SPE

Society of Petroleum Engineers of AIME

SPE 10371

Physicochemical Mechanics of the Propagation of the Stabilized Oil Bank Formed During Dilute Surfactant Flooding

by Gregory R. King,* Turgay Ertekin,* C. Drew Stahl,* J. H. Jones, R. Nagarajan, and A.J. Yarzumbeck, *The Pennsylvania State University*

*Member SPE-AIME

ABSTRACT

Recent displacement tests have indicated that under certain conditions the stabilized oil bank formed during dilute surfactant flooding may be composed of as many as three distinct oil banks. These secondary oil banks are characterized by the arrival of high oil cuts, high sulfonate concentrations, and low interfacial tensions in the effluent stream. The mechanisms governing the formation of these three banks, although different for each bank, are related to the interactions between the oil, rock, surfactant solution, and mobility buffer.

To determine the mechanisms governing the formation of these banks, a series of core floods was designed to isolate and study each bank separately. The experimental results, including the production histories and effluent analysis of these tests are presented and discussed.

The results of these tests indicate that two of the banks are formed by the chromatographic separation of high and low equivalent weight sulfonates, while the third is formed by the desorption of sulfonate during the injection of low saline fluids (mobility buffers). Also discussed are the means to alter the production profiles of displacement tests by manipulation of these mechanisms.

INTRODUCTION

Previous investigators[1,2,3] have attempted to describe the mechanisms governing the development and propagation of the stabilized oil bank formed during surfactant/polymer flooding. Davis and Jones[1] presented experimental results which indicated a region of high oil cut at oil breakthrough. The oil cuts decreased and eventually stabilized later in the flood. This behavior was attributed to the mobile water bank advancing on and beyond the stabilized oil bank. The oil cut was observed to decrease as the water bank invaded the oil bank.

Gladfelter and Gupta[2] reported a similar trend

References and illustrations at end of paper.

in their experimental work. Using a microwave scanning apparatus, they observed a "hump" region in the oil saturation profile of linear sandstone cores at the leading edge of the stabilized oil bank. This region of high oil saturation was followed by a steady state region of lower oil saturation. They determined that the "hump" was formed through the hysteresis in the relative permeability curves and the related hysteresis in the fractional flow curve. The growth of the "hump" was found to be solely dependent on the extent of hysteresis and the fraction of oil flowing in the lower steady state region.

Wasson et al.[3] described the development and production of two oil banks formed during low concentration surfactant flooding. The formation of these two oil banks was found to be related to the mobilities of the injected fluids. The first bank was formed by the fingering of the low viscosity slug through the more permeable channels of the core. The surfactant solution in these channels came into contact with enough oil to form an oil bank. The second bank was formed during the injection of the mobility buffer. It was believed that the plug flow associated with high viscosity fluids was responsible for the formation of this bank.

Production histories of early displacement tests in this study indicated that three distinct oil banks were being produced. Examples of these banks are shown in Figures 1-3. The arrivals of the first two banks were observed after 50% PV and 100% PV of fluid production. The third bank, similar to that observed by Wasson, was produced at the end of the buffer injection. The purpose of this paper, therefore, is to give a detailed description of the stabilized oil bank formed by the low concentration slugs studied and attempt to describe the mechanisms governing the formation of these secondary oil banks.

MATERIALS

CRUDE OIL

The crude oil chosen for this study was the

Bradford crude oil. This was a 46.5° API, paraffinic based crude which had a viscosity of 4.5-5.5 cp at test conditions (approximately 70°F and 14.3 psia).

SURFACTANT SOLUTIONS

All surfactant solutions used in this study were made from mixtures of the petroleum sulfonates TRS 16[A] and PRL 7A[B]. Table 1 lists the composition and properties of these sulfonates. The total active sulfonate concentration remained 0.5% (by weight) throughout the experiments. The salt concentration in the solutions was 1.0% (by weight) NA_2CO_3. No cosurfactant or polymer was present in the solutions. The oil recovery characteristics of these solutions are given in Figure 4.

MOBILITY BUFFER SOLUTIONS

Following the surfactant slug, a 50% PV mobility buffer was injected. These solutions consisted of Kelzan[C] mixed in various concentrations with a low saline brine (ranging from 0.02% to 1.0% (by weight) NaCl). The polymer concentration was varied, depending on the salt concentration, to maintain an apparaent viscosity of 10 cp.[D]

BRINE

Both the interstitial water and drive fluid were either 1.0% or 2.0% (by weight) NaCl brine. All fluids injected into the core were filtered, in line, through a 0.45 micron filter.

POROUS MEDIA

All core floods were conducted in 2-in. diameter Berea sandstone cores,[E] with the length varying between 1-ft and 4-ft. The absolute permeabilities of the cores ranged from 100 md to 325 md, while the porosities remained 20.8% ± 2.0%. A fresh core was used in each run. Properties of the test cores are given in Table 2.

EXPERIMENTAL PROCEDURE

CORE PREPARATION

Cores were initially sealed with phenoline 300[F] and mounted in steel jackets. The ends perpendicular to flow were sealed by bolting end plates onto the jackets. The end plates were fitted to allow for the injection and production of fluids.

