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Nature of the porosity in American coals

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The nature of the porosity in a number of 40 X 70 (i.e. - 40 + 70) mesh size American coals, varying in rank from anthracite to lignite, has been studied using the following characterization techniques: gas adsorption, helium and mercury displacement, and mercury porosimetry. Surface areas calculated from carbon dioxide adsorption at 298 K are consistently higher than those calculated from nitrogen at 77 K, indicating the molecular sieve character of the coals. Total pore volumes have been measured in the diameter range 12–29 600 Å and then divided into macropores (300–29 600 Å), transitional pores (12–300 Å), and micropores (4–12 Å). Coals vary widely in their total pore volumes (porosities range between 4.1 and 23.2%). In the lower-rank coals (carbon content less than 75%), porosity is primarily due to the presence of macropores. In coals having a carbon content in the range 76–84%, about 80% of the total open pore volume is due to micro and transitional pores, whereas in the coals of higher carbon content microporosity predominates. Coals having about 35–55% of their total open pore volume in the transitional range are expected to be most suitable for use for adsorption of organic molecules from solution. Thus, they are of interest as possible materials to be used in water purification. In general, these results are considered to be of importance in understanding the extent and rate of interaction of coals with gases and liquids.

Application of physical methods to the study of coal structure has indicated that coal possesses a unique pore system. Hirsch¹, from X-ray diffraction measurements, has demonstrated that, broadly, three types of structure are present in a wide range of coals: (1) the 'open structure' characteristic of low-rank coals with high porosity; (2) the 'liquid structure' of the coking coals with very little porosity; and (3) the 'anthracite structure' of the high-rank coals with high porosity. Anderson, Hall, Lecky and Stein² studied the adsorption of gases and vapours on a number of American coals. The following observations on the pore structure were made: (1) coals have significant pore volume with porosities varying from 2.5 to 18.0%; (2) from the relative sorption of normal and isobutane, it was shown that an appreciable fraction of the pores have openings (diameters) of 4.6 to 5.6 Å* at 0°C; and (3) the low-temperature nitrogen isotherms give the area of pores with diameters larger than 4 to 5 Å.

Most of the sorption work on coals refers to total pore volume. A systematic study of the pore size distribution of various ranks of American coals has not been made. Size distribution may be of prime importance in processes involving diffusion and the availability of internal area. As an example, the problem of methane release from coal would be better understood from a knowledge of pore size distribution rather than from that of pore volume alone. In a proposed method of removing organic compounds from waste water by filtering through a bed of coal³, a knowledge of the pore size distribution would be of great help in selecting the best coal for the process. From these considerations the present investigation was made. This is a study of the

pore structure of coals as characterized by such parameters as total pore volume from helium and mercury densities, pore surface areas from adsorption of nitrogen at 77 K and carbon dioxide at 298 K, macropore size distribution from mercury porosimetry, and size distribution of pores below 300 Å calculated from nitrogen isotherms measured at 77 K.

EXPERIMENTAL

Samples

The chemical analyses of the 27 samples used are given in *Table 1*. Attempts have been made to select samples of all ranks, with high vitrinite content and from all important coal fields of the United States. Sample PSOC-106 was an exception, it having a relatively low vitrinite content and high exinite, micrinite, and fusinite contents. However, detailed study has been restricted to twelve samples, the remainder being used only for nitrogen and carbon dioxide surface area measurements. The samples, originally available in a -20 mesh size, were sieved to a particle size range of (40 X 70) US standard mesh. Because a sieved fraction has been used, the samples do not represent the whole coal. In the attainment of adsorption equilibrium, particle size has an important effect; and work has been done with particles with a rather narrow size range so that comparative data would be obtained.

Apparatus

A volumetric gas adsorption apparatus, of essentially the same design as described by Emmett⁴, was used to

