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**Effect of Surface Area and Pore Size Distribution on Oil Recovery
at Breakthrough, Oil Recovery at Floodout, Residual Oil Saturation,
and Wettability**

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by

Dr. Robert W. Watson

The Pennsylvania State University

Fathi Boukadi

The Pennsylvania State University

ABSTRACT

Waterflood experiments were conducting using radial Berea sandstone cores. Statistical analyses indicated that the frequency distributions of average irreducible water saturation, average residual oil saturation, porosity, average initial oil saturation, tortuosity, oil recovery at breakthrough, and oil recovery at floodout are close to a normal distribution.

24 core plugs were extracted from each of the 22 waterflooded Berea sandstone cores and were used in the wettability and porosimetry studies. Amott's method was used to determine the average wettability indices. Results indicated that the wettability of Berea Sandstone rocks is heterogeneous with hydrophilic dominance. Furthermore, regression analysis indicated that the average wettability index was directly proportional to the average irreducible water saturation and inversely proportional to the average residual oil saturation, and wettability was directly proportional to oil recovery at breakthrough and oil recovery at floodout.

Mercury porosimetry data were used to calculate or infer petrophysical characteristics. Based on pore-size distribution curves, Berea sandstone pores tested are classified as capillary (pores diameters vary from 0.0002 to 0.508 mm). The heterogeneous pore radii in Berea sandstone rocks appear to be the primary cause of mercury trapping by bypassing and snap-off mechanisms. Regression analyses indicated that oil recovery at breakthrough and oil recovery at floodout are related to the rock surface area.

Median pore-throat size is related to rock tortuosity expressed in terms of the wetting phase retention time. Tortuosity was found to be inversely proportional to the median pore-throat size of Berea sandstone.

INTRODUCTION

The most common secondary oil recovery technique is waterflooding. A prerequisite for the understanding of waterflood performance is a knowledge of the basic properties of reservoir rock (Morrisy, 1963). These consist of two main types: (1) properties of the rock skeleton alone, such as porosity, permeability, pore-size distribution, and surface area, and (2) combined rock-fluid properties such as capillary pressure (static) characteristics, and relative permeability (flow) characteristics (Forrest, 1971). In this study, characterization of surface area was accomplished using mercury porosimetry. In 1981, Lowell and Shields pointed out that the experimental method of mercury porosimetry for the determination of porous properties of solids is dependent on several variables such as wetting or contact angle between mercury and the surface of the solid. To monitor changes in these variables, Ritter and Drake in 1945 used a resistance wire in the capillary stem. They also developed one of the first high pressure porosimeters and measured the contact angle between mercury and a variety of materials. The contact angle was found to be between 135° and 142° with an average value of 140° . Mercury porosimetry theory for determining surface area, capillary pressure variations, cavity radius, sample volume, apparent density, and pore-size distribution is based on an equation developed by Washburn in 1921. Washburn's equation was developed using the Young-Dupre equation which establishes the criteria for wettability. In mercury porosimetry, capillary pressure variations and intrusion-extrusion hysteresis have been attributed to "ink-bottle" shaped pores (Orr, 1970). In pores of this type, intrusion cannot occur until sufficient pressure is attained to force mercury into the narrow neck, whereupon the entire pore will fill. However, on depressurization, the wide pore body cannot empty until a lower pressure is reached, leaving entrapped mercury in the wide inner position. Reverberi et al. in 1966 proposed a method for calculating the sizes of narrow and wide portions of the pore from intrusion-extrusion curves based on the fact that such pores exhibit "ink-bottle" shapes. This method involves scanning the hysteresis loop by means of a series of pressurization and partial depressurization cycles in order to determine the volume of the wide inner portion of pores having neck radii in various radius intervals.

Wettability is described as a major factor controlling the location, flow and distribution of fluids

in a reservoir. Changes in wettability have been shown to affect waterflood behavior, irreducible water saturation (S_{iw}) and residual oil saturation (S_{or}) (Raza et al., 1968; Wagner and Leach, 1959) Therefore, if core analysis is to accurately predict reservoir behavior, the wettability of the core must be the same as the wettability of the undisturbed reservoir rock. Historically, all petroleum reservoirs are believed to be strongly water-wet. This supposition was based on the observations that almost all clean sedimentary rocks are strongly water-wet and sandstone reservoirs were deposited in aqueous environments into which oil migrated at some later time and displaced the connate water (Anderson, 1984). It is assumed that the connate water prevented oil from touching the rock surfaces.

Wettability is defined as "the tendency of one fluid to spread on or to advance to a solid surface in the presence of other immiscible fluids" (Craig, 1971). In a rock-oil-brine system, it is a measure of the preference that the rock has for either the oil or water. When the rock is water-wet, there is a tendency for the water to occupy the small pores and contact the majority of the rock surface. Similarly, in an oil-wet system, there is a tendency for the rock to be in contact with the oil. The location of the two fluids is reversed from the water-wet case, and oil will occupy small pores and contact the majority of the rock surface. Wettability is described as the wetting preference of any rock and does not necessarily refer to the fluid that is in contact with the rock any time. Depending on the specific interactions of rock, oil, and brine, the wettability of a system can range from strongly water-wet to strongly oil-wet. When the rock has no strong preference for either oil or water, the system is said to be neutral or of intermediate wettability. When the system is in equilibrium, the wetting phase will occupy the smallest pores and be in contact with the majority of the rock surface. The non-wetting phase will occupy the larger pores and form isolated ganglion in the vicinity of the rock.

A number of methods have been used to measure wettability. Three quantitative methods are used today: contact angle method, Amott method, and the USBM method. The contact angle method is best for measuring the wettability of pure fluids and polished surfaces where there is no possible wettability alteration arising from compounds such as surfactants. However, there are some difficulties involved in applying contact angle measurements to reservoir cores and moreover, the hysteresis phenomenon is encountered. With the Amott method, which combines imbibition and centrifugal dis-

placement to measure the average wettability of a core, both the reservoir core and fluids can be used.

The object of this study of reservoir characterization is to study the effect of surface area and pore size distribution on oil recovery at breakthrough, oil recovery at floodout, residual oil saturation and wettability.

EXPERIMENTAL PROCEDURE

Waterflooding Experiments:

All waterflooding experiments were conducted using radial unfired Berea sandstone cores¹. The experimental apparatus used was a fully automatic core flooding station developed by Core Test Systems². This system permitted simulation of both reservoir temperature and overburden pressure. The cores used were 12.7 cm in diameter and 5.08 cm long. Prior to mounting in a cylindrical core holder, an injection well located at the center was drilled through the core. A .159 cm clearance between the core and the core holder around the circumference was maintained. This clearance was necessary to permit the development of radial flow behavior. The core was evacuated using a vacuum pump for a period of 24 hours. Brine, the wetting phase, was then permitted to saturate the core. The pore volume was determined by measuring the amount of brine used in the saturation process. The brine used consisted of 1.5% by weight sodium chloride³, 0.3% by weight Formalin³ and 98.2% by weight distilled water⁴. The Formalin was used to preserve the brine and prevent bacterial growth. The non-wetting phase is a binary system containing 70% by volume Blandol⁵ and 30% by volume of Soltrol⁶. This combination was selected to yield a viscosity of 10 cp at 35°C. This viscosity was chosen to simulate the viscosity of a common reservoir oil. Before mixing and prior to each experimental run, the wetting and the non-wetting phases were filtered through a 0.45 µm Metrical filter⁷. The containment pressure on the cores was maintained at 3447.3 kPa. This pressure permitted water injection without the inducement of fractures in the sandstone cores. Temperature was maintained at 35°C

[1] Cleveland Quarries, Amherst, Ohio

[2] Core Test Systems, Inc., Mountain View, CA

[3] Fisher Scientific, Fair Lawn, New Jersey

[4] Roaring Spring Bottling Co., Roaring Spring, PA

[5] Witco Corporation, New York, NY

[6] PHILLIPS 66 COMPANY, Bartlesville, OK

[7] Gelman Science, Inc., Ann Arbor, MI

throughout the experimental runs. To model a field situation where water advance is moderate, displacement studies were conducted at injection rates equivalent to a field drainage rate of 0.6096 meters/day in the waterflooding experiments, this was equivalent to injection rate of 0.61 cc/min or 36.6 cc/hr. The waterflooding experiments were used to obtain the average irreducible water saturation, the average residual oil saturation, oil recovery at breakthrough and oil recovery at floodout.

