

Fundamental Properties of Green River Oil Shale
as Determined from Nitrogen Adsorption and
Desorption Isotherms

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Oil shale, a major potential source of liquid fuels, consists of a complex mixture of organic and inorganic constituents in variable proportions. Understanding of its fundamental properties and structure may aid in improving existing methods for converting the organic matter to useful liquid and gaseous products and in devising new methods (7,8,9,10,12).

A previous publication (14) presented data on particle size, particle-size distribution, and particle-size classification of the primary inorganic particles. Included were photomicrographs showing the geometric form of many of these particles. The paper also described the method used in preparing the organic-free mineral constituents for that work and the current study.

The present paper presents information on surface area, pore structure, and pore volume of oil shale and its mineral constituents, and the manner in which the organic matter is distributed through the shale. Based on the surface area of the mineral constituents and some logical assumptions, the maximum amount of organic matter in contact with the surface of the inorganic matrix is calculated.

EXPERIMENTAL

Preparation of Oil-Shale Samples

Two samples of approximately 200 pounds each were prepared by compositing random samples of EF and B bed shales from the Bureau of Mines experimental oil-shale mine near Rifle, Colorado (13). The composite sample from EF bed assayed 28.6 gallons a ton and that from B bed 75 gallons a ton. These were crushed to pass a 2-mesh-per-inch screen. A representative sample from each of the crushed oil shales was reduced to pass a 0.375-inch screen and a representative portion of this reduced further to pass a 200-mesh screen. The particles smaller than 44 microns were removed using a screening and washing technique. The remaining particles, 44 to 77 microns, were used to determine surface area, micropore structure, and pore volume. This particle-size range was selected to obtain a representative sample of the initial shale within a 4 to 5 gram sample, limited by the size of the adsorption bulb; to expose any naturally existing micropore structure, and to eliminate the surfaces of the extremely fine particles created during crushing. The 44 to 77 micron particles represented 53.4 and 42.6 weight percent of the respective 28.6- and 75-gallon-per-ton shales ground to pass 200-mesh. Chemical analyses indicated that their organic-inorganic ratios were quite similar to those of the 200-mesh shales prior to removing the particles smaller than 44 microns.

Apparatus

The low-temperature adsorption apparatus and technique employed for this study were similar to those described by Emmett (4), Joyner (1), and Reis (11). The

Pyrex-glass adsorption apparatus, fabricated in this laboratory, consisted of an adsorption bulb, calibrated gas burettes, mercury manometer, McLeod gauge, nitrogen-vapor-pressure thermometer, high vacuum system capable of 10^{-6} mm. of Hg., purification trains for nitrogen and helium, and reservoirs for the purified gases. The purity of the two gases exceeded 99.9 mole percent as determined by mass spectrometer.

Procedure

Oil Shale, 44 to 77 Microns. A sample of known weight was packed tightly into the adsorption bulb and degassed at 220°F. for 72 to 96 hours to attain a constant pressure of 10^{-6} mm. Hg. This degassing temperature was selected to clean the shale's surfaces without significantly changing its chemical or physical structure. To determine the effect of degassing time, runs as short as 8 hours were made. After degassing, the dead-space volume within the adsorption bulb was measured with helium at the temperature of liquid nitrogen. Subsequently the helium was pumped from the adsorption bulb and the sample again degassed at 220°F. for 30 minutes before determining its adsorption isotherm.

A complete adsorption isotherm at the temperature of liquid nitrogen was obtained by measuring the quantity of nitrogen adsorbed at pressures from a few millimeters to the saturation pressure of the nitrogen. Adsorption equilibrium was reached rapidly below a relative pressure of 0.35. Fifteen minutes was allowed for equilibrium before each successive known volume of nitrogen was admitted into the adsorption bulb. Above 0.35, two hours were allowed for equilibrium to be attained. This appeared ample time for the heat of adsorption to dissipate and for equilibrium to be established. To determine if equilibrium had occurred, the time was extended to six hours at several different relative pressures. No significant differences were noted when compared with two hours time. After completing the adsorption isotherm, the data for the desorption isotherm were obtained by removing a known volume of nitrogen and allowing the system to come to equilibrium before removing the next known volume of nitrogen. This was continued until the relative pressure dropped to 0.2. Equal time was allowed for desorption at the different relative pressures as was allowed for adsorption. Several adsorption-desorption runs were made for each of the two shales using different representative samples for each run. The loss in weight, probably due to decarboxylation and loss of volatile organic matter, ranged from 0.20 to 0.34 weight percent of the samples charged to the adsorption bulb.