(A)   Commercial sulfonate from the Witco Chemical
      Company, Petrolia, PA.
(B)   Experimental sulfonate from the Penn State
      Research Laboratories, University Park, PA.
(C)   Polysaccharide polymer from the Kelco Company, Los Angeles, CA.
(D)   Measured at 6 rpm on variable speed Brookfield viscometer.
(E)   Cleveland Quarries, Amherst, OH.
(F)   Phenol-formaldehyde plastic from the Carboline Corporation, St. Louis, MO.

After mounting, the core was evacuated for 24 hours and allowed to imbibe the brine to be used as interstitial water. After a soak period of 24 hours, brine was injected into the core until a pressure of 500 psig was reached. The total volume of brine taken by the core was then considered the pore volume.

An oil flood was conducted to partially saturate the core. Oil was injected at a pressure drop of approximately 300 psig until a producing WOR of 1/100 was obtained. To reduce the oil saturation to residual, the core was waterflooded until oil production ceased. The core was then ready for the displacement test.

DISPLACEMENT TEST

All displacement tests were conducted with the apparatus shown in Figure 5. Prior to the coreflood, all lines were purged with the slug to be tested. The core was then connected to the displacement apparatus and the test begun. The approximate volume of slug to be used was set on the calibrated barrel of a Ruska[A] positive displacement pump and injected at a constant frontal advance rate of 1 ft/day. Injection of the mobility buffer and drive water was similar to that of the surfactant solutions. Drive water injection continued until a WOR of 100 was obtained. This completed the displacement test.

DISCUSSION OF RESULTS

It has been reported that as a chemical slug travels through a porous medium and is being adsorbed, there is a zone of the medium in equilibrium with the slug.[4,5] As the solute stripped slug moves through the medium, the equilibrium zone follows, with the flood front traveling on the order of 2.0 – 3.0 times faster. If two solutes travel through a porous medium with one preferentially adsorbed, the solution in front of the equilibrium zone will be stripped of the adsorbed solute but will still contain the less adsorbed solute. Behind the equilibrium zone the slug will contain both solutes. Thus, as the slug travels through the medium a chromatographic separation will occur.

This is the case with slugs made from blended sulfonates, such as those used in this study, with the higher equivalent weight sulfonate being preferentially adsorbed. The chromatographic separation of the high and low equivalent weight sulfonates in these slugs has been experimentally verified by Gale and Sandvick.[6] It is believed that this chromatographic separation is responsible for the formation of the first two banks.

To study the adsorption/chromatographic behavior of the TRS 16/PRL 7A slugs, dynamic adsorption studies were conducted in 2-ft, consolidated Berea cores. In these tests, no oil was present in the cores ($S_{oi} = 0.0\%$). Sulfonate concentrations in the effluent were determined by means of the Jones' dye extraction technique.[7] Interfacial tensions

---

(A)   Ruska Instrument Corporation, Houston, TX.

between the produced aqueous phase and Bradford crude were measured via a Du Nouy ring apparatus. The results of one of these tests is presented in Figure 6.

In this figure the breaks marked "slug" and "buffer" indicate the intervals where these fluids would be produced during perfect plug flow. The two peaks in the sulfonate concentration curve indicate that a chromatographic separation has occurred. It should be mentioned that the appearance of this curve would be different if oil had been present. Sulfonate concentrations and recovery (≈64%) are artificially high because no sulfonate is being lost through phase entrapment.[5,8,9] Also, the sulfonate breakthrough takes place later since the slug is miscible with 100% of the saturating fluids (If oil had been present, plug flow would not have occurred.). Although these two mechanisms would tend to shift the curve, they would not influence its shape.

A similar plot for the case of oil partially saturating the core is presented in Figure 7. As expected, the sulfonate bank was produced earlier and the sulfonate recovery was lower (≈47%). However, two peaks were again produced. Also shown in this figure is the oil banking in front of these peaks.

If a single sulfonate was used during the preparation of the surfactant solution, the chromatographic separation described earlier would not take place. Research on slugs of this type are currently being conducted.[10] The sulfonate used in these tests, CIII-48,[(A)] is manufactured from a similar process and feedstock as the PRL 7A sulfonate.[11,12] A typical production history is shown in Figure 8.

As expected, both a sulfonate bank and an oil bank with single peaks were produced. From the data presented in this figure, it cannot be determined whether the bank formed by the CIII-48 slugs corresponds to the second or the third bank, formed by the TRS 16/PRL 7A slugs. The high oil cut at the end of the buffer injection, however, indicates that the two banks may have merged in this test. This is of little concern. What is important is that a single peak in the sulfonate concentration curve (and a related peak in the oil cut) was obtained from a slug made with a single sulfonate.

The last bank produced in the displacement tests of Figures 1-3 was observed by Wassan et al.[3] He attributed it to the injection of the low mobility buffer solution. The more efficient oil displacement of the polymer solution was found to be responsible for the increased oil cuts.

Hurd[13] and Enedy[14] discuss the desorption of sulfonate in low saline fluids. In this study the salt concentration of the polymer solution was low (0.02% by weight) as compared to that in the slug (1.0% by weight) and drive water (2.0% by weight). In Figure 6, the slope of the sulfonate concentration curve changes with the production of the buf-

fer. Although the concentration is low it is enough to keep the interfacial tension low and possibly keep the oil mobile.

To determine if the desorption of sulfonate, indeed, had any effect on the third bank, tests were conducted in which the salt concentrations of the interstitial water, slug, buffer, and drive water were kept at 1.0% (by weight). With this system it was hoped to keep desorption to a minimum. The value of salinity was chosen because it was determined to be the optimum salinity for the slugs studied. Any change in the slug salinity would have rendered the results of these tests incomparable to those of previous tests. In order to maintain comparable buffer viscosities, the polymer concentration had to be increased from 500 ppm to 800 ppm. The results of this test are shown in Figure 9.