Wettability Experiments:

The Amott method was used to measure the average wettability of the 24 plugs per core which were extracted from the waterflooded cores. The core plugs extracted were 1.27 cm. in diameter and 1.69 cm. long. The core plugs were cleaned prior to testing by soaking for 24 hours in a solution containing 50 % by volume of acetone and 50 % by volume isopropyl alcohol. This procedure was followed by an additional soaking for 24 hours in a solution containing only acetone. The core plugs were then permitted to dry in a vacuum oven for 24 hours. The Amott method was selected in this case because the core and fluids used in the waterflooding experiments could be used in the wettability determination. The Amott method is based on the fact that the wetting fluid will generally imbibe spontaneously into the core, thereby displacing the non-wetting phase. The ratio of spontaneous imbibition to forced imbibition is used to reduce the influence of other factors, such as relative permeability, viscosity, and the initial saturation of the rock because only the surface forces are changed (Anderson, 1984). According to Donaldson et al. in 1976, wettability measurements are made as quickly as possible because changes in temperature, pressure and exposure to air produce physical and chemical changes that could alter the wettability. Consequently, these experiments were conducted in such a way that the measurements on the tested core plugs were made quickly with minimum air exposure.

Mercury Porosimetry:

Following the wettability experiments, the core plugs were cleaned in the same manner described in the wettability experiments section. Samples were evacuated in a Micromeritics Pore Size 9220⁸ to a pressure of 50 microns of mercury. The sample chambers were then filled with mercury and pres-

[8] Micromeritics, Norcross, Georgia

surized incrementally to a pressure of 413,685 kPa. Prior to the increase to the next higher pressure value, equilibrium was attained by setting the porosimeter equilibrium value to 15 seconds. With each pressure increment, smaller pore throats were invaded by mercury. Pore-throat size information is obtained from mercury intrusion curves based on the assumption of cylindrical pore-throat configuration. The Berea sandstone core plugs used in the wettability experiments were used in determining surface area, median pore-throat size, pore-throat size distribution, and effective porosity. Although pore radii have been known to assume all regular geometric shapes and in most instances highly irregular shapes, pore radii measurements in mercury porosimetry are based on the "equivalent cylindrical diameter". This is the diameter of a pore which would behave in the same manner as the core plug diameter being measured in the same instrument. Surface areas calculated from core plug cylindrical diameters will establish the lower limit using the implicit assumption of the cylindrical geometry of pores, and by ignoring the highly irregular nature of rock surfaces.

RESULTS AND DISCUSSION

Waterflood Results:

Statistical descriptions of the different waterflood experiments variables are listed in Table 1. Such variables include average initial oil saturation, average irreducible water saturation, average residual oil saturation, porosity, tortuosity (expressed in terms of retention time), oil recovery at breakthrough, and oil recovery at floodout. Figure 1 contains a plot of average residual oil saturation versus average initial oil saturation. This plot indicates that there is a tendency for residual oil to increase as the initial oil saturation increases. For strongly water-wet rocks such as the Berea sandstone cores studied, capillary forces affect the distribution of fluids while viscous forces have only a minimum influence on residual oil saturation. Consequently, at a low capillary number (the ratio of capillary to viscous forces), the residual non-wetting saturation is generally a well-defined quantity. Such a behavior in Berea sandstone rocks suggests that oil recovery by waterflooding is controlled by pore geometry, and a unique residual non-wetting phase saturation exists for a given set of initial conditions. Trapping in such cores is governed solely by capillary forces. The magnitude of the viscous and gravity forces compared to the capillary forces gives rise to the initial-residual saturations relationship

which appears to be unique in the case of Berea sandstone cores studied. Pickell et al. in 1966, Wardlaw et al. in 1976, Chatzis and Dullien in 1981, and Wyman in 1977 conducted displacement tests and indicated that residual oil saturation can be strongly dependent on initial oil content. Our findings are in agreement with these previous investigations concerning the initial-residual oil saturations relationship. Morrow in 1970 also pointed out that for a waterflood carried out at a low capillary number, the residual non-wetting saturation is a defined quantity for a definitive initial saturation. Chatzis et al. in 1983 noted that Berea sandstone usually retains a high residual oil saturation, approximately 35 %, following waterflooding. The vast majority of the population of oil blobs from Berea sandstone are trapped as singlet and doublet structures. This behavior is typical of pore networks having a high aspect ratio of pore-body size to pore-throat size. In Berea sandstone, the pore throat diameters were shown by Chatzis et al. in 1983 to vary from 10 to 30 μm , while pore-body sizes vary from 40 to 200 μm . Ruzyla et al. in 1982 found that high irreducible oil saturations are characteristic of heterogeneous pore systems. However, low values of irreducible oil saturation would be expected for rocks with pore systems of a homogeneous nature. Morrow in 1970 indicated that the magnitude of irreducible wetting phase saturation and consequently the initial oil saturation is mostly a function of pore system heterogeneity; that is, the way pores and throats of different sizes are distributed within the matrix. Geffen in 1951 also came to the same conclusion that for water-wet core plugs, the residual oil saturation increases as the initial oil saturation increases.

Wettability Results:

Using the Amott-Harvey method to measure the relative displacement index, Berea sandstone surface wettability indices were determined and shown to vary from a minimum value of + 0.45 to a maximum value of + 1.00 or absolute water wettability. The wettability index statistical description is shown in Table 2. The wettability scale adopted and presented in Table 3 is based on the scale used at L'institut Francais de Petrole. The mean wettability of the rocks was found to be functionally related to the amount of hydrophilic or hydrophobic surface area present in each core sample. Wettability variations in the less permeable rocks were more pronounced. This was attributed to the relative abundance of shaley streaks in the tighter cores and led to the conclusion that with respect to the plugs

tested, the wettability is heterogeneous or "dalmatian" with some parts of the surface area being water-wet and others being oil-wet.

The wettability index frequency distribution plot on Figure 2 is skewed to the left since the median of the distribution is larger than the mean. However, the average wettability indices frequency distribution on Figure 3 assumes an exponential distribution. Wettability controls the distribution of fluids in the porous media. Wettability of Berea sandstone cores governs the irreducible water saturation and residual oil saturation values. The wetting phase tends to occupy smaller intergranular pores than the non-wetting phase. Wardlaw in 1983 agreed that wettability may strongly affect S_{iw} and S_{or} and the fractional flow of fluids for a given saturation, and areal and volumetric sweep efficiencies. Wardlaw also emphasized that changes in wettability can greatly change the arrangement of water and oil within a pore system. He also noted that for a given rock, the critical end points S_{iw} and S_{or} may differ greatly for different conditions of wettability. Figure 4 shows that the average wettability index was found to be directly proportional to average irreducible water saturation. Moreover, Figure 5 indicates that the average residual oil saturation in Berea sandstone rocks is inversely proportional to the average wettability index. Figures 6 and 7 indicate that oil recoveries at breakthrough and oil recovery at floodout correlate to the average wettability index in Berea sandstone rocks. Scatter plots relating the indicated variables show elliptical envelopes of the data points. The major axis of the ellipses indicate a direct proportionality between oil recovery at floodout and average wettability, and between oil recovery at breakthrough and average wettability index in Berea sandstone cores. Wardlaw in 1983 indicated that oil recovery by waterflooding and the average residual oil saturation are greatly affected by the arrangement of fluids, which is related to wettability, in the porous media. Kyte in 1961, Owens in 1971, and Mungan in work published in 1966 and 1972 found that relative permeability becomes progressively less favorable to oil production as the degree of water-wetness decreases and that residual oil saturation increases as the cores become less water-wet.

Mercury Porosimetry Results:

The experimental results indicated that the large pores and interparticle voids of 0.033 μm in diameter were filled with mercury at pressures of 34473.8 kPa. Incremental Intrusion above a capillary

pressure of 137895.1 kPa was found to be approximately zero in most of the cases studied. At pressures of approximately 413,685.4 kPa, evidence of compression was noted in a number of core plugs. An abrupt increase in mercury intrusion would suggest this conclusion. Grain compression was also noted in a number of core plugs and was indicated by the steep curvature noted in the pressure curves.