Inorganic Constituents. Previous work (14) indicated that a high percentage of the primary inorganic particles were smaller than 44 microns. The term "primary" refers to the initial size of the particles. To retain their initial size and to maintain representation of the initial shales, a composite sample consisting of several hundred pieces, 0.25 to 0.375 inch, was selected from each of the two shales crushed to pass a 0.375-inch screen. The organic matter was removed from these samples by a thermal treatment which did not exceed 750°F. (14), and then each organic-free shale residue was blended to give two uniform samples before their respective adsorption and desorption isotherms were determined.

New inorganic particles, mainly calcium sulfate, were formed when the organic matter was removed. Because the calcium sulfate could exist as extremely fine particles and hence have an appreciable surface area, it was leached from a portion of each residue. Adsorption isotherms were determined on the water-soluble-free residues to compare their surface areas with those of the initial residues. The leached material represented 1.7 and 8.4 weight percent of the initial residues from the 28.6- and 75-gallon-per-ton shales. Because the residue from the rich shale contained such a high percentage of water-soluble material, both its adsorption and desorption isotherms were determined.

A sample, 5 to 6 grams, from each of the residues was packed tightly into separate adsorption bulbs, degassed at 600°F. for 16 hours, and then the dead-space volume determined. The sample was again degassed at 600°F. under high vacuum for 30 minutes before determining the respective isotherms. The time allowed for equilibrium to be

attained after each addition of nitrogen was 15 to 30 minutes for relative pressures below 0.35 and two to three hours for those above 0.35. In obtaining the desorption data, the reverse time intervals were used for desorption to attain equilibrium. In a number of instances, the time between addition or removal of nitrogen was increased to 10 hours in the relative pressure region above 0.75. Comparison of these data with those from the shorter periods indicated that two to three hours was ample time for either adsorption or desorption to occur at the higher relative pressures.

INTERPRETATION OF RESULTS

The experimental data can be expressed in graphic form as adsorption and desorption isotherms. These relate volume of nitrogen adsorbed or desorbed per gram of sample as a function of the relative pressure, P/P_0 , where P is the measured pressure within the adsorption bulb and P_0 is the liquefaction pressure of nitrogen. The adsorption-desorption isotherms of the two oil shales, the primary inorganic particles from each shale, and those from the rich shale free of water-soluble material are presented in Figures 1, 2, 3, 4, and 5.

As classified by Brunauer (2), all of the adsorption isotherms are of the sigmoid or S-shaped type, also referred to as Type II, with an asymptotic approach to the P_0 line. They were interpreted according to the method of Brunauer, Emmett, and Teller (3) who showed that S-shaped adsorption isotherms can be plotted according to the equation:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_0} \quad \text{where}$$

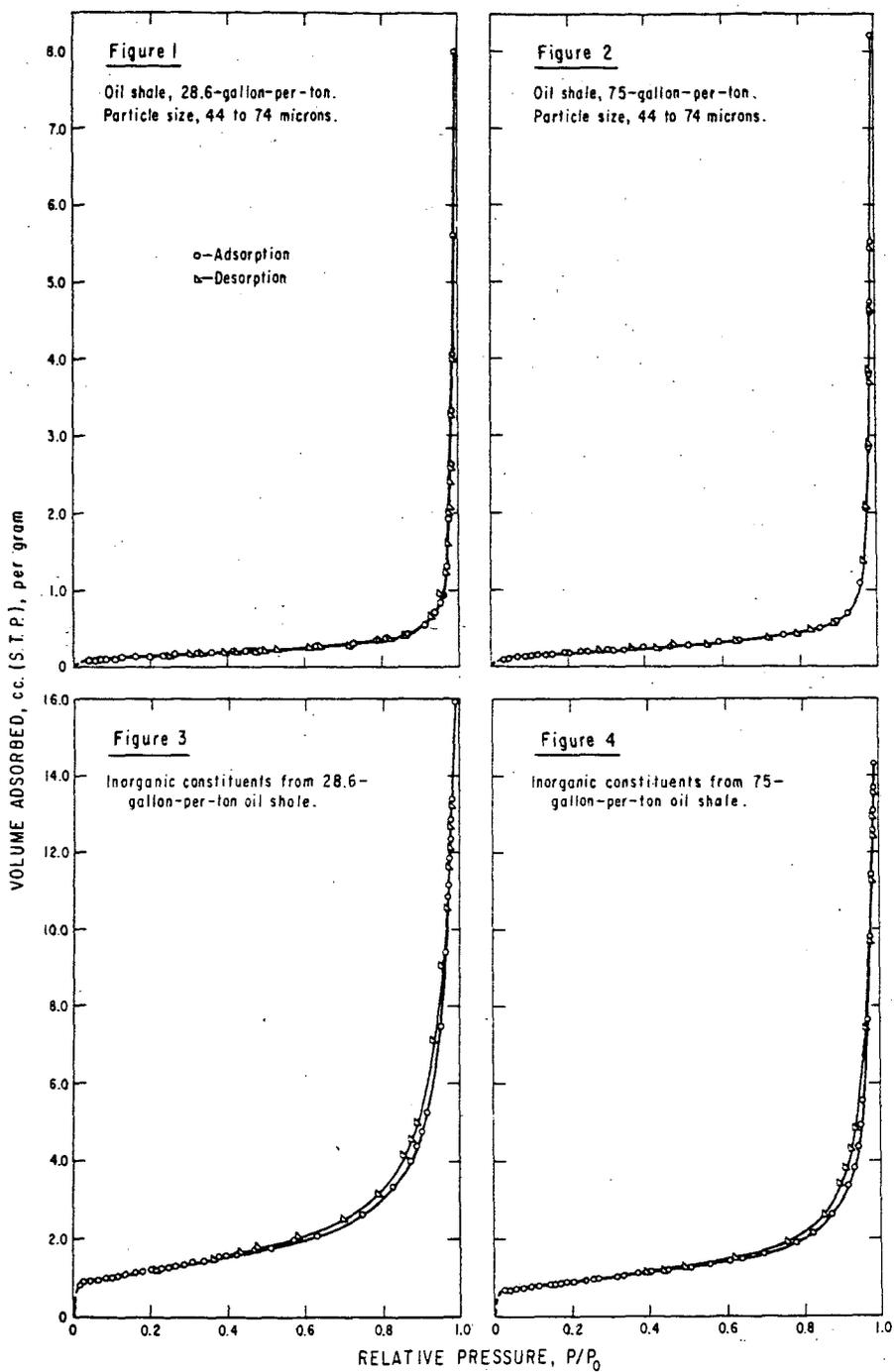
- P = measured pressure
- P_0 = liquefaction pressure of the adsorbate
- V = volume of gas adsorbed at pressure P
- V_m = volume of gas required to form a monolayer
- C = constant relating to heat of adsorption