In the production history presented in Figure 9, the first two banks were produced as usual, but the third was not. In this test 7% less sulfonate was recovered, compared to those tests in which the salt concentration of the buffer solution was 0.02%. More important, however, was the difference in the ultimate oil recoveries. In this test the oil recovery was 56.4% of the residual oil, as compared to the 66.0% which had normally been recovered.

Varying the salinity of the buffer and brine would not be detrimental to the phase behavior of the system because 1.0% was determined to be the optimum for the slug. Increasing the polymer concentration by 300 ppm would slightly alter the phase behavior in the mixing zone at the trailing edge of the slug. This change, however, is not believed to have been sufficient enough to reduce the oil recovery by 10%.

CONCLUSIONS

From the work presented, the following conclusions have been drawn:

1. Displacement tests using slugs made from blended sulfonates indicate that oil banks with multiple peaks may be produced. These peaks are believed to be secondary oil banks. The arrival of these banks coincide with the arrival of high sulfonate concentrations and low interfacial tensions in the produced fluids.

2. Two banks are believed to be formed by the chromatographic separation of the high and low equivalent weight sulfonates in the slug. These banks were observed to be produced after 50% PV and 100% PV of fluid production.

3. Desorption of sulfonate in the low saline, polymer solutions accounts for approximately 7% of the recovered sulfonate. The amount of sulfonate desorbed in the buffer is sufficient to keep the oil mobile. This mechanism coupled with the efficient displacement associated with high viscosity fluids, may be responsible for the recovery of as much as 10% of the residual oil.

(A) Experimental sulfonate from the Penn State Research Laboratories, University Park, PA.

NOMENCLATURE

S_{o_i} = oil saturation prior to waterflooding.

WOR = water-oil ratio.

REFERENCES

1. Davis, J. A., and Jones, S. C.: "Displacement Mechanisms of Micellar Solutions," J. Pet. Tech. (Dec., 1968) 1415-1428.

2. Gladfelter, R. E., and Gupta, S. P.: "Effect of Fractional Flow Hysteresis on Recovery of Tertiary Oil," Soc. Pet. Eng. J. (Dec., 1980) 508-520.

3. Wasson, D. T., Perl, J. P., and Milos, F. S.: "Microwave Spectroscopic Analysis of Surfactant/ Polymer Flooding: Interrelationships Between Chemical Slug Properties, Coalescence Phenomena and Tertiary Oil Recovery," paper SPE 8327 presented at the 54th Annual Fall Technical Conference and Exhibition, Las Vegas, Sept. 23-26, 1979.

4. Calhoun, J. C., Stahl, C. D., Preston, F. W., and Nielson, R. F.: "A Review of Laboratory Experiments on Wetting Agents for Waterflooding," Prod. Monthly (Nov., 1951) 15-23.

5. Preston, F. W., and Calhoun, J. C.: "Applications of Chromatography to Petroleum Production Research," Prod. Monthly (March, 1952) 22-32.

6. Gale, W. W., and Sandvick, E. I.: "Tertiary Surfactant Flooding: Petroleum Sulfonate Composition-Efficacy Studies," Soc. Pet. Eng. J. (Aug., 1973) 191-199.

7. Schmidt, C. R.: "Some Analytical Methods and Problems in Tertiary Oil Recovery," M.S. Thesis, The Pennsylvania State University (1979).

8. Foster, W. R.: "A Low Tension Flooding Process," J. Pet. Tech. (Feb., 1973) 204-210.

9. Trogus, F. J., Sophany, T., Schecter, R. S., and Wade, W. H.: "Static and Dynamic Adsorption of Anionic and Nonionic Surfactants," Soc. Pet. Eng. J. (Oct., 1977) 337-344.

10. Dudenas, P. J.: Research in progress, presented at the Annual Review of Enhanced Oil Recovery Research, The Pennsylvania State University, June 11, 1981.

11. Klaus, E. E., Jones, J. H., Nagarazan, R., Ertekin, T., Fan, J. J., Lin, D. M., Yarzumbeck, A. J., and King, G. R.: "Oxidized Petroleum Fractions as Co-Surfactants and as Feedstocks for the Tertiary Recovery of Oil," paper SPE 9006 presented at the SPE International Symposium on Oilfield and Geothermal Chemistry, Stanford, May 1980.

12. Klaus, E. E., Jones, J. H., Nagarazan, R., Ertekin, T., Chung, Y. M., Arf, G., Yarzumbeck, A. J., and Dudenas, P.: "Generation of Ultralow Tensions over a Wide EACN Range Using Penn State Surfactants," paper SPE 9784 presented at the 2nd Annual Joint Symposium on Enhanced Oil Recovery, Tulsa, April 5-8, 1981.

13. Hurd, B. G.: "Adsorption and Transport of Chemical Species in Laboratory Surfactant Waterflooding Experiments," paper SPE 5818 presented at the Improved Oil Recovery Symposium of the Society of Petroleum Engineers, Tulsa, March 22-24.

14. Enedy, S. L.: "Evaluation of a Low Tension Flooding Process Using Dilute Surfactant Solutions," M.S. Thesis, The Pennsylvania State University, 1979.