Ellenburger (Amthor et al., 1988), however, pressurized his samples up to 103,421.4 kPa (Hg-air) and Hunton (Amthor et al., 1988) pressurized his samples up to 137,895.1 kPa (corresponding to an opening of 30 angstroms wide). These pressures are both considerably greater than those reached in any published studies of this type (Amthor et al., 1988). Ghosh et al. in 1987 pressurized their samples to 34,473.8 kPa, and Jennings in 1987 used 13,789.5 kPa as his maximum pressure value. Most of Wardlaw's work (Wardlaw and Taylor, 1976; Wardlaw et al., 1988) has covered pressure ranging up to 10,342.1 kPa. This is apparently not a significant factor for the rock cores tested in this study because the increase in incremental intrusion at very high pressures which would occur if significant volumes of microfractures were opened, was observed in the testing of a number of samples. Further, if these fractures are open in our experimental apparatus, they would then be open in the subsurface environment under comparable pressure conditions (Amthor et al., 1988). After intrusion measurements were completed, extrusion data were collected as pressure was incrementally reduced to atmospheric pressure (101.4 kPa).

Figure 8 indicates that the rock surface wettability depends on the rock surface area. A large surface area on which the fluid can adhere and spread results in a higher affinity for that fluid by the rock surface. The scatter plot relating the average wettability index to the surface area indicates a direct proportionality between the the average wettability index and the average rock surface area. Melrose in 1982 and Collins in 1988 described thin aqueous wetting films, separating rock and oil, which are stabilized by the electrostatic repulsive force acting between electrical double layers at the oil-brine and mineral-brine interfaces. Both Melrose and Collins concluded that the larger the surface area the greater the electrostatic forces. Figure 8 would support this conclusion that the relative magnitude of the rock's wettability increased with larger surface area.

Figures 9 and 10 contain plots of oil recovery at breakthrough to surface area and oil recovery at

floodout to surface area respectively. These plots indicate that for water-wet rocks, oil recovery at breakthrough and oil recovery at floodout is higher for the cores with a larger surface area. These plots suggest that oil recovery is a function of a larger surface area. Surface area controls the wettability of the porous medium which in turn, controls the fluid distribution in the vicinity of the rock and dictates the oil recovery. Large surface areas are observed in a strong water-wet system where hydrophilic behavior is dominant. In 1985, Wardlaw and Li reported similar findings. They expressed the view that wettability and topology, the relative amount of surface area, are the main factors which determine whether snap-off occurs in throats, in pores, or at pore-throat junctions. Wherever it occurs, the effect is to disconnect the nonwetting phase and ultimately, to cause its entrapment. Wardlaw et al. in 1986 also indicated that within single pores, the trapping of oil is a function of the shape of the water-oil interface which is controlled by the contact angle and the shape of the pore surface and consequently, the rock surface area.

Candido et al. in 1985 reported that oil recovery diminishes as rock-pore heterogeneity increases. He also noted that oil recovery is governed by pore-size distribution. Such conclusions are in accordance with our experimental findings. Figures 11, 12 and 13 contain plots of the pore-throat size distribution for the cores tested. These plots indicate that the distributions are centered around a median pore-throat size of approximately 15 μm and that the pore structure can be considered to be homogeneous. Irregularities, or small peaks, in the pore-throat size distribution plots reflect small amounts of intrusion in the discontinuous ranges of pores. These types of pores are classified as "ink well" pores or pores having a "bottle" shaped configuration.

Figures 14 and 15 contain plots of the depressurization and pressurization cycles for Berea cores where the S_{or} measured after waterflooding was 34.46 % and 29.21 % respectively. The location of the depressurization cycle above the pressurization cycle indicates that the hysteresis loop does not close and suggests that some mercury is entrapped in the pores. Similar intrusion-extrusion curves behavior was observed by Lowell and Shields in 1981. They attributed the hysteresis behavior to the fact that mercury exhibits two or more intrusion contact angles for a given material. Thus, superposition of the intrusion-extrusion curves can not be achieved. Orr in 1970 suggested that intrusion-

extrusion hysteresis is due mainly to "ink-bottle" shaped pores. In pores of this type, intrusion can not occur until sufficient pressure is attained to force mercury into the narrow neck. With the attainment of this pressure level, the entire pore will fill with mercury. However, upon depressurization, the wide-pore body can not empty until a lower pressure is reached, leaving entrapped mercury in the wide inner portion.

For strongly water-wet systems, Wardlaw et al. in 1983 indicated that mercury-air capillary pressure curves adequately characterize oil-water capillary pressure behavior. The hysteresis curves obtained from these studies provide insight into the trapping mechanisms of the non-wetting phase and the role of pore-throat size distribution on oil recovery by waterflooding and consequently, the rock surface area effect on oil recovery by waterflooding. The differences observed in the hysteresis curves shown on Figures 14 and 15 indicate that the mercury entrapment attendant to the curve on Figure 14 exceeded that on Figure 15. This suggests that the difference between the S_{or} measured after waterflooding resulted from oil entrapment in "ink-bottle" shaped pores. The results of these experiments are supportive of the findings of Wardlaw and his co-workers.

Figure 16 indicates that the median pore-throat size of Berea sandstone is inversely proportional to the rock tortuosity expressed in terms of the the wetting phase average retention time. This finding is consistent with the observations made by Burdine et al. in 1950 and Burdine in 1952. In 1950, Burdine and his co-workers concluded that specific permeability, a function of the square of the radius of the flow pathways, was inversely proportional to the tortuosity factor and in 1952, Burdine indicated that the tortuosity factor was inversely proportional to pore radii.

CONCLUSIONS

The following conclusions can be drawn from this investigation:

- In water-wet reservoirs where conditions favor a hydrophilic dominance, surface wettability conditions permit low saturation levels of the non-wetting phase.
- In a strongly water-wet system, wettability controls fluid distribution in the porous medium. Wettability determines the values of the irreducible water saturation and initial oil saturation.

- Pore size distribution in water-wet systems is the principal factor in a direct proportionality relationship between the average initial oil saturation and the average residual oil saturation. Pore-size distribution controls capillary pressure behavior and capillary forces, which are the dominant forces in a strongly water-wet medium.
- Wettability is related to the rock surface area. The amount of wetting phase present in the Berea sandstone cores is a function of the exposed and unexposed surface area of the medium upon which the wetting phase adheres or spreads.
- Wettability affects oil recovery in strongly water wet systems because the relative permeability to oil increases as the degree of water-wetness increases.
- The rock surface area affects the wettability of a porous media and consequently is a factor in the amount of oil recovery realized by waterflooding. Oil recoveries by waterflooding are larger for porous media with more rock surface area and a higher degree of water-wetness than for porous media with less rock surface area and a lower degree of water-wetness.
- Pore size distribution and median pore-throat size affect rock tortuosity expressed in terms of the wetting phase retention time in a water-wet medium.

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NOMENCLATURE

Q_1 = lower quartile of the frequency distribution.

Q_3 = lower quartile of the frequency distribution.

St. Dev. = standard deviation of given experimental data.

ϕ = porosity, fraction

τ = tortuosity (expressed in terms of retention time), s.

Abbreviations

Av = average

cm = centimeter

Hg = mercury

kPa = kilo-Pascal

Min = minimum

Max = maximum

S = saturation

s = second

St. Dev. = standard deviation of given experimental data

Subscripts

i = irreducible

o = oil

r = residual

w = water

Table 1: Statistical Description of Waterflood Experiments Variables

Variable	Mean	Median	Min.	Max.	Q_1	Q_3	St. Dev.
	Dimension of Variable	Dimension of Variable	Dimension of Variable	Dimension of Variable	Dimension of Variable	Dimension of Variable	%
Oil Recovery @ ∞ WOR	0.4399	0.4362	0.3986	0.5130	0.4210	0.4497	2.928
Oil Recovery @ BT	0.3225	0.3269	0.2005	0.3766	0.3123	0.3447	4.054
S_{oi}	0.5441	0.5484	0.4658	0.6193	0.5094	0.5779	3.950
S_{wi}	0.4559	0.4515	0.3807	0.5382	0.4220	0.4905	3.950
S_{or}	0.3041	0.3107	0.2446	0.3488	0.2807	0.3314	3.234
ϕ	0.1955	0.2009	0.1688	0.2183	0.1779	0.2148	1.893
τ	652.0	666.9	347.1	897.0	572.4	743.7	139.1