A plot of $P/V (P_0 - P)$ as a function of P/P_0 is linear within the relative pressure range of 0.05 to about 0.35 provided the adsorption isotherm is of the sigmoid or S-shaped type. Deviations from linearity occur below and above this relative pressure range. They are negative up to 0.05 and positive above 0.35.

The experimental data for the two shales and the primary inorganic particles were plotted according to the BET equation and they are presented in Figures 6, 7, and 8. These adsorption isotherms are in excellent agreement with the BET theory. The volume of nitrogen, V_m , required to form a monolayer was calculated from the slope and intercept of these isotherms and then translated into area units, sq. meters per gram, using 16.2 \AA . (6) as the area of the adsorbed nitrogen molecule.

Oil Shale

Surface Area. The surface areas of the two shales are presented in Table I. That of the rich oil shale remained essentially constant with respect to degassing time while that from the leaner shale differed by about 0.14 sq. meter per gram. Why the surface area dropped was not known because the samples did not appear to be completely degassed before 96 hours. The values selected to represent the shale particles, 0.75 and 0.58 sq. meter per gram, were those after degassing for 96 hours. These values when converted to surface areas per cubic centimeter, were very close, 1.22 and 1.24 sq. meters per cc. respectively. They are about 20 times the surface area of nonporous spheres with a diameter midway between 44 to 74 microns when packed in a rectangular pattern and each successive layer resting in the depressions provided by the previous layer.



NITROGEN ADSORPTION-DESORPTION ISOTHERMS.

Table I. - Surface Area of Oil Shale, Particle Size, 44 to 74 Microns

Oil Shale	Weight, gms.	Degassing Temp., °F.	Degassing Time, hrs.	V _m cc./g.	Surface Area, Sq. M/g.	Surface Area, Sq. M/cc.
28.6 GPT ^{1/}	5.056	220	8	0.850	0.73	1.57
"	5.271	220	24	0.838	0.70	1.50
"	5.080	220	96	0.690	0.59	1.27
"	4.885	220	96	0.646	0.58	1.24
75 GPT	3.609	220	8	0.616	0.75	1.22
"	3.609	220	60	0.594	0.72	1.17
"	3.930	220	96	0.616	0.75	1.22

^{1/} Gallons per ton

Much of the surface area of the shale particles was probably contributed by surface roughness, induced fractures in the inorganic crystals exposed at the surfaces of these particles, and induced fractures in the organic matter itself brought about when the shale particles were prepared. Some of the surface area may be attributed to naturally occurring pores or capillaries with diameters less than 10 Å. If such exist, their surface area could not be determined directly from the adsorption-desorption isotherms nor their presence detected, because within the relative pressure region, 0.05 to 0.35 capillary condensation presumably does not occur and hysteresis therefore would not be evident. The coverage of nitrogen on the adsorbate within this region varies from less than a monolayer up to about 1.5 monolayers (5). The small measured surface area of the shale particles indicates that surfaces attributed to capillaries or pores accessible through openings less than 10 Å., if they occur, are not very large.

