to the time of exposure. Thus, it was recognized that the results of short-term laboratory tests would be optimistic relative to conditions in the reservoir where the exposure times are much greater. To scale up to reservoir conditions, the laboratory data, shown in Table 8, were calibrated to a kinetics model for long-term consumption. The converted laboratory data were then used in the simulator to predict performance in the reservoir.

Slug Optimization Study With Two Dimensional Simulator

A two-dimensional model study was conducted to study the effects of slug size, alkaline concentrations, chemical consumption, and relative permeability adjustments. With the aid of these simulations, a decision can be made on the optimum slug design for the field. An area in the Fo₁ and Fo₂ sands in the southeast section of the pilot was chosen (Figure 7).

The grid used for these studies was 14 cells (east to west) by 27 cells (north to south). The cells measured 38 by 38 feet. The study area included two injection wells and four producing wells.

The basic reservoir and operating data for this area are shown in Table 9. The reservoir rock properties for the Fo₁ and Fo₂ sands are combined. The relative permeability and long-term consumption data used for the model were previously described. It was further assumed that the injection and postflush fluids were softened and contained 1.0 percent added sodium chloride.

Various simulations were conducted to evaluate the effects of alkali consumption, slug size, concentration of alkali, and the relative permeability adjustment procedure. Final results are shown in Table 10 and Figure 8. The results, in general, show that the smaller, more concentrated slugs produced faster oil recovery response but it is not as sustained as the recovery response from larger, more dilute slugs. A slug with variable concentrations was also evaluated.

The large, more dilute slugs gave better results in the simulator predictions because of improved mobility control over a long period of time. The optimum slug size is a 60 percent pore volume slug containing 0.4 percent sodium orthosilicate. These slug specifications were used for the final design. The procedure used to adjust permeabilities appeared to be important in the computed recoveries.

The simulations indicated that oil recovery could potentially be improved in spite of the time-dependent adsorption losses. As subsequently discussed, adsorption losses appeared much more critical in the larger pore volume systems due to the longer residence times.

Pilot Area Simulations with Seven-Layered, Three Dimensional Model

Simulations were conducted to predict the performance from the pilot area. These simulations used seven layers: Fo_1 , Fo_2 , Fo_3 , F, H, G, and G_4 . The properties of the layers and the four areas which comprise the pilot area are given in Tables 1 and 2. The grid in each layer was 11 cells (east to west) by 23 cells (north to south). The area of each grid block was 200 by 300 feet.

A base case waterflood prediction was made using the appropriate injection and production conditions, the drilling of new infill wells, and the plugging of certain subzones to reduce channeling. Using the same conditions, two alkaline predictions were made. Both simulations were made assuming 60 percent pore volume slugs of 0.4 percent sodium orthosilicate and 1.0 percent salt. One of these cases used the linearly prorated (Case 1) and the other a minimum-threshold alkaline flood (Case 2) relative permeability adjustment. The predictions are shown in Table 11 and Figure 9.

The predicted incremental oil recovery was 651,000 barrels which is about 1.9 percent of the oil-in-place. This compares with about 7.25 percent of the oil-in-place as predicted from the smaller two-dimensional pattern. The three-dimensional simulations are very

disappointing. The parameter which appears to account for the low total oil recovery and the differences between the two-dimensional and three-dimensional results is the long-term consumption of alkaline fluids. The consumption appears to affect the larger area (as for the three-dimensional simulations) much more severely than smaller areas due to the greater residence times and larger surface area. Additional simulations appear to support this conclusion.

MINI-INJECTION TEST

A one-well injectivity test was conducted during the period of June 6 to August 17, 1977, in preparation for the full scale pilot. The major purpose of the mini-test was to evaluate the injection performance of the alkaline fluids. The test was conducted in Well B-836I (Figure 5). The following are the major steps taken during the mini-injection tests:

1. Preflush Injection. About 62,000 barrels of a softened water with 1 percent added sodium chloride was injected into the well beginning on June 6, 1977. The initial average injection rate of 5,000 barrels per day was reduced for a period of time to 2,000 barrels per day, due to storm damage which prevented the blending of the designed quantities of salt.
2. Alkali Injection. About 237,000 barrels of 0.1 percent sodium hydroxide in softened fresh water was injected into the well beginning on June 20, 1977. Initial injection rates were 5,000 barrels per day. The well was backflowed after 10 days of injection, but only 2 barrels of fluid was recovered from the wellhead. The small volume of produced fluid was attributed to low bottom hole pressure. Injection continued thereafter until the test terminated on August 17. Bottom hole samples were collected on July 8 and at the end of the test.

The following conclusions were derived from the test:

1. Injectivity of the preflush and alkaline fluids was satisfactory.
2. Profile surveys indicated no significant change in fluid flow distributions.
3. Chemical analyses of backflow samples indicated a substantial increase of fluid alkalinity. However, it was not determined if the increased alkalinity was due to NaOH or to the conversion of HCO_3^- to $\text{CO}_3^{=}$ in the reservoir.
4. No determination could be made on the amount of consumption of the alkaline fluids.
5. The fill in the wellbore at the end of the test appeared to come from backflow as opposed to the formation of precipitates from chemical reactions.
6. The logistics for the handling of chemicals and the injection of fluids was satisfactory.

SPECIFICATION OF INJECTED FLUIDS

The specification of the types and volumes of chemicals to be injected was based upon simulation studies, laboratory testing, and the mini-injection test. Table 12 lists the quantities of injected fluids and the period of time over which the fluids were injected. The following paragraphs discuss the basis for the chemical design.

Initially, a 10.2 percent pore volume of a softened fresh water with 1 percent added NaCl was injected. The purpose of the preflush is to remove excessive hardness from the reservoir and to establish a salinity level which allows the injected alkaline fluids to efficiently displace oil. Table 13 shows the composition of the formation water (as

estimated from a reported synthetic water analysis). As shown, the hardness levels are in the range of 670 ppm. This level greatly exceeds the tolerance limits of injected alkaline fluids. The composition of two softened waters used for injection are shown in Tables 14 and 15. As shown, the hardness levels are low (10 ppm, 25 ppm), which would greatly reduce adverse reactions with injected alkaline fluids. The key issue, as discussed later, is the ability of the softened preflush to adequately reduce the hardness to an acceptable level.

Sodium orthosilicate was selected as the preferred alkaline agent based upon laboratory tests. It appears to be more suitable than sodium hydroxide because of a lower interfacial tension, better oil recovery, and greater resistance to hardness. As discussed later, the selection of orthosilicate resulted in the creation of magnesium silicate scale in producing wells.

A 67 percent pore volume slug of a 0.39 percent sodium orthosilicate with 0.67 percent added salt was injected. This volume and concentration was selected based upon simulation studies.

Softened fresh water was subsequently injected to protect the alkaline fluid from the hardness of the injection water.

SURFACE FACILITIES

Figure 10 shows the schematic for the surface facilities. These facilities were designed to inject (1) softened water with added salt during the preflush; (2) softened water with added salt, and blended with separate streams of sodium silicate and sodium hydroxide, during the alkaline fluid injection; and (3) softened water with added salt, during the postflush. The facilities for preflush injection were completed in 1979, with completion of total facilities in March 1980.

Plans were prepared for the installation of additional production handling facilities if emulsion problems were encountered. These facilities were not needed.

PROJECT IMPLEMENTATION

This section discusses project operation and significant events which occurred during the life of the project.

OPERATIONS

All fluids were successfully injected into the reservoir within the general time frame that had been anticipated. The injection took place over the following times:

Preflush	January 1979 - March 1980
Alkaline Slug	March 1980 - December 1983
Postflush	December 1983 - June 1984

Table 12 lists the volumes and compositions of each injected fluid. No major problems were encountered with the surface facilities for the blending and injection of chemicals.

Numerous workovers were required throughout the project. Most of the problems were in producing wells where injected alkaline fluids had broken through. Table 16 lists many of the workovers that were conducted during the period of January 1976 to December 1985. This list is incomplete, but illustrates the types of remedial treatments conducted. Most of the treatments were designed to overcome the plugging effects of scale in producing wells. A later section discusses the scale problem in more detail.

INJECTION AND PRODUCTION WELL PERFORMANCE

Ranger Economic Block 9

Figure 11 shows the performance of Ranger Economic Block 9 through most of 1985. Block 9 represents the primary basis for evaluation since it is confined by two rows of injectors.

Figure 11 shows that the total injection into the pattern remained around 30,000 barrels per day until mid-1983. Thereafter, the injection rates fluctuated and a steeper decline began after mid-1984. The decline was due in part to the shut-in of wells B-107-I and B-836-I for repair.

Gross oil production declined significantly after 1982. The declining gross oil production is attributed to reduced injection rates and to the scale problems in producing wells.

Total fluid production declined, reflecting the reduced injection and plugging problems in producing wells.

The water-oil ratio (WOR) increased beyond the projected trend in 1982 and began a steady decline in 1983. The decline in the WOR reflects the reduced water production observed in some of the wells (Table 18). This table indicates the total WOR at the affected wells has been reduced. Figure 12 shows the oil cut versus cumulative oil production for Block 9.

Northern Area

Figure 13 shows the performance of wells in the Northern Area. There are wide swings in the gross and net production, reflecting workovers which were periodically conducted. There are also wide variations in the WOR, with a long-term gradual increasing trend. The WOR appears to be level for the past two years.

Figure 14 shows the oil cut versus cumulative oil production of the Northern Area.

Southern Area

Figure 15 shows the performance of wells in the Southern Area. As shown, there is a gradual decline in the gross and net production, reflecting the reduced injection into the pattern. The WOR is gradually increasing with time.

Figure 16 shows the oil cut versus cumulative production for the Southern Area. The trend is toward a reduced oil cut, but some stabilization has occurred.

SCALE PROBLEMS

Scale deposition has been a major problem in the project. Scale and precipitates have occurred in a number of producing wells, resulting in restricted production and the fouling of downhole equipment. The scales include calcium carbonate, magnesium silicate, and amorphous silica. Calcium carbonate was initially identified as a scale problem. With time, scales evolved into a mixture of calcium carbonate and magnesium silicate. Later, an amorphous silica gel occurred in the submersible pumps in some of the wells.

The conditions of the alkaline project are favorable for the formation of scales and precipitates. These include the existence of multivalent cations, carbonates, bicarbonates, hydroxides, and silicates. The pH of the system also plays a key role. The pH controls the formation of many scales, particularly carbonates, hydroxides, and silicates. The solubility of each component varies considerably, both over the range of pH and the type and concentration of multivalent cations present.

The following is a discussion of the types of scales and examples of where such scales have occurred in the field.

Carbonate Scale

Carbonate scales result from reactions between multivalent cations with bicarbonate ions, carbonate ions, and indirectly with dissolved CO₂ in water (CO₂ can ultimately ionize to carbonate ions under the proper pH conditions). Carbonate scales readily form in regions of high pressure drops, flow turbulence, and by mixing with other fluids. Calcium carbonate is the predominant form of carbonate scales, due to its lower solubility. Carbonate scales are readily soluble in most mineral acids such as hydrochloric acid and hydrofluoric acid.

For example, the conditions in Well No. B-834-A are favorable for the formation of calcium carbonate scale. Figure 17 shows the analyses of fluids produced from Well B-834-A. These analyses include pH, hardness (Ca⁺⁺ + Mg⁺⁺), total salinity, and the silicate content. The significant aspects of the analyses are the rapid increase in hardness in 1982 and the approximately level values of pH and silica content over the same time period. The productivity of the well declined with the increased hardness levels, suggesting the formation of calcium carbonate scale. This well has been successfully treated by the continuous injection of a scale inhibitor down the annulus.

Well No. B-105 is another example of a group of wells where carbonate scale has occurred. As shown in Figure 18, a sharp increase in the silica content was observed in late 1981 with no corresponding increase in the pH. The water production also declined during the time period, suggesting that scale was being formed. The calcium carbonate occurred in and around the pump but not in the liner. Use of hydrochloric acid and scale inhibitor treatments down the annulus allowed this and similar wells to be successfully produced.

Silicate Scale

The formation of silicate scales is very complex chemically and is a function of the degree of polymerization of the silicate ions, pH value, and concentration. In general, silicates will precipitate with most

multivalent metal cations over specific pH ranges under certain conditions of temperature, time, and pressure. Magnesium silicate scales are more common than the calcium silicate, due to its lower solubility. The domain over which silicate scales form overlays those of other scales. Thus, the resulting precipitate or scale may be a complex mixture of compounds. The silicate scales are generally amorphous in nature and highly hydrated. They do not readily adhere to metal surfaces, but can be readily absorbed by carbonate scales and oxide surfaces. The silicates precipitate rapidly and do not readily dissolve in acid solutions due to low solubility. Certain sequestrants, such as EDTA, may be of limited value in preventing silicate scale formation, but cannot dissolve the scales after they have been formed.

An amorphous silica gel may form where a high-pH, high-silica content fluid is diluted with a low-pH fluid. Such gels contain only small amounts of other multivalent scales or precipitates. Alkaline fluids can dissolve such gels. Acids are ineffective in breaking such gels and may even promote further gelation.

Well B-712 is an example of a well where silicate scale was formed. As shown in Figure 19, a sharp increase in the silica content occurred in 1982, with a corresponding increase in the pH. These represent favorable conditions for the formation of magnesium silicate scale. Earlier, calcium carbonate scale was detected and successfully treated. Treatments to handle the magnesium silicate were unsuccessful and the well was shut in.

Treatment

As earlier discussed, wells with calcium carbonate scale were successfully treated by a combination of acid and scale inhibitor injections. Wells with magnesium silicate scale were much more difficult to treat. The following discussion focuses on the treatment of such wells.

Magnesium silicate scaling problems occurred in Wells B-101-A, B-712, B-830, and B-838. Analysis of fluids from these wells indicated high pH and relatively high concentrations of silica. Initial analyses of the scale from centrifugal pumps showed high concentrations of carbonate, silica, calcium, magnesium, and iron; and low concentrations of sodium, aluminum, potassium, and zinc. The first treatment for this type of scale was conducted in Well B-712 where a stimulation treatment using hydrochloric acid and hydrofluoric acid was unsuccessful.

The subsequent work focused on the use of scale inhibitors to prevent the formation of scale. These investigations evaluated polyacrylates and phosphate ester inhibitors. The investigations ultimately determined that a combination of scale and corrosion inhibitors would be the most effective treatment.

A treatment was performed in Well B-838 in July 1983. The treatment consisted of an initial acid squeeze (HCl and HF) followed by scale/corrosion inhibitor (amino methylene phosphonate) injection. The well produced for 25 days, but the pump failed following the breakthrough of a high pH fluid. A semi-solid mass was found in the pump after the treatment. Analysis of the material indicated the mass to contain particulates from the formation consisting of feldspar, clays, quartz, and indeterminate amounts of amorphous siliceous materials.

In November 1983, a similar treatment was conducted in Well B-101-A. The well produced for 29 days after treatment, but once again failed. Once again, analysis of the produced fluids indicated a sharp increase in the pH following treatment. Analysis of the precipitate found in the tubing indicated that calcium carbonate/magnesium silicate had been controlled. However, further analysis indicated the deposit to contain mostly silica, with smaller amounts of aluminum oxide. It was speculated that most of the silica was the result of silica dissolution in the formation. The amorphous silica probably precipitated in the wellbore due to the mixing with other fluids.

Overall, it appears that the conventional-type scale problems could be controlled by a combination of acid stimulation treatment and injection of scale inhibitors. The most severe problems appear to be caused by the reaction of alkaline materials with the constituents of the formation.

PROJECT EVALUATION

This discussion addresses the performance of the project and provides our opinions on the specific aspects of the project that might have been better conducted. The discussion is divided into categories, as follows:

OIL RECOVERY PERFORMANCE

Economic Block 9 is the primary area for evaluation of the project since it is confined between rows of injectors. Wells in this area are more likely to be influenced by the injected alkaline fluids and less affected by other ongoing operations within the field. The Northern and Southern areas provide secondary sources for evaluation. These areas are not within a confined area but still provide useful information about the project.

Figure 11 shows the performance of Economic Block 9. Note that the oil production in early 1983 declined below the projected trend. This decline was accompanied by an increase in the water-oil ratio. During this same period, injection rates had decreased, as well as the gross fluid production. The reduced oil production and increased WOR probably resulted from the numerous scale problems, as later discussed.

Figure 12 shows the oil cut versus cumulative oil recovery (since 1976) for Economic Block 9. This plotting procedure is useful since it removes some of the uncertainties caused by rate fluctuations. Analysis of the data shows a uniformly declining oil cut extending through the time of the project, with a period of reduced oil cuts below the prevailing trend. These data indicate that there was no improvement in oil recovery and, perhaps, even a loss of some oil production. Improved oil recovery would be indicated by an increased oil cut.

It has been speculated that the alkaline process may have been effective in improving sweep efficiency. The period of reduced oil cuts suggests that the sweep efficiency was not improved. Improved sweep efficiency would be indicated by an increased oil cut. However, there is evidence that the alkaline fluids reduced the circulation of water through some of the more permeable channels. Table 18 shows the wells which experienced reduced water production. With one exception, there is evidence that the injected alkaline fluids changed the chemistry of the produced fluid. The table shows that both the oil and water production were reduced, with the water reduced to a greater degree. The composite WOR was reduced at the affected wells, suggesting that the alkaline fluids were reducing flow. Much of the reduced flow at the producers was observed before actual breakthrough of chemicals. Thus, it appears that the alkaline fluids were reducing water circulation within the interwell area.

Figures 13 through 16 show the performance history for the Northern and Southern areas. These curves show trends similar to Block 9. Oil producing rates and oil cuts show a declining trend. However, we believe that the evaluation is less certain in those areas since the producers are affected in only one direction by injection wells. A pre-project baseline performance is also less certain in these areas, due to periodic workovers and the drilling of additional wells.

LABORATORY PROGRAM

For purposes of review, the laboratory work was separated into four subject areas. These areas are routine core analysis, special core analysis, core flood testing, and miscellaneous laboratory testing, including oil-water interfacial tension measurements. Each of these subjects is discussed below.

Routine Core Analysis

Ranger Zone core material was obtained from Wells B-827 and B-110-IA. The cores were retrieved in plastic sleeve core barrels and were frozen.

The cores were obtained using a polymer based mud as the drilling fluid. Core plug samples used in laboratory tests were obtained from these preserved cores.

Routine core analysis included measurement of air permeability, helium porosity, grain density, oil saturation, and water saturation. These data are presented in Table 3. The results of routine core analysis appear to be consistent with the unconsolidated nature of the reservoir sand. Liquid saturation measurements indicate a significant quantity of residual oil is still present in the Ranger Zone core material. The oil saturation values reflect the high oil saturation within the Ranger Zone even after waterflooding.

Special Core Analysis

A large number of special core analysis tests were performed for this project. The majority of these tests are waterflood susceptibility and unsteady-state water-oil relative permeability tests. Other tests include cation exchange capacity measurements (for log analysis purposes) and electrical resistivity measurements.

Results of the waterflood susceptibility tests are provided in Table 4. The details of laboratory procedures used to obtain waterflood susceptibility tests results were not provided. The percent of oil-in-place after waterflood susceptibility tests ranged from 38.8 to 68.1 percent and averaged 49.4 percent. This indicates an average displacement efficiency of oil by the water phase.

Unsteady-state water-oil relative permeability data were obtained for a large number of core plug samples. After waterflooding, each of these core plug samples were resaturated and flooded again with an alkaline solution. Relative permeability data were obtained during both tests. Only complete data for test numbers 39A through 62B were found in the annual reports. These data are provided in Table 7. The unsteady-state relative permeability tests were performed at a constant flow rate of one foot per day. Under these test conditions (unconsolidated high

permeability sand saturated with viscous oil), such a low flow rate often yields unreliable results due to potential gravity segregation. Higher rates may have improved the relative permeability data. However, it was appropriate to conduct the alkaline fluid tests at the low rate to more realistically represent the performance in the reservoir. As discussed in the appendix, low IFT processes are strongly influenced by rate.

After waterflooding, an endpoint or final relative permeability measurement (to water) was obtained. A comparison of the waterflood and the alkaline flood tests indicates the waterflood tests consistently have higher endpoint relative permeabilities to water than the alkaline flood tests. In addition, the oil saturation is generally lower in the alkaline flood tests. This is opposite to what would be expected. This flow behavior suggests that the alkaline fluids may be dispersing fines or reacting with the rock to produce materials which plug the pore throats. A change of rock wettability may also be occurring.¹⁵

Cation exchange capacity (CEC) measurements and electrical resistivity tests were performed on Ranger Zone core material for log analysis purposes. Cation exchange capacity measurements are presented in Table 5 and average 4.8 milliequivalents per 100 grams of reservoir rock. Since clay minerals are the main contributors to cation exchange capacity, the CEC values may be used as an indicator of the presence of clay minerals. The wide range of CEC values suggest a variable amount of clay minerals exist within the Ranger Zone. This is consistent with the geological descriptions provided within the annual reports submitted to the DOE. A further discussion of the cation exchange capacity measurements is provided in Appendix I.

The CEC measurements presented were obtained for log analysis. However, cation exchange is known to play an important role in the success or failure of chemical flooding. We believe that tests should have been performed to investigate the relationship between cation exchange and the alkaline flooding process as it applies to the Wilmington Field.

Alkaline Waterflood Tests

In order to investigate the alkaline waterflood process at the Wilmington Field, a substantial number of alkaline flood tests were performed. These tests were performed primarily by an independent testing laboratory, Petroleum Testing Services. Some additional laboratory tests were performed by California State University at Long Beach, by Dr. Van T. Lieu.⁹

The results of 62 alkaline flood tests are presented in Table 6. The test conditions such as alkali concentration, slug size, and preflush size were varied to maximize oil recovery. In laboratory core flood tests, the entrapment process did not recover a significant amount of additional incremental oil. The entrapment process should work in field applications if the process reduces permeability in the contacted areas. It is difficult to evaluate the entrapment process for sweep improvement in these tests in the laboratory since oil recovery response is normally not expected in linear systems. Therefore, the tests performed to evaluate the entrapment process in the Ranger Zone were inconclusive.

The entrainment process for recovering oil by caustic flooding appeared very promising from the data obtained in the laboratory. Due to the erratic results, however, conclusions concerning other test variables could not be made. The erratic core flood test results are attributed to inconsistent testing methods. Each core sample used in these tests possessed different mineralogy and rock characteristics. During laboratory testing, ten different crude oil samples with different crude oil acid numbers and different crude oil viscosities were utilized. The Wilmington crude oils are known to be highly variable in their

properties depending particularly on the depth. These problems may have been avoided by using composite sand for preliminary testing with sand packs and by using a representative crude oil. If a representative crude oil did not exist, then a composite oil sample may have been used.

During some of the alkaline waterflood tests (tests 39B through 62B), the concentration of selected ions and pH of the core effluent was measured. These data provide insight into the chemical reactions that occur during alkaline flooding. A review of test number 39B indicates that, during the test, the concentrations of potassium, sulfate, aluminum, silica, and carbonate increase as the alkali concentration and pH increase. The concentrations of magnesium, calcium, and bicarbonate are reduced to very low levels. The potassium, aluminum, and carbonate ions do not occur naturally in the formation brine at any appreciable level. Their presence suggests that, due to fluid-rock interactions, minerals exposed to the alkali may have been partially dissolved. This results in the release of these ions and the release of silica which is also seen in the effluent. This dissolution process results in a loss of alkalinity and the deterioration of the alkaline fluid.

A summary of alkali consumption measurements performed during flow tests is presented in Table 8. In addition to these flow tests, static equilibrium (jar) tests were performed using alkali and Ranger Zone core material. Results of these tests indicate that alkali consumption is dependent upon initial alkali concentration and the extent of alkali-rock contact time. The duration of these tests was limited to 36 days of contact time. During an actual alkaline flood in the field, the contact time would be much longer and, therefore, the alkali consumption values (Table 8) are lower than the consumption to be expected in the field. Alkali consumption measured during these tests varied from 8.6 milliequivalents of alkali per 100 grams to 16.9 milliequivalents of alkali per 100 grams of rock for a duration of 36 days. These values are equivalent to a consumption of approximately 14.7 pounds to 29.0 pounds of alkali per barrel of pore volume. The consumption values assume that sodium orthosilicate is the alkali and the reservoir rock

has a grain density of 2.66 grams per cubic centimeters and 25.0 percent porosity. The consumption values indicate a high loss of alkalinity during alkaline flooding of the Ranger Zone sand.

The high loss values observed during alkaline flooding of the Ranger Zone sand can be attributed to the mineralogy of the core material used for these tests. An earlier discussion of chemical reactions that occur during alkaline flooding suggested that rock dissolution may be occurring during the core flood tests. This is indicated by the appearance of potassium, aluminum, and carbonate in the effluent of the core flood tests. Further evidence of unfavorable reactions of alkali with Ranger Zone core material was provided by Lieu.⁹ His data indicate the presence of 1.0 percent sulfate and 0.5 percent carbonate in the core material. The presence of these anions strongly suggests the presence of calcium sulfate and carbonate minerals which would have an adverse effect on an alkaline flood utilizing sodium hydroxide or sodium orthosilicate. When rock dissolution, alkali reaction with calcium sulfate, and cation exchange are occurring simultaneously, the loss of alkalinity may be quite high. The laboratory data indicate these processes are occurring and that alkali loss is, in fact, high.

Miscellaneous Laboratory Testing

Several miscellaneous laboratory tests were performed to support this alkaline waterflood project. These tests include the measurement of oil to water interfacial tension, oil-to-water dehydration testing, and analysis of produced fluids and are described below.

To determine the interfacial tension (IFT) between the oil and water phases during an alkaline waterflood, measurements of IFT by the pendant drop and the spinning drop methods were performed. Initially, the IFT between crude oil and sodium hydroxide in distilled water was measured by the pendant drop method. IFT's are known to vary depending upon the time. All measurements were made after five minutes of spinning to provide a standard for comparison of results. The results indicated

that the addition of sodium hydroxide to distilled water could significantly reduce the oil to water IFT over a wide range of sodium hydroxide concentrations. During these tests, the IFT was found to decrease below a level of 0.001 dynes per centimeter. Additional tests were performed using the spinning drop method to determine the IFT between produced crude oil and produced brine. Sodium hydroxide and sodium orthosilicate were added to the produced brine to reduce the IFT. Results of these tests are shown in Figures 20 through 23.

The measurements obtained with produced brine indicate the lowest values of IFT were obtained with sodium orthosilicate. The lowest interfacial tension values were near 0.01 dynes per centimeter at the designed level of alkali concentration. As the alkali concentration decreased, the IFT values increased sharply to levels in excess of 1.0 dyne per centimeter. These data suggest that, even with optimum alkali concentration, the low values of IFT needed to mobilize oil may not be obtained during the alkaline flood. It is anticipated that alkali consumption and dilution will decrease concentrations into a range where IFT's are relatively high. The result is poorer than anticipated recovery.

Dehydration tests were performed to determine if emulsions produced during alkaline flooding with sodium hydroxide could be treated effectively to remove the water. Results of these tests indicate that addition of commercially available demulsifiers would eliminate the emulsion problems. A flocculation was observed during testing which appeared to be precipitated calcium, magnesium, and iron hydroxide or carbonates. The presence of these compounds is typical when sodium hydroxide is added to oil field brines. Laboratory filtration tests indicated the flocculations could be removed by addition of a surface active polymer followed by filtration. The emulsions formed by addition of sodium orthosilicate were not investigated and it is unclear if the same chemical treatments would be as effective with sodium orthosilicate as they were with sodium hydroxide in breaking emulsions and removing flocculation.