Table 1. Composition and Properties of Sulfonates

Name	EW	Active Material, Wt. %	Unreacted Oil, Wt. %	Volatiles,[A] Wt. %	Salt, Wt. %
TRS 16	455	61.3	33.7	4.9	0.1
PRL 7A	298	60.6	1.1	28.0	10.2

[A]Water and/or Alcohol

Table 2. Core Properties of Two Foot Cores

Property	Average Value	Maximum Value	Minimum Value	Standard Deviation	Percent of Cores Within One Standard Deviation of Average Value
Pore Volume	255.4 cc	273.1 cc	235.0 cc	10.10	65.2
Porosity	20.8%	21.1%	19.9%	0.79	52.2
Permeability	262.9%	330.0 md	143.0 md	43.20	78.3
S_{oi}	63.6%	69.2%	57.0%	2.87	69.6
S_{or}	32.4%	38.9%	26.9%	2.48	78.3
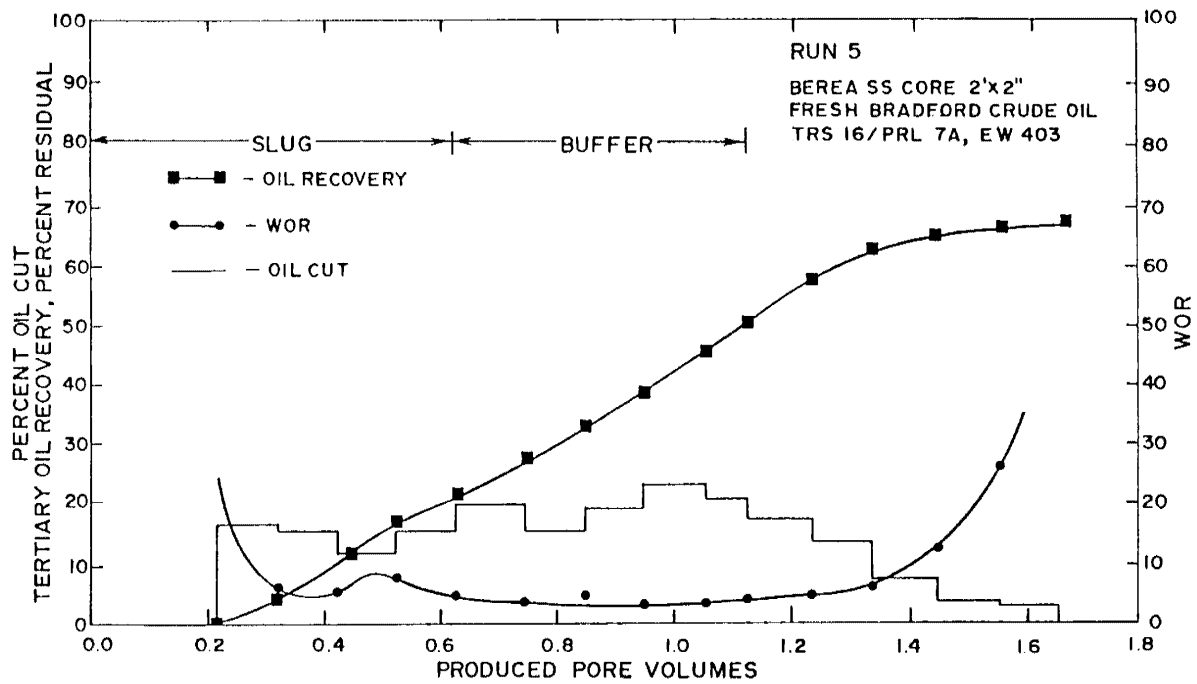