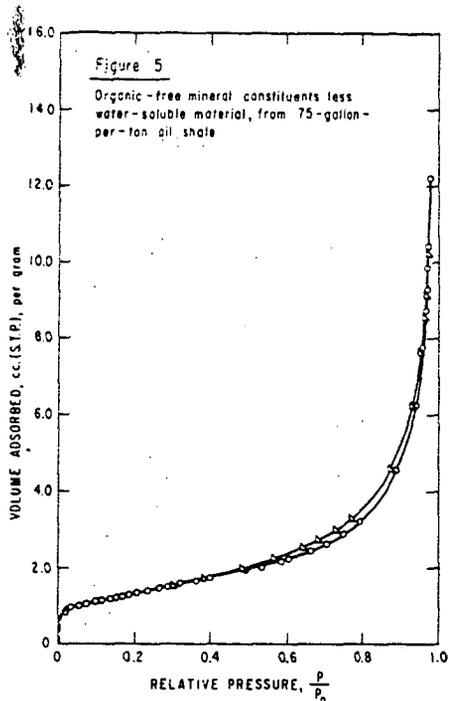
Pore Structure. Pore size, pore-size distribution, and pore volume of the adsorbent is obtained from adsorption-desorption isotherms and Kelvin's equation which relates the radius of a capillary to the relative pressure at which condensation takes place (11). Kelvin's equation is expressed as follows:

$$\ln \frac{P}{P_0} = \frac{-2\sigma V \cos \theta}{rRT}$$

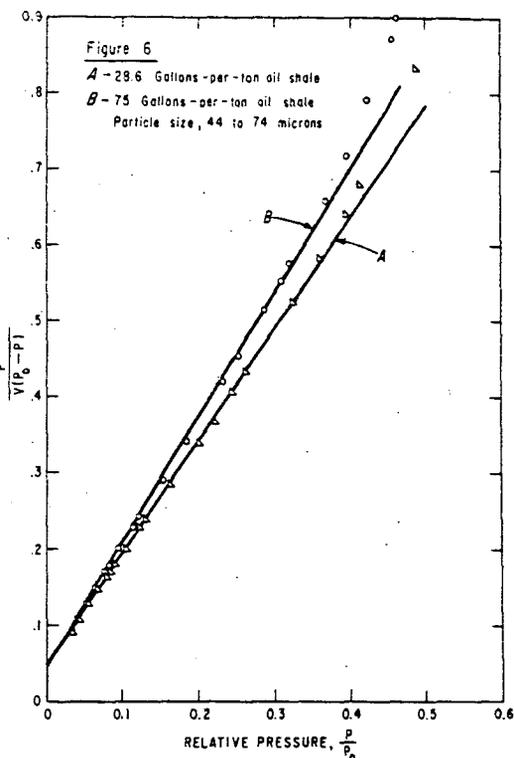
where

$\frac{P}{P_0}$	=	relative pressure
r	=	capillary radius
σ	=	surface tension of the adsorbate
V	=	molar volume of liquid adsorbate
θ	=	angle of contact
R	=	gas constant
T	=	absolute temperature

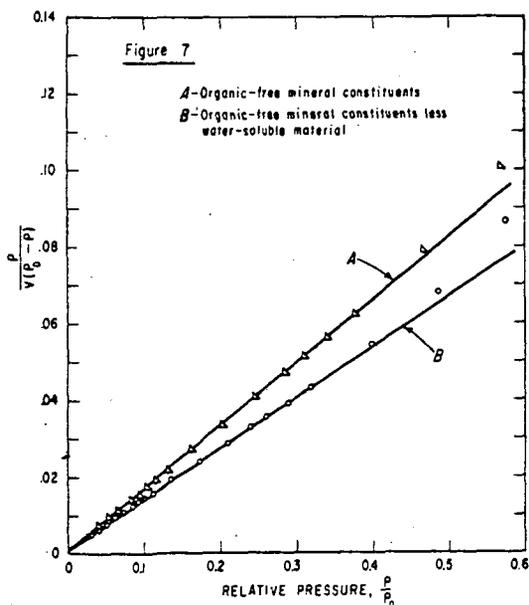
When capillary condensation occurs, the desorption isotherm usually lies well above the adsorption isotherm down to a relative pressure, near 0.4, which corresponds to the thickness of two monolayers of adsorbate. The nature of the pore structure determines the contour of the hysteresis loop in the desorption isotherm. Those which have hysteresis loops with plateaus followed by steep portions in the isotherm indicate a narrow pore-size distribution whereas curves free of inflection points indicate a broad pore-size distribution.