A series of water analyses was performed during the alkaline waterflood project. These water analyses aid in monitoring the progress of the alkaline flood and assist in the evaluation of preflush efficiency and alkaline loss. The results of this series of analyses for three producing wells are shown in Figures 17 through 19. The information provided by these analyses includes salinity, silica concentration, water hardness levels, and the pH. Generally, the data is provided from 1979 through 1985. These analyses provide some useful information. However, for the purpose of evaluating the progress of an alkaline flood, the analyses are incomplete. Emphasis should be placed on the source of the alkalinity of the produced fluids by determination of carbonate and bicarbonate concentrations, total alkalinity, and pH. An elevated pH may be due to the presence of the alkaline slug or it may be due to the presence of chemical compounds produced when the alkaline slug reacts with reservoir brine and rock (i.e., calcium hydroxide, calcium carbonate). Therefore, an increase in the pH of produced fluids does not necessarily indicate a successful propagation of the alkaline slug. A periodic analysis specifically for magnesium, calcium, sulfate, potassium, and aluminum would also be useful in monitoring the extent of alkali consumption during this project.

PREFLUSH DESIGN

The preflush plays an important role in the performance of an alkaline project. The preflush was to perform the following functions for the Wilmington project:

1. Displace the excessive hardness associated with the formation brine and reservoir rock. The formation water contains around 670 ppm of divalent cations (Ca^{++} and Mg^{++}). Much of the injected alkaline fluids would be lost due to precipitation. For example, the contact of sodium hydroxide with the formation water would lead to the precipitation of insoluble calcium hydroxide, calcium carbonate, and other insoluble compounds. Contact of orthosilicate

with the formation water would lead to the formation of insoluble magnesium silicate, calcium carbonate, and other insoluble compounds.

The preflush is also needed to remove the multivalent cations which are associated with the clay minerals in the formation. Without such removal, the injected alkaline fluids will react with the associated multivalent cations to form insoluble compounds. These reactions reduce the amount of alkaline fluids available for displacing oil.

2. Establish a salinity level that permits efficient displacement of oil by the following alkaline fluids. Oil recovery is maximized in surfactant and alkaline processes where the salinity of the in-place water is within a particular range of concentrations. For Wilmington, the preflush contained about 12,000 ppm total dissolved solids, achieved by adding 1 percent sodium chloride to a softened fresh water.
3. Prevent the formation of scale, by eliminating or reducing the contact of divalent ions with the injected alkaline fluids. As previously discussed, major scale problems were encountered with calcium carbonate, magnesium silicate, and amorphous silica.

Overall, the softened water preflush was not effective in achieving the objectives. The following are some of the indications:

1. The hardness of produced waters remained high even after large volumes of softened water injection. Typically, hardness (Ca^{++} and Mg^{++}) concentrations in the range of 200 to 300 ppm existed during the later stages of the project. It is recognized that the concentrations as measured in the producing well reflect the flow from various sub-layers within the Ranger Zone. Thus, it is likely that hardness concentrations were lower in the more permeable zones

where greater softened water injection had occurred. Regardless, the high hardness levels, coupled with a lack of oil response, suggests that the preflush was not effective in removing hardness.

Figures 24 and 25 show the results of produced water tests conducted on wells where a defined pH increase occurred. The increased pH suggests the arrival of the orthosilicate at the well. As shown, the rise in pH is accompanied by a large reduction in the hardness of produced waters to a range of 100 to 200 ppm. These reductions suggest that the calcium and magnesium ions are reacting with the injected alkaline fluids and reducing their concentrations in the produced fluids.

2. Scale problems were severe in a number of the producing wells. Scale formation would have been less severe if the preflush had been effective in reducing hardness of the connate water. As above, some scale problems would have occurred even if the preflush had been effective due to the mixing of high hardness fluids from unswept zones with the produced carbonates and silicates.

The total salinity of produced fluids was generally in the range of 12,000 ppm, which is at a level required for efficient recovery.

A question to be addressed is how the preflush design could have been improved. As earlier indicated, the preflush consisted of injecting 11,500,000 barrels (10.2 percent PV) of a softened fresh water with 1.0 percent added salt.

We doubt that the preflush could have been improved, when considering both the technical and economic factors. This conclusion is based upon a recent study in which a statistical analysis was made of the critical factors affecting the performance of micellar-polymer projects.¹⁹ The strongest conclusion from that study was that preflushing is generally ineffective in removing hardness from the reservoir, even if large volumes of a softened and/or less saline water had been used in prior

waterflooding. It is judged that hardness is more critical in alkaline flooding than in micellar-polymer flooding. The failure of preflushes can be due to several reasons: (1) insufficient volume; (2) crossflow of higher salinity, higher hardness waters from unswept zones to swept zones; (3) release of higher salinity, higher hardness formation water which may have been previously shielded by oil (as in oil wet reservoirs); (4) incomplete release of multivalent cations from clay mineral surfaces; and (5) presence of gypsum or anhydrite which continuously release calcium ions regardless of the volume of preflush.

Preflushing can be improved by methods which accelerate the transfer of multivalent ions from clay minerals into the injected waters or neutralize the effects of the ions in some other way. Such methods include: (1) the use of a high-concentration sodium chloride slug followed by the design-level concentration; (2) sequestering agents such as sodium tri-polyphosphate; and (3) low-cost agents to precipitate the multivalent ions. Although such methods might improve performance, we doubt that they could be economically justified.

The existence of gypsum in the Ranger Zone may have been a major contributor toward the release of calcium into the alkaline fluids. As earlier discussed, preflushing with a softened water is ineffective if gypsum is present, since calcium is continuously released. The continual feed of calcium into the water would have contributed toward the loss of orthosilicate through precipitation.

The preferred approach toward improving the process efficiency is through improved tolerance of the chemicals for hardness. These ideas will be discussed in a later section.

CHEMICAL SLUG DESIGN

This section discusses the basis for the design of the chemical system for the project. Much of the basic data for the design were based upon

laboratory tests, which are discussed separately. Laboratory tests determined that sodium orthosilicate was preferred to sodium hydroxide because of better oil recovery, greater resistance to hardness, and lower interfacial tension.

Chemical Selection

The choice of orthosilicate appears justified upon the basis of laboratory tests. It was recognized that this choice could lead to problems with magnesium silicate scale. It was not realized, however, the degree to which the scaling problems would occur. It was assumed that the fresh water preflush would remove much of the hardness and thereby minimize scale problems.

Quantity of Chemicals

Laboratory tests provide the major source of data needed to design the quantity of orthosilicate to be injected. Early tests were promising because of the relatively low losses that were observed. However, as additional data became available, it was observed that the losses were a function of the residence time. Losses increased with longer residence time. Losses in the reservoir, given years of residence time, could be extremely high. Even after a residence time of 36 days in laboratory tests (refer to Table 8), losses of orthosilicate were at a high level of 16.9 meq/100 gm of rock. This corresponds to a computed loss of about 28.6 pounds/barrel of pore space when converted to practical terms. When scaled to the project pattern, the injected quantity of orthosilicate (65,000,000 pounds) was computed to be adsorbed with 0.2 percent of the pore volume. The conclusion is that the alkaline slug would penetrate very little of the reservoir and oil recovery would be poor.

Simulation studies using a kinetically controlled adsorption loss showed a similar conclusion that the recovery from alkaline injection would be about the same as for waterflooding (refer to Figure 9).

The key question is whether the project should have been initiated in view of the excessive losses that were being observed in the laboratory and the predictions indicating poor recovery. On hindsight, the project probably should not have been initiated. However, many of the basic studies with alkaline fluids were just becoming available at the time. On balance, the decision to proceed at that point in time was reasonable even though there was a significant risk of failure.

The concentration of the injected orthosilicate (0.4 weight percent) appears reasonable based upon the laboratory tests and the results of numerical simulation studies. As shown in Figures 20 and 22, the interfacial tension (IFT) of 0.4 weight percent solutions appeared to be near the minimum range. Solutions still exhibit low IFT even when considerably diluted (up to the 0.05 to 0.07 weight percent range), as would be the case in a reservoir application. The data as shown in Figures 20 and 22 are for softened water. As shown in Figures 21 and 23, the level of IFT is higher with produced water and occurs over a narrower range. Thus, the alkaline fluids would lose their ability to displace oil efficiently if the preflush fluid does not adequately displace the in-place water. As earlier discussed, the preflush did not adequately displace the in-place water. Thus, it is likely that the alkaline fluids had little ability to displace oil because of mixing with the connate waters.

Mobility Control

The alkaline fluids as injected had a significantly higher mobility than the combined mobility of oil and water which flows ahead of the alkaline slug. The unfavorable mobility between the driven and driving phases is due, in part, to the viscous nature of the Wilmington crude oil (23 cp average). The result is a tendency of the alkaline fluids to finger through the oil-water bank, with the consequence of lower oil recovery. The mobility specifications were computed based upon the relative permeability curve as shown in Figure 26. These computations indicate

that the alkaline fluids would need to have a viscosity of about 11 cp to match the mobility of the oil-water bank. Polymers could be added to achieve this viscosity level, requiring a resistance factor in the range of 20.

The addition of polymers to the alkaline fluids would likely have improved the performance both from the standpoint of improved mobility and improved displacement (as discussed in the appendix). Some oil response may have been realized, which would have been largely due to the polymer. Although the polymer would have improved performance, there is still the question of the incremental benefits versus the added cost. Also, the presence of divalent ions would have a detrimental effect on the polymer. In general, polymers should be added to alkaline fluids to achieve mobility. It is judged, however, that caustic consumption dominated the process for Wilmington and that polymer addition would not have been sufficient to compensate for that problem.

ANALYSIS OF PRODUCED FLUIDS

The fluids from the producing wells were periodically analyzed to monitor the progress of the project. Typically, the testing included analysis for pH, hardness, silica, and salinity content. Figures 17, 18, 19, 24, and 25 illustrate the types of the data collected for individual wells. The following are some observations and conclusions based upon these analyses.

pH

The pH was observed to increase in Wells B-101-A, B-112, B-410, B-711, B-712, B-830, and B-838. Figures 25, 24, 19 show the responses at Wells B-112, B-711, and B-712, respectively. An increase in the pH may indicate the arrival of the alkaline fluids or the presence of chemical compounds produced by the reaction of the alkaline slug with reservoir

rock and brine. Thus, an increase of pH at a well does not necessarily indicate the arrival of alkaline fluids. However, the lack of any change in the pH indicates that alkaline fluids have not arrived at that well.

Most of the wells experiencing an increase of the pH are located in the first row of producers from the injectors. There was little evidence of breakthrough of alkaline fluids in the second row of producers or anywhere within the northern pattern.

Well B-838 experienced considerable difficulty with scaling problems. This well produced for 25 days after an acid/scale inhibitor treatment had been performed, after which the breakthrough of a high-pH fluid occurred and the pump failed. The breakthrough of the high-pH fluids was attributed to the failure of a cement job in an offset injector and the subsequent channeling of the injected fluids through sands other than the Ranger Zone. The pump was pulled and observed to contain a considerable amount of semi-solid material. The analysis of the solid is shown in Table 19. Wet chemical analysis indicated the existence of iron oxide/iron sulfide, calcium carbonate, barium sulfate, and silica. An analysis of elements indicated a predominance of silica, aluminum, potassium, calcium, magnesium, iron, and sodium. These elements appear to be the reaction products of alkaline fluids and the reservoir rock.

A similar problem occurred in Well B-101-A. This well produced for 29 days after an acid/scale inhibitor squeeze treatment, at which point the pump failed. Shortly before pump failure, the well had experienced a sharp increase in the pH of the produced water. A small acid job failed to free the pump. When pulled, the pump was plugged with a solid, brownish material. A wet chemical analysis indicated a predominance of oil, iron salts, and silica. Further analyses were made, confirming an abundance of silica. The following was a typical analysis:

<u>Chemical Compound</u>	<u>Concentration</u>
SiO ₂	91.6 percent
MgO	3.8 percent
CaO	1.7 percent
Fe ₃ O ₄	2.7 percent
Na ₂ O	3.3 percent
K ₂ O	0.066 percent
Al ₂ O ₃	0.21 percent

The large amount of silica is thought to be a reaction product of the alkaline fluids with the formation. Laboratory tests have verified that soluble silicate (SiO₂) can be produced by reaction of alkaline fluids with clay minerals. In particular, the presence of aluminum in the sample is an indication that the alkaline fluids were reacting with the clays.

The observed pH increases indicate that the injected alkaline fluids were influencing reservoir flow behavior to the first row of producers. It is not clear if the pH increases were due to the breakthrough of alkaline fluids or to the reaction products of alkaline fluids with the rock. As discussed in the laboratory section, the periodic measurement of total alkalinity would have been helpful in defining the mechanism for the pH increase. Even with the uncertainty on the interpretation of the pH measurements, it appears that the influence of the alkaline fluids did not extend beyond the first row of wells. This would indicate a high degree of alkali consumption.

Hardness

As earlier noted, the hardness of the produced waters remained high even after large volumes of softened water injection. Typically, hardness levels remained in the 200 to 300 ppm range, even during the latter stages of the project. The formation water contained a hardness level

of about 670 ppm. Thus, the process as designed was not effective in reducing the hardness level to an acceptable level. The high levels of hardness can be attributed to some combination of the following factors:

- (1) failure of the softened water preflush in removing the hardness;
- (2) release of hardness from the clay minerals due to ion exchange;
- (3) dissolution of water-soluble minerals such as anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and epsomite ($\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$). It is suspected that all three of these factors have played a role. The reservoir is known to contain a significant amount of clays which could result in a high cation exchange capacity. The reservoir is also known to contain gypsum⁹ which could result in a continuous release of calcium ions with continued throughput. The presence of gypsum is especially detrimental since the calcium cannot be removed by preflushing.

Regardless of the sources of hardness, the injected alkaline fluids cannot perform their function in displacing additional oil in the presence of the multivalent ions. The orthosilicate will react with such waters to form insoluble magnesium silicate, calcium carbonate, and other insoluble compounds.

We believe that additional analyses should have been performed on waters produced from the individual wells. In addition to measurements for pH, hardness, total salinity, and silica content, analyses should have been made for sulfate, potassium, and aluminum. Such measurements would have provided additional information on rock-alkali reactions and dissolution of gypsum and/or anhydrite. Although such analyses would have helped to explain the mechanisms, no actions could have been taken at that point to improve oil recovery.

Salinity

The total salinity of produced fluids was routinely measured. The total salinity of produced fluids was generally in the range of 12,000 ppm. This is about the level which had been determined as optimum. Thus, the total salinity levels are not thought to have adversely affected performance.

Silica

The silica content of produced waters was routinely measured on produced fluid samples. Many of the analyses indicated a background level of silica, even before breakthrough of any alkaline fluids could have been expected. It is presumed that the background level is due to the production of colloidal-sized clay mineral particles.

Well B-712 is an example of a well where a sharp increase in silica occurred, as shown in Figure 19. This increase was accompanied by an increase in pH and a decrease in hardness. As earlier discussed, plugging also occurred in this well. Magnesium silicate was determined to be the major cause for plugging in the well. Similar problems occurred in other wells. The increased silica content in this well appears to be the breakthrough of the injected orthosilicate into the well. It points out the need for achieving a low hardness condition, so that damaging scale deposits can be avoided.

In general, the low level of silica observed in the produced wells indicates that much of the orthosilicate had been consumed within the reservoir. As previously discussed, the evidence is strong that the orthosilicate was being consumed by reactions with the clays in the formation.

No conclusions can be drawn on the amount of the orthosilicate which might have been consumed by reaction with the quartz sand. Such reactions are expected to occur slowly, but could be highly significant given years of residence time. The work of Southwick¹⁴ suggests that an equilibrium is eventually established. He further suggests that alkali-quartz reactions can be minimized by injecting an alkaline solution which has been formulated to be in equilibrium with quartz.

SIMULATION STUDIES

Figure 27 shows the comparison of the computed and actual performance for the project. As shown, the actual performance was much less than had been predicted. The figure shows the simulation for Case II, which used a minimum-threshold relative permeability adjustment. It also contained a kinetically-controlled consumption function, which accounts for the long-term loss of alkaline fluids as they move through the reservoir. The Case II predictions tracked very closely the performance that had been predicted for waterflooding.

The significant differences between actual and computed performance is attributed to the wellbore plugging problems. The severity of these problems was not anticipated.

The simulation studies were well conceived and conducted. It was necessary to make significant adjustments in the model to simplify the many complexities of the process. These adjustments were reasonable. The simulation studies also incorporated the key parameters observed in laboratory tests, particularly the consumption tests. In particular, the inclusion of a kinetically-controlled consumption loss was important to match the observations that were being determined from laboratory tests.

CONCLUSIONS

The major purposes of this report are to independently evaluate the performance of the project and to determine how the project could have been improved. The following are some of the major conclusions from this study.

1. The performance of the project was poor. There was no increase of oil recovery compared to waterflooding. However, water production was decreased in some wells.
2. The key factors for the lower than expected oil recovery were attributed to:
 - a. High consumption, as indicated by only limited breakthrough of alkaline fluids and/or reaction products at the first row of producers. The high consumption appears to be due in part to the mixing and precipitation of alkaline fluids with high hardness waters and to the dissolution of reservoir minerals by the alkaline fluids. A significant amount of calcium may have been continuously released into the injected fluids by the existence of gypsum in the rock.
 - b. Wellbore plugging problems. Oil production was greatly curtailed by the formation of scales and precipitates in producing wells. Calcium carbonate scales could be successfully treated, but no long-term treatments were successful for the control of magnesium silicate scale or for silicate-containing precipitates.
3. Overall, the project was well developed and executed. It is doubtful that performance could have been significantly improved with the basic chemical systems used in the project. On hindsight, we question whether the project should have been implemented in view of the excessive losses observed in laboratory tests and the predictions indicating marginal recovery.

4. Several changes in the project may have resulted in improved performance. However, these are considered to be secondary when compared to the more dominant effects created by alkali consumption. These are:
 - a. Improved Preflush Design. The preflush was ineffective in removing hardness, as evidenced by the high concentrations of calcium and magnesium in the waters from producing wells. The preflush could potentially be improved by (1) using a larger volume, (2) inclusion of a brine more effective in releasing hardness from the clays (e.g., high concentration of sodium chloride), (3) use of a brine to precipitate divalent ions (e.g., sodium carbonate), and (4) use of sequestering agents (e.g., EDTA). The relative benefits and costs should be evaluated when considering any of these methods.
 - b. Addition of Polymers. The mobility of the alkaline fluid bank was higher than the leading oil-water bank. The tendency is for reduced sweep and poorer oil recovery. The addition of polymers would have improved recovery by improving sweep.
5. Interpretation of the project could have been improved by additional analyses on the produced waters from the field. These analyses would help in determining the extent to which the process is being affected by alkali-rock reactions and by the release of calcium ions through solubilization of gypsum or anhydrite.

RECOMMENDATIONS FOR RESEARCH

The performance of the Wilmington and other projects creates some real concerns about the viability of the alkaline flooding process. The process has the inherent advantage of being low in cost. Thus, the process can be potentially attractive even if the incremental oil recovery is low. The inherent disadvantage is the extreme sensitivity of the process to hardness in the formation waters and in the reservoir. This problem is especially severe where the hardness in the native formation water is high or where the reservoir contains a significant amount of clay minerals or even minor amounts of gypsum or anhydrite. It is doubtful that preflushing can ever be a practical, wide-scale practice for removing hardness.

We believe that the emphasis in research should be in improving the hardness tolerance of the chemicals. Previous investigations have evaluated the use of co-surfactants and additional synthetic surfactants for improving hardness tolerance. Polymer addition can further help by providing better mobility control. Such studies are useful and should be pursued. However, the costs versus the benefits should be continually assessed. The costs for these "improved systems" can potentially approach those for micellar-type formulations. Where this may be occurring, the more fruitful approach could be in the evaluation of the new-generation, high hardness synthetic surfactants as an alternative chemical system.

TABLE 1

RESERVOIR PARAMETERS
ALKALINE PILOT AREA*

Type of Reservoir Rock	Interbedded unconsolidated to semi-consolidated shaly sand
Average Porosity	See Table 2
Average Oil Gravity	See Table 2
Average Gross Zone Thickness	305 Feet
Average Net Sand Thickness	See Table 2
Bottom Hole Temperature	125°F
Initial Average Water Saturation	See Table 2
Average Oil Viscosity at Reservoir Conditions	23 cp
Average Solution Gas-Oil Ratio	160 cu ft/bbl
Average Formation Volume Factor	1.10 bbl/bbl
Oil-in-Place (Layer Composite)	1,260 bbl/acre-foot

<u>Floodable Reservoir Volumes</u>	<u>Pattern Area</u>	<u>Northern Area</u>	<u>Southern Area</u>
Area - Acres	93	59	41
Volume - Acre-Feet	26,900	15,800	12,500
Tank Oil-in-Place - M/bbl	33,900	19,900	15,700

* Based on 1,600 psi confining pressure core analysis and quantitative log analysis data obtained in special coring and logging programs, Task 13.

TABLE 2

LAYER PROPERTIES
ALKALINE PILOT AREA

<u>Subzone</u>	<u>Average Net Thickness, Feet</u>	<u>Porosity, Fraction*</u>	<u>Air Permeability, md*</u>	<u>Initial Water Saturation, Fraction</u>	<u>Oil Gravity, °API</u>	<u>Oil-In-Place at Center of Pattern</u>
Fo ₁	40	0.260	314	0.270	15-18	0.1347
Fo ₂	45	0.254	298	0.278	15-18	0.1464
Fo ₃	24	0.270	194	0.318	15-18	0.0784
F	52	0.274	321	0.270	15-18	0.1845
H	41	0.246	179	0.325	16-23	0.1208
X	48	0.265	173	0.328	18-26	0.1517
G	29	0.289	220	0.302	18-26	0.1038
G4	26	0.270	131	0.360	20-28	0.0797

* Based on 1,600 psi confining pressure core analysis data obtained in special coring and logging programs, Task 13.

TABLE 3

SUMMARY OF ROUTINE CORE ANALYSIS TESTS
 ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE, LONG BEACH UNIT
 WILMINGTON FIELD, CALIFORNIA

Depth, Feet	Air Permeability, md		Helium Porosity, Percent		Grain Density, gram/cc	Liquid Saturation, Percent Of Original Helium Pore Volume	
	Original psi	Confining Pressure 350 psi	Original psi	Confining Pressure 350 psi		Oil	Water
Well B-827 No. 1, ERDA							
4,062'6"	271		32.5		2.67	25.1	48.4
4,064'9"	169		35.9		2.67	32.7	52.4
4,067'7"	723		44.6		2.63	10.1	81.6
4,073'1"	232		32.7		2.72	14.3	83.5
4,075'11"	67		27.7		2.65	32.5	53.1
4,091'9"	1,150		46.6		2.60	16.0	75.5
4,099'6"	412		37.5		2.72	38.4	59.5
4,102'9"	178		31.2		2.71	20.5	69.0
4,105'11"	935		37.1		2.68	29.2	58.1
4,121'1"					2.65	54.4	37.5
Well B-827 No. 1, RD No. 1, ERDA							
4,098'11"	110		33.3	31.6	2.63	0	98.6
4,104'11"	13	840	29.6		2.62	0	97.4
4,132'11"	893		34.2		2.67	33.9	59.1
4,135'11"	1,100		38.0		2.67	33.3	56.0
4,138'11"	1,280		35.5		2.68	37.4	48.5
4,141'11"	1,000		33.6		2.68	35.8	44.6
4,144'10"	1,190		37.2		2.68	34.9	48.8
4,160'11"	1,560		36.3		2.69	52.3	36.2
4,163'11"	1,610		34.4		2.69	23.0	44.4
4,165'11"	1,390		33.2		2.68	37.0	43.4
4,171'11"	1,410		32.0		2.67	35.3	46.3
4,174'11"	1,720		24.3		2.67	47.9	47.9
4,177'11"	1,700		25.7		2.66	34.5	54.1
4,180'11"	2,780		32.1		2.66	32.8	48.7
4,183'11"	2,500		33.2		2.66	33.3	45.6
4,186'11"	832		31.2		2.66	35.8	49.6
4,188'11"	717		34.2		2.66	33.4	48.4
4,189'5"	75		27.0		2.69	40.2	78.8
4,192'5"	1,530		33.5		2.66	13.3	50.9
4,195'5"	1,460		32.1		2.67	36.3	49.0
4,198'5"	1,380		33.2		2.67	35.2	43.1
4,204'5"	1,050		32.1	31.8	2.67	43.4	28.8
4,207'5"	727		33.2		2.68	27.8	54.9
4,210'5"	1,510		19.6		2.66	33.9	44.2
4,213'5"	2,660		31.8		2.68	27.7	42.6
4,220'1"	1,040		39.8		2.67	32.0	57.1
4,222'11"	311		41.7		2.64	26.6	56.6
4,226'11"	422		32.5		2.67	29.3	37.5
4,228'10"	1.4		28.8		2.64	0	98.3

TABLE 3 - CONTINUED

SUMMARY OF ROUTINE CORE ANALYSIS TESTS- CONTINUED

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE, LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

Depth, Feet	Air Permeability, md		Helium Porosity, Percent		Grain Density, gram/cc	Liquid Saturation, Percent Of Original	
	Original psi	350 psi	Original psi	1,600 psi		Oil	Water
4,239'7"	952	870	34.7	32.3	2.67	38.0	49.4
4,242'5"	246		35.1		2.68	40.0	51.5
4,245'4"	954		31.0		2.65	31.2	51.0
4,259'2"	514		38.3		2.65	41.7	49.8
4,266'5"	269		39.0		2.68	35.1	46.0
4,269'2"	744		38.5		2.67	37.2	54.4
4,271'7"	8.0		29.3		2.65	0.8	95.0
4,274'3"	38.0		29.8		2.60	8.2	87.9
4,277'2"	12.		29.8		2.68	4.3	92.3
4,284'0"	12.	10	31.7	31.3	-	-1.3	91.5
4,287'11"	25		31.5		2.65	16.3	78.3
4,290'10"	420		40.1		2.68	41.1	51.5
4,293'10"	357		33.4		2.66	38.6	49.8
4,297'2"	18		30.2		-	-22.4	63.7
4,300'4"	365		35.8		2.69	40.3	40.0
4,303'5"	830		32.8		2.67	38.4	42.3
4,356'10"	6.8		31.5		2.65	0.8	97.0
4,361'11"	478		37.9		2.66	40.5	48.7
4,364'10"	172		32.9		2.64	18.7	69.6
4,367'10"	988		32.5		2.67	33.1	48.4
4,370'11"	772	682	32.9	30.8	2.66	29.3	55.0
4,372'10"	1,110		32.6		-	-1.3	82.2
4,375'9"	933		30.5		2.61	5.0	86.4
4,378'10"	895		30.5		2.65	2.2	83.1
4,438'3"	233		30.3		2.69	1.4	94.0
4,441'4"	0.7		29.1		-	8.5	84.7
4,444'8"	21		27.1		2.64	0	98.0
4,447'4"	11		32.2		2.65	0	98.7
4,450'4"	8.3		29.6		2.66	24.8	48.6
4,454'4"	27.6		27.6		2.66	26.9	49.0
4,457'10"	655		32.7		2.64	1.2	97.3
4,460'10"	2.4		28.6		2.73	31.9	50.9
4,463'10"	210		32.9		2.64	33.5	43.4
4,468'4"	974		31.5		2.64	29.4	46.0
4,471'4"	203	166	31.9	28.6	2.65	29.4	54.5
4,474'4"	749		33.3		2.67	42.6	32.2
4,477'4"	29		17.3		2.64	24.7	52.3
4,591'10"	283		28.2		-	-	-