Table 2: Statistical Description of Wettability Indices*

Core #	Top Layer	St. Dev., %	Middle Layer	St. Dev., %	Bottom Layer	St. Dev., %
1	0.836	6.49	0.807	9.11	0.813	4.23
2	0.935	5.21	0.954	4.48	0.975	1.83
3	0.971	1.59	0.971	1.59	0.958	2.16
4	0.965	2.03	0.958	2.05	0.961	2.05
5	0.923	2.30	0.901	3.88	0.921	2.78
6	0.937	3.61	0.954	1.73	0.941	3.79
7	0.897	3.01	0.895	3.36	0.922	1.64
8	0.929	2.69	0.969	1.63	0.956	3.50
9	0.936	3.35	0.952	3.49	0.941	3.97
10	0.958	2.29	0.961	2.10	0.969	2.67
11	0.963	2.17	0.972	2.04	0.959	1.43
12	0.959	1.79	0.966	1.94	0.969	1.96
13	0.977	1.40	0.962	1.73	0.967	1.58
14	0.952	3.02	0.955	2.36	0.959	2.32
15	0.929	4.24	0.930	3.91	0.951	2.79
16	0.933	5.02	0.941	2.83	0.919	6.01
17	0.711	5.21	0.749	6.77	0.737	4.13
18	0.887	12.82	0.906	8.67	0.893	2.70
19	0.858	5.03	0.857	3.92	0.910	6.45
20	0.767	13.87	0.776	10.83	0.784	11.92
21	0.907	1.70	0.890	2.33	0.935	2.43
22	0.934	8.48	0.974	1.65	0.958	2.50

*Average wettability is based on arithmetic average over 8 sandstone core plugs

WI	-1	-0.3	-0.1	+0.1	+0.3	+1
		Slightly oil wet	Neutral	Slightly water wet		
WETTABILITY	OIL WET	INTERMEDIATE			WATER WET	