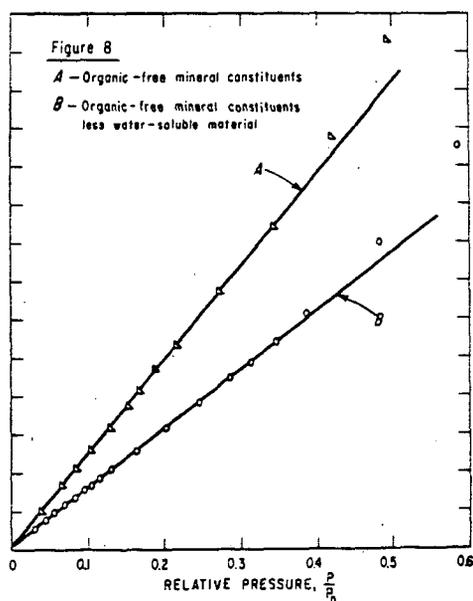
NITROGEN ADSORPTION-DESORPTION ISOTHERM.



NITROGEN ADSORPTION ISOTHERMS ACCORDING TO THE BET EQUATION.



NITROGEN ADSORPTION ISOTHERMS ACCORDING TO THE BET EQUATION.



The isotherms in Figures 1 and 2 show practically no hysteresis therefore little, if any, capillary condensation and evaporation. Deposition and removal of nitrogen apparently involved similar physical forces. This phenomenon indicates that the shale particles contained no appreciable amount of pores and/or capillaries with radii of the pore openings ranging from 10.5 to 235 A. as determined by Kelvin's equation.

Pore Volume. The pore volume can be calculated, from the quantity of nitrogen adsorbed between the relative pressure of 0.4 to 1.0. In Type II adsorption isotherms, however, which approach P_0 asymptotically; the relative pressure at which capillary condensation is complete and interparticle condensation begins is not readily discernible. In Figures 1 and 2 the relative pressure selected for calculating pore volume was the intercept between the extrapolated near linear portions of each adsorption isotherm. In both isotherms the intercept occurred at 0.96. At this point all capillary condensation should be completed and all pores accessible through openings with radii up to 235 A. should be filled with liquid nitrogen. Reis (11) points out that there is reason to believe that in Type II isotherms, adsorption above a relative pressure of 0.90 may be interparticle condensation principally.

The pore volumes of the shale particles calculated from two different relative pressures, 0.96 and 0.90, are given in Table II. The value 0.808 was used as the density of nitrogen at the liquefaction pressure. As noted in Table II, the relative pressure selected to represent completion of capillary condensation significantly influences the calculated pore volume. The actual value may be somewhere between these two limits.

Table II. - Pore Volume of Oil-Shale Particles, 44 to 77 Microns

	Weight, gms.	Pore Volume			
		$\frac{P}{P_0} = 0.96$		$\frac{P}{P_0} = 0.90$	
		cc./gm.	Vol. %	cc./gm.	Vol. %
Oil Shale					
28.6 GPT	4.885	0.0013	0.28	0.0005	0.11
75 GPT	3.930	0.0013	0.21	0.0006	0.10

The pore volumes calculated from either relative pressure are small. These values, although small, may be higher than the true pore volume. Induced minute fractures in the shale particles as result of crushing and interparticle condensation probably contribute to these volumes. Because the isotherms in Figures 1 and 2 exhibit practically no hysteresis, they indicate absence of pore volume accessible through pore openings with radii smaller than 100 A.

Inorganic Constituents

Surface Area. The surface area of the primary inorganic particles free of organic matter and those free of both organic matter and water-soluble material were calculated from their respective BET plots, Figures 7 and 8, and presented in Table III. The particles free of water-soluble material had the higher value. This was not expected because of the calcium sulfates present. The increase in surface area over the initial inorganic particles may be attributed to separation of the platelet structure of some clay minerals, etching on the surface of minerals slightly soluble in water, removal of material other than calcium sulfate or a combination of these factors.