Well B-827 No. 1, RD No. 1, ERDA-Continued

TABLE 3 - CONTINUED

SUMMARY OF ROUTINE CORE ANALYSIS TESTS- CONTINUED

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE, LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

Depth, Feet	Air Permeability, md		Helium Porosity, Percent		Grain Density, gram/cc	Liquid Saturation, Percent Of Original Helium Fore Volume	
	Original psi	350 psi Confining Pressure	Original psi	350 psi Confining Pressure		Oil	Water
Well B-827 No. 1, ERDA-Continued							
4,610'4"	420	300	33.8	28.1	2.65	29.8	43.5
4,616'3"	725	439	32.2	27.0	2.64	25.2	43.7
4,617'2"	446	299	30.6	26.2	2.65	22.4	37.1
4,621'4"	215	8.4	34.1	27.8	2.69	14.6	65.4
4,624'4"	458	206	34.1	28.0	2.69	12.4	80.2
4,627'1"	362	348	33.0	30.6	2.65	30.1	43.8
4,629'10"	296	110	37.6	30.6	2.65	30.5	52.1
4,654'2"	6.9	-	31.0	-	2.66	0	98.0
4,666'2"	3.2	-	29.5	-	2.63	3.7	94.5
4,670'10"	4.5	-	26.5	-	2.62	3.8	94.1
4,673'10"	124	84	37.0	26.7	2.63	24.4	37.4
4,679'20"	16	6.7	18.0	15.0	2.72	24.3	39.5
4,681'7"	29	1.4	30.1	24.1	2.68	2.8	96.0
4,684'4"	761	225	33.4	26.1	2.65	20.3	78.1
4,687'4"	1,520	457	44.0	32.2	2.67	14.6	83.1
4,690'4"	153	41	33.7	27.4	2.60	21.0	62.1
4,693'4"	237	86	34.8	28.5	2.64	22.6	71.5
4,767'1"	252	79	33.9	27.1	2.64	0	97.5
4,771'9"	8.9	-	30.7	-	2.62	0	92.8
4,774'5"	5.8	-	34.9	-	2.67	37.8	48.7
4,777'5"	555	400	36.7	30.3	2.66	27.0	54.2
4,780'5"	572	300	35.8	28.9	2.67	34.4	48.3
4,782'5"	512	350	34.5	27.5	2.66	31.6	42.6
4,785'5"	465	318	34.2	28.2	2.63	0	97.5
4,788'5"	7.2	-	32.9	-	2.65	12.3	73.5
4,791'5"	70	13	33.6	28.8	2.65	31.5	45.8
4,794'5"	425	146	36.9	29.3	2.65	28.7	54.8
4,796'10"	389	158	33.8	27.6	2.64	36.0	50.1
4,799'10"	767	143	34.3	28.2	2.72	0	92.8
4,802'10"	443	250	34.3	28.5	2.64	41.1	48.2
4,805'10"	0.1	-	3.9	-	2.64	17.0	74.1
4,844'5"	473	181	36.2	29.1	2.65	28.6	59.9
4,847'5"	151	41	32.4	26.8	2.66	28.9	58.6
4,850'5"	306	76	35.7	27.9	2.65	33.5	43.3
4,853'5"	544	339	38.0	25.1	2.69	20.6	62.1
4,856'5"	100	77	31.5	24.8	2.67	34.1	49.8
4,860'5"	2.3	-	16.3	-	2.65	36.0	46.9
4,863'5"	524	247	35.9	29.1	2.62	14.6	69.8
4,866'5"	615	319	36.4	29.5	2.66	0	98.0
4,869'5"	699	233	32.7	25.5	2.67	0	98.0
4,872'5"	56	21	35.8	29.4	2.65	0	98.0

TABLE 4

SUMMARY OF WATERFLOOD SUSCEPTIBILITY TEST DATA

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE
 LONG BEACH UNIT
 WILMINGTON FIELD, CALIFORNIA

Well Number	Sample Number and Depth, Feet	Porosity, Percent	Pore Volume, cc	Absolute Brine Permeability, md	Initial Conditions			Final Conditions			Oil Recovery	
					Saturation, Percent	Oil* Permeability, md	Oil Saturation, Percent	Water Permeability, md	Relative Permeability To Water, Percent	Percent	Oil-In-Place	
B-102	5,749	30.6	9.93	452	24.1	382	39.6	117	30.6	36.4	47.9	
B-102	6,279	28.9	9.24	94	23.8	313	39.4	80	25.6	36.8	48.3	
B-319	4,059-1	34.3	12.08	203	36.4	116	27.2	29	25.0	36.3	57.2	
B-319	4,190	35.6	11.74	845	13.0	300	53.2	109	36.3	33.7	38.8	
C-338	3,929	31.8	10.16	857	20.4	149	44.9	76	51.0	34.7	43.6	
C-338	4,260-1	28.6	8.27	452	29.2	147	22.6	48	32.6	48.2	68.1	
J-555	4,432-1	25.5	7.28	1,210	27.7	314	42.3	265	84.4	30.0	41.4	
J-555	4,722-1	28.8	7.38	1,320	27.7	212	36.3	83	39.2	36.0	49.8	
				Average	25.3		38.2				49.4	

* Base permeability used in calculating relative permeability.

TABLE 5

CATION EXCHANGE CAPACITY TEST RESULTS

THUMS LONG BEACH COMPANY
WELL B-827 NO. 1, R.D. NO. 1, ERDA
WILMINGTON FIELD
LOS ANGELES, CALIFORNIA

<u>Depth, Feet</u>	<u>Cation Exchange Capacity, Milliequivalents per 100 grams</u>
4,104'11"	11.5
4,183'11"	3.3
4,239'7"	3.7
4,293'10"	3.9
4,303'5"	3.2
4,463'10"	7.9
4,616'3"	3.6
4,684'4"	3.0
4,791'5"	5.7
4,860'5"	<u>2.6</u>
	Average 4.8

TABLE 6

SUMMARY OF LABORATORY CORE FLOOD TESTS
ALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE, LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

Test Number	Alkali	Alkali Concentration, Weight Percent		Alkali Salinity-Sodium Chloride Concentration, Weight Percent		Alkali Slug Size, Percent Pore Volume		Water-Oil Ratio at Start of Preflush		Oil Viscosity, Centipoise	Incremental Oil Recovery, Percent Pore Volume		Core Material, Source Well	Crude Oil Acrid Number
		Alkali	NaOH	Alkali	NaOH	Slug Size, Percent Pore Volume	Preflush Size, Percent Pore Volume	Ratio	Total		Incremental			
1*	NaOH	0.10	0.10	0	20.0	none	5	24	24	Not measured			B-827-A	Not measured
2*	NaOH	0.10	0.10	0	20.0	20.0	5	24	24	Not measured			B-827-A	Not measured
3	NaOH	0.10	0.10	0	20.0	20.0	5	24	24	Not measured		6.0	B-827-A	Not measured
4*	NaOH	0.10	0.10	0	20.0	20.0	5	24	24	Not measured			B-827-A	Not measured
5	NaOH	0.10	0.10	0	20.0	20.0	5	24	24	Not measured		-2.5	B-827-A	Not measured
6	NaOH	0.10	0.10	0	20.0	20.0	5	24	24	Not measured		1.5	B-827-A	Not measured
7	NaOH	0.10	0.10	1.0	Continuous	20.0	5	24	24	Not measured		2.0	B-827-A	Not measured
8	NaOH	0.10	0.10	1.0	Continuous	20.0	5	24	24	Not measured		5.0	B-827-A	Not measured
9	NaOH	0.20	0.20	1.0	Continuous	20.0	** WBT	74	74	54	14.0		B-827-A	2.05 mg KOH/gm
10	NaOH	0.20	0.20	1.0	Continuous	20.0	WBT	74	74	49.5	16.0		B-827-A	2.05 mg KOH/gm
11	NaOH	0.40	0.40	1.0	Continuous	20.0	WBT	74	74	69	20.0		B-827-A	2.05 mg KOH/gm
12	NaOH	0.40	0.40	1.0	Continuous	20.0	WBT	74	74	50.5	1.0		B-827-A	2.05 mg KOH/gm
13	NaOH	0.20	0.20	0	Continuous	40.0	WBT	74	74	53.5	1.5		B-827-A	2.05 mg KOH/gm
14	NaOH	0.20	0.20	1.0	Continuous	20.0	WBT	32	32	50.5	11.0		B-827-A	0.86 mg KOH/gm
15	NaOH	0.20	0.20	1.0	Continuous	20.0	WBT	32	32	57	13.0		B-827-A	0.86 mg KOH/gm
16*	NaOH	0.15	0.15	1.0	Continuous	20.0	WBT	32	32	-	-		B-827-A	0.86 mg KOH/gm
17*	NaOH	0.15	0.15	1.0	Continuous	20.0	WBT	32	32	-	-		B-827-A	0.86 mg KOH/gm
18*	NaOH	0.10	0.10	1.0	Continuous	20.0	WBT	32	32	-	-		B-827-A	0.86 mg KOH/gm
19	NaOH	0.10	0.10	1.0	Continuous	20.0	WBT	32	32	49	12.5		B-827-A	0.86 mg KOH/gm
20	NaOH	0.25	0.25	1.0	Continuous	20.0	WBT	32	32	53.5	10.0		B-827-A	0.86 mg KOH/gm
21	NaOH	0.25	0.25	1.0	Continuous	20.0	WBT	32	32	51	18.5		B-827-A	0.86 mg KOH/gm
22	NaOH	0.10	0.10	1.0	Continuous	20.0	WBT	32	32	58.5	14.5		B-827-A	0.86 mg KOH/gm
23	NaOH	0.10	0.10	1.0	Continuous	20.0	WBT	32	32	55	11.5		B-827-A	0.86 mg KOH/gm
24	Na4SiO4	0.20	0.20	1.0	Continuous	20.0	WBT	32	32	44	11.5		B-827-A	0.86 mg KOH/gm
25	Na4SiO4	0.20	0.20	1.0	Continuous	20.0	WBT	32	32	52.5	10.0		B-827-A	0.86 mg KOH/gm
26	NaOH	0.20	0.20	1.0	Continuous	20.0	WBT	26.7	26.7	57	17.0		B-827-A	2.25 mg KOH/gm
27	NaOH	0.20	0.20	1.0	Continuous	20.0	WBT	26.7	26.7	53	4.5		B-827-A	2.25 mg KOH/gm
28	NaOH	0.30	0.30	0	Continuous	20.0	WBT	39.6	39.6	51	3.0		B-827-A	Not measured
29	NaOH	0.30	0.30	0	Continuous	20.0	WBT	39.6	39.6	46	2.0		B-827-A	Not measured
30	NaOH	0.25	0.25	1.0	Continuous	5.0	WBT	39.6	39.6	39.5	7.5		B-827-A	Not measured
31	NaOH	0.25	0.25	1.0	Continuous	5.0	WBT	39.6	39.6	34.5	7.5		B-827-A	Not measured
32	NaOH	0.3	0.3	1.0	Continuous	5.0	WBT	51.1	51.1	40.5	5.0		B-827-A	0.92 mg KOH/gm
33	NaOH	0.2	0.2	1.0	Continuous	5.0	WBT	51.1	51.1	41	5.0		B-827-A	0.92 mg KOH/gm
34	NaOH	0.2	0.2	1.0	Continuous	5.0	WBT	51.1	51.1	41	1.0		B-827-A	0.92 mg KOH/gm
35	NaOH	0.2	0.2	1.0	Continuous	5.0	WBT	51.1	51.1	40.5	0		B-110-IA	0.92 mg KOH/gm
36	NaOH	0.2	0.2	1.0	Continuous	5.0	WBT	51.1	51.1	45.5	0		B-110-IA	0.92 mg KOH/gm
37	NaOH	0.2	0.2	1.0	Continuous	20.0	WBT	51.1	51.1	43	0.5		B-110-IA	0.92 mg KOH/gm
38	NaOH	0.2	0.2	1.0	Continuous	20.0	WBT	51.1	51.1	43	3.5		B-110-IA	0.92 mg KOH/gm

* Some data for these tests are unavailable

** WBT - at water breakthrough

TABLE 6 - CONTINUED

SUMMARY OF LABORATORY CORE FLOOD TESTS
 ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE, LONG BEACH UNIT
 WILMINGTON FIELD, CALIFORNIA

Test Number	Alkali	Alkali Concentration, Weight Percent	Alkali Salinity-Sodium Chloride Concentration, Weight Percent	Alkali Slug Size, Percent Pore Volume	Preflush Size, Percent Pore Volume	Water-Oil Ratio at Start of Preflush	Oil Viscosity, Centipoise	Incremental Oil Recovery, Percent Pore Volume		Core Material, Source Well	Crude Oil Acid Number
								Total	Incremental		
39	NaOH	0.2	1.0	Continuous	20.0	WBT	47.8	43.5	1.5	B-110-IA	1.17 mg KOH/gm
40	NaOH	0.2	1.0	Continuous	20.0	WBT	47.8	54.3	9.0	B-110-IA	1.17 mg KOH/gm
41	NaOH	0.2	1.0	Continuous	5.0	WBT	47.8	56.0	7.0	B-110-IA	1.17 mg KOH/gm
42	NaOH	0.2	1.0	Continuous	5.0	WBT	47.8	51.2	3.0	B-110-IA	1.17 mg KOH/gm
43	Na4SiO4	0.2	1.0	Continuous	5.0	WBT	47.8	56.2	9.5	B-110-IA	1.17 mg KOH/gm
44	Na4SiO4	0.2	1.0	Continuous	5.0	WBT	47.8	59.3	10.5	B-110-IA	1.17 mg KOH/gm
45	Na4SiO4	0.4	1.0	Continuous	5.0	WBT	41.6	47.4	5.0	B-110-IA	1.17 mg KOH/gm
46	Na4SiO4	0.4	1.0	Continuous	5.0	WBT	41.6	53.6	6.0	B-110-IA	1.17 mg KOH/gm
47	Na4SiO4	0.6	1.0	Continuous	5.0	WBT	41.6	67.7	15.0	B-110-IA	1.17 mg KOH/gm
48	Na4SiO4	0.6	1.0	Continuous	5.0	WBT	41.6	54.1	1.0	B-110-IA	1.17 mg KOH/gm
49	Na4SiO4/NaOH	0.4/0.2	1.0	Continuous	5.0	WBT	41.6	52.6	0	B-110-IA	1.17 mg KOH/gm
50	Na4SiO4/NaOH	0.4/0.2	1.0	Continuous	5.0	WBT	41.6	51.3	2.0	B-110-IA	1.17 mg KOH/gm
51	Na4SiO4	0.4	1.0	Continuous	5.0	WBT	39.7	47.0	5.0	B-110-IA	1.17 mg KOH/gm
52	Na4SiO4	0.4	1.0	Continuous	5.0	WBT	39.7	43.9	0.5	B-110-IA	1.17 mg KOH/gm
53	Na4SiO4	0.4	1.0	0.5	5.0	WBT	39.7	35.4	-5.5	B-110-IA	1.17 mg KOH/gm
54	Na4SiO4	0.4	1.0	0.5	5.0	WBT	39.7	38.3	-9.0	B-110-IA	1.17 mg KOH/gm
55	Na4SiO4	0.4	1.0	1.0	5.0	WBT	39.7	44.1	-1.0	B-110-IA	1.17 mg KOH/gm
56	Na4SiO4	0.4	1.0	1.0	5.0	WBT	39.7	45.5	-4.0	B-110-IA	1.17 mg KOH/gm
57	Na4SiO4	0.4	1.0	1.0	5.0	WBT	39.7	37.7	2.0	B-110-IA	1.17 mg KOH/gm
58	Na4SiO4	0.4	1.0	1.0	5.0	WBT	43.8	38.2	3.0	B-110-IA	1.17 mg KOH/gm
59	Na4SiO4	0.4	1.0	2.0	5.0	WBT	43.8	41.1	-1.0	B-110-IA	1.17 mg KOH/gm
60	Na4SiO4	0.4	1.0	2.0	5.0	WBT	43.8	32.5	1.5	B-110-IA	1.17 mg KOH/gm
61	Na4SiO4	0.4	1.0	Continuous	198.0	WBT	43.8	42.2	0.5	B-110-IA	1.17 mg KOH/gm
62	Na4SiO4	0.4	1.0	Continuous	216.0	WBT	43.8	37.8	2.5	B-110-IA	1.17 mg KOH/gm

TABLE 7

SUMMARY OF COREFLOOD TEST
UNSTEADY-STATE RELATIVE PERMEABILITY DATAALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE
LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

Test Number*	Depth, Feet	Porosity, Percent	Pore Volume, cc	Air Permeability, md	Initial Conditions			Final Conditions			Relative Permeability, Percent	Oil Recovery Percent
					Water Saturation, Percent	Oil** Permeability, md	Oil Saturation, Percent	Water Permeability, md	Oil Saturation, Percent	Water Permeability, md		
39A	4,941.5	21.0	44.80	57	35.6	34.2	21.7	0.392	1.15	42.6	66.3	
39B	4,941.5	21.0	44.80	57	35.6	34.0	20.8	1.93	5.68	43.5	67.6	
40A	4,942.0	20.9	44.70	75	19.3	38.8	36.9	4.39	11.3	43.8	54.3	
40B	4,942.0	20.9	44.70	75	19.3	35.2	26.3	4.17	11.8	54.3	67.3	
41A	4,942.5	20.5	43.44	90	15.9	53.1	36.1	5.01	9.44	48.0	57.0	
41B	4,942.5	20.5	43.44	90	15.9	43.3	28.2	4.22	9.75	56.0	66.6	
42A	4,943.0	19.6	41.39	117	25.8	57.5	30.9	3.81	6.63	43.2	58.3	
42B	4,943.0	19.6	41.39	117	25.8	54.6	23.0	3.90	7.14	51.2	69.0	
43A	4,944.0	19.2	42.52	128	22.9	70.2	32.9	6.38	9.09	44.2	57.3	
43B	4,944.0	19.2	42.52	128	22.9	63.7	20.9	3.94	6.19	56.2	72.8	
44A	4,944.5	21.3	44.45	107	21.4	56.8	33.8	7.01	12.3	44.9	57.1	
44B	4,944.5	21.3	44.45	107	21.4	50.9	19.4	6.38	12.5	59.3	75.4	
45A	4,945.0	18.0	45.21	83	18.1	56.9	34.0	1.11	1.95	47.8	58.4	
45B	4,945.0	18.0	45.21	83	18.1	58.6	34.4	1.66	2.82	47.4	57.9	
46A	4,945.5	18.0	44.46	95	17.6	57.9	32.7	6.28	10.8	49.8	60.4	
46B	4,945.5	18.0	44.46	95	17.6	59.4	28.8	1.81	3.05	53.6	65.1	
47A	4,946.0	17.8	39.11	74	8.46	51.8	48.0	5.18	10.0	43.5	47.5	
47B	4,946.0	17.8	39.11	74	8.46	51.3	23.8	0.10	0.195	67.7	74.0	
48A	4,946.7	18.3	48.46	62	18.7	40.9	27.5	4.82	11.8	53.9	66.2	
48B	4,946.7	18.3	48.46	62	18.7	42.0	27.2	1.71	4.08	54.1	66.5	
49A	4,947.2	17.6	44.36	70	17.0	20.7	30.2	19.6	19.6	52.8	63.6	
49B	4,947.2	17.6	44.36	70	17.0	20.9	30.4	10.2	10.2	52.6	63.3	
50A	4,947.7	18.9	46.77	40	34.8	19.3	14.9	3.45	17.9	50.2	77.1	
50B	4,947.7	18.9	46.77	40	34.8	19.1	13.9	1.52	7.97	51.3	78.7	

* A - Waterflood test

B - Alkaline flood test

** Base permeability used to calculate relative permeability.

TABLE 7 - CONTINUED

SUMMARY OF COREFLOOD TEST
UNSTEADY-STATE RELATIVE PERMEABILITY DATA - CONTINUEDALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE
LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

Test Number*	Depth, Feet	Porosity, Percent	Pore Volume, cc	Air Permeability, md	Initial Conditions			Final Conditions			Oil Recovery	
					Water Saturation, Percent	Oil** Permeability, md	Oil Saturation, Percent	Water Permeability, md	Relative Permeability To Water, Percent	Pore Volume	Percent	Pore Volume
51A	5,023.4	22.2	54.52	332	21.8	174	39.6	9.69	5.57	38.6	49.3	
51B	5,023.4	22.2	54.52	332	21.8	175	31.1	8.73	4.99	47.0	60.1	
52A	5,024.1	23.2	52.37	364	25.2	203	34.4	7.42	3.66	40.4	54.0	
52B	5,024.1	23.2	52.37	364	25.2	183	31.0	7.10	3.88	43.9	58.6	
53A	5,033.0	24.5	55.59	337	26.4	182	31.3	11.9	6.54	42.4	57.4	
53B	5,033.0	24.5	55.59	337	26.4	148	38.4	7.28	4.92	35.4	47.9	
54A	5,036.1	23.9	53.52	523	21.1	294	33.7	10.3	3.50	45.3	48.6	
54B	5,036.1	23.9	53.52	523	21.1	281	40.5	8.90	3.17	38.3	57.4	
55A	5,038.8	21.5	47.68	478	19.2	234	35.4	29.6	12.7	45.4	56.1	
55B	5,038.8	21.5	47.68	478	19.2	188	36.7	2.96	1.57	44.1	54.6	
56A	5,055.6	23.4	54.90	809	17.2	468	33.8	13.0	2.78	48.9	59.1	
56B	5,055.6	23.4	54.90	809	17.2	471	37.3	10.9	2.31	45.5	54.9	
57A	5,030.0	28.1	68.39	325	23.5	177	41.3	15.7	8.87	35.2	46.1	
57B	5,030.0	28.1	68.39	325	23.5	177	38.7	13.1	7.40	37.7	49.3	
58A	5,031.4	25.5	60.96	284	24.6	145	39.2	10.7	7.38	36.2	48.0	
58B	5,031.4	25.5	60.96	284	24.6	146	37.2	10.4	7.12	38.2	50.6	
59A	5,039.7	23.0	53.33	520	21.3	312	37.0	6.96	2.23	41.7	53.0	
59B	5,039.7	23.0	53.33	520	21.3	298	37.5	9.48	3.18	41.1	52.3	
60A	5,050.1	23.1	55.54	271	32.1	73.2	35.6	5.38	7.35	32.3	47.5	
60B	5,050.1	23.1	55.54	271	32.1	75.5	35.4	6.01	7.96	32.5	47.8	
61A	5,052.8	25.1	61.89	509	23.6	335	38.9	5.03	1.50	37.5	49.0	
61B	5,052.8	25.1	61.89	509	23.6	297	34.3	17.1	7.76	42.2	55.2	
62A	5,053.4	23.6	59.99	432	19.2	246	46.3	8.0	3.25	34.5	42.7	
62B	5,053.4	23.6	59.99	432	19.2	232	43.0	23.3	10.00	37.8	46.8	

* A - Waterflood test

B - Alkaline Flood test

** Base permeability used to calculate relative permeability.

TABLE 8
CHEMICAL CONSUMPTION FLOW TESTS

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE
 LONG BEACH UNIT
 WILMINGTON FIELD, CALIFORNIA

B-110-1A Composite Sand
 125°F Test Temperature

Elapsed Time	Sodium Hydroxide* Alkalinity (N)	Weight Percent as NaOH	Chemical Consumption, (meq/100g)	Reversible Adsorption, (meq/100g)	Sodium* Orthosilicate Alkalinity (N)	Weight Percent as NaOH	Chemical Consumption, (meq/100g)	Reversible Adsorption, (meq/100g)
Day 0	0.022	0.088	1.9	0.99	0.013	0.052	2.0	0.70
	0.046	0.184	2.8	1.1	0.027	0.108	2.9	0.90
	0.124	0.496	3.6	1.6	0.074	0.296	3.4	1.60
Day 2	0.238	0.952	2.1	2.9	0.152	0.608	3.7	1.70
	0.018	0.072	3.7	0.8	0.011	0.044	4.8	0.50
	0.043	0.172	6.2	1.7	0.025	0.100	5.7	0.80
Day 9	0.112	0.448	6.4	1.1	0.072	0.288	7.1	0.70
	0.235	0.940	7.0	1.8	0.148	0.592	6.9	1.70
	0.013	0.052	8.5	0.7	0.008	0.032	7.4	0.40
Day 36	0.038	0.152	9.1	1.0	0.021	0.084	9.4	0.60
	0.110	0.440	10.2	1.9	0.070	0.280	11.8	0.70
	0.228	0.912	11.2	1.3	0.144	0.576	13.0	1.0
Day 36	0.007	0.028	13.6	1.2	0.007	0.028	8.6	0.80
	0.032	0.128	14.9	1.8	0.019	0.076	11.1	0.50
	0.106	0.424	16.4	1.9	0.064	0.256	14.8	0.70
	0.212	0.848	16.7	2.2	0.134	0.520	16.9	0.50

* Prepared in 1 percent NaCl brine

These tests were performed by California State University, Long Beach, California.