Table 3: Wettability Index Scale Description

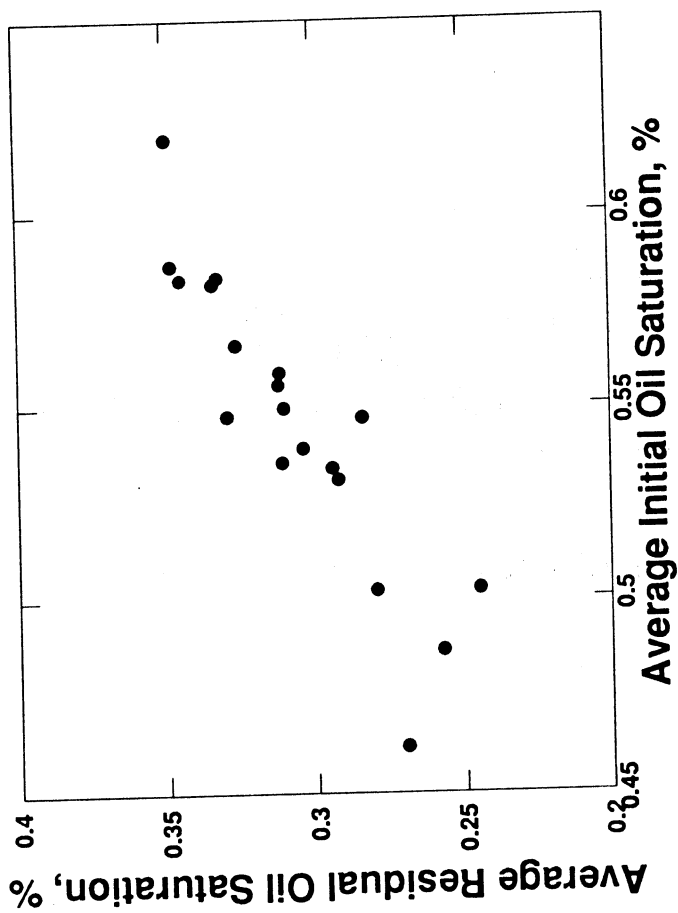


Fig. 1: Av. Residual Oil Saturation vs Av. Initial Oil Saturation

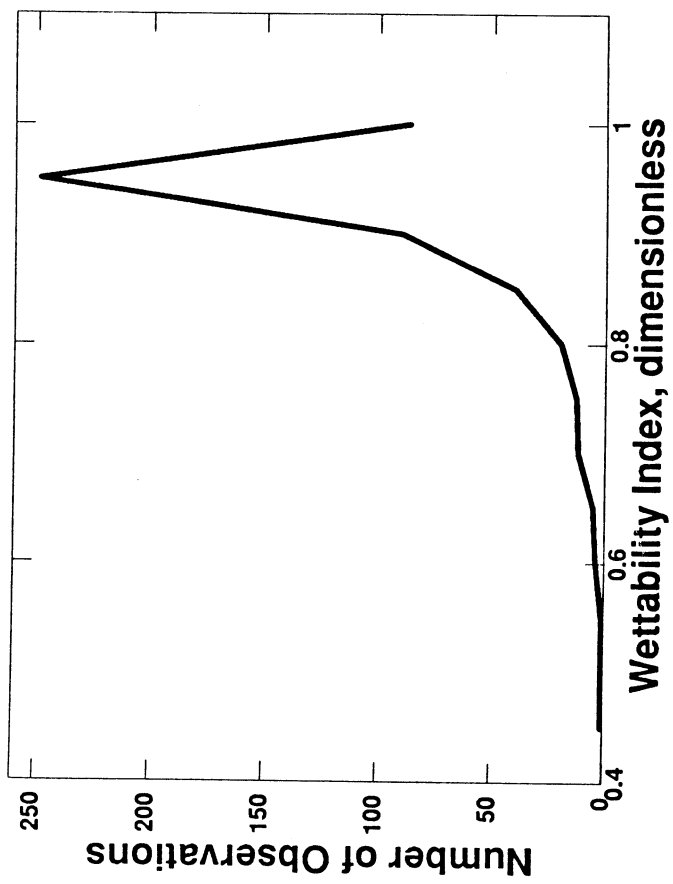


Fig. 2: Wettability Index Frequency Distribution Plot

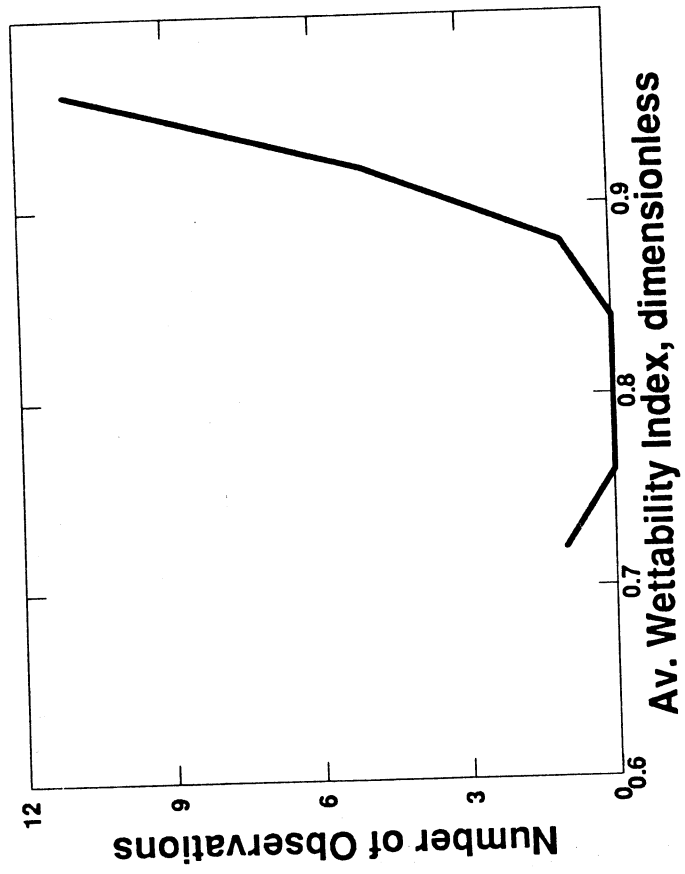


Fig. 3: Average Wettability Index Frequency Distribution Plot

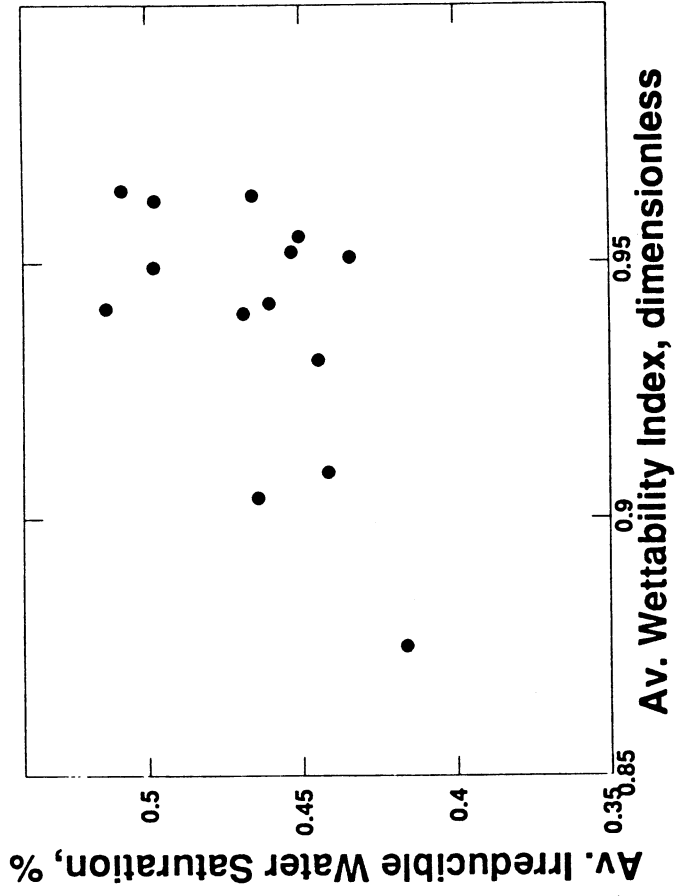


Fig. 4: Average Irreducible Water Saturation vs Average Wettability Index

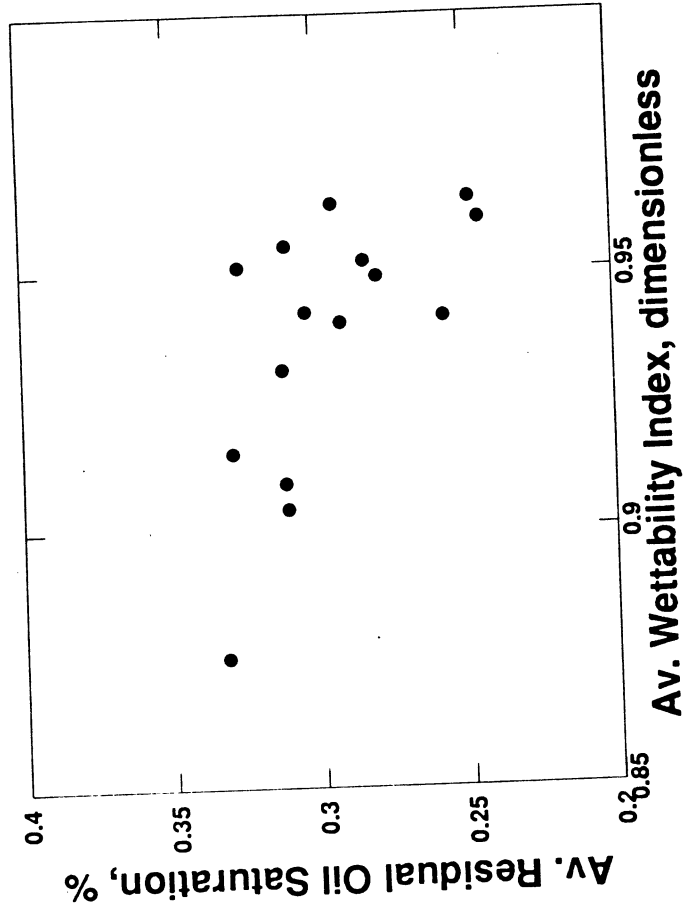


Fig. 5: Average Residual Oil Saturation vs Average Wettability Index

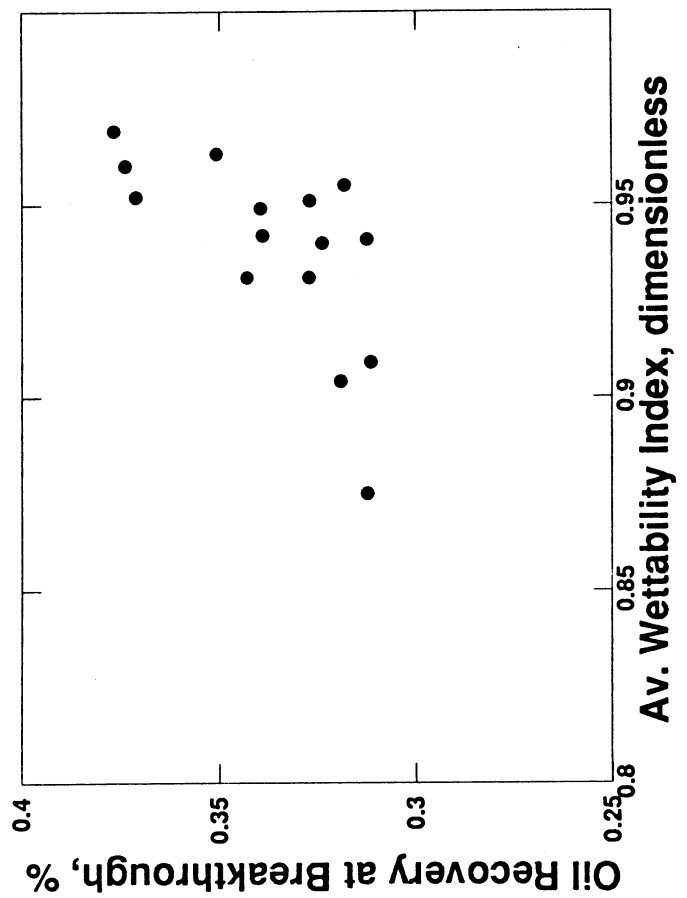