Pore Structure. In Figures 3, 4, and 5 the desorption isotherms exhibit hysteresis characteristic of porous materials yielding Type II isotherms. The hysteresis loops in

Table III. - Surface Area of Primary Inorganic Particles

Primary Inorganic Particles	Weight, gms.	Degassing Temp., °F.	Degassing Time, hrs.	V _m cc./g.	Surface Area Sq. M./g.
28.6 GPT Oil Shale <u>1/</u>	6.261	600	16	0.969	4.24
75 " " <u>1/</u>	6.915	600	16	1.081	4.73
28.6 " " <u>2/</u>	5.711	600	16	0.713	3.12
75 " " <u>2/</u>	6.323	600	16	1.029	4.15

1/ Initial2/ Free of water-soluble material

the respective figures begin at relative pressures near 0.96, 0.97, 0.97 and all join the adsorption isotherms near 0.4. The smooth contours indicate that the pore openings in the primary inorganic particles have random pore-size distribution. Calculated from Kelvin's equation, the pore radii extend from 10.5 A. to 235 A. within the relative pressure region of 0.4 to 0.96 and 10.5 A. to 312 A. within 0.4 to 0.97. However, if condensation above a relative pressure of 0.90 is considered to be interparticle principally (11), the upper limit of the pore radii would be about 100 A.

Pore Volume. Pore volume per gram and percent porosity of the primary inorganic particles calculated from their respective isotherms, Figures 3, 4, and 5, are presented in Table IV. The volume occupied by the organic matter in 28.6- and 75-gallon-per-ton

Table IV. - Pore Volume of Primary Inorganic Particles

Primary Inorganic Particles	Weight, gms.	Pore Volume			
		$\frac{P}{P_0}$ at 0.96		$\frac{P}{P_0}$ at 0.90	
		cc./g	Vol.%	cc./g.	Vol.%
28.6 GPT Oil Shale <u>1/</u>	6.261	0.0096	2.66	0.0050	1.39
75 " " <u>1/</u>	5.711	0.0086	2.36	0.0029	0.80
75 " " <u>2/</u>	6.232	0.0079	2.16	0.0048	1.31

1/ Initial2/ Free of water-soluble material

oil shales is 0.151 and 0.417 cc. per gram respectively. The maximum amount of the organic matter in the respective shales that could exist within the pores or capillaries of the primary inorganic particles is 6.36 and 2.06 volume percent based on the pore volumes obtained at a relative pressure of 0.96. The corresponding volume percents with respect to 0.90 relative pressure are 3.31 and 0.70. The pore volumes presented in Table IV show that the primary inorganic particles are not very porous and that the distribution of the organic matter in the shales appear to be essentially interparticle and not intraparticle.

Organic Matter in Contact with the Mineral Constituents.

Using surface area data and some logical assumptions an estimate can be made of the amount of organic matter in contact with the mineral constituents. The assumptions were: The organic molecules were spheres, 10 or 20 A. in diameter; the total surface of the mineral constituents was accessible for contact; and the spherical molecules formed a rectangular pattern on the surface. Based on the organic matter's density, 1.07, the approximate molecular weights of the 10 A. and 20 A. molecules would be 340 and 2700 respectively. The amount of organic matter represented by one monomolecular layer in contact with the surface is presented in Table V. This table also presents the number of monolayers the total organic could form if evenly distributed over the surface. These estimates suggest that only a small part of the organic matter is bonded either chemically or physically to the surface of the mineral constituents.

Table V. - Estimated Amount of Organic Matter in Contact with the Mineral Constituents

Mineral Constituents	Surface Area, Sq. M./g.	Dia. of Organic Molecule, A.	Organic Matter Represented by One Monolayer, Wt. %	No. of Monolayers from Total Organic Matter
28.6 GPT Oil Shale	4.24	10	3.11	32
" "	4.24	20	1.57	64
75 GPT	3.12	10	0.57	175
" "	3.12	20	0.29	345

SUMMARY

Data from low-temperature nitrogen adsorption-desorption isotherms on Green River oil shale and its mineral constituents provide a better understanding of its basic physical structure. These data indicate that oil shale is a highly consolidated material with no significant micropore structure, pore volume, or internal surface. This type of physical structure is not favorable to surface dependent chemical or physical processes as it restricts reactive fragments or molecules to the interface. It appears that access to the interior must be preceded by removing, either chemically or physically, successive monolayers or molecules of organic or inorganic matter.

The primary inorganic particles contain pores and/or capillaries with random pore-size distribution. Their pore radii extend from 10.5 A. to 235 A. The pore volume accessible through these pore openings is about 0.01 cc. per gram and the amount of organic matter in the 28.6- and 75-gallon-per-ton oil shales that could exist within these pore spaces was calculated as 6.36 and 2.06 volume percent respectively. These values are considered as maximum volumes. If condensation above a relative pressure of 0.90 was interparticle condensation principally, the volume percents would be about one half. The data show that the distribution of the organic matter within the inorganic matrix is essentially interparticle and not intraparticle.