TABLE 9

ALKALINE SLUG OPTIMIZATION STUDIES
BASE DATA FOR STUDY AREA

(Includes B-101, B-711, B-712, B-838, B-831-I, B-836-I)

Reservoir Pore Volume of 4 Producers, 2 Injectors Fo ₁ + Fo ₂ Area (PV)	1,879,000 Res. Bbl.	(298,700 Res.m ³)
Initial Oil-in-Place (TOIP)	1,231,000 St. Bbl.	(195,700 St.m ³)
Waterflood Oil Recovery:		
To 5-01-79	562,000 St. Bbl.	(89,400 St.m ³)
Percent TOIP		45.65
Percent PV		29.91
Waterflood Oil Recovery 5-01-79		
To economic limit of 150 WOR (11-01-85)	84,800 St. Bbl.	(13,500 St.m ³)
Cumulative Waterflood Oil Recovery	646,800 St. Bbl.	(102,800 St.m ³)
Percent TOIP		52.54
Percent PV		34.42
Injection Rate 5-01-79 to End (7.5 P/Yr.±)	4,806 B/D	(764 m ³ /D)
Start of Alkaline Injection 5-24-80		
Preflush Injection - 1.0 Percent Salt-Soft Water Solution (390 Days)	1,874,340 St. Bbl.	(298,000 St.m ³)
Percent PV		99.75

TABLE 10

ALKALINE SLUG OPTIMIZATION STUDY
OIL RECOVERY DATA
5-01-79 to Economic Limit

Alkaline Slug Description	Long Term Consumption	Oil Recovery		Economic Limit (150 WOR) Date	Incremental Oil Recovery Above Waterflood	
		MST Bbl./ (m) ³	% TOIP		M Bbl./ (m) ³	% PV
Waterflood	-	84.8 (13,480)	-	11-01-85	-	-
<u>Pro-Rated Alkaline Relative Permeability Adjustment</u>						
60 PV % 0.4% Alkali, 1% Salt	Accelerated Rate	174.0 (27,660)	7.25	07-03-89	89.2 (14,180)	4.75
32 PV % 9.8% Alkali, 1% Salt	Accelerated Rate	137.9 (21,920)	4.31	09-01-86	53.1 (8,440)	2.83
32 PV % 0.8% Alkali, 1% Salt	Constant Rate	143.5 (22,820)	4.77	06-05-86	58.7 (9,330)	3.12
32 PV % 0.8% Alkali, 1% Salt	None	159.8 (25,410)	6.09	07-01-86	75.0 (11,920)	3.99
24 PV % 1% Alkali, 1% Salt	Accelerated Rate	122.1 (19,410)	3.03	12-06-85	37.3 (5,930)	1.99
24 PV % 1% Alkali, 1% Salt	None	142.3 (22,620)	4.67	10-21-85	57.5 (9,140)	3.06
48.6 PV % Variable Alkali Content* 1% Salt	Accelerated Rate	162.0 (25,760)	6.30	02-16-88	77.5 (12,320)	4.12
* 0.4% orthosilicate for first 1.5 years, 1.0% for next 1.0 year, 0.8% for 1.0 year, 0.4% for 1.0 year, and 0.2% for 2.0 years.						
<u>Minimum Threshold Alkaline Relative Permeability Adjustment</u>						
60 PV % 0.4% Alkali 1% Salt	Accelerated Rate	226.0 (35,930)	11.47	05-28-90	141.2 (22,450)	7.51

TABLE 11

PATTERN AREA PERFORMANCE THROUGH 1994

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE
 LONG BEACH UNIT
 WILMINGTON FIELD
 LOS ANGELES, CALIFORNIA

Subzone	Waterflood Cumulative Oil		Alkali Case 1 Cumulative Oil		Alkali Case 2 Cumulative Oil	
	10 ³ STB	stock-tank-m ³	10 ³ STB	stock-tank-m ³	10 ³ STB	stock-tank-m ³
Fo	4,390	698,000	4,497	715,000	4,758	756,000
F	2,871	456,000	2,990	475,000	3,048	485,000
H	1,742	277,000	1,751	278,000	1,762	280,000
X	3,560	566,000	3,580	569,000	3,622	576,000
G	1,787	284,000	1,791	285,000	1,795	285,000
G ₄	699	111,000	706	112,000	715	114,000
Total	15,049	2,392,000	15,315	2,434,000	15,700	2,496,000

TABLE 12

SPECIFICATION OF INJECTED FLUIDS

<u>Fluid</u>	<u>Volume, bbls</u>	<u>Components</u>	<u>Injection Period</u>
Preflush	11,500,000 (10.2% PV)	Softened fresh water with 1% added salt (38,300,000 pounds added salt)	January 1979 - March 1980
Alkaline Slug	40,927,000 (67% PV)	Softened fresh water with 0.67% added salt (97,000,000 pounds) 0.391% sodium othosilicate (30,222,650 pounds sodium silicate plus 34,816,700 pounds sodium hydroxide)	March 1980 - December 1973
Postflush		Softened fresh water with 0.75% added salt	December 1983 - June 1984

TABLE 13

ANALYSIS OF FORMATION BRINE

<u>Radicals</u>	<u>Milligrams Per Liter</u>
Sodium (Na)	6,938
Ammonium (NH ₄)	149
Calcium (Ca) ⁴	355
Magnesium (Mg)	315
Sulfate (SO ₄)	-
Chloride (Cl)	11,911
Carbonate (CO ₃)	-
Bicarbonate (HCO ₃)	1,306
Borate (B ₄ O ₇)	123
Silica (SiO ₂)	-
	<u>21,097</u>

TABLE 14

ANALYSIS OF SOFTENED EL DORADO FRESH WATER
CONTAINING 1 PERCENT SODIUM CHLORIDE,
CAUSTIC FLOOD PLANT, ISLAND WHITE

<u>Radicals</u>	<u>Milligrams Per Liter</u>
Sodium (Na)	4,500
Ammonium (NH ₄)	TR 1
Calcium (Ca)	8
Magnesium (Mg)	2
Barium (Ba)	TR 1
Iron (Fe)	0.2
Sulfate (SO ₄)	350
Chloride (Cl)	6,600
Hydroxide (HO)	0
Carbonate (CO ₃)	0
Bicarbonate (HCO ₃)	120
Borate (B ₄ O ₇)	TR 1
Iodide (I)	TR 1
Silica (SiO ₂)	9
*Organic Acids	6
Total Hardness (CaCO ₃)	27
Total Suspended Solids (TSS)	1.1
Salinity as Salt (NaCl)	10,900
Total Solids	11,600
Specific Gravity, @ 60°F	1.011
Resistivity, Ohm Cm @ 75°F	55.7
pH Value	7.94

* Included in Bicarbonates

TABLE 15

ANALYSIS OF SOFTENED ISLAND WHITE MUD WATER
CONTAINING 1 PERCENT NaCl

<u>Radicals</u>	<u>Milligrams Per Liter</u>
Sodium (Na)	4,800
Ammonium (NH ₄)	1
Calcium (Ca) ⁴	15
Magnesium (Mg)	10
Barium (Ba)	TR 1
Iron (Fe)	TR 0.05
Sulfate (SO ₄)	250
Chloride (Cl)	7,200
Hydroxide (HO)	0
Carbonate (CO ₃)	4
Bicarbonate (HCO ₃)	120
Borate (B ₄ O ₇)	TR 2
Iodide (I)	1
Silica (SiO ₂)	10
*Organic Acids	10
Total Hardness (CaCO ₃)	79
Salinity as Salt (NaCl)	11,900
Total Solids	12,400
Specific Gravity, @ 60°F	1.010
Resistivity, Ohm Cm @ 75°F	52.4
pH Value	8.34
Temperature, °F	60
Dissolved Oxygen	6.5
Total Suspended Solids	1.3
Scaling Index	-0.67

* Included in Bicarbonates

TABLE 16

WELL WORKOVERS, STIMULATIONS, AND SHUT-IN DATA

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE, LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

Date	Workover					Stimulation				Shut-In Wells	New Wells	
	Redrill	Install Liner	Nonroutine Pump Change	Bridge Plug In or Out	Clean Out Fill	Reset Packer	Thermal	Acid Squeeze	Scale Inhib. Squeeze			
Jan-76												
Feb-76												
Mar-76												
Apr-76												
May-76												
Jun-76												
Jul-76												
Aug-76												
Sep-76												
Oct-76												
Nov-76												
Dec-76	B-827A						B-711					
Jan-77		B-712					B-1191	B-1191				
Feb-77							B-712					
Mar-77												
Apr-77	B-110IA											
May-77												
Jun-77	B-826IA											
Jul-77	B-828IA											
Aug-77												
Sep-77	B-831IA	B-410										
Oct-77												
Nov-77												
Dec-77		B-834										

TABLE 16 - CONTINUED

WELL WORKOVERS, STIMULATIONS, AND SHUT-IN DATA

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE, LONG BEACH UNIT
 WILMINGTON FIELD, CALIFORNIA

Date	Workover				Stimulation				Shut-In Wells	New Wells		
	Redrill	Install Liner	Nonroutine Pump Change	Bridge Plug In or Out	Clean Out Fill	Reset Packer	Thermal	Acid Squeeze			Acidize	Scale Inhib. Squeeze
Jan-78		B-108										
Feb-78												
Mar-78		B-711	B-108							B-709I		
Apr-78			B-410									
May-78				B-834	B-709I							
Jun-78				B-116								
Jul-78			B-834									
Aug-78										B-831IA	B-110IA	
Sep-78			B-101A							B-826IA		
Oct-78				B-116	B-828IA	B-110IA					B-828IA	
Nov-78				B-834							B-836I	
Dec-78			B-106	B-120	B-836I	B-836I						
Jan-79		B-120										
Feb-79												
Mar-79				B-116	B-110IA							
Apr-79		B-834A			B-119I							
May-79					B-110IA	B-110IA						
Jun-79					B-116	B-116						
Jul-79												
Aug-79					B-116	B-116						
Sep-79					B-107I	B-107I						
Oct-79										B-710	B-831IB	
Nov-79		B-830			B-826IA	B-826IA				B-710	B-828IA	
Dec-79					B-831IB	B-831IB						

TABLE 17

STATIC PRESSURES - 3,000 FEET DATUM PSI

ALKALINE WATERFLOODING DEMONSTRATION PROJECT
 RANGER ZONE
 LONG BEACH UNIT
 WILMINGTON FIELD
 LOS ANGELES, CALIFORNIA

<u>Area</u>	<u>Well Number</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>	<u>1979</u>	<u>1980</u>
Block 9	B-108	1294				
	B-112		1009			
	B-114	1308	1110			
	B-117		1139			
	B-410		1312	1354		
	B-712	1216			1102	
	B-827	1231	1170	1197	1099	1141
	B-834	1306	1103	1221	1036	1020
	B-837		1160	1227	1196	
	B-838		973			
	B-839		1295	1152		1286
	B-107I				1645	
	B-110I				1430	
	B-119I					
	B-828I					
	B-709I				1660	1440
	B-826I				1335	
	B-831I					
	B-836I					
Northern	B-105		1102	1081	1137	1179
	B-106					
	B-111					
	B-120					
	B-121					
	B-124					
	B-710					
Southern	B-101	1212				
	B-705					
	B-706			886	879	843
	B-707A					
	B-711	1169	1107			931
	B-830		1043	1138	1102	961
Adjacent Wells	A-237					
	A-242I					
	A-303A		1136	1029	992	877
	B-102I					
	B-116I					
	B-124					
	B-133					
	B-825		1107			
	B-829I					
	B-832		1107	977	1087	995

TABLE 18

DOE ALKALINE PILOT
PRODUCERS SHOWING REDUCED WATER PRODUCTION

Well Number	Location	Prior Rates			Current Rates (May 1986)			Change In Produced Water Chemistry To Alkaline	Change In Produced Water Chemistry To Normal Injection Water (2)	Date Simulator Predicted First Alkali*	
		B/D	Gross	BO/D	WOR	FOP	Date				B/D
***R-101-A	Southern Area, Row B	1,370	70	18.57	284'	12/80	-	-	-	2nd half '81	
***B-105 (2)	Northern Area, Row A	1,690	75	21.53	363'	08/81	-	-	-	2nd half '81	
***B-111	Northern Area, Row A	1,850	95	18.47	318'	01/81	-	-	-	1st half '83	
***B-112	Pattern Area, North Row	850	45	17.89	107'	09/81	-	-	-	1st half '81	
B-117	Pattern Area, North Row	1,550	130	10.92	28'	01/81	1,100	70	14.71	97'	1st half '82
B-121	Northern Area, Row A	1,250	80	14.63	255'	01/81	605	35	16.29	27'	1st half '84
***B-410	Pattern Area, North Row	1,600	65	23.62	18'	11/80	-	-	-	1st half '82	
B-705	Southern Area, Row D	1,550	115	12.48	245'	01/81	610	110	4.55	268'	1st half '83
B-706	Southern Area, Row D	930	105	7.86	88'	04/81	730 (1)	70 (1)	9.43 (1)	160'	2nd half '86
***B-707	Southern Area, Row D	1,150	45	24.56	1,419'	03/81	1,120 (1)	15 (1)	73.67 (1)	43'	2nd half '86
***B-711	Southern Area, Row B	1,800	40	44.00	435'	03/81	-	-	-	1st half '81	
***B-712	Pattern Area, South Row	790	45	16.56	501'	02/81	-	-	-	2nd half '83	
***B-830	Southern Area, Row B	900	(?) 2	450.00	6'	01/81	-	-	-	2nd half '81	
B-834-A	Pattern Area, South Row	2,500	90	26.78	877'	03/81	425	45	8.44	120'	2nd half '81
***B-838	Pattern Area, South Row	1,570	55	27.55	202'	02/81	-	-	-	3rd Qtr. '80	
***B-839 (2)	Pattern Area, North Row	1,550	55	27.18	404'	04/81	-	-	-	1st half '82	
TOTALS (excluding B-101, B-105, B-111, B-112, B-410, B-707, B-711, B-712, B-830, B-838, B-839)		7,780	520	13.96			3,470	330	9.52		

* Alkaline flood simulation #2; other wells producing first alkali:
1st half 1984 B-114

** Excluded from totals because of non representative recent test data or lack of tests following recent work.

*** Excluded: down at month end.

(1) Stabilizing after pump and/or rotation changes: stimulation.

(2) Idled during 5/86: high cut.

TABLE 19

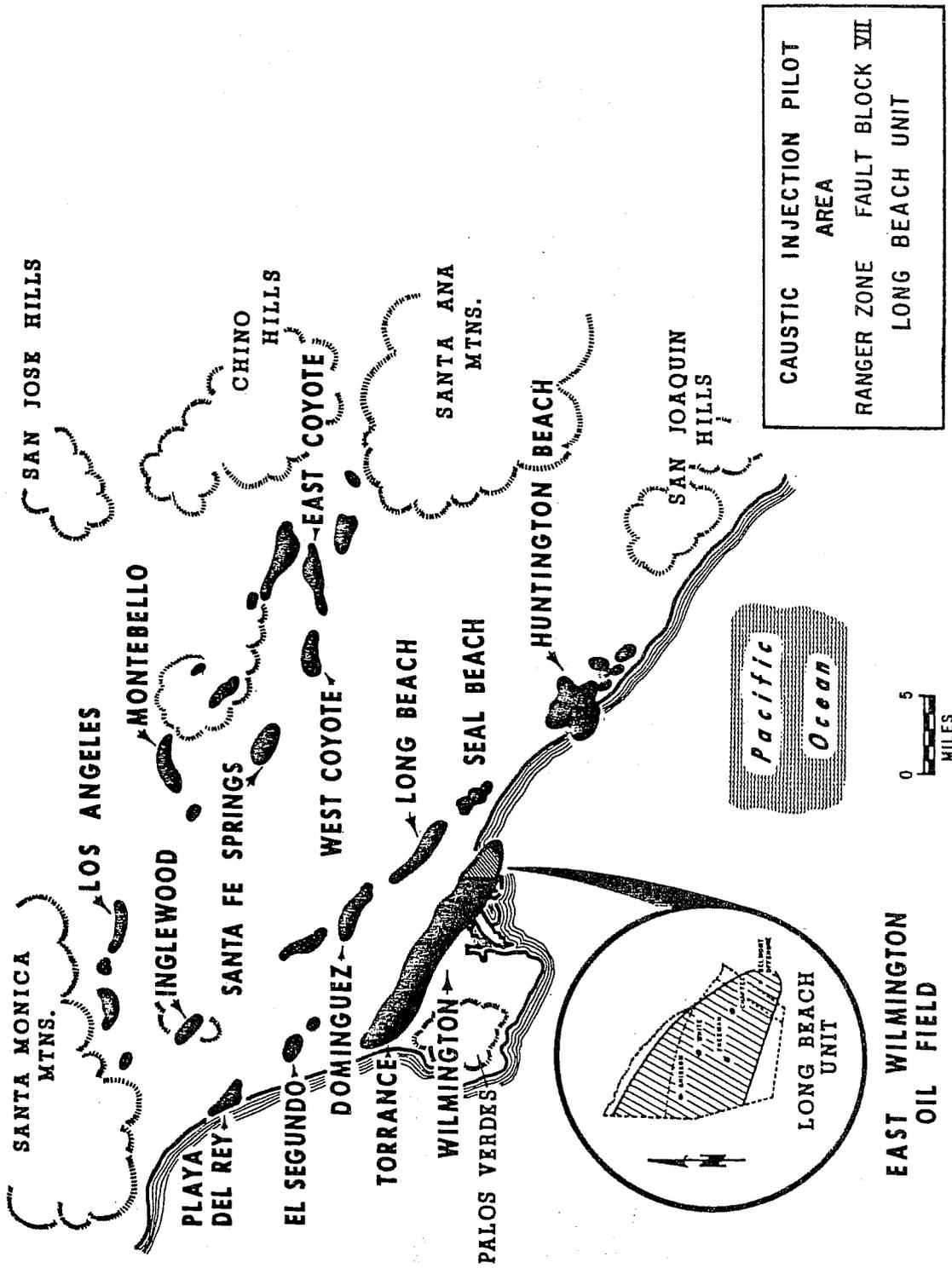
WET CHEMISTRY ANALYSES OF SOLIDS FROM PRODUCTION STRING

B-838

Location	Hydrocarbon	Iron Oxide/ Iron Sulfate	Calcium Carbonate	Barium Sulfate	Silica
First Joint of Tubing Above Pump (Coarse Solids)	6.2%	14.59%	41.10%*	-0-	37.11%
First Joint of Tubing Above Pump (Fines)	2.4%	2.26%	4.60%	-0-	90.47%
Top Pump Impeller	1.8%	5.09%	1.17%	3.14%	89.80%
Middle Pump Impeller	1.64%	14.46%	4.68%	2.69%	76.53%
Bottom Pump Impeller	1.39%	18.19%	6.14%	2.17%	72.11%
Pump Intake	2.13%	39.21%	26.67%	3.41%	28.58%

*Possibly cement resulting from casing failure.

FIGURE 1



LOS ANGELES BASIN

EAST WILMINGTON
OIL FIELD

FIGURE 2

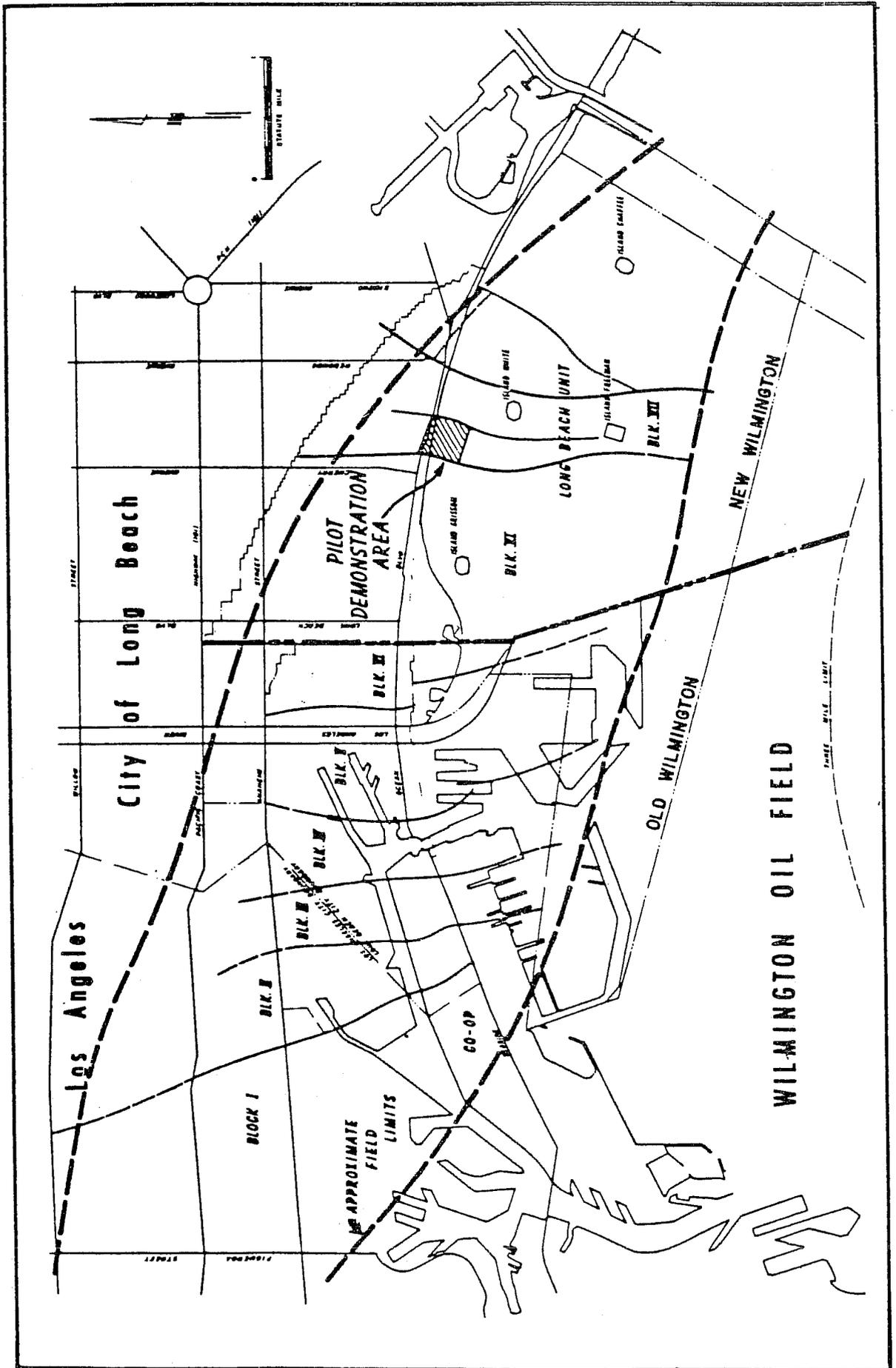


FIGURE 3

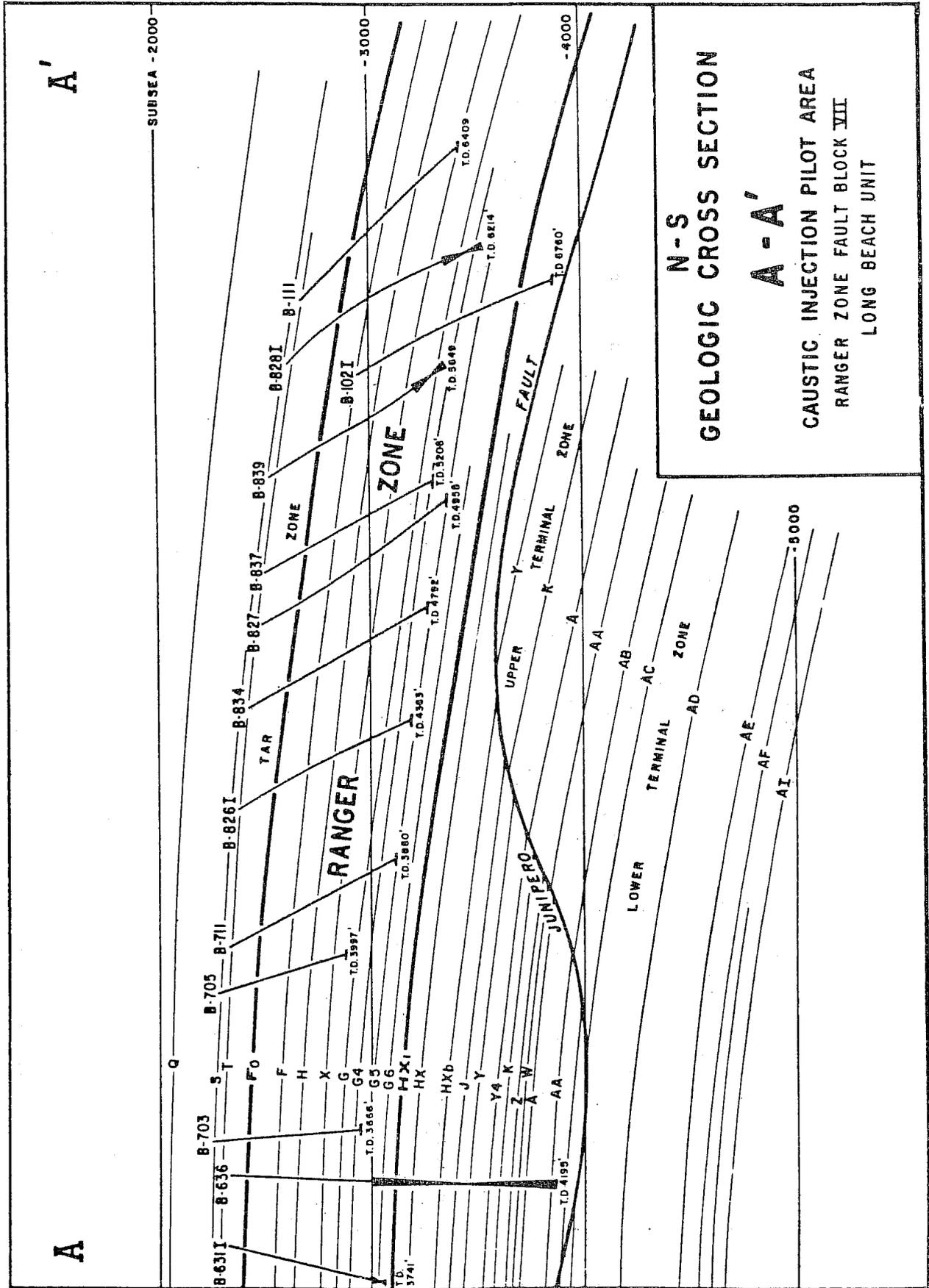


FIGURE 4

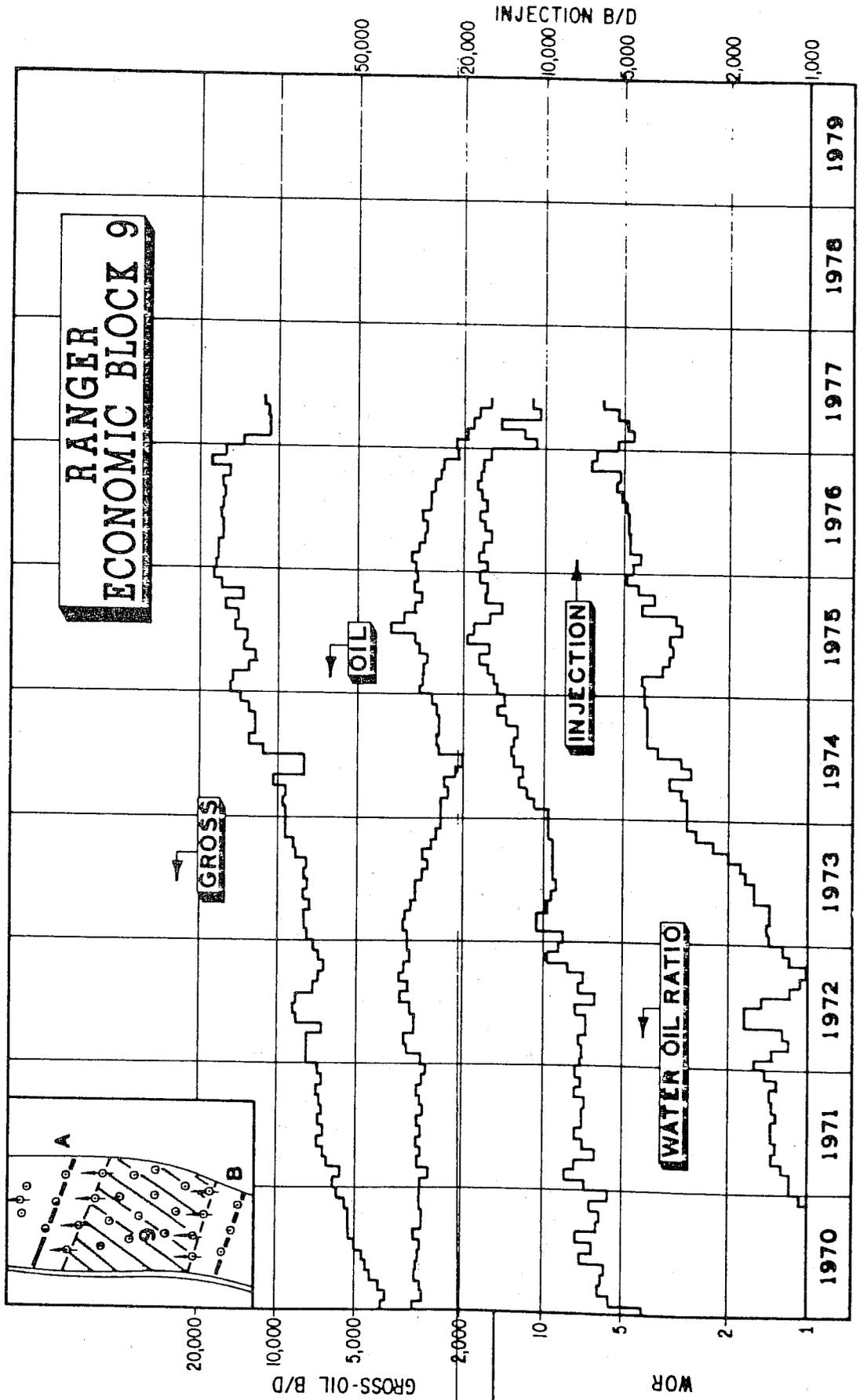
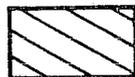