Fig. 6: Oil Recovery at Breakthrough vs Average Wettability Index

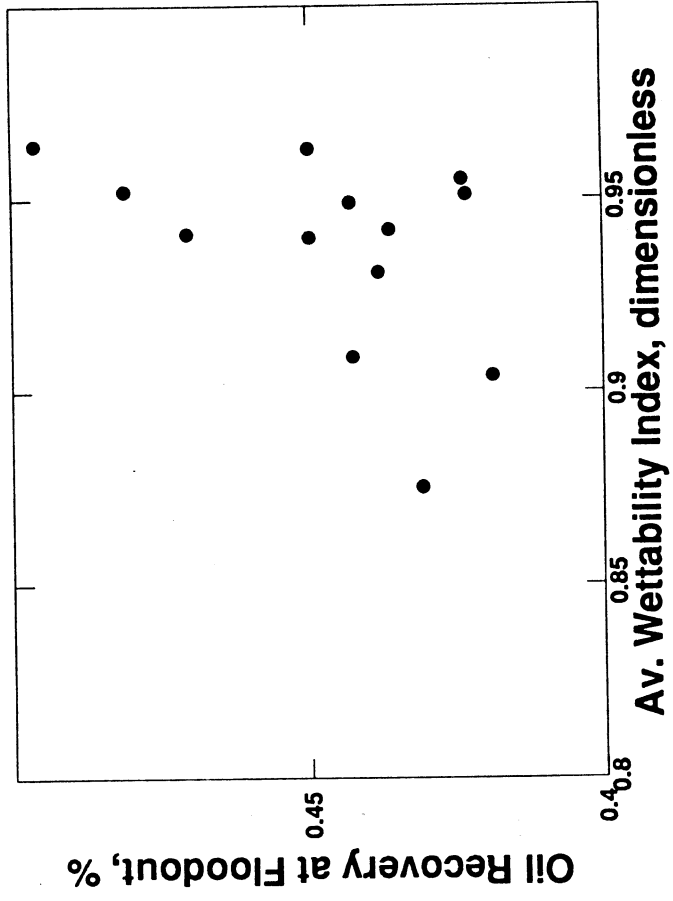


Fig. 7: Oil Recovery at Floodout vs Average Wettability Index

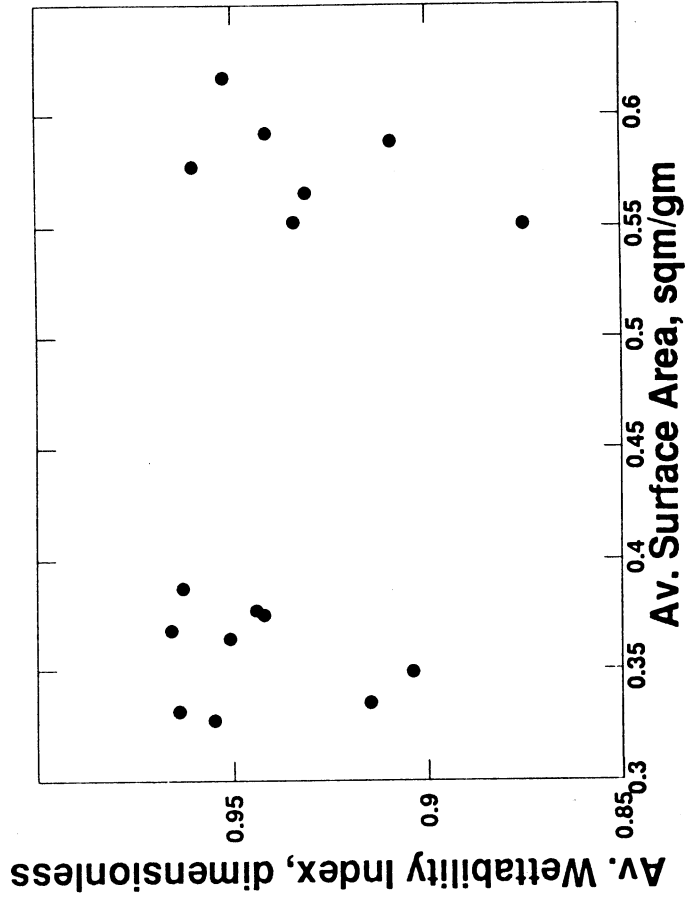


Fig. 8: Average Wettability Index vs Average Surface Area

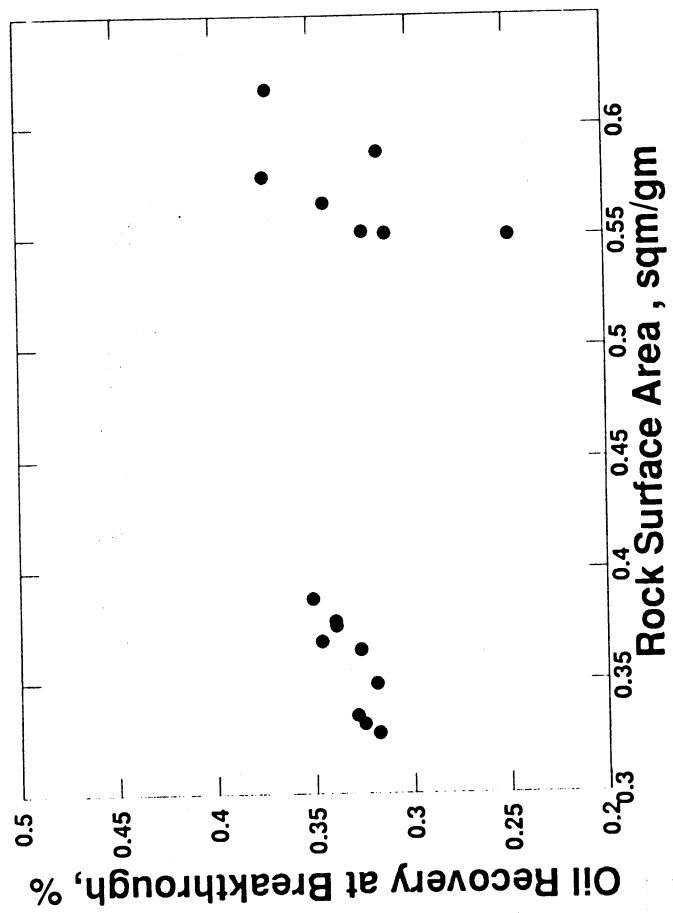


Fig. 9: Oil Recovery at Breakthrough vs Average Surface Area

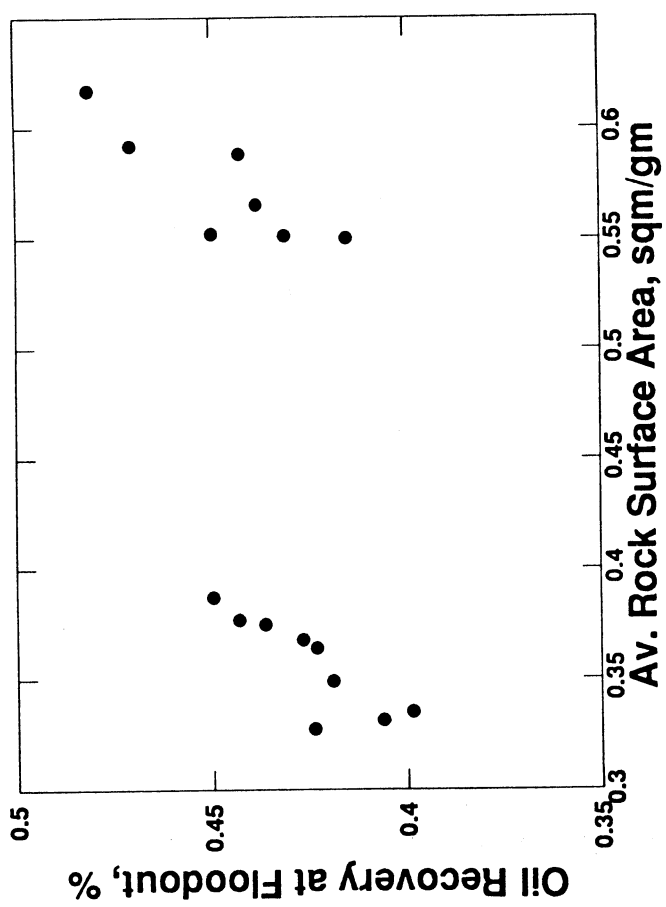


Fig. 10: Oil Recovery at Floodout vs Average Surface Area

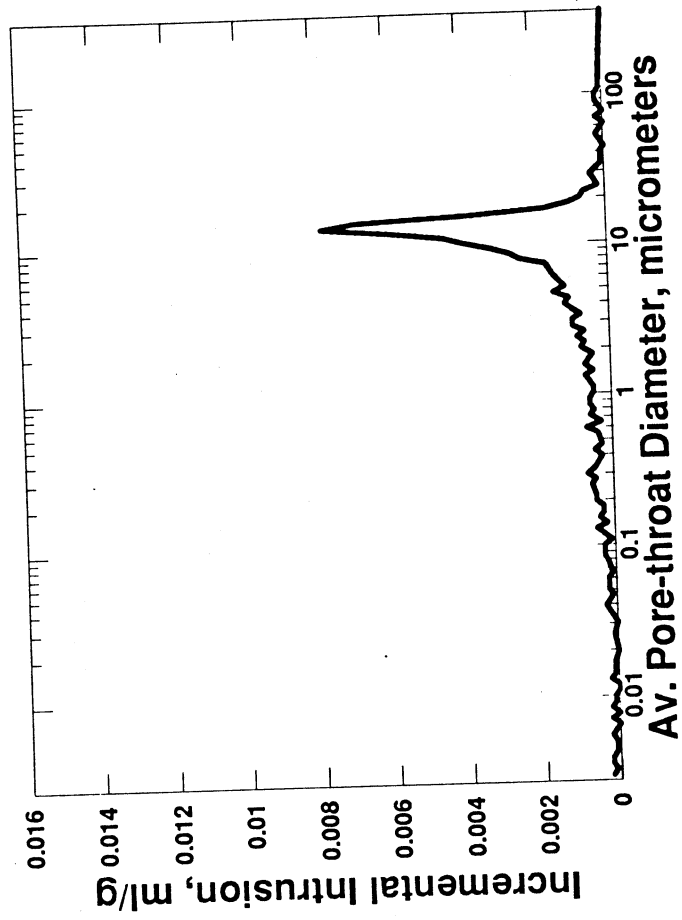


Fig. 11: Incremental Intrusion vs Average Pore-throat Diameter ($k=62.767$ md)