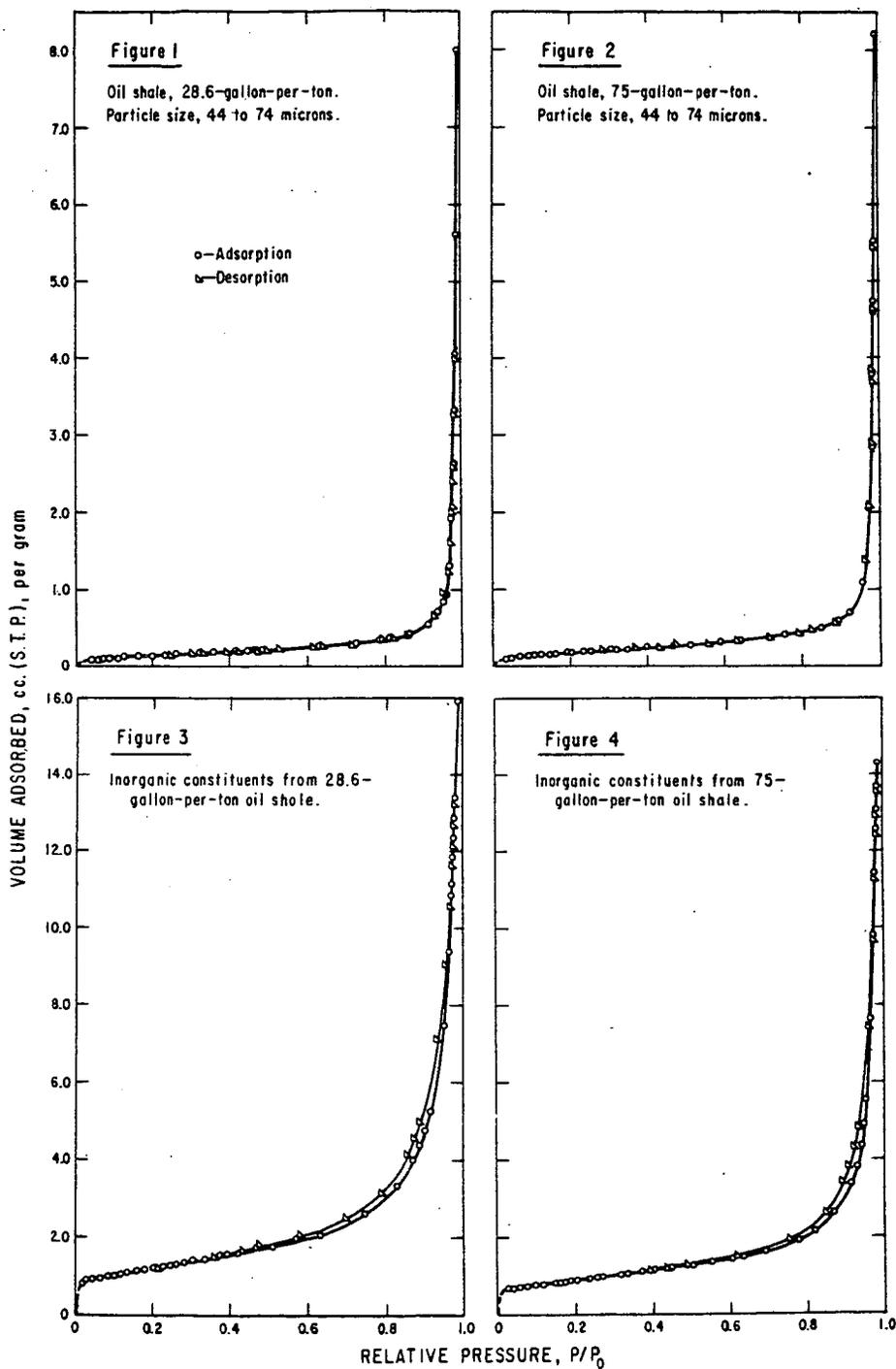
The primary inorganic particles contain no extensive micropore structure as evidenced by the surface area, about 4 sq. meters per gram. Estimates made from surface area values and logical assumptions suggest that only a small percentage of the organic matter is in direct contact with the surfaces of the mineral constituents.

ACKNOWLEDGMENT

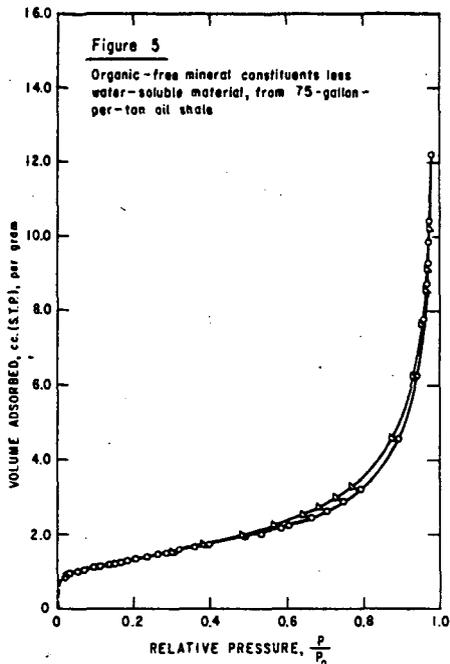
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Literature Cited