FIGURE 5



RANGER AREA 9



SOUTHERN AREA



NORTHERN AREA



A-171I



A-209I



A-213I



A-234



A-221



A-219A



A-222



A-229



A-230



A-233



A-237



B-240I



A-241I



A-242I



A-260



A-262



A-261



A-303 A



A-266



A-265



A-263



A-304



A-301



A-269



A-319I



A-307I



A-305I



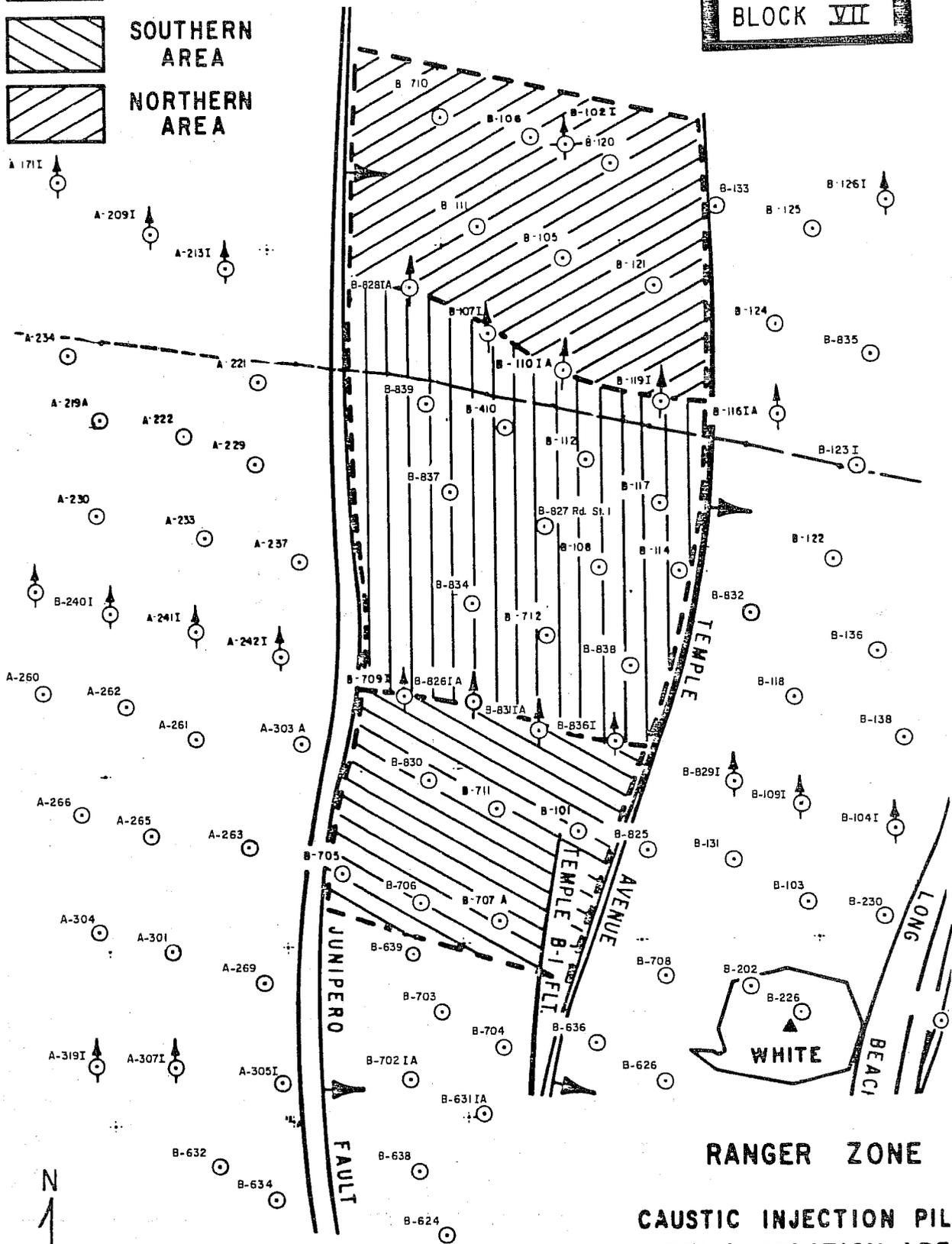
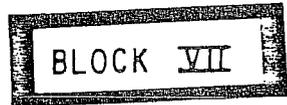
B-632



B-634



B-113I



RANGER ZONE
CAUSTIC INJECTION PILOT
DEMONSTRATION AREA

LONG BEACH UNIT

FIGURE 6

CORE FLOOD AND SIMULATOR FLOOD MATCH

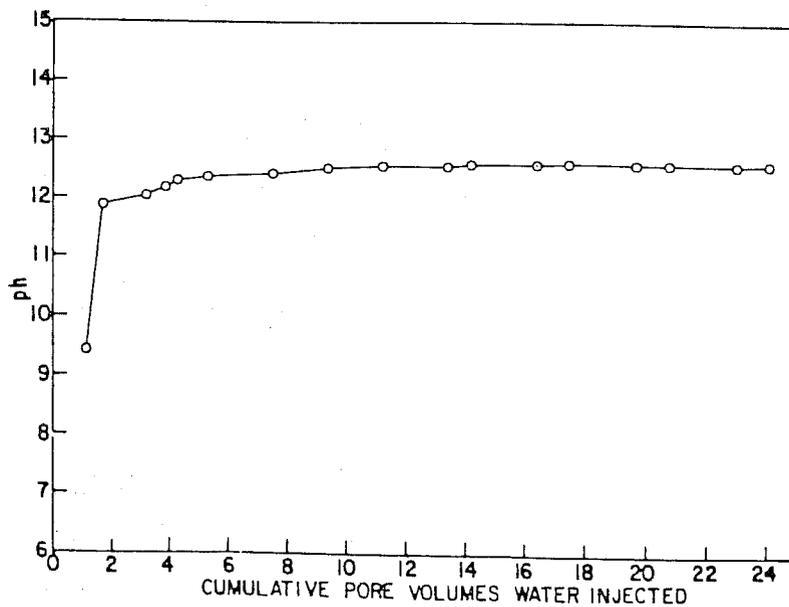
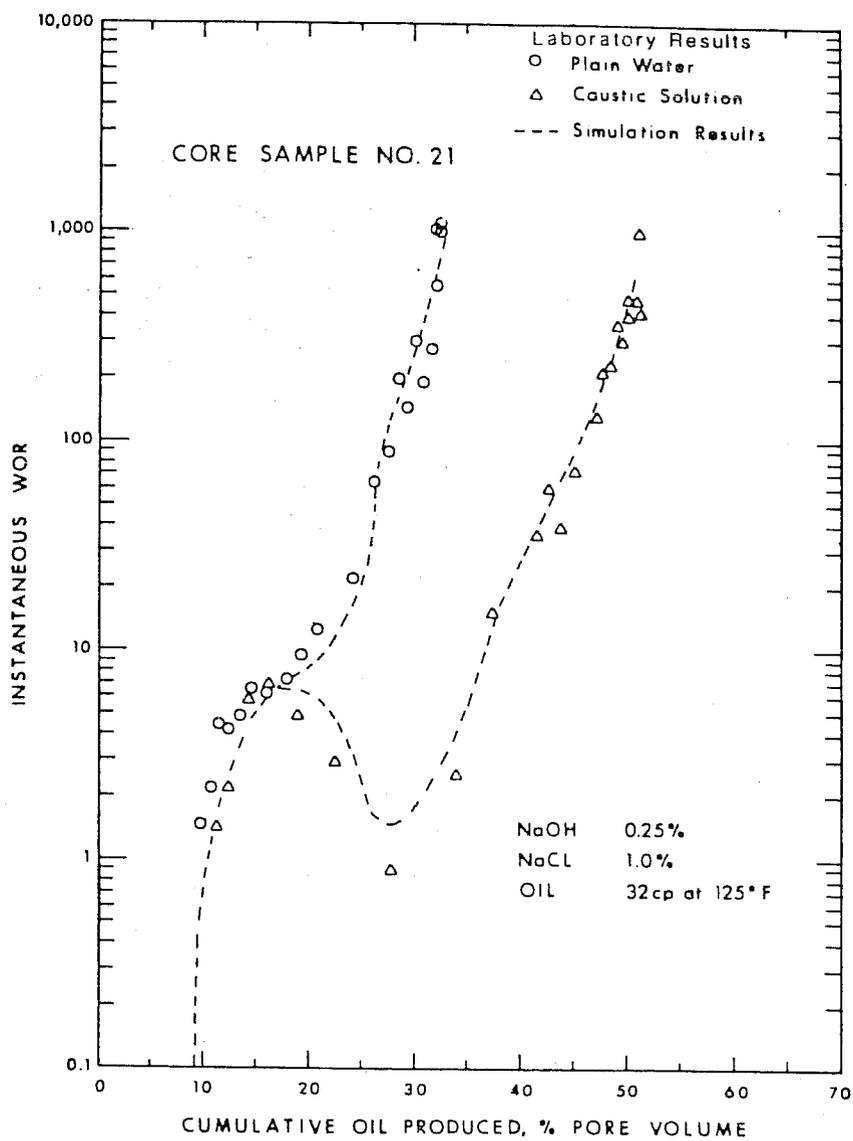


FIGURE 7

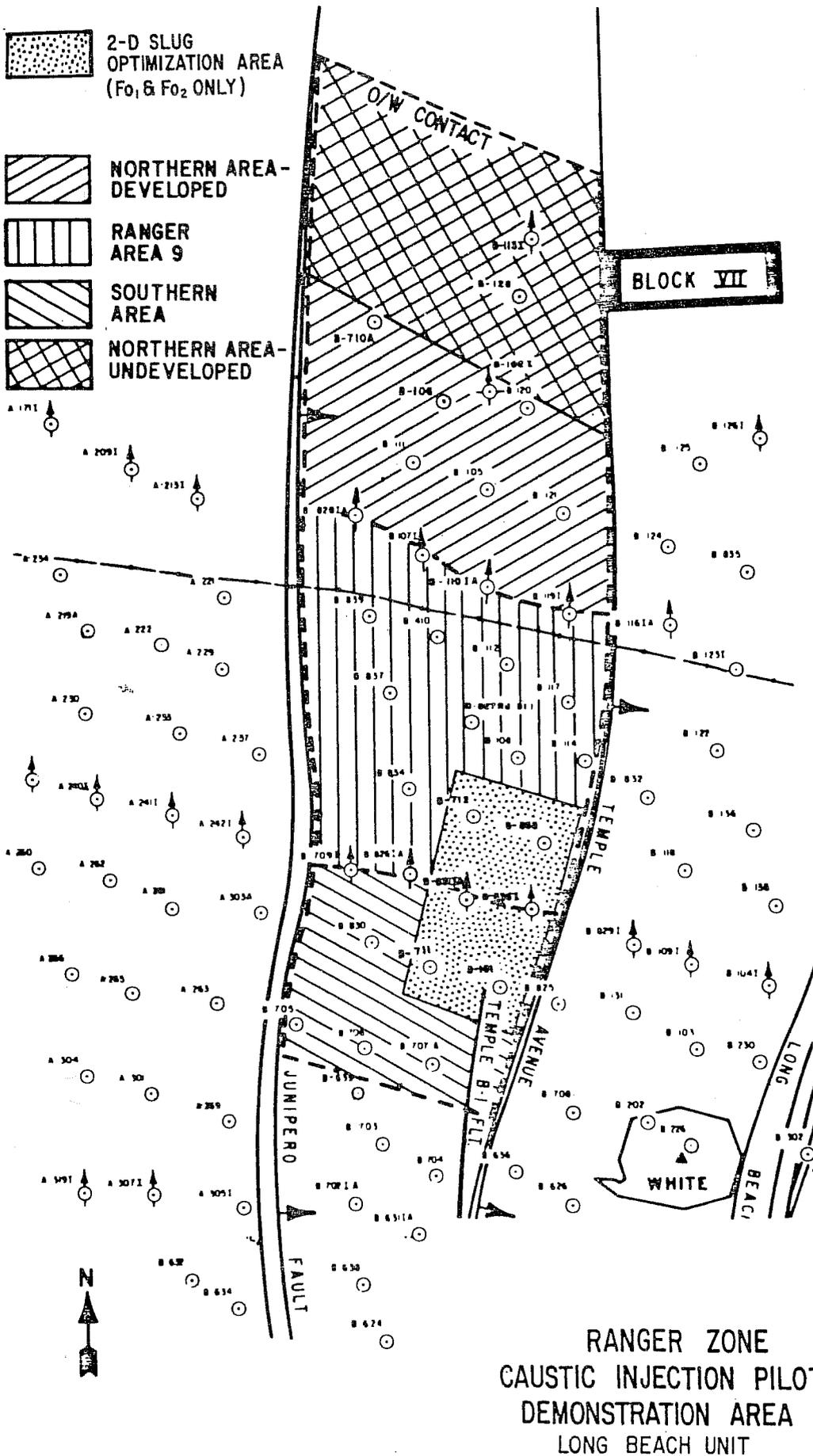
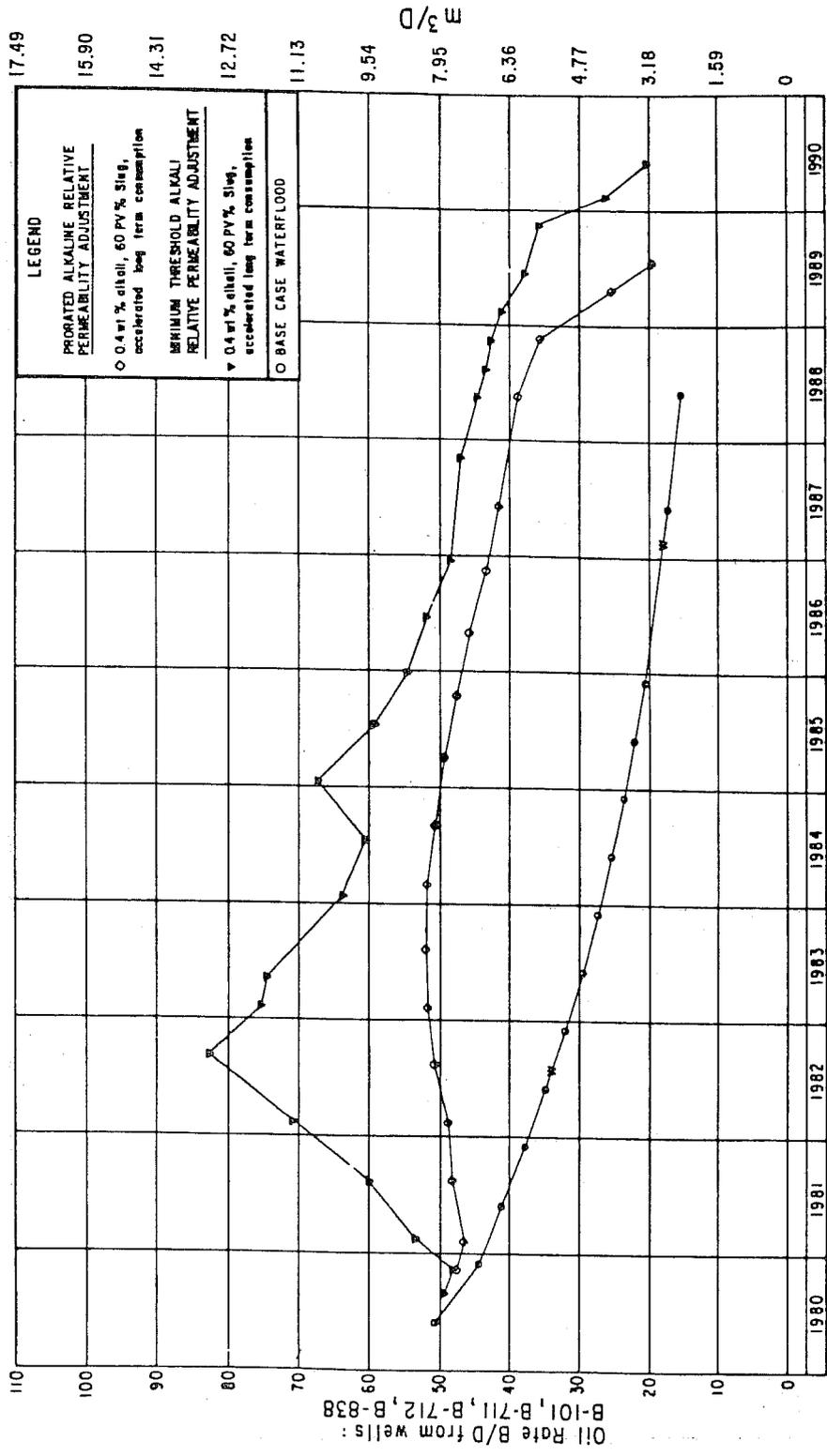