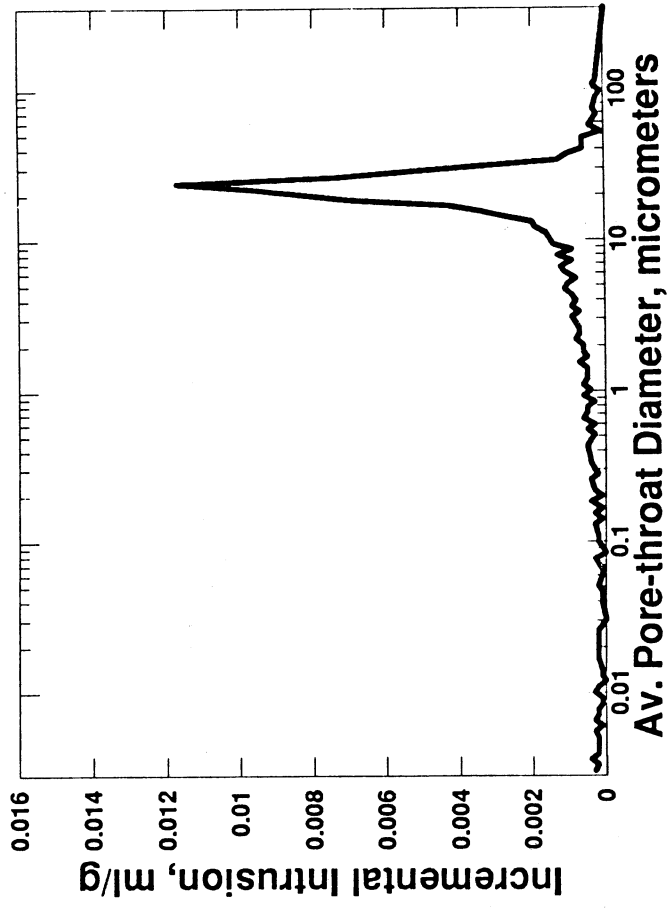


Fig. 12: Incremental Intrusion vs Average Pore-throat Diameter ($k=332.584$ md)

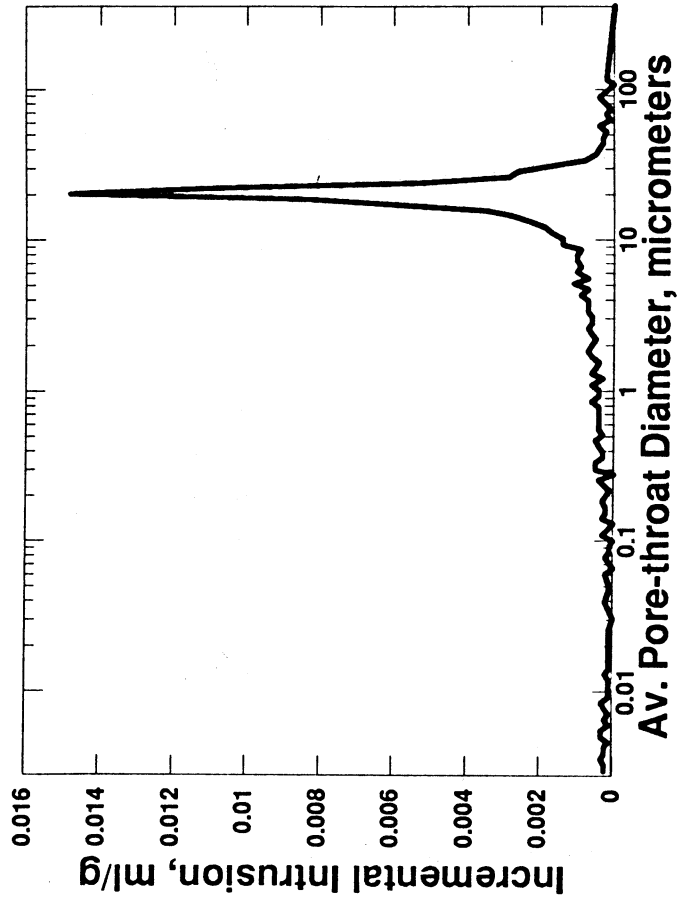


Fig. 13: Incremental Intrusion vs Average Pore-throat Diameter (k=509.028 md)

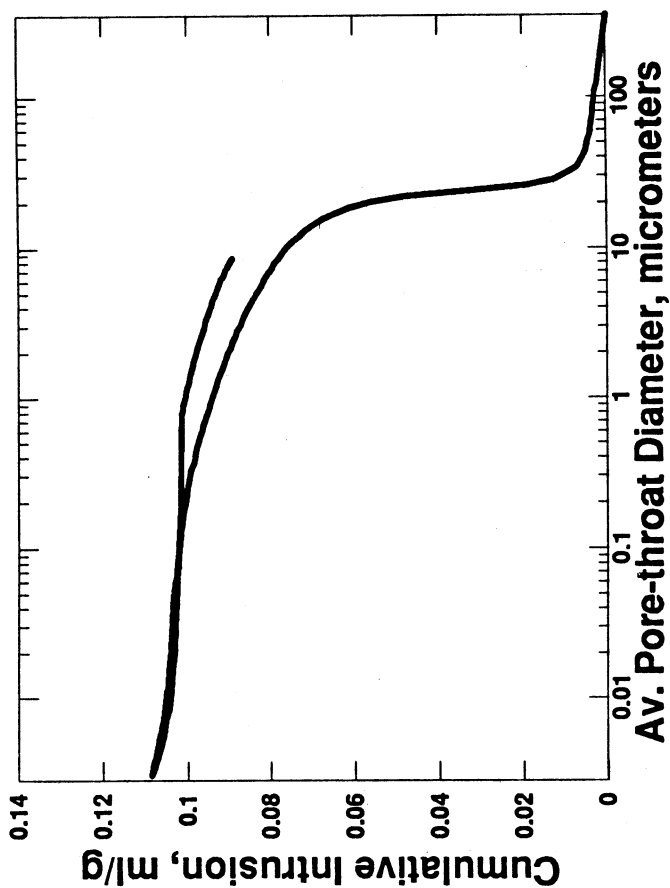


Fig. 14: Cumulative Intrusion vs Average Pore-throat Diameter ($k=332.5$ md, $S_{\alpha}=34.46$ %)

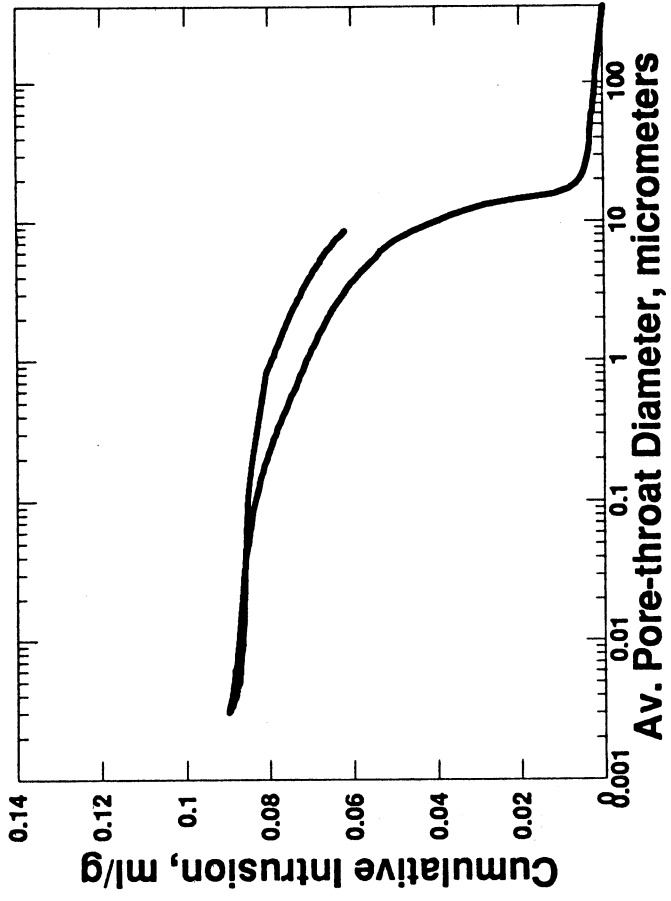


Fig. 15: Cumulative Intrusion vs Average Pore-throat Diameter ($k=62.7$ md, $S_{cr}=29.21$ %)