Fig. 1 – Production history of Run 5.
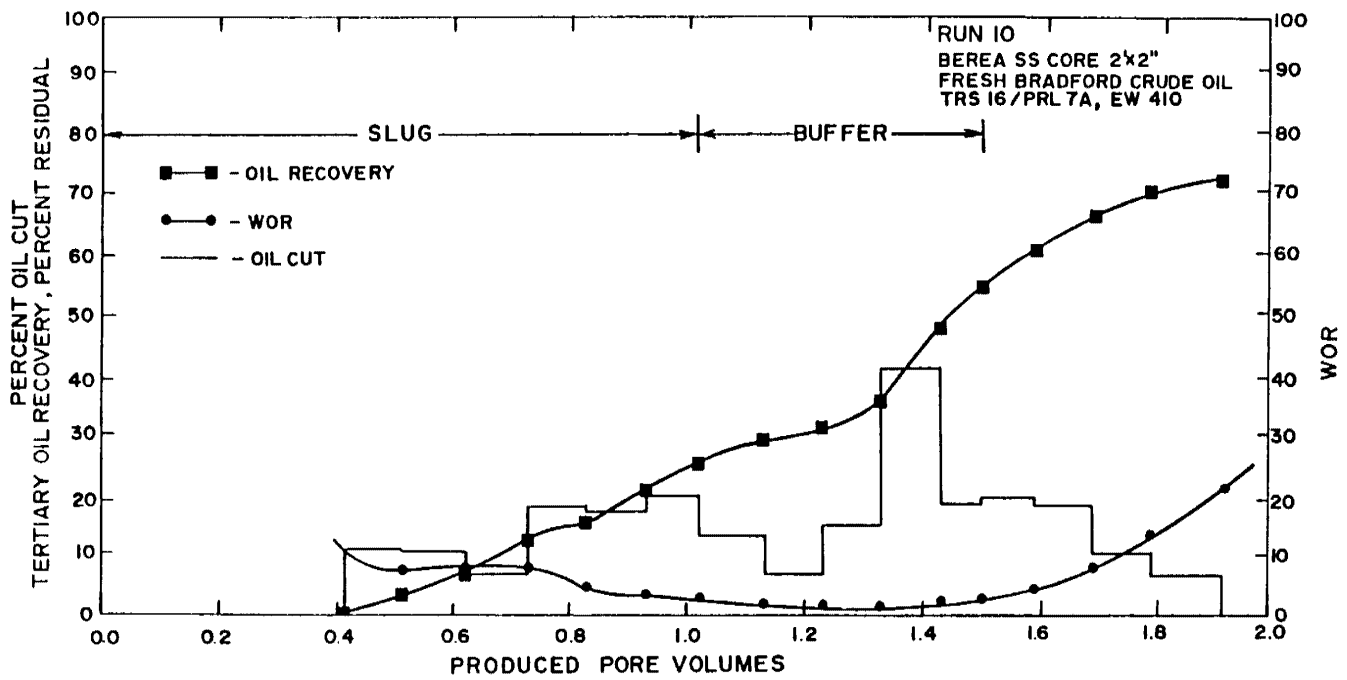
Fig. 2 – Production history of Run 10.
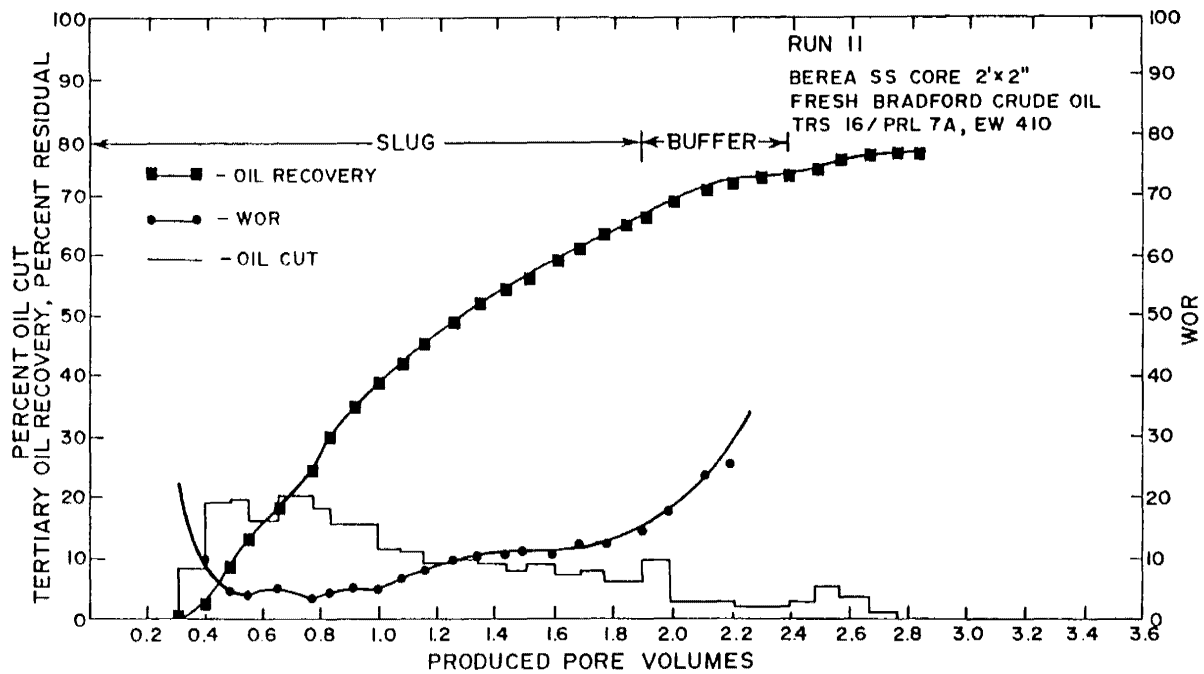
Fig. 3 — Production history of Run 11.
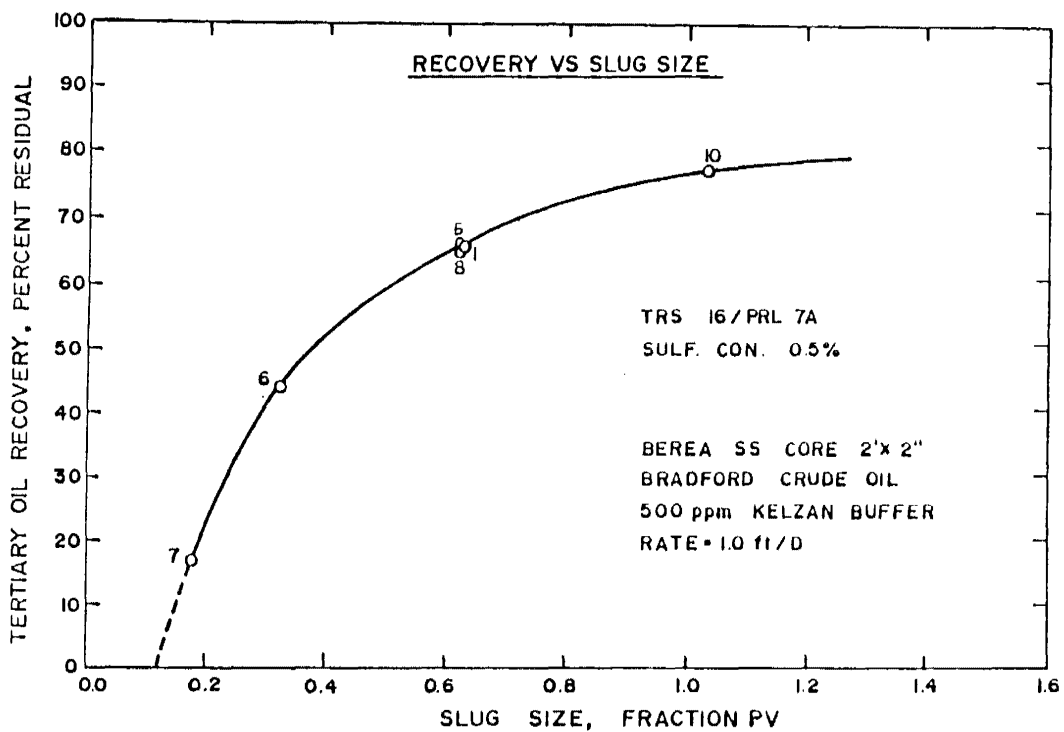
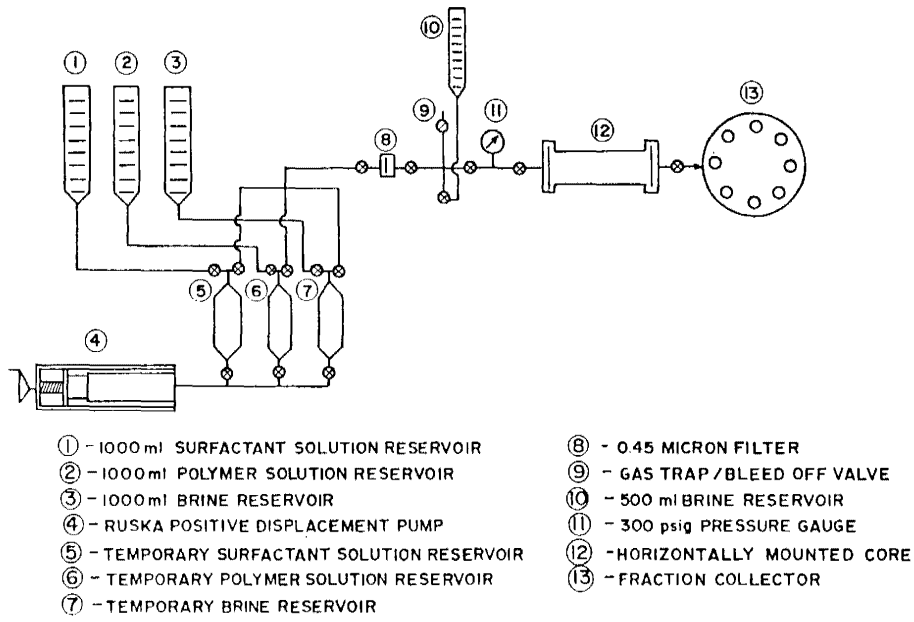**Fig. 4** — Tertiary oil recovery as a function of slug size.