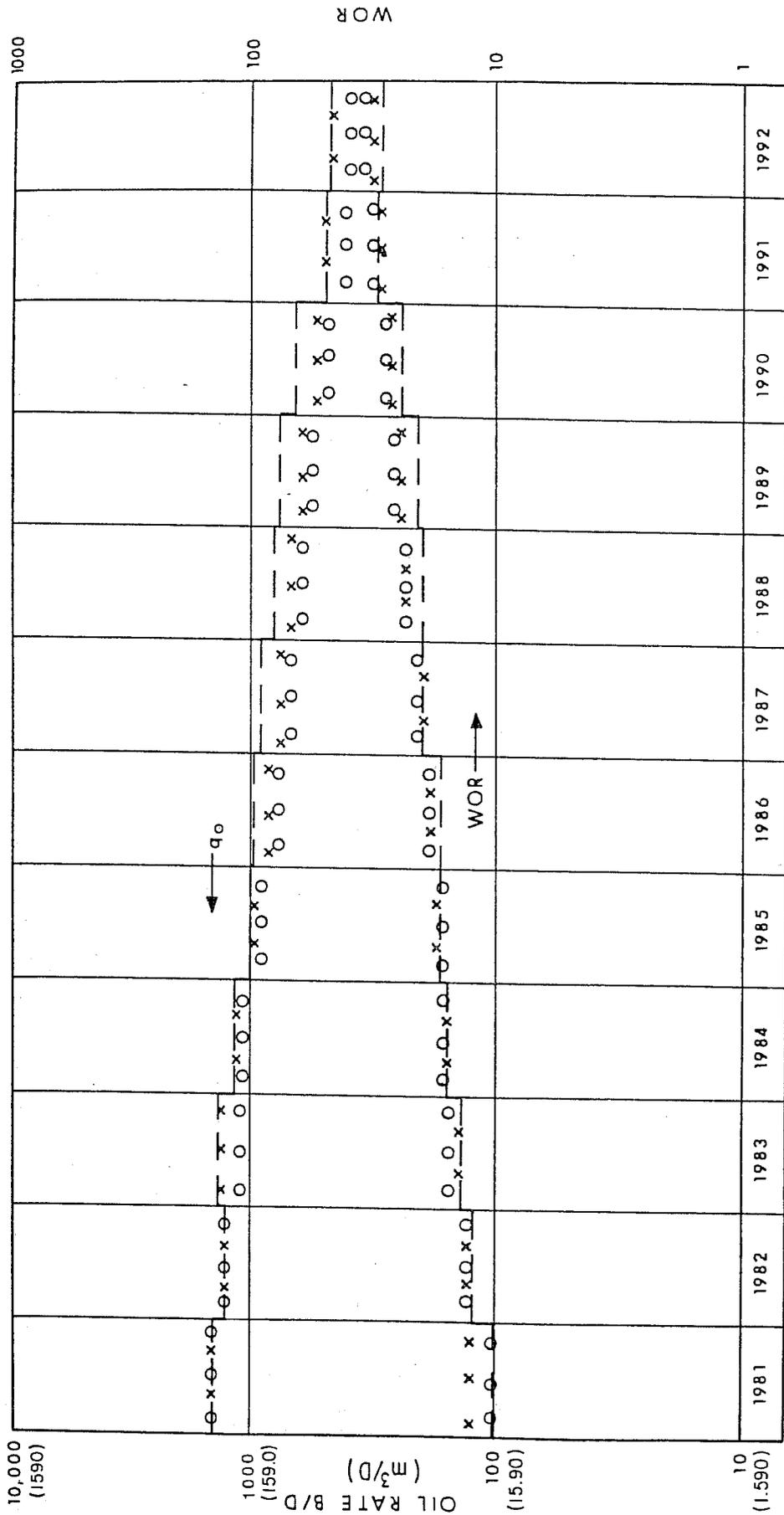
FIGURE 8



OIL RATE AS RESULT OF RELATIVE PERMEABILITY ADJUSTMENT
SLUG SIZE OPTIMIZATION STUDY

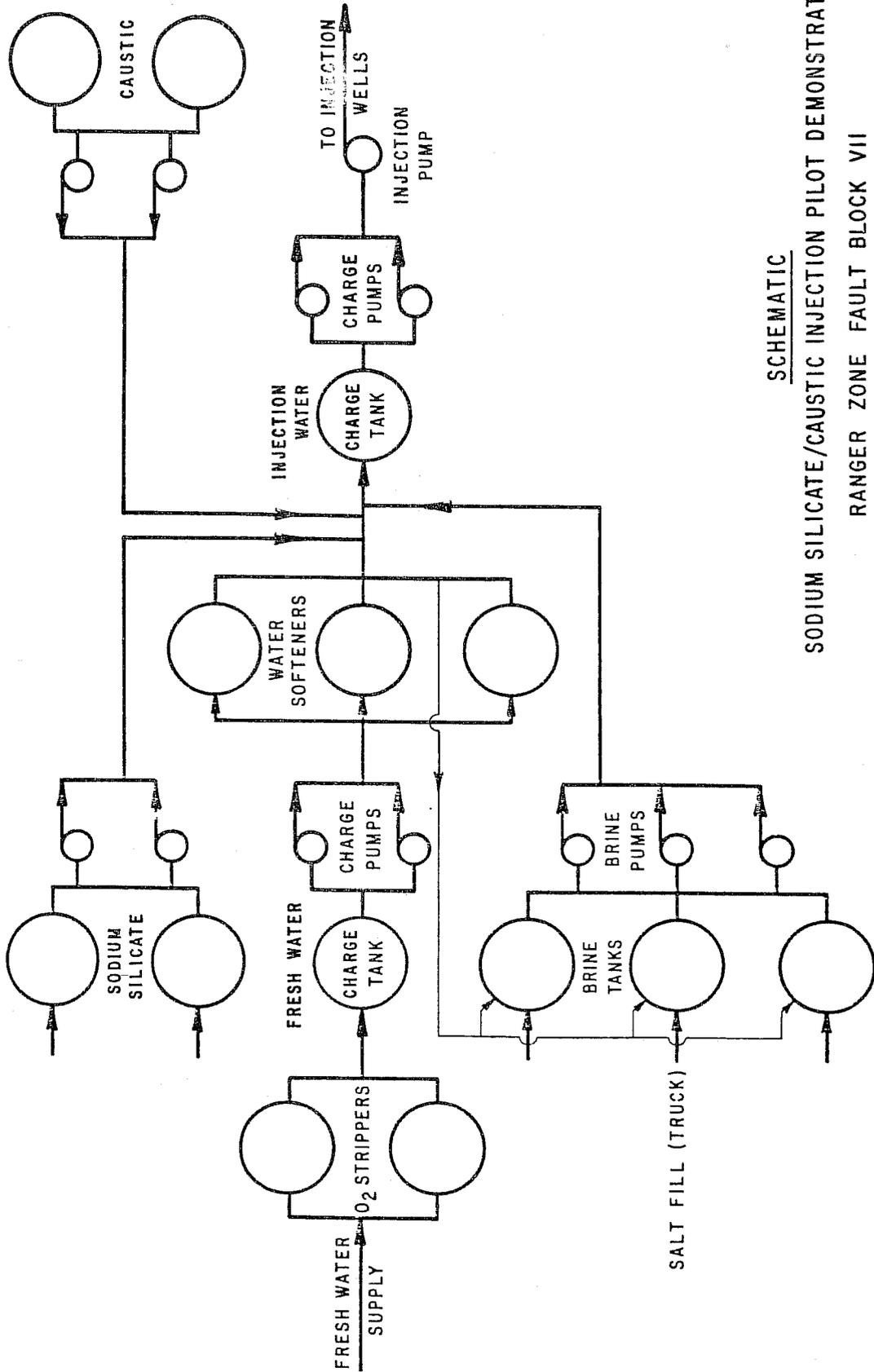
FIGURE 9

COMPARISON OF PREDICTIONS
PATTERN AREA



O O O BASE CASE WATERFLOOD
 x x x CAUSTIC FLOOD CASE I
 — CAUSTIC FLOOD CASE II

FIGURE 10



SCHEMATIC

SODIUM SILICATE/CAUSTIC INJECTION PILOT DEMONSTRATION

RANGER ZONE FAULT BLOCK VII

LONG BEACH UNIT

FIGURE 11

PRODUCTION DATA
RANGER ECONOMIC BLOCK 9

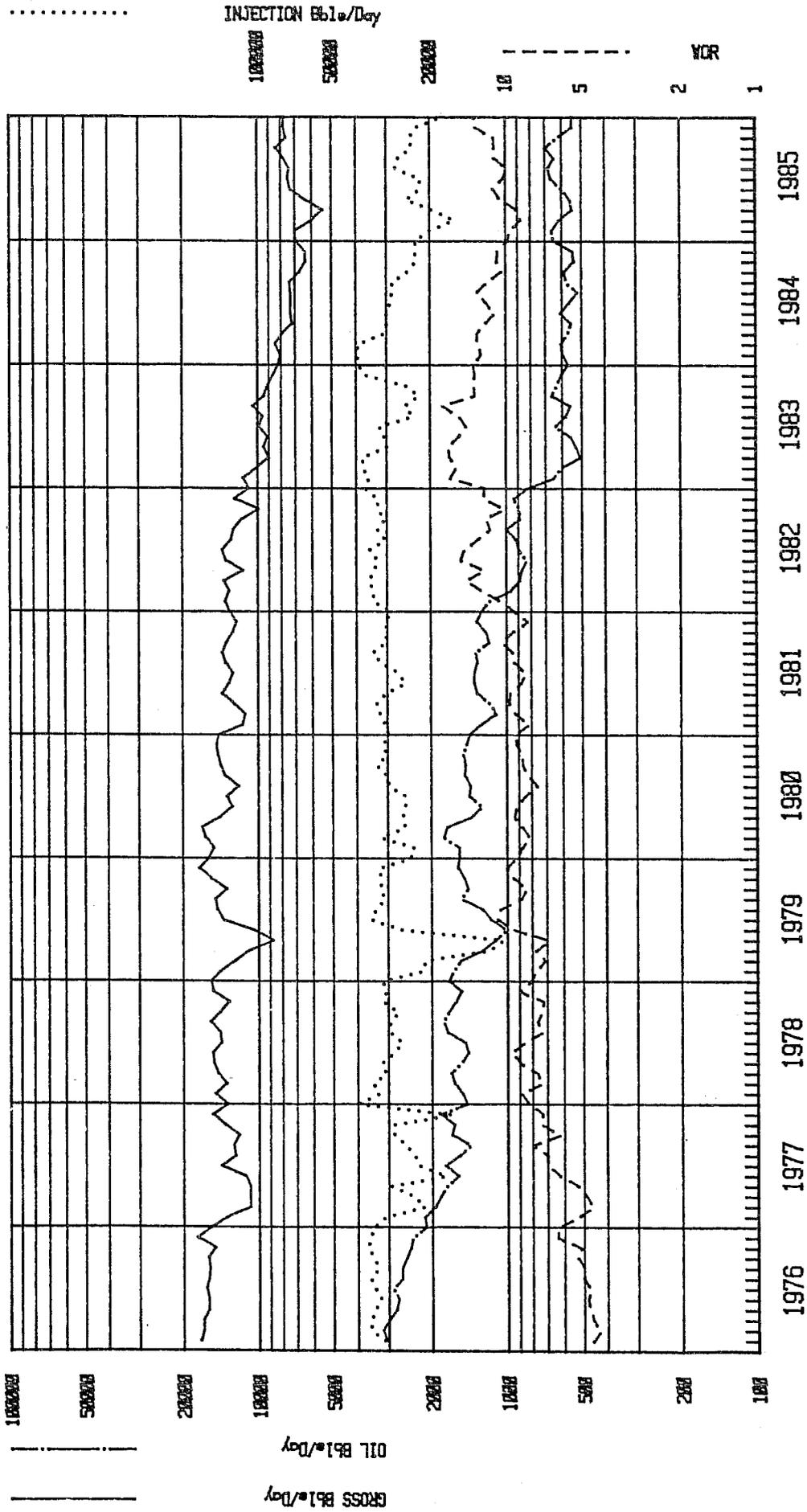


FIGURE 12

OIL CUT vs CUMULATIVE OIL (Since 1/1/76)
RANGER ECONOMIC BLOCK 9

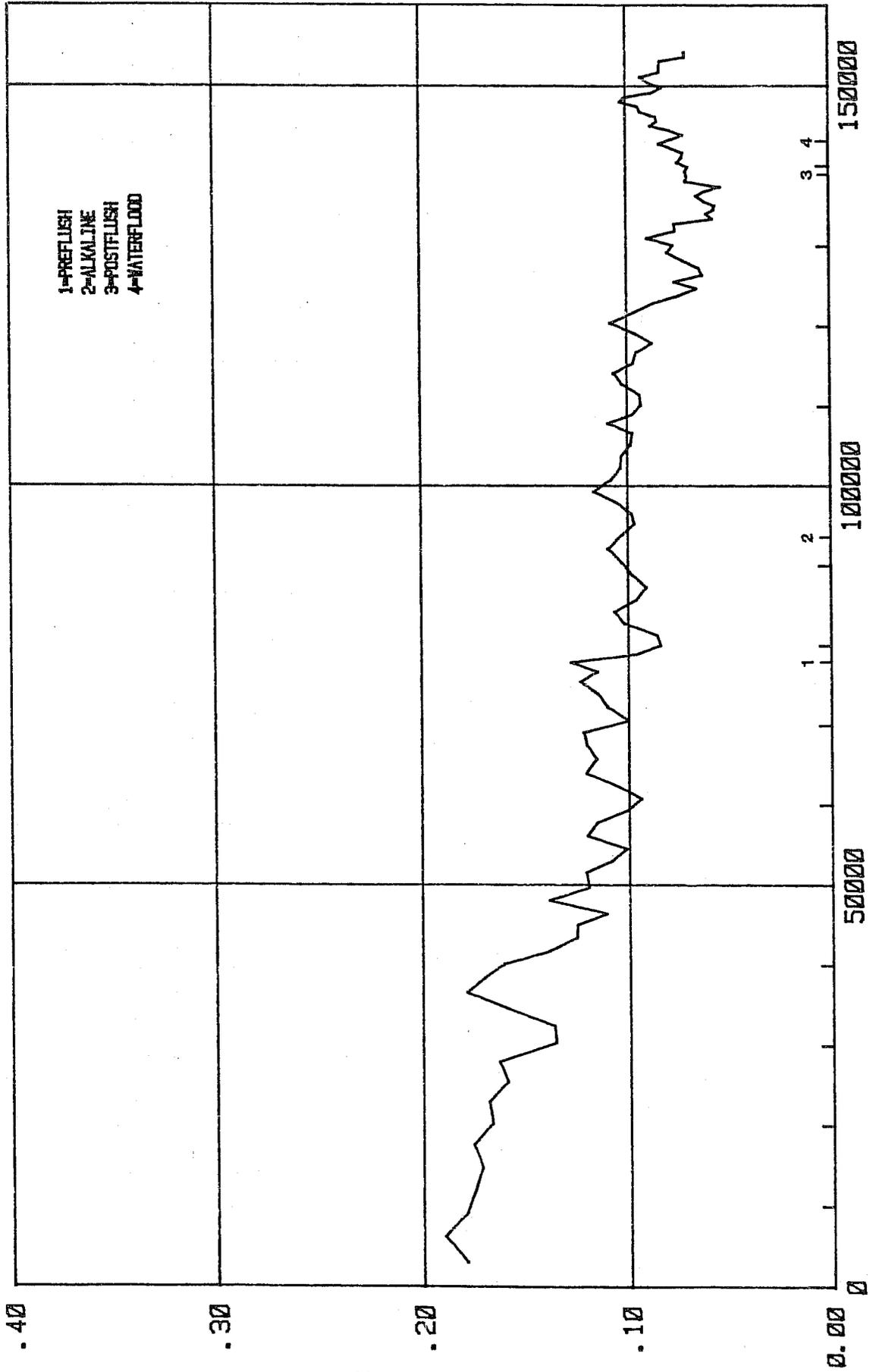


FIGURE 13

PRODUCTION DATA NORTHERN AREA

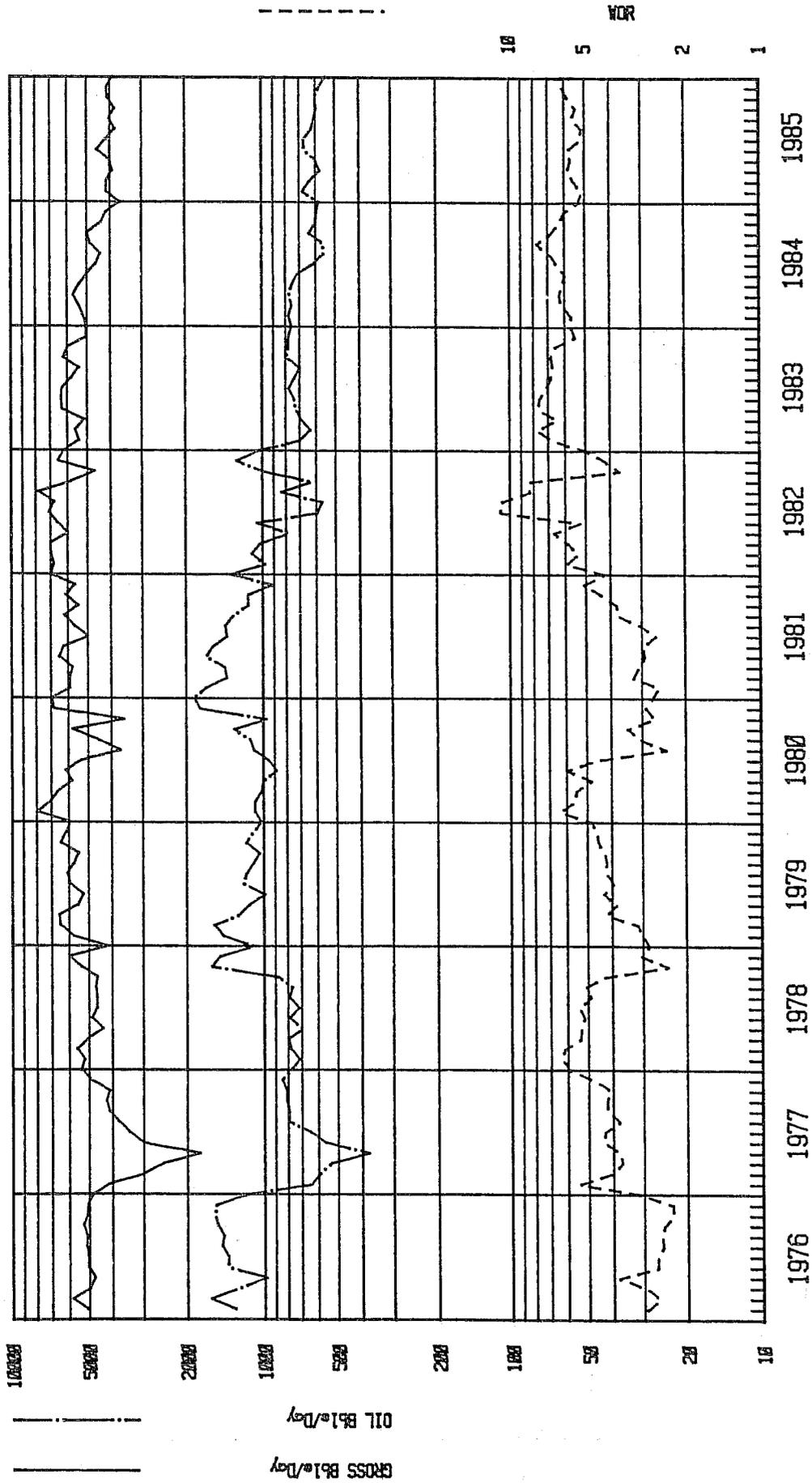


FIGURE 14

OIL CUT vs CUMULATIVE OIL (Since 1/1/76)
NORTHERN AREA

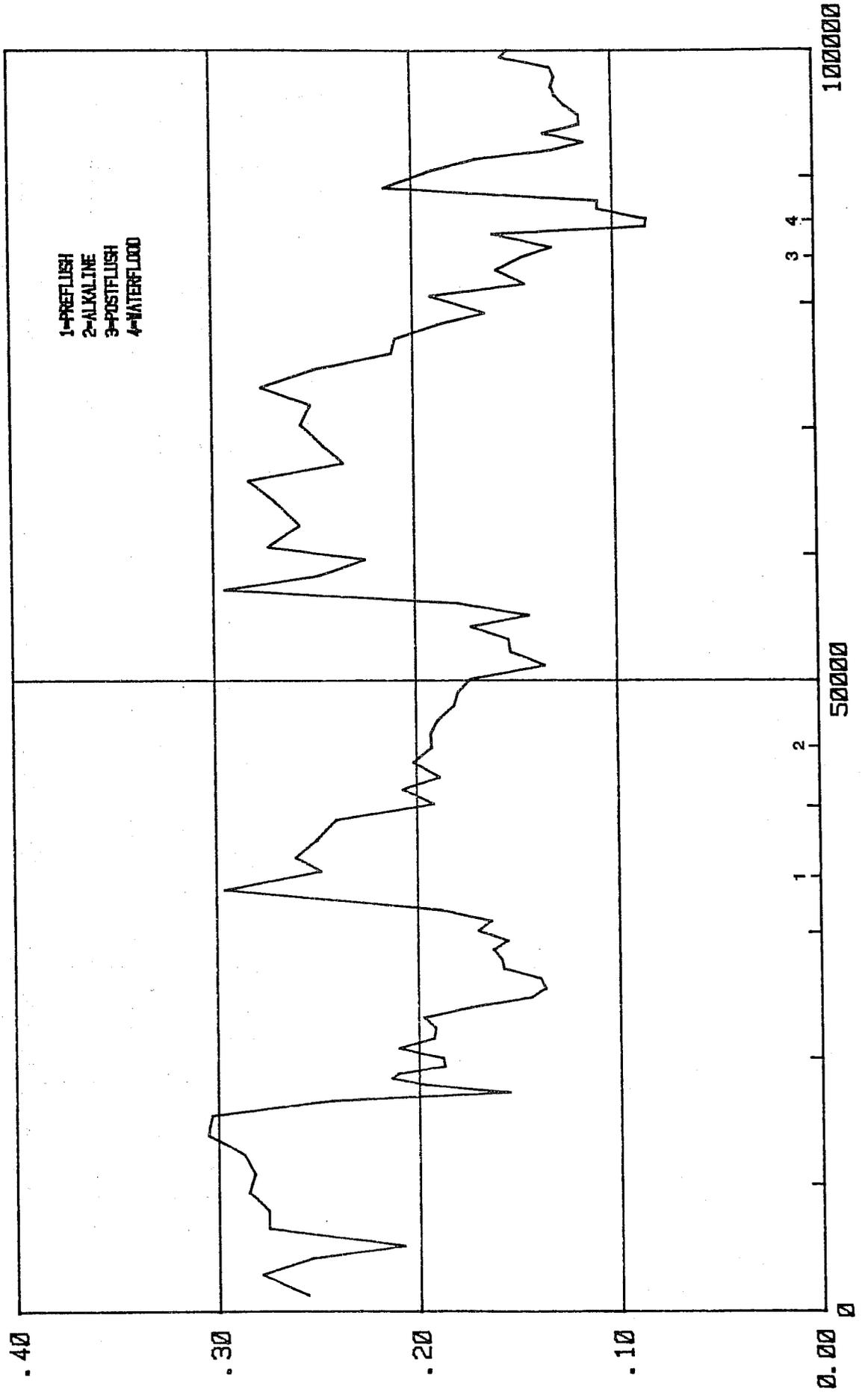


FIGURE 15

PRODUCTION DATA
SOUTHERN AREA

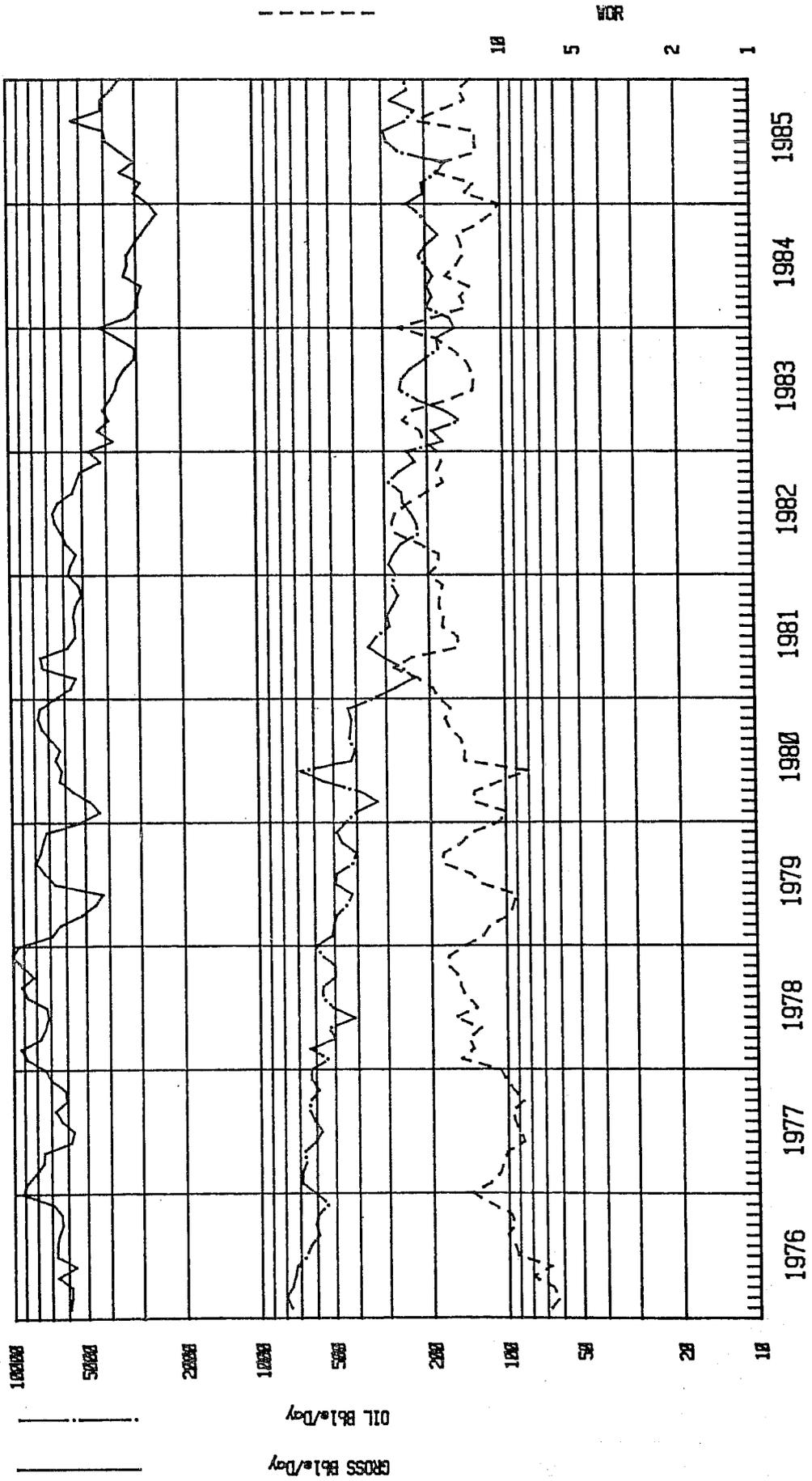


FIGURE 16

OIL CUT vs CUMULATIVE OIL (Since 1/1/76)
SOUTHERN AREA

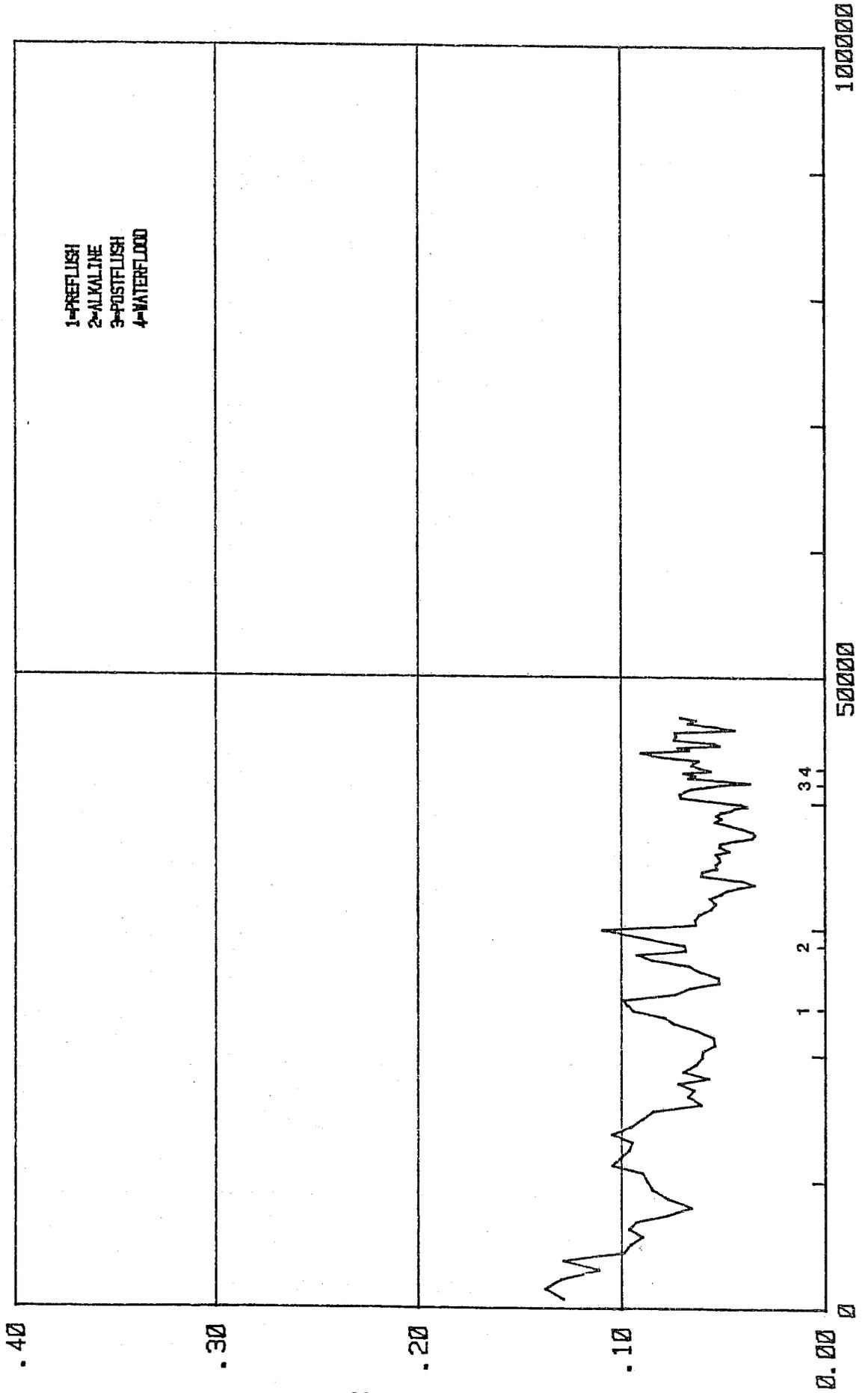


FIGURE 17