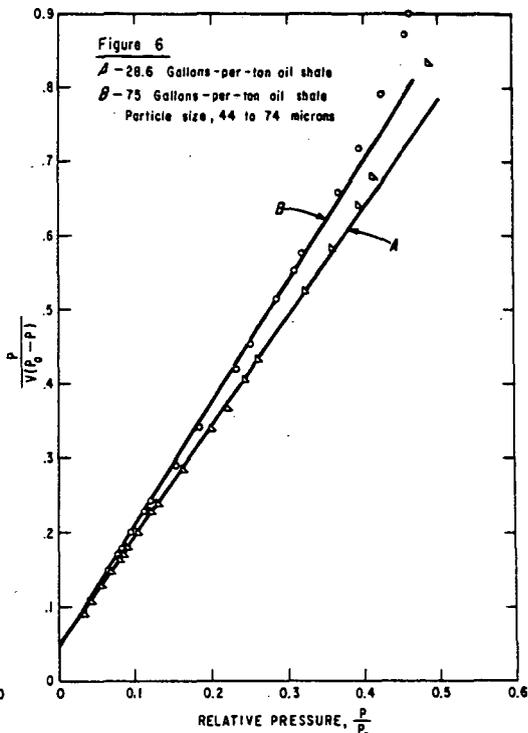
1. Barr, W. E., and Anhorn, V. J., "Scientific and Industrial Glass Blowing and Laboratory Techniques," p. 257, Industrial Publishing Co., Pittsburgh, Pa., 1949.
2. Brunauer, S., "The Adsorption of Gases and Vapors," p. 95, Princeton University Press, Princeton, N. J., 1943.
3. Brunauer, S., Emmett, P. H., Teller, E. J., J. Am. Chem. Soc. 60, 309 (1938).
4. Emmett, P. H., "Catalysis," Vol. 1, p. 31, Reinhold Publishing Corp., New York, 1954.
5. Emmett, P. H., Ind. Eng. Chem., 37, 639 (1945).
6. Emmett, P. H., Brunauer, S., J. Am. Chem. Soc., 59, 1553 (1937).
7. Hull, W. Q., Guthrie, B., Sippelle, E. M., Ind. Eng. Chem. 43, 2 (1951).
8. Matzick, A., Ruark, J. R., Putman, M. W., U. S. Bur. of Mines Rept. Invest. 5145, November 1955.
9. McKee, R. H., "Shale Oil," p. 150, The Chemical Catalog Co., Inc., New York, 1925.
10. "Oil Shale and Cannel Coal," Vol. 2, p. 345, The Institute of Petroleum, Mason House, 26 Portland Place, London, W 1, 1951.
11. Reis, H. E., Jr., "Advances in Catalysis," Vol. 4, p. 87, Academic Press Inc., Publishers, New York, 1952.
12. Ruark, J. R., Berry, K. L., Guthrie, B., U. S. Bur. of Mines Rept. Invest. 5279, November 1956.
13. Stanfield, K. E., Frost, I. C., McAuley, W. S., Smith, H. N., U. S. Bur. of Mines Rept. Invest. 4825, p. 18, November 1951.
14. Tisot, P. R., Murphy, W. I. R., J. Chem. Eng. Data, Vol. 5, No. 4, 558 (1960).



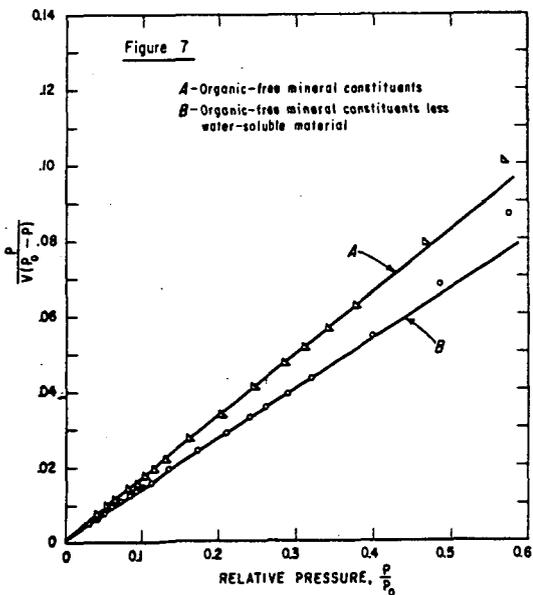
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