① - 1000 ml SURFACTANT SOLUTION RESERVOIR   ⑧ - 0.45 MICRON FILTER
② - 1000 ml POLYMER SOLUTION RESERVOIR   ⑨ - GAS TRAP/BLEED OFF VALVE
③ - 1000 ml BRINE RESERVOIR   ⑩ - 500 ml BRINE RESERVOIR
④ - RUSKA POSITIVE DISPLACEMENT PUMP   ⑪ - 300 psig PRESSURE GAUGE
⑤ - TEMPORARY SURFACTANT SOLUTION RESERVOIR   ⑫ - HORIZONTALLY MOUNTED CORE
⑥ - TEMPORARY POLYMER SOLUTION RESERVOIR   ⑬ - FRACTION COLLECTOR
⑦ - TEMPORARY BRINE RESERVOIR

Fig. 5 – Experimental apparatus.
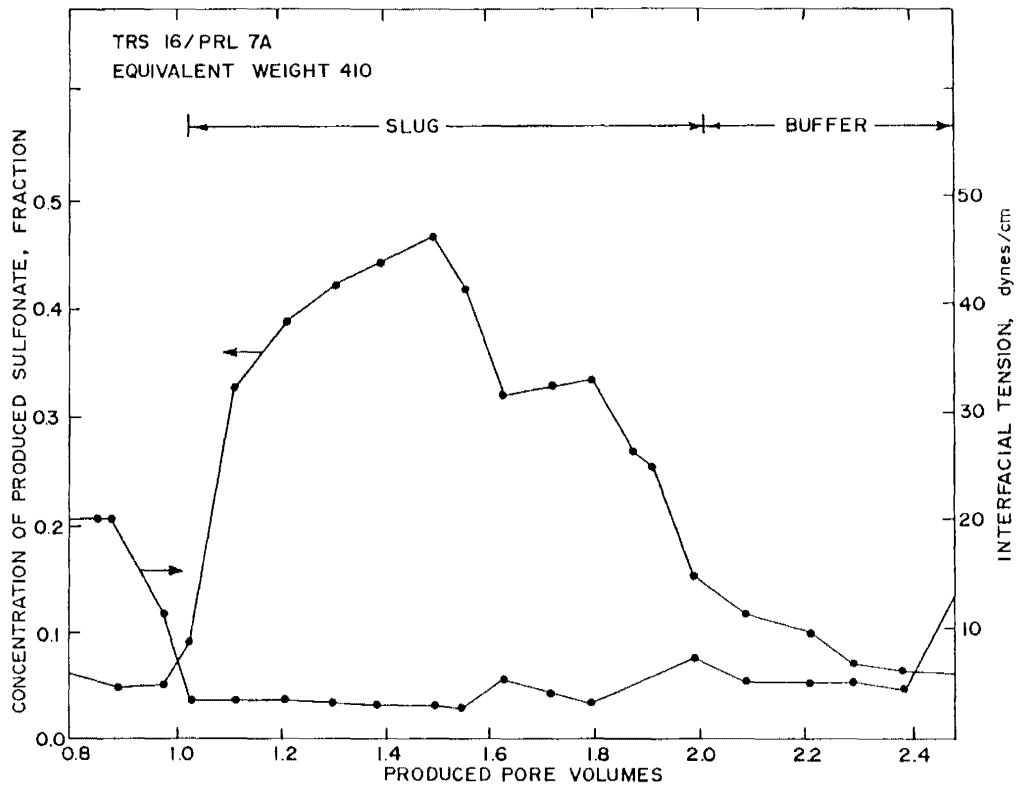
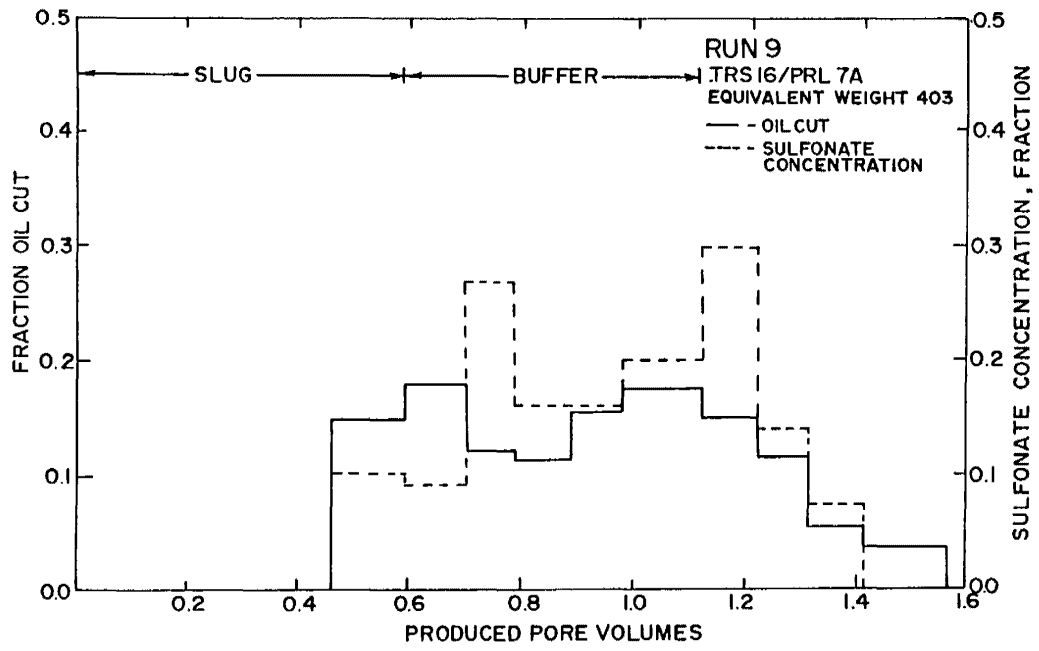**Fig. 6** – Results of dynamic adsorption test.

Fig. 7 – Production history of Run 9.