PRODUCED WATER TESTS
WELL B-834A RANGER ECONOMIC BLOCK 9

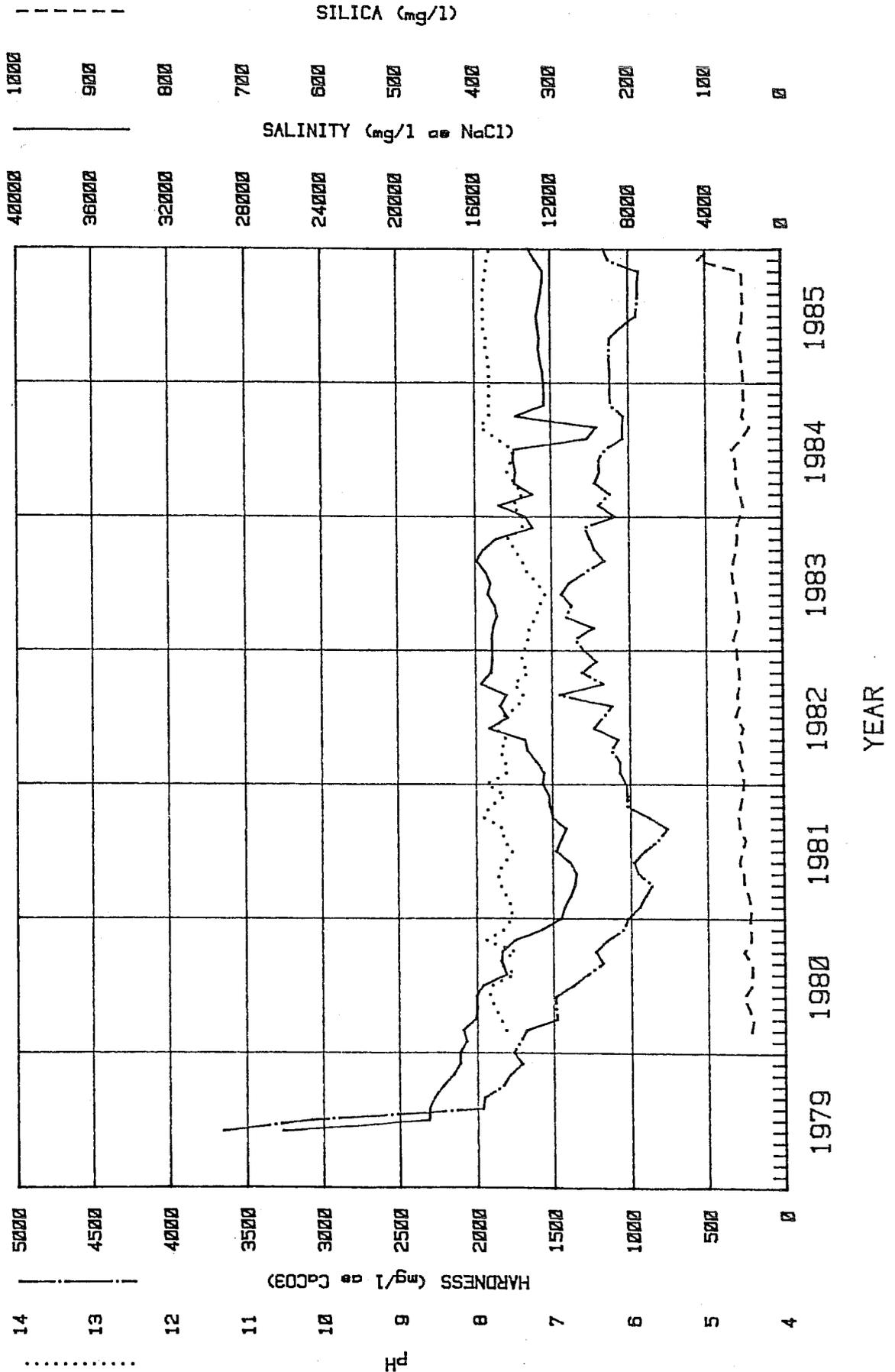


FIGURE 18

PRODUCED WATER TESTS
WELL B-105 NORTHERN AREA

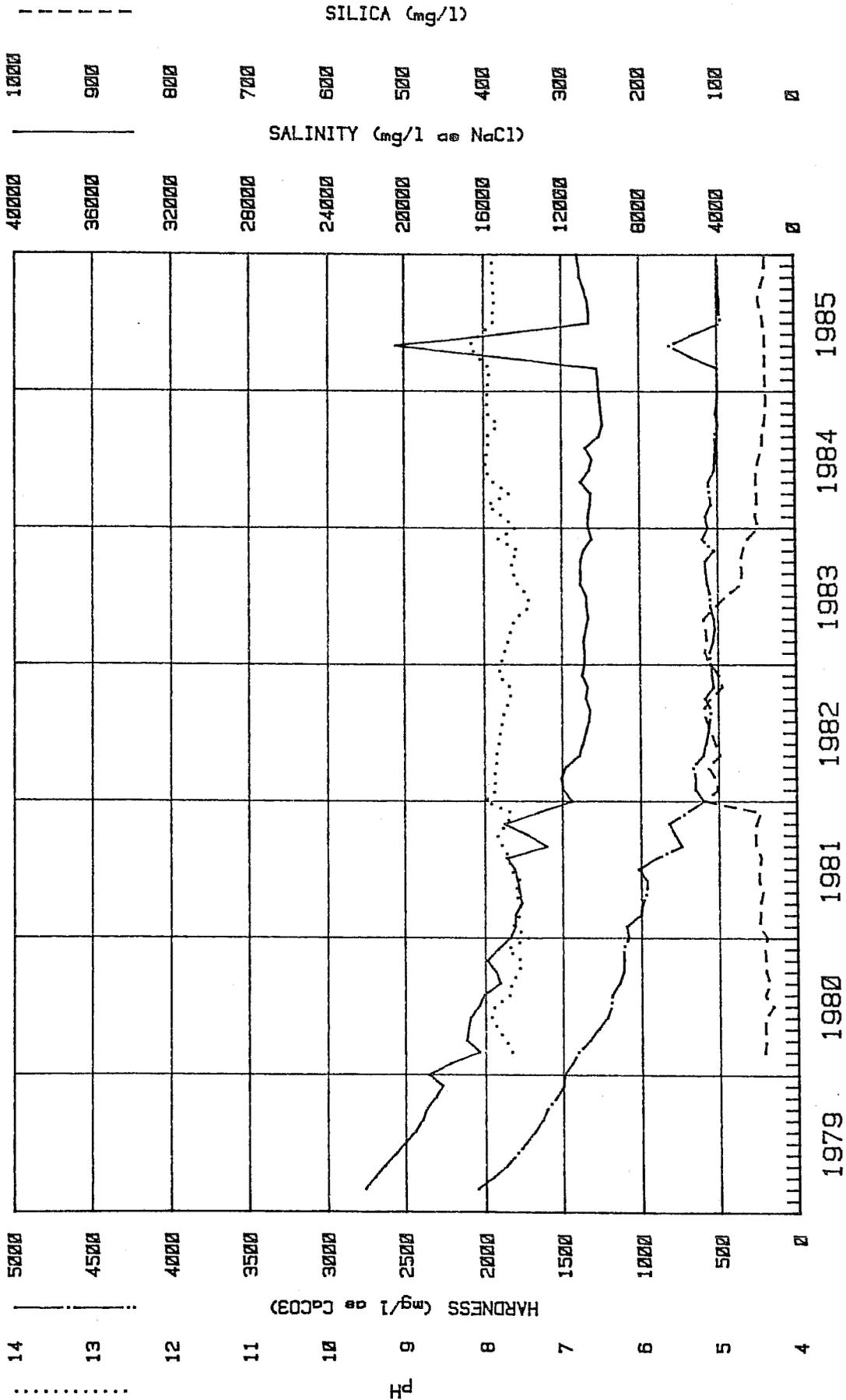
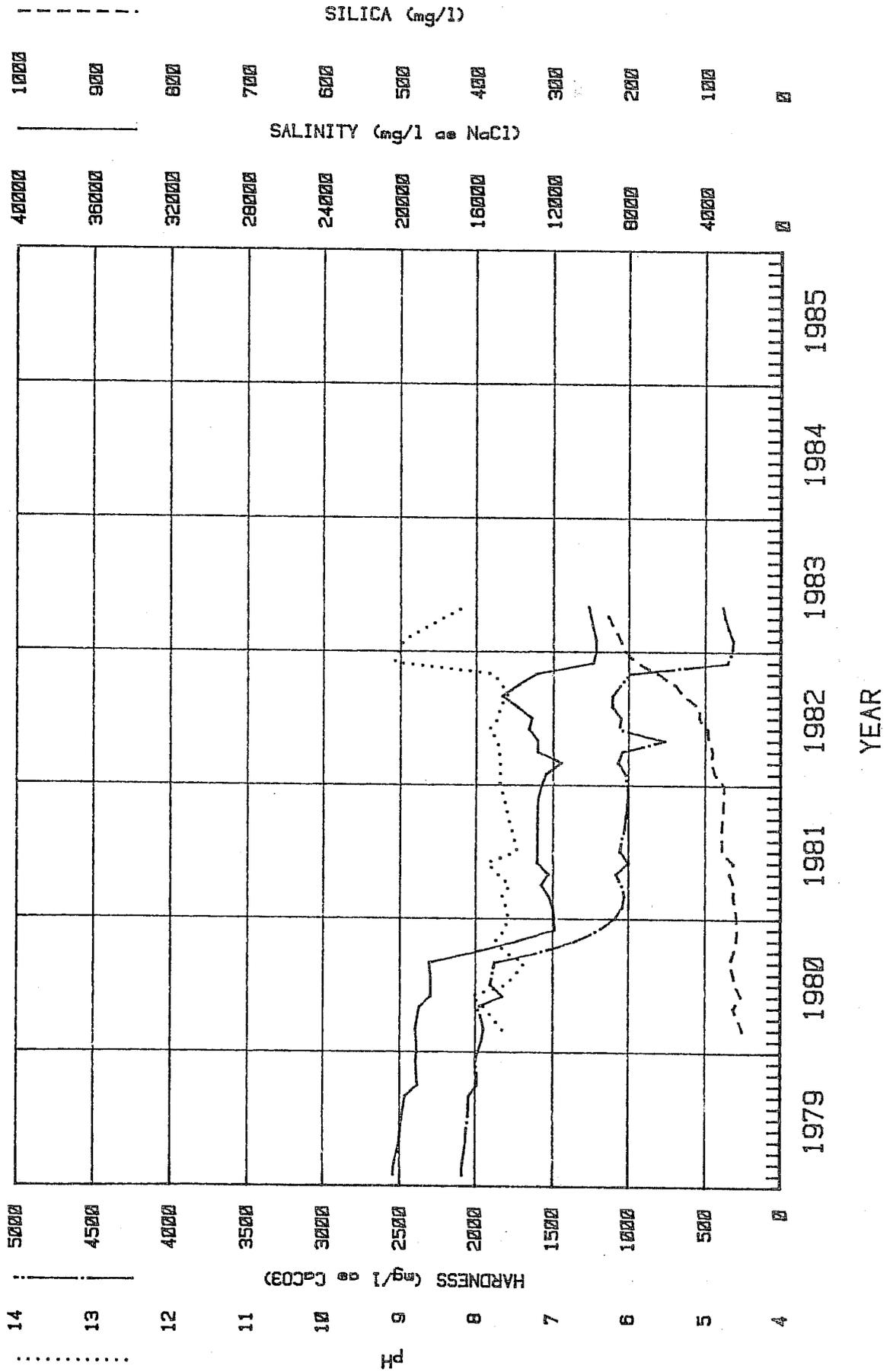


FIGURE 19

PRODUCED WATER TESTS
WELL B-712 RANGER ECONOMIC BLOCK 9



SPINNING DROP
INTERFACIAL TENSION VALUES
FOR C-331 CRUDE OIL (32cp)
VS

SODIUM HYDROXIDE AND SODIUM ORTHOSILICATE
IN SOFTENED WATER WITH 1% Na Cl

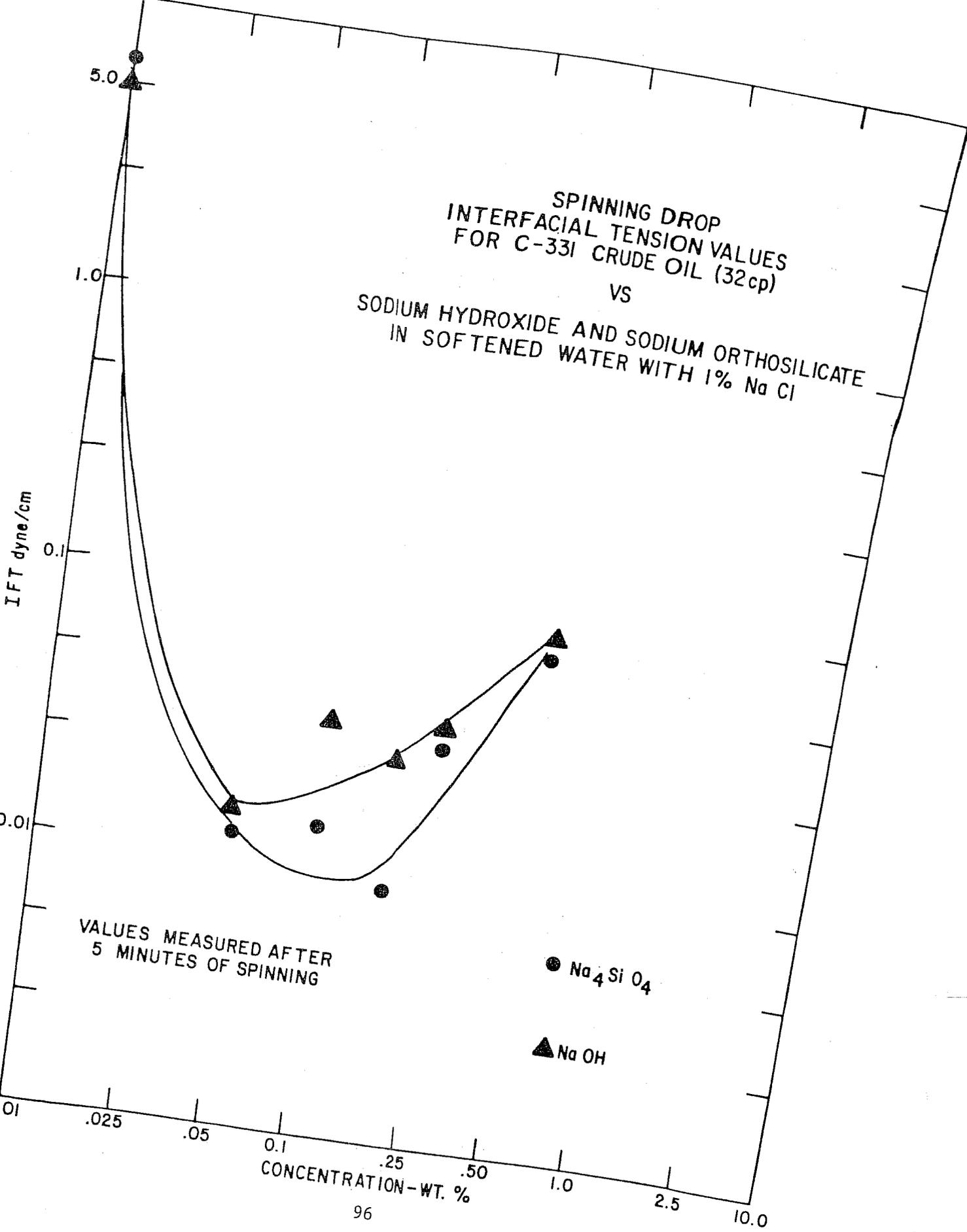


FIGURE 21

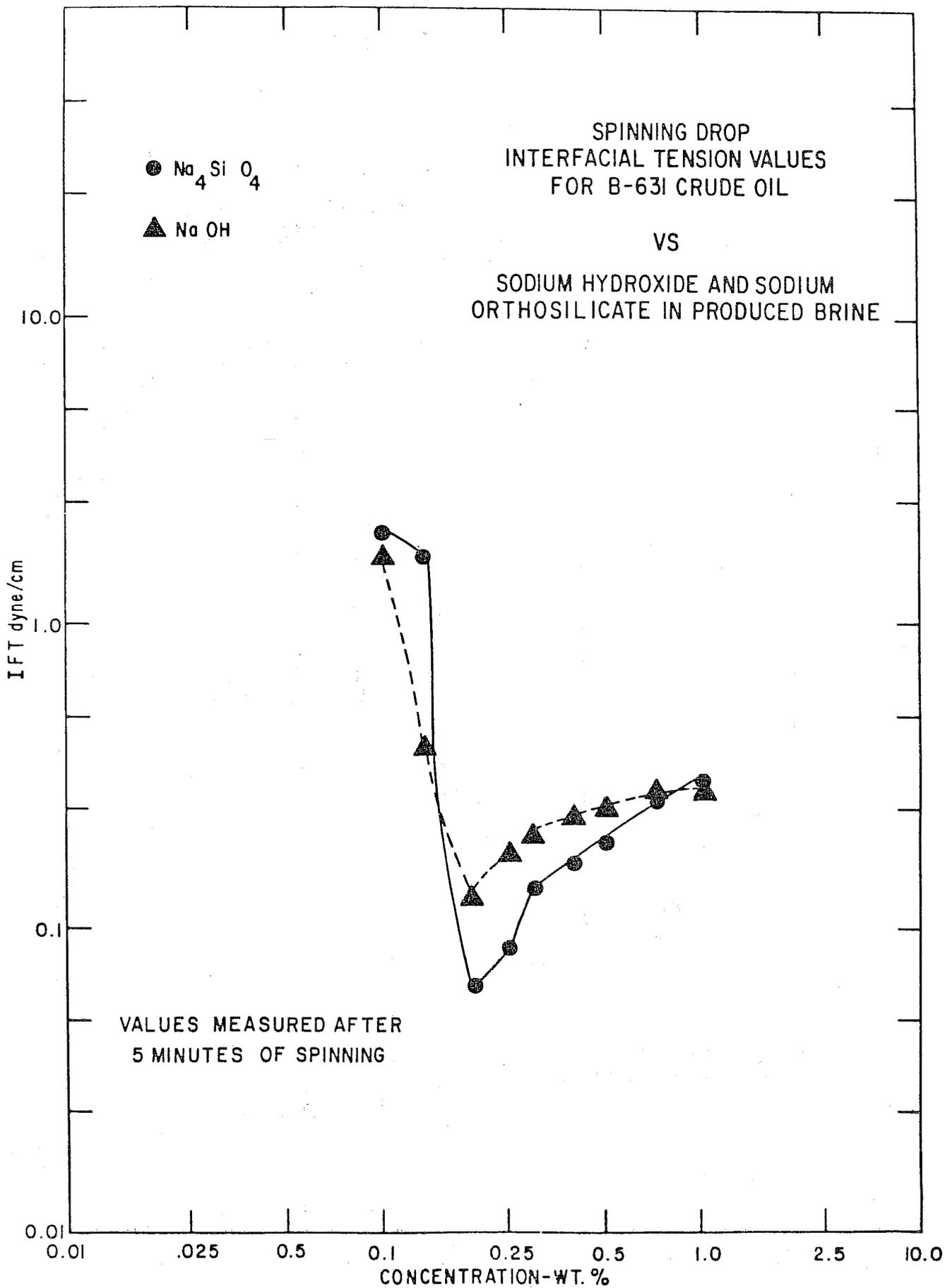


FIGURE 22

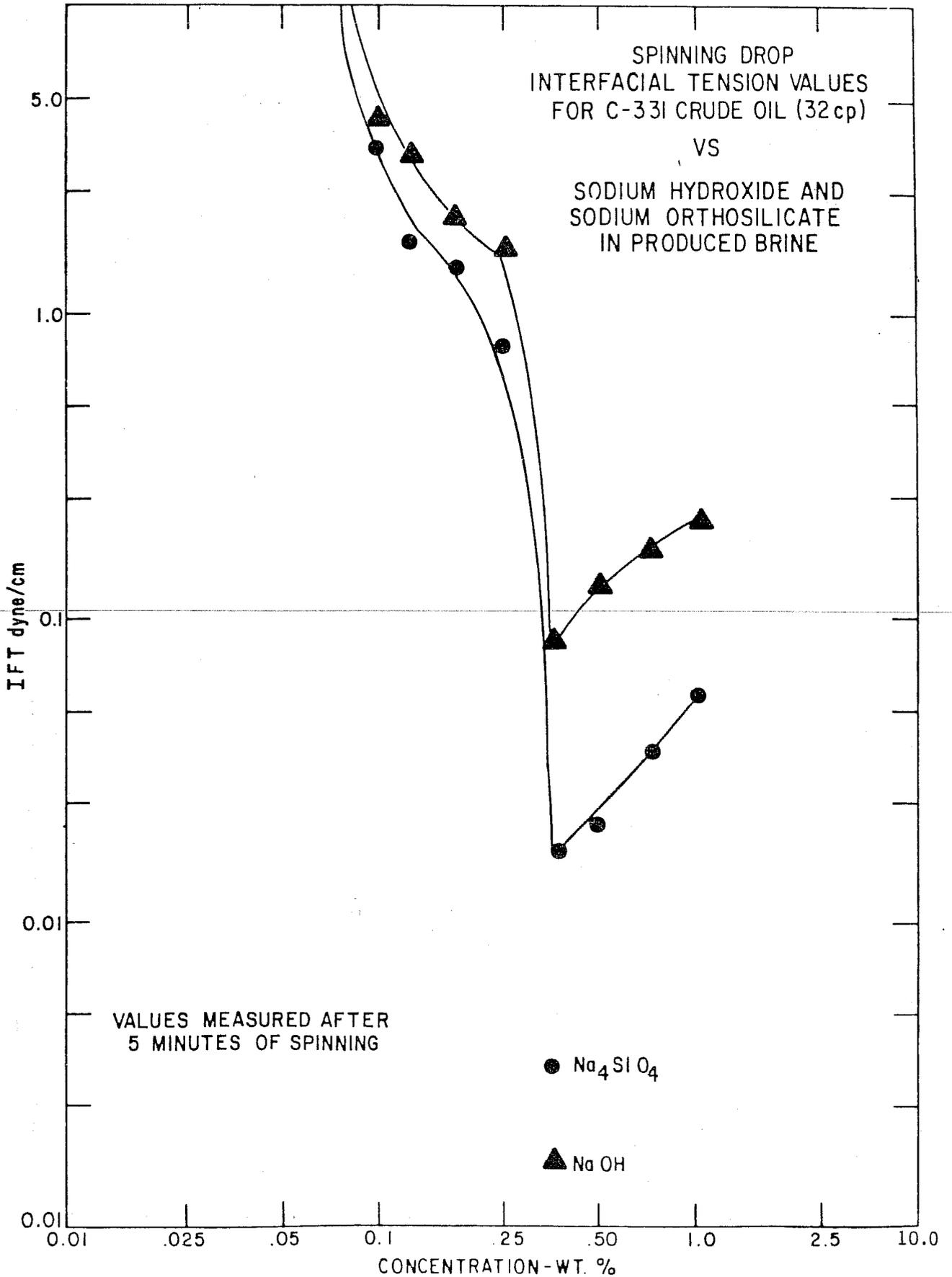


FIGURE 23

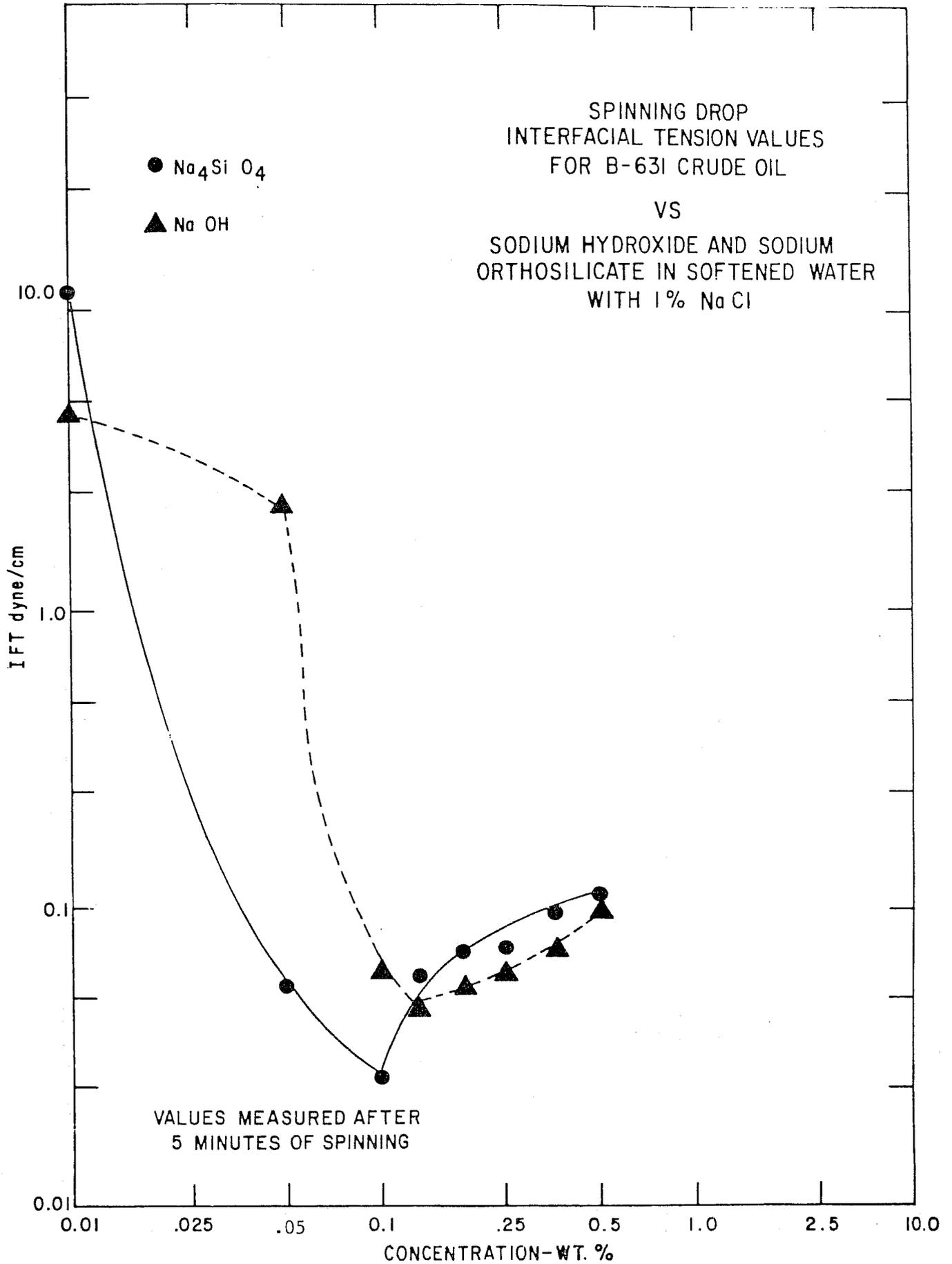


FIGURE 24

PRODUCED WATER TESTS WELL B-711 SOUTHERN AREA

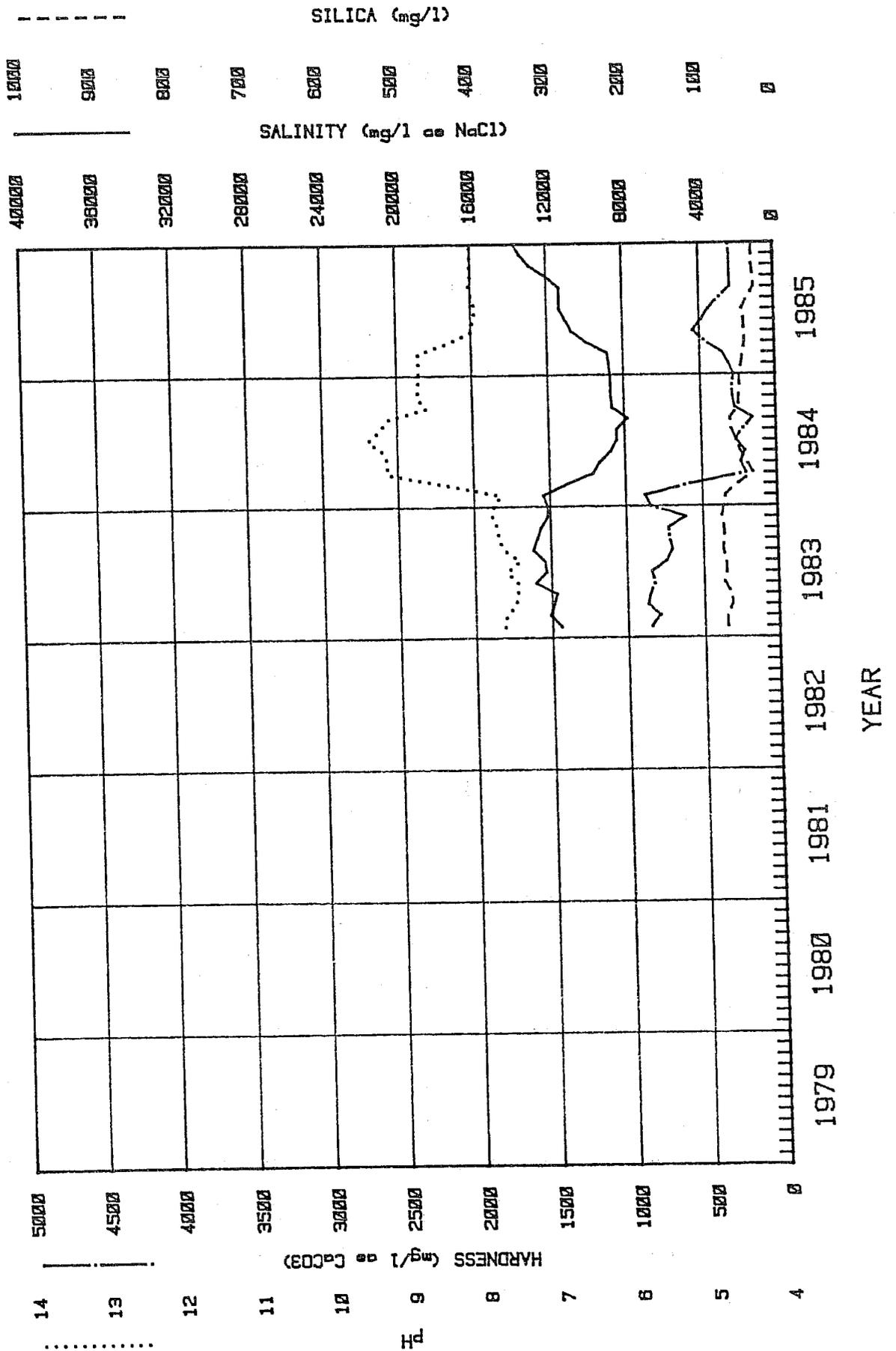


FIGURE 25

PRODUCED WATER TESTS
WELL B-112 RANGER ECONOMIC BLOCK 9

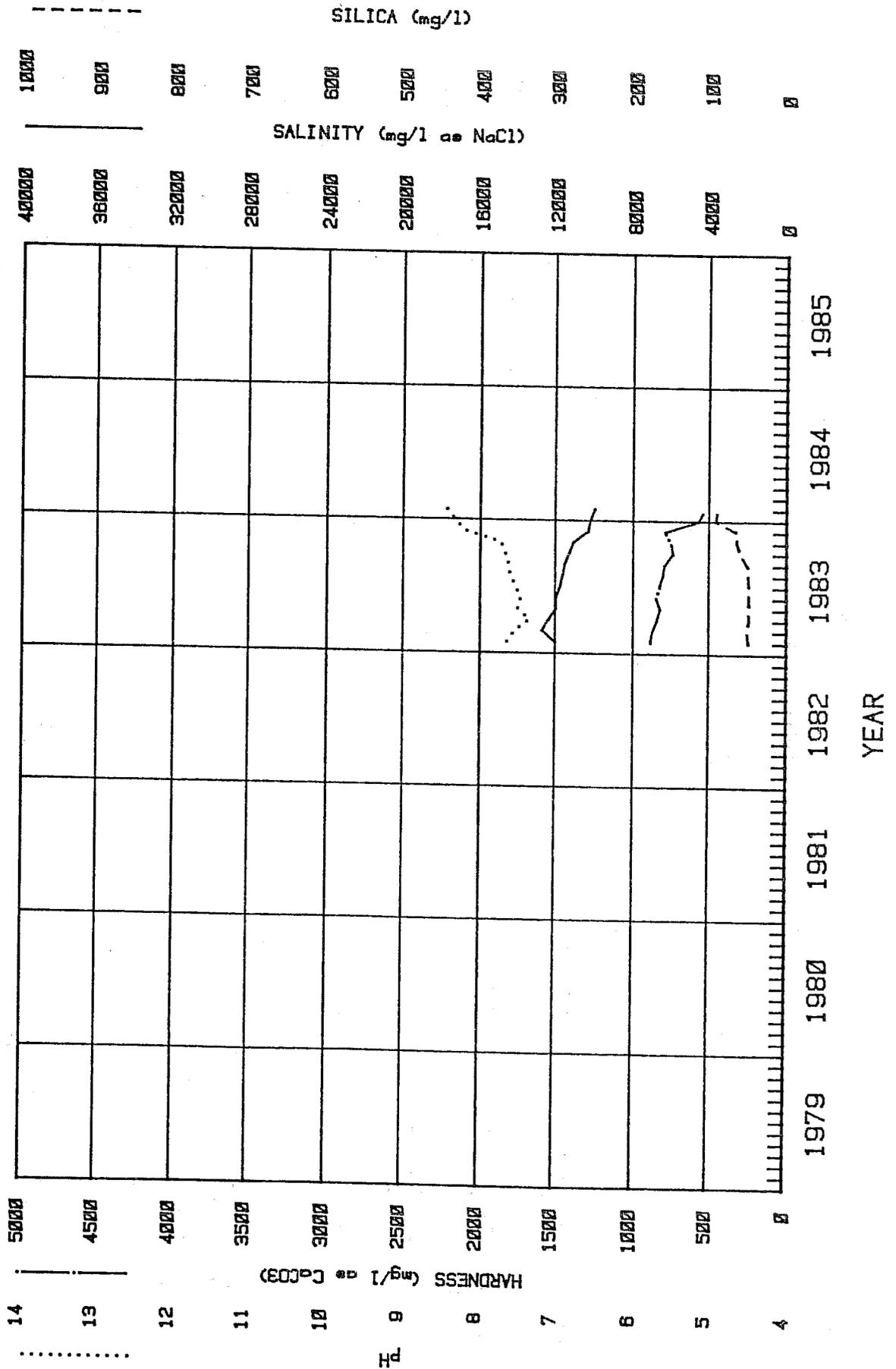


FIGURE 26

UNSTEADY-STATE WATER-OIL RELATIVE PERMEABILITY TEST RESULTS
ALKALINE WATERFLOODING DEMONSTRATION PROJECT
RANGER ZONE, LONG BEACH UNIT
WILMINGTON FIELD, CALIFORNIA