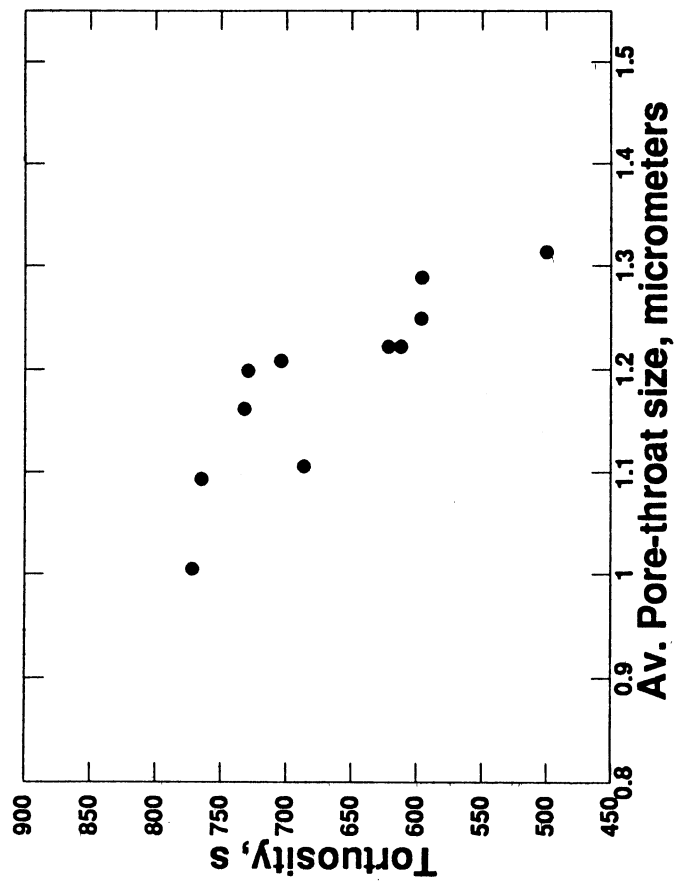


Fig. 16: Tortuosity vs Average Pore-throat Diameter



Table 1.

APEX Volume Classification used in
Bivariate Distribution Functions

Class	Volume range (nanoliters)
10	2.2 - 3.1
15	12.5 - 17.7
20	70.7 - 99.9
25	400 - 565
30	2,260 - 3,200
35	12,800 - 18,100

Table 2.

Comparison of Archie's Lithologic Exponent Values

	APEX Estimate		Measured
	Tower	higher	
<u>Small Samples (1/2" x 1/2")</u>			
Berea sandstone 1	1.72	1.93	(1.78)
Berea sandstone 2	1.68	1.99	(1.78)
San Andres dol 1	1.66	1.94	(1.96)
San Andres dol 2	1.64	2.04	(1.96)
Berea sandstone	1.76	1.95	(1.75)
Bentheim sandstone	1.86	1.94	(1.78)
Moldic dolomite	2.00	2.23	[2.2-2.3]
Belridge diatomite	3.15	4.33	(2.94)
<u>Large Samples (1" x 1")</u>			
Berea Sandstone	1.77	1.82	1.75
Castlegate sandstone	2.00	2.13	2.03
Moldic dolomite	2.00	2.18	[2.2-2.3]
Moldic limestone	2.26	2.44	2.54

() - measured on adjacent sample

[] - estimated

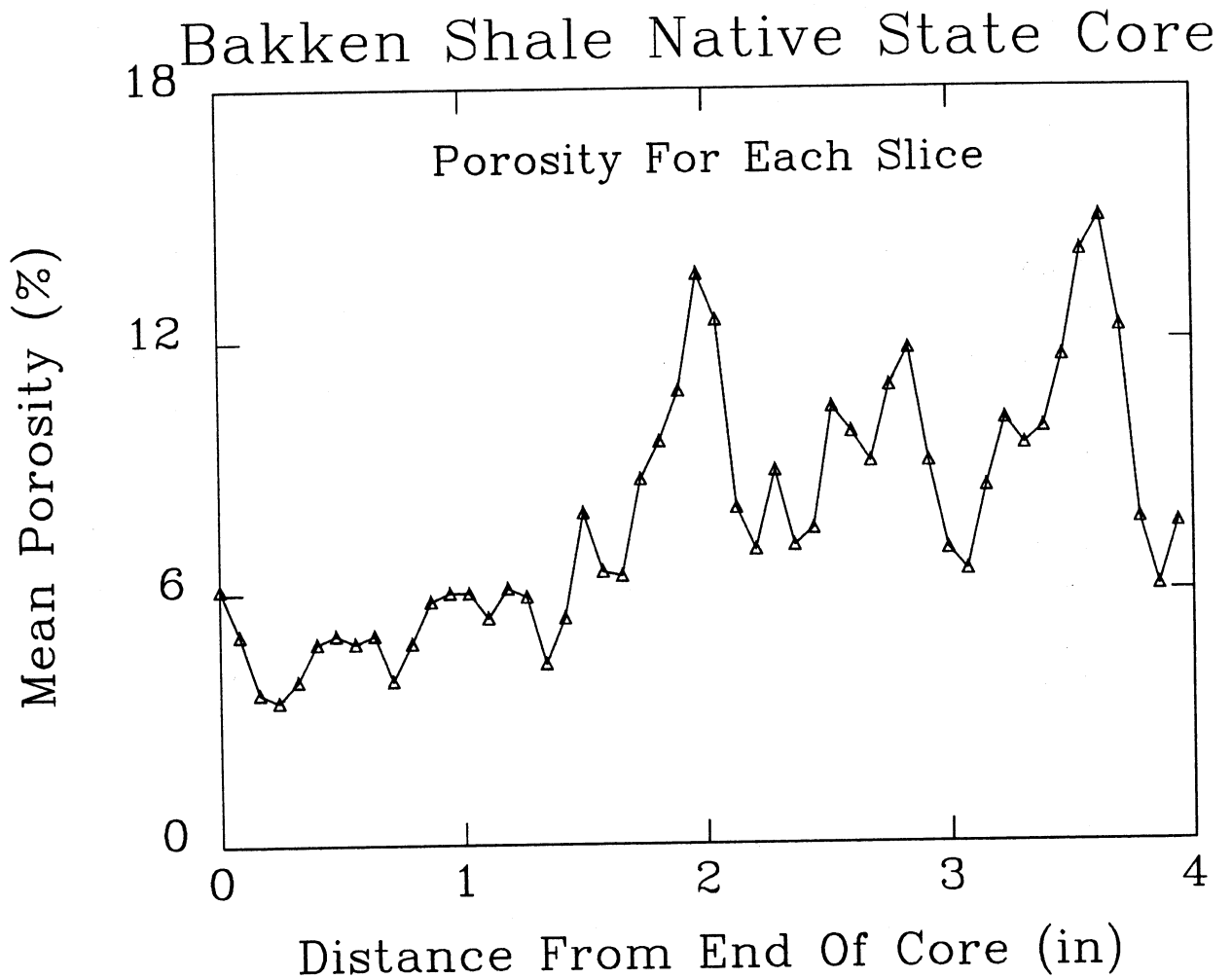


Figure 9 - The mean porosity as a function of distance from the end of the core for the Bakken shale sample. These whole core data correspond well to the individual porosity image in Figure 8.

Figure 10 - The differences in the experimental setup for the Monterey shale experiment and the coal experiment. The addition of the plastic spacer greatly reduced beam hardening by minimizing the annulus and prehardening the beam. It also helped in centering the sample.

Figure 11 - Porosity data after 30 seconds for the coal sample. The image is normalized to the gas density in the annulus (white on this scale). The fractures are already filled, and some adsorption is already taking place. The xenon gas was at 20 psig.

Figure 12 - A comparison of the evacuated CT number image (left) and the porosity image (right) after 30 seconds for the coal sample. The dark areas in the CT number image are fractures. The white areas in the CT number image are probably sand.

Figure 13 - Porosity data after 4.3 days for the coal sample. The green ring is the gas in the annulus (relative density = 1). The sample has absorbed 2.9 times the density of the surrounding gas on average. The nominal pressure at the time of this image was 86 psig.