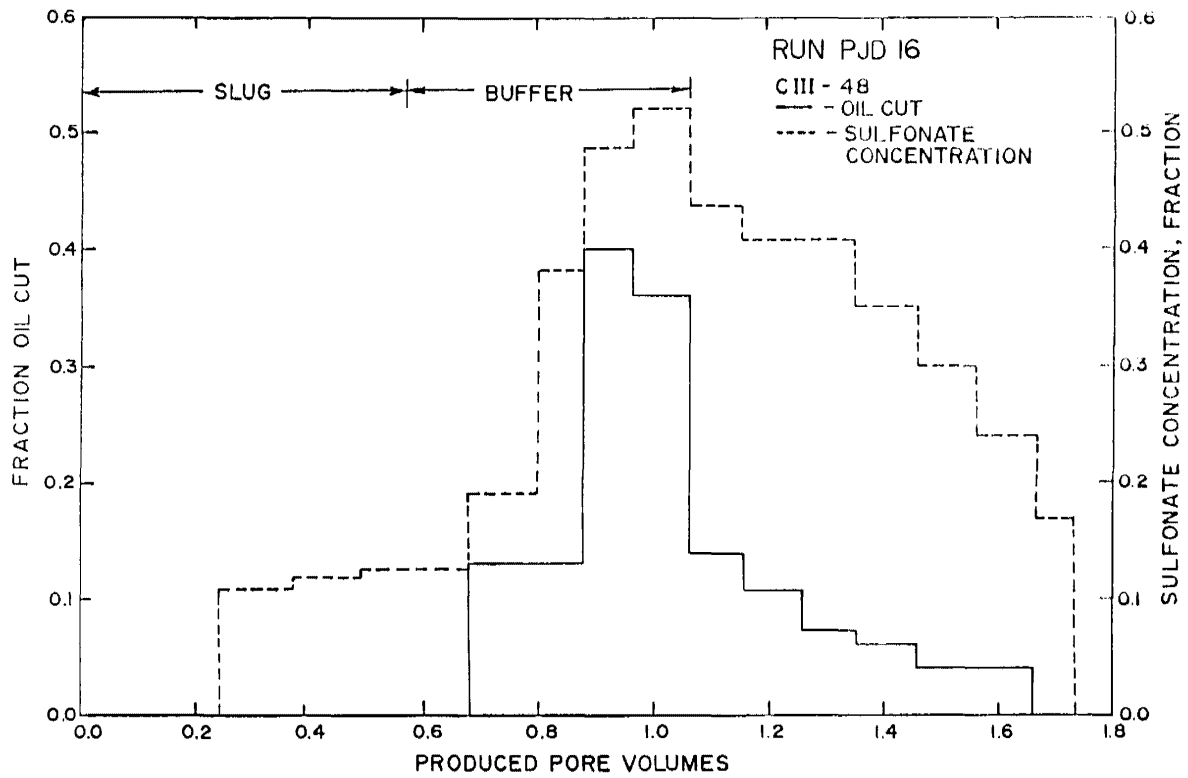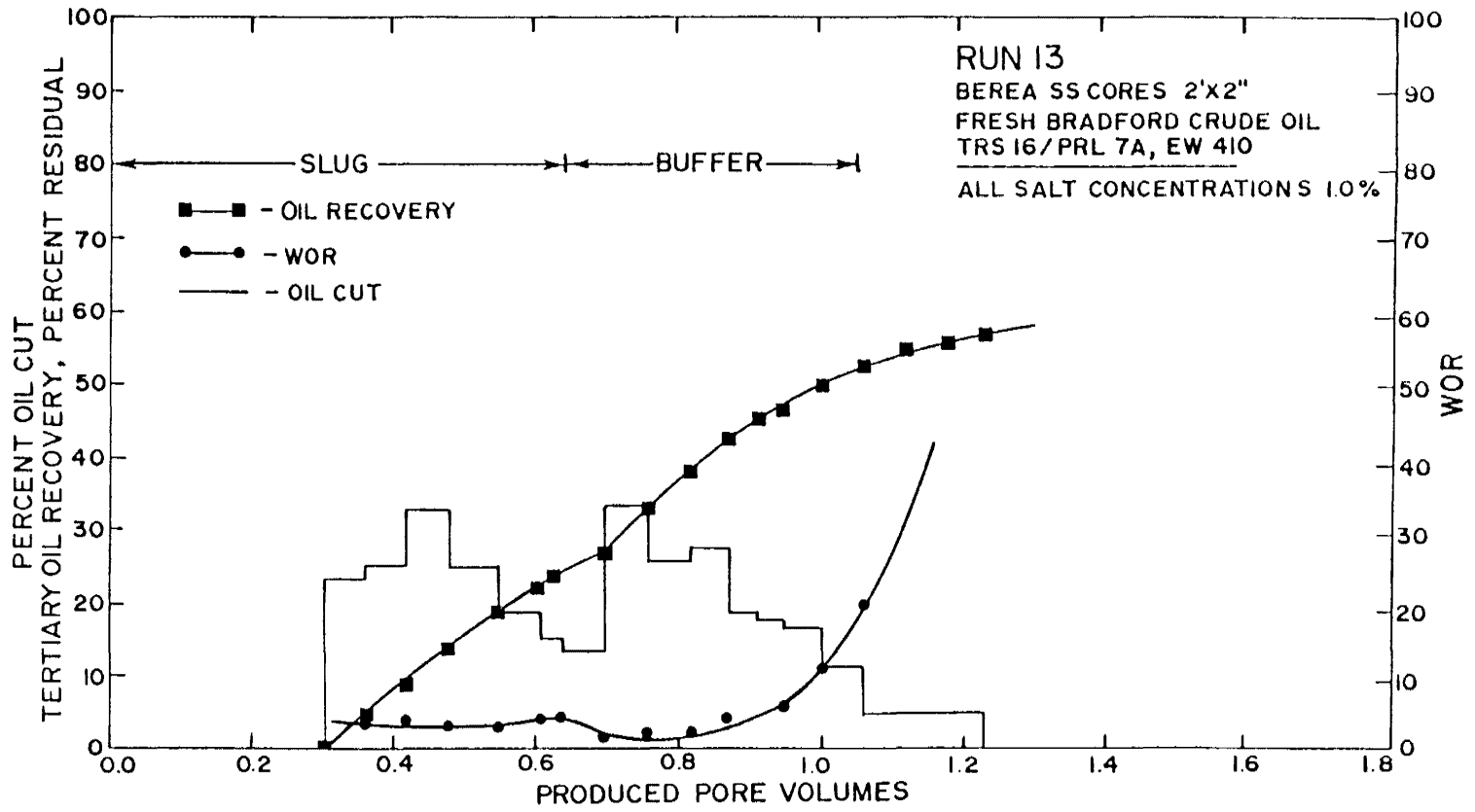**Fig. 8** – Production history of PJD 16 (after Dudenas).

Fig. 9 — Production history of Run 13.