WELL B-110

Core Number 51B Oil Permeability @ 21.8% Swi = 175 md Porosity = 22.2%

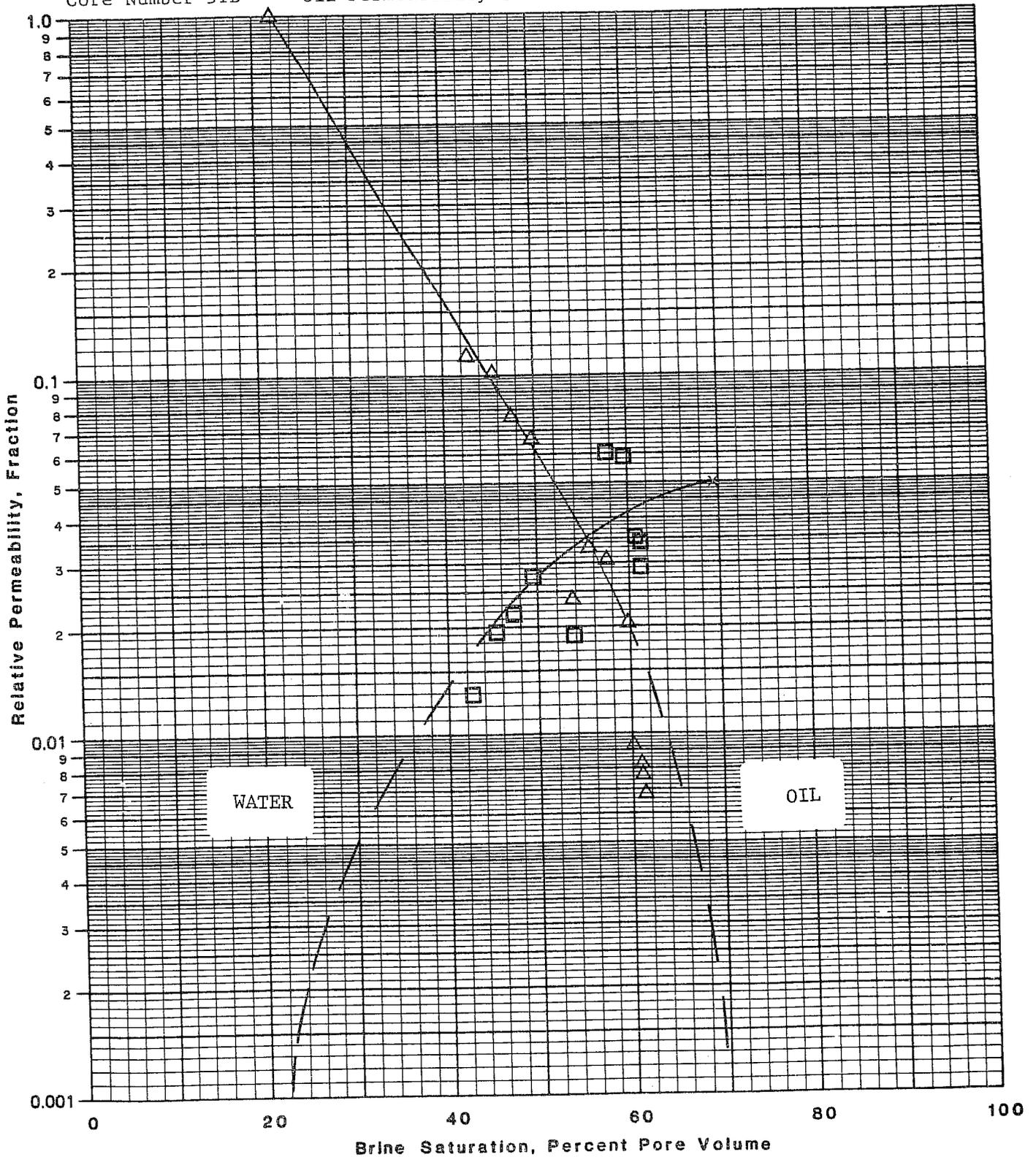
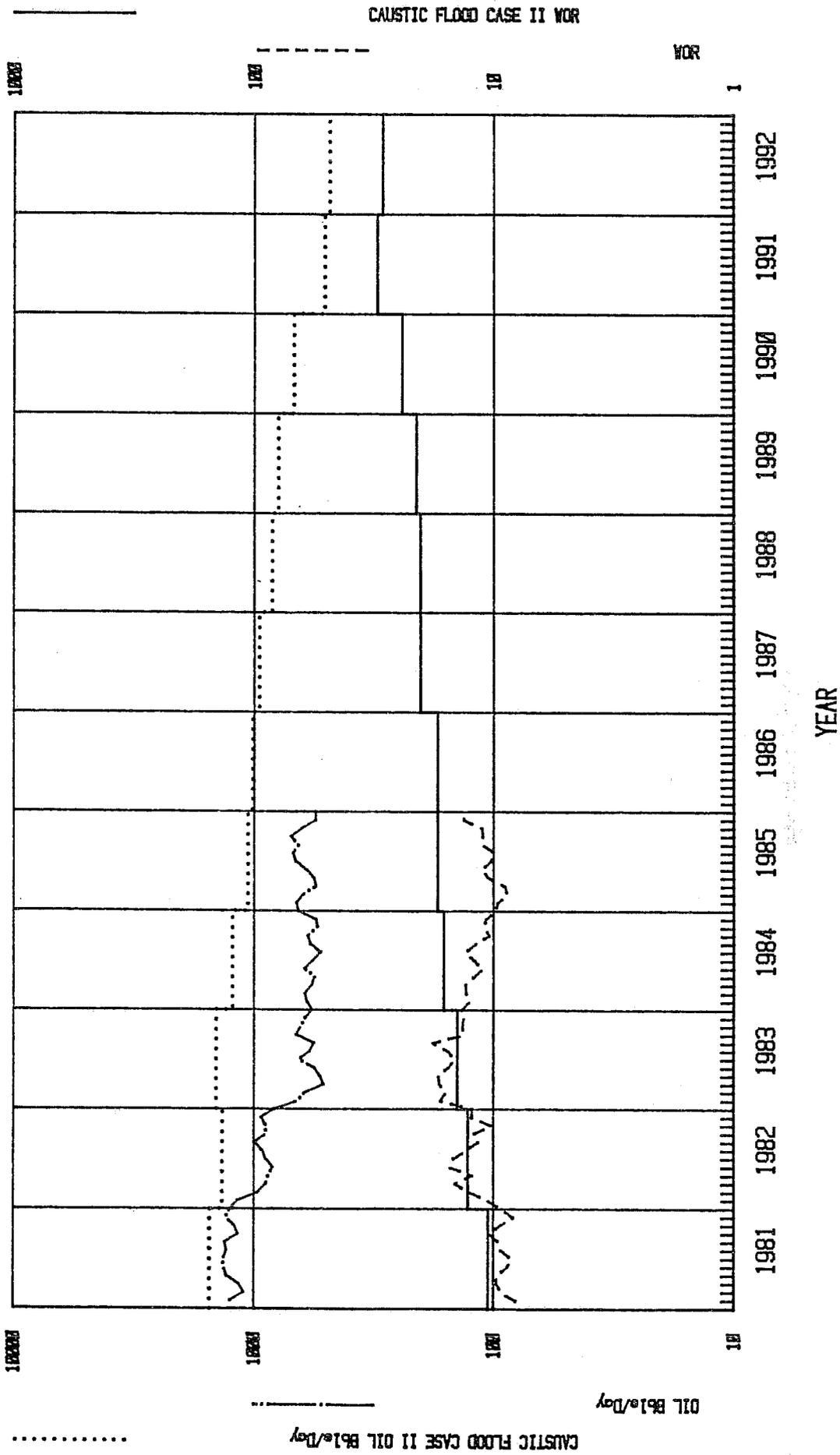


FIGURE 27

COMPARISON OF ACTUAL with PREDICTIONS
RANGER ECONOMIC BLOCK 9



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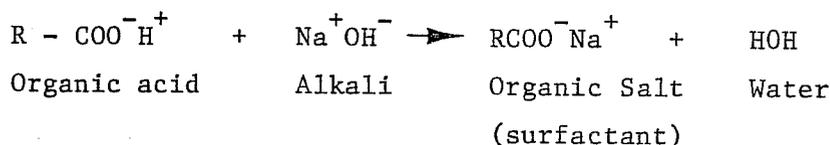
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APPENDIX I
STATE-OF-THE-ART IN ALKALINE FLOODING

INTRODUCTION

The concept of alkaline waterflooding to enhance the recovery of oil from a reservoir was proposed as early as 1917. At that time, F. Squires¹ proposed that the recovery of oil could be enhanced with the addition of alkali to the injection water. Since that time, a considerable amount of research has been directed towards improving oil recovery by the alkaline waterflood process. This discussion provides a review of this EOR process.

Alkali enhances oil recovery due to the reaction of alkali with reservoir oil. A general reaction of alkali with reservoir oil is given by:



The result of this reaction is the formation of a petroleum soap or surfactant, which emulsifies oil and water and aids in the recovery of oil.

The purpose of this appendix is to discuss, in general terms, the state-of-the-art of alkaline flooding. The proposed mechanisms of oil displacement by alkaline waterflooding and the interaction or reaction of alkali with reservoir rock, oil, and brine are outlined.

MECHANISM OF ALKALINE RECOVERY

There are several proposed mechanisms for the recovery of oil by alkaline waterflooding. The most significant recovery mechanism has not been clearly established. During the alkaline flood, each of these

mechanisms or a combination of these mechanisms may be responsible for improving oil recovery. These mechanisms are 1) lowering of interfacial tension, 2) wettability reversal, 3) emulsification and entrainment, 4) emulsification and entrapment, and 5) emulsification and coalescence. A brief description of each mechanism is described below.

Interfacial Tension and Capillary Number

Taber³ and others have reported an increase in oil recovery when the water-oil interfacial tension (IFT) during a coreflood is lowered. Taber described the "critical displacement ratio" necessary to mobilize residual oil as a ratio defined by the equation $\frac{\Delta P}{\sigma L}$, where ΔP is the

pressure drop across the length, L , and σ is the interfacial tension between wetting and non-wetting phases (such as water and oil).

Stegemeir⁴ included a relative permeability term, k_r , into the capillary number definition which resulted in a dimensionless number defined by $\frac{v \mu}{k_r \sigma}$

where v is the velocity term, μ is the viscosity, and σ is the interfacial tension. Chatzis and Morrow² included the specific permeability to water or air, k_w or k_a to define the capillary number as $\frac{k_w \Delta P}{L \sigma}$ or $\frac{k_a \Delta P}{L \sigma}$. Many capillary number relationships have appeared in

the literature to define the ratio of viscous to capillary forces. Most of these relationships include the interfacial tension term.

Taber³ demonstrated that changing the pressure drop across the length, L , resulted in a change of capillary number and, therefore, a change in residual oil saturation. However, when the pressure drop required to mobilize residual oil in laboratory corefloods was scaled to field rates, the pressure was unreasonable. Since the length, L , of the system is not a variable in the field, Taber adjusted the interfacial tension in order to improve oil recovery. Typically, the interfacial tension between the wetting and non-wetting phases must be lowered by several orders of magnitude to achieve a substantial reduction in residual oil.

The alkaline waterflood process, when properly designed, is capable of lowering the interfacial tension between oil and water by several orders of magnitude. Although the reduction of interfacial tension may be transient²⁸, increased oil recovery is still feasible. In addition to increasing the capillary number, lowering the water-oil interfacial tension aids in the formation of emulsions. These emulsions are an integral part of other proposed recovery mechanisms discussed in this appendix.

Wettability Reversal: Wettability reversal has been proposed as a mechanism in alkaline flooding by several researchers. The reversal of rock wettability from an oil-wet to a water-wet condition has been proposed by Wagner and Leach⁵, Leach, et al.⁶, Mungan⁷, and Erlich, et al.⁸ The reversal of rock wettability from a water-wet to an oil-wet nature under certain conditions was proposed by Cooke, et al.⁹ The resulting changes in relative permeability by wettability reversal and changes in oil-water interfacial tension contribute, in part, to these recovery mechanisms.

One cause of wettability reversal suggested by Castor, et al.¹⁰ was the migration of the surface active agents from solution to the rock surface where they adsorb and alter rock wettability. Nelson, et al.¹¹, proposed that wettability reversal during alkaline flooding was related to the optimum salinity requirement of the surfactant system. They proposed that a wettability change from a water-wet to an oil-wet condition was due to over-optimum salinity and a change from an oil-wet to a water-wet condition was due to an under optimum salinity. Although the mechanisms of wettability reversal have not been clearly elucidated, there is a significant quantity of laboratory data that indicates that wettability reversal does occur during alkaline flooding. The changes in wettability result in a reorientation of the oil and water phases within the reservoir which improves waterflood efficiency. This can be better understood by considering the change in rock wettability from an oil-wet to a water-wet condition. As the wettability change occurs, the relative permeability to water decreases as oil on the rock surfaces is replaced by water. This results in mobilization of the oil and the improvement of waterflood recovery.

Emulsification and Entrainment

The process of emulsification and entrainment was first proposed by Subkow.¹² The process results from the formation of a stable oil-in-water emulsion and the entrainment of the emulsion into the flowing alkaline solution. The oil is eventually produced as the alkaline flood continues through the reservoir. An important aspect to the emulsification step is the formation of an oil-in-water emulsion having the capability of being mobilized by the alkaline flood. In order to improve the emulsification step, the salinity of the alkaline solution is adjusted to obtain an optimum salinity. This results in an emulsion with smaller droplets and a lower surface tension which aids in its propagation through the reservoir. A reduced water-oil interfacial tension is required to initiate this emulsification step as discussed earlier. Using the emulsification and entrainment process, the residual oil saturation in laboratory core tests has been reduced to levels well below that achieved by conventional waterflooding.

Emulsification and Entrapment

A third mechanism of alkaline flooding proposed by Jennings, et al.¹³, is called the emulsification and entrapment process. This process results in the emulsification of oil, as in the emulsification and entrainment process; however, the emulsion droplets are large and have a higher surface tension. This is due to the absence of salinity i.e., an under-optimum salinity condition. The emulsion droplets are larger than the pore throats of the reservoir rock and behave much like hard spheres as they become lodged in the pores of the rock. This results in an improvement of waterflood sweep efficiency as flow is diverted to more permeable areas within the reservoir and an improvement in oil recovery.

Emulsification and Coalescence

Emulsification and coalescence has been proposed as a fourth mechanism of oil recovery by alkaline flooding.¹⁰ This process is very similar to emulsification and entrainment which results in the mobilization of an

emulsion. However, the coalescence mechanism includes the formation of an unstable water-in-oil emulsion followed by a coalescence step. During coalescence, the emulsions begin to break and form oil droplets or areas of high oil saturation. As this process continues, additional droplets are formed and eventually an oil bank is formed. It has been shown that the formation of an oil bank eventually results in higher oil recovery as the oil bank accumulates additional residual oil.

In order for the coalescence process to work as an alkaline flooding mechanism, the water-in-oil emulsions produced during alkaline flooding must be unstable enough to break and allow the formation of the oil droplets. In addition, the emulsification step should be spontaneous. This requires the optimization of the phase behavior of alkali produced surfactants in a manner similar to the way the phase behavior of oil-brine-surfactant systems is optimized for surfactant flooding projects.

FACTORS AFFECTING ALKALINE WATERFLOODING

During an alkaline waterflood, a number of factors can influence the success or failure of an alkaline waterflood. These include the oil-water interfacial tension, the cation exchange capacity and the presence of divalent and multivalent cations, the presence of minerals within the reservoir rock which have the ability to consume large quantities of alkali, and unfavorable mobility of the injected alkaline solutions. The effects of each of these factors is described below.

Interfacial Tension

The reduction of interfacial tension at the crude oil-water interface is due to the presence of surface active agents, or surfactants, generated during the alkaline flood. These surfactants are the products of a reaction between acidic components within the crude oil and the alkali in the flooding solution. Work performed by Jennings¹⁴ indicated that crude oils with acid numbers higher than 0.5 mg of KOH contain a sufficient quantity of acidic components to produce surfactants which,

in turn, reduced interfacial tension. The acid number is a measure of the acidity of crude oils and reflects the amount of potassium hydroxide necessary to neutralize one gram of oil. Therefore, the reservoir crude oil must have a sufficient quantity of acidic components to generate surfactants and reduce interfacial tension before an alkaline flood can be considered as a viable process.

The enhancement of oil recovery by alkaline flooding has been shown to be related to the interfacial tension. In order to lower interfacial tension to the lowest values, the salinity of the flooding solution and the concentrations of the alkali must often be adjusted. Several authors^{9,10,11,15} have shown the necessity of adjusting the concentration of salts in the flooding solution to achieve optimum salinity. Trujillo¹⁶ demonstrated the dependence of interfacial tension on alkali concentration. Generally, the optimum salinity and alkali concentration necessary to achieve the lowest interfacial tension is unique for each reservoir crude oil.

Once the surfactants are generated by the reaction of alkali and reservoir crude oil and the interfacial tension is reduced, the surfactants may react with divalent and multivalent cations (such as calcium, magnesium, and aluminum) to form precipitates such as oil soluble calcium soaps. This reaction reduces the concentration of the surfactant available to lower the interfacial tension, and the interfacial tension increases to high levels. Jennings, et al.¹³, demonstrated that for one of the crude oils tested, the addition of less than 25 ppm of calcium increased the interfacial tension by an order of magnitude. Several authors^{9,13,14,16,28} have discussed the effects of calcium on interfacial tension and demonstrate the harmful effects of water hardness on alkaline waterflood.

Cation Exchange Capacity

One method of reducing the level of harmful cations, such as calcium, is to flush the reservoir with a low hardness brine before chemical injection. This preflush, in theory, sweeps the reservoir of calcium

ions and replaces them with the low hardness preflush solution. It is during this process that cation exchange capacity begins to become a significant factor. The removal of calcium from the reservoir is hindered by the attraction of calcium to the reservoir rock.^{20,21} The cation exchange capacity is an indicator of the amount of calcium and other cations that will be adsorbed onto the surface of the reservoir rock. During the chemical flood, changes in the ionic strength of the injected fluids and the in-place reservoir fluids will initiate an exchange process. This exchange process results in the release of calcium back into solution and allows it to react with alkali or surfactants. The results of this exchange process is the deterioration of the alkaline slug.

Another cation exchange process that can effect an alkaline flood is the exchange of hydrogen and sodium. This reversible process allows the release of hydrogen during the alkaline flood. The free hydrogen reacts with hydroxide ions to produce the neutral water molecule. As the alkaline slug passes, the hydrogen and sodium exchange process is reversed and sodium is released back into solution. The net result of this process is the delay of the alkaline front as it passes through the reservoir and a lowering of the pH as the flood front broadens and becomes diluted. This type of exchange, known as hydrogen exchange capacity, was investigated by Bunge and Radke¹⁸ and by Novosad and Novosad.¹⁹ Since the movement of caustic through the reservoir controls the rate of oil production during the alkaline flood, complete information concerning cation exchange is desirable. Laboratory investigations have shown that as the pH of the flooding solution is increased, the delay of alkaline breakthrough due to ion exchange is decreased. This suggests that the alkaline slug design must consider ion exchange as well as optimum interfacial tension.

Chemical Losses by Alkali/Rock and Alkali/Brine Interaction

The reaction of alkali with reservoir rock is considered to be the most significant factor in alkali consumption. A number of studies of alkali consumption have been published.^{13,22-27} Interest has been

focused on the amount of consumption attributable to reservoir rock, and the rate at which the alkali/rock reactions occur. Studies have shown that the reaction of alkali with reservoir rock is a complex process that depends on the composition of the rock and the composition of the alkali used for flooding.

The degree of consumption depends on the temperature, concentration and type of alkali, the surface area of the rock, and the chemical composition or mineralogy of the rock. Generally, clay minerals have been shown to have a high degree of consumption due to composition and high surface area. High consumption due to the presence of gypsum has also been noted due to the formation of calcium hydroxide precipitate. Quartz shows one of the lowest degrees of consumption for a given time period. Therefore, knowledge of the mineralogy of the reservoir rock should give clues as to the amount of caustic consumption over a given time period.

The reaction rate is another factor in increasing alkali consumption. A chemical reaction rate is a measure of the amount of alkali chemical that reacts with reservoir rock over a given time period. For example, the reaction of kaolinite clays with alkali occurs at a faster rate than the reaction of quartz with alkali.^{24,26} The reaction rate is dependent upon reservoir temperature and on the type and concentration of the alkali. It has been shown that slow reaction rates do not appear to be significant in laboratory core flood tests, but these low reaction rates become a significant factor during long term alkaline flooding in the field. This is because the injection of alkali during field trials is a long term process which results in the consumption of an considerable amount of alkali.

Finally, chemical consumption can also occur due to the reaction of alkali with reservoir brine. If the reservoir brine contains divalent and trivalent cations, such as calcium and magnesium, the alkali will react with these cations to form insoluble precipitates such as magnesium hydroxide or magnesium silicate. Calcium can react with sodium hydroxide to precipitate calcium hydroxide, which is slightly

soluble. All of these reactions reduce the concentration of hydroxide or the level of alkalinity to an undesirable level. If the level of alkalinity is reduced, the ability to form surfactants and emulsions by the reaction of alkali with reservoir crude oil will be reduced and the alkaline flood may be unsuccessful.

ENHANCEMENT OF ALKALINE FLOODING WITH CHEMICAL ADDITIVES

As previously discussed, the success of an alkaline waterflood is dependent upon several factors. The alkali must be able to generate low interfacial tension, be resistant to low levels of hardness and higher levels of salinity, and be able to propagate efficiently through the reservoir in order to improve the recovery of oil. Using the same techniques developed for chemical flooding (surfactant/micellar), the efficiency of the alkaline flood can be significantly enhanced. These techniques include the addition of polymer for mobility control, addition of surfactants to aid in lowering interfacial tension, and the addition of cosurfactants to improve the salinity tolerance of alkali-generated surfactants.

Alkaline/Polymer Flooding

A number of reservoirs amenable to alkaline flooding produce viscous crude oils. One difficulty in recovering these oils with alkaline waterflooding is the poor mobility control of the injected alkaline solution. A comparison of the large viscosity differences between injected alkaline solutions (1.0 cp) and the reservoir crude oil (20 to 70 cp) gives an indication of mobility control problems. To improve mobility control and improve sweep efficiency, the addition of polymer to the alkaline solution has been studied. Schuler, et al.¹⁵, and Nelson, et al.¹¹, provide laboratory data to evaluate the alkaline/polymer flood process. Both studies indicate the recovery of oil can be improved by the addition of polymer to the injected alkaline or alkaline/micellar fluid. The combination of alkali and polymer has a synergistic effect on oil recovery: the recovery of oil by the alkaline/polymer process is much higher than the oil recovery by either the alkaline or the polymer process separately.

A field trial of the alkaline/polymer process has been initiated at the Isenhour Unit, Sublette County, Wyoming. Preliminary results indicate a favorable response to the alkaline/polymer flood process. A report by T. E. Doll¹⁷ indicates oil recovery has been increasing at the rate of 20 percent per year since the start of the project.

Micellar/Alkaline/Polymer Flooding

The combination of micellar, alkaline, and polymer fluids to improve oil recovery has been studied by Schuler, et al.¹⁵, and Nelson, et al.¹¹ Both groups found that the micellar/alkaline/polymer process can significantly enhance the recovery of oil above the recovery observed with alkaline/polymer processes and are equivalent to micellar/polymer processes. Schuler, et al.¹⁵, observed that chemical costs and chemical consumption were reduced when the micellar/alkaline/polymer process was used in coreflood tests. Measurements of interfacial tension of the core effluent indicated a longer period of production of fluids with low interfacial tension when the micellar/alkaline/polymer solutions were injected compared to the injection of only micellar/polymer or alkaline/polymer solutions.

Nelson, et al.¹¹, suggested the alkaline waterflood process was a special case of surfactant flooding. The same concepts of phase behavior and salinity control apply to alkaline flooding as well as to surfactant flooding. To improve salinity tolerance and phase behavior during alkaline flooding, Nelson, et al., recommended using a cosurfactant. During their study, they found that flooding with a well designed cosurfactant-enhanced alkaline/polymer solution will recover as much oil as a well designed chemical flood (surfactant). This is consistent with the findings of Schuler, et al.¹⁵, and suggests the micellar/alkaline/polymer process or the cosurfactant-enhanced alkaline flood may provide significant improvement in oil recovery over more traditional enhanced oil recovery processes.

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