* 1 Å = 0.1 nm

Table 1 Analyses of coals

Sample	Location (State)	Seam	Ultimate analysis (% daf)*					Vitrinite content (volume %, mmcb)**
			Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen (by diff.)	
PSOC-85	Pa	No.8 Leader	91.2	3.8	0.60	1.1	3.1	97.5
PSOC-80	Pa	Buck Mountain	90.8	2.6	0.76	0.64	5.1	96.3
PSOC-130	W. Va	Pocahontas No.3	90.5	4.3	1.1	0.55	3.4	72.7
PSOC-127	Pa	Lwr Kittanning	89.5	5.0	1.0	0.83	3.6	77.7
PSOC-134	Alabama	Pratt	89.3	4.7	1.5	1.0	3.3	75.5
PSOC-135	Alabama	Pratt	88.3	4.9	0.25	0.65	5.7	83.1
PSOC-4	Kentucky	Elkhorn No.3	83.8	5.7	1.5	0.88	7.9	67.3
PSOC-102	Pa	Pittsburgh	83.4	5.2	1.1	1.4	8.7	72.8
PSOC-106	Indiana	Indiana No.1 Block	82.7	5.5	0.55	0.69	10.4	26.2
PSOC-95	Washington	Queen or No.4	81.6	6.0	1.0	1.7	9.4	89.6
PSOC-105A	Indiana	Indiana No.1 Block	81.3	5.7	1.0	1.8	9.9	62.5
PSOC-215	Kentucky	Kentucky No.9	81.3	5.7	1.6	4.5	6.7	79.4
PSOC-24	Illinois	No.2 Colchester	80.0	5.5	1.0	4.5	8.8	88.1
Rand	Indiana	—	79.9	5.2	1.5	4.3	8.9	—
PSOC-213	Kentucky	Kentucky No.9	78.8	5.6	1.7	4.2	9.4	73.4
PSOC-22	Illinois	Illinois No.6	78.7	5.8	1.5	2.8	11.0	88.3
PSOC-26	Illinois	Illinois No.6	77.2	5.6	1.1	7.4	8.3	88.5
POC-197	Pa	'B' Seam (Lwr Kittanning)	76.5	5.6	1.2	4.5	12.2	85.3
PSOC-189	Illinois	Illinois No.1	75.9	5.6	1.0	5.5	11.8	78.0
PSOC-190	Illinois	Illinois No.6	75.5	5.3	1.0	3.3	14.6	88.9
PSOC-97	Wyoming	No.80	75.0	5.5	0.58	1.3	17.5	86.7
PSOC-138	Texas	Darco	74.3	4.9	0.37	0.75	19.6	75.1
PSOC-100	Wyoming	Wyodak-Roland	72.0	5.2	0.81	0.55	21.2	86.0
PSOC-141	Texas	Darco	71.7	5.2	1.3	0.90	20.8	75.3
PSOC-90	Montana	Lower Lignite Seam— Tongue River Member	71.5	4.8	0.83	0.50	22.2	60.9
PSOC-87	N. Dakota	Zap	71.2	5.2	0.56	0.69	22.2	64.7
PSOC-89	N. Dakota	Harmon	63.3	4.6	0.47	1.5	29.9	70.3

* dry, ash-free basis

** mineral-matter-containing basis

measure nitrogen isotherms at 77 K and carbon dioxide isotherms at 298 K. Samples, dried in an air oven at 105°C for 1 h, were then degassed at 130°C for 12 h at a pressure of 10^{-5} torr* before measuring adsorption. Nitrogen adsorption isotherms were followed up to a p/p_0 value of 0.93 (where p is the equilibrium pressure and p_0 is the saturation pressure of the adsorbate at the temperature of measurement). An equilibrium time of 30 min was allowed for adsorption. Nitrogen isotherms were used for the computation of pore size distribution.

An Aminco laboratory porosimeter⁵ was used to determine mercury densities and pore volume distributions for pores greater in diameter than 200 Å. The samples were dried in an oven at 105°C for 1 h and then degassed at room temperature for 2 h before being filled with mercury.

Helium densities were determined in an apparatus described in detail by Bessant⁶. The apparatus (thermostatted to maintain temperature within $\pm 0.1^\circ\text{C}$ in the range 30 to 35°C) was of a constant-pressure type; that is, after the expansion of helium into the sample tube, the pressure was brought back to the initial value by decreasing the apparatus volume using mercury displacement. Equilibrium time for a run was 30 min. The samples were degassed at 130°C for 12 h before the introduction of helium. All helium densities were measured at $32.5 \pm 0.1^\circ\text{C}$.

A 'Low Temperature Asher' (LTA), manufactured by Tracerlab, Inc, was used to determine the mineral matter content of some samples. Details of its instrumentation and techniques are discussed by Gluskoter⁷. In essence, the organic part of the coal is reacted away with atomic oxygen; the sample is not exposed to a temperature higher than 180°C.

* 1 torr = 133 N/m²

RESULTS AND DISCUSSION

Nitrogen and carbon dioxide surface areas

Excellent reviews^{8,9} have appeared recently on the problem of determining surface areas of coal. Areas calculated from nitrogen isotherms at 77 K using the BET equation are associated with the external area of the particles plus that area contained in pores of diameter greater than about 5.0 Å. On the other hand, areas calculated from carbon dioxide adsorption at 298 K, also using the BET equation, are considered to be the closest approximation to the 'total surface area of coals'¹⁰. Marsh and Siemieniowska¹¹ have suggested the use of the Dubinin-Polanyi (DP) equation to calculate surface area of coals from carbon dioxide adsorption data at 298 K. The interesting point about this equation is that surface areas can be calculated from adsorption below 1 atm pressure, if a linear extrapolation of the data to the volume axis is assumed. Walker and Patel¹² compared surface areas calculated by the BET and DP equations (from carbon dioxide adsorption at 298 K but in different pressure ranges) measured in two different pieces of apparatus for a number of coals and chars. They found excellent agreement between the area values in all cases. Consequently in this investigation carbon dioxide areas have been calculated using the DP equation. It may be added that the term 'monolayer equivalent' rather than 'surface area' should be used in discussing results on coals, but the more familiar term has been retained because it is still adequate to describe the phenomenon.

The nitrogen and carbon dioxide surface areas of the coals, on a mineral-matter-containing basis, are reported in Table 2. O'Gorman found the nitrogen surface area of the mineral matter obtained from the low-temperature ashing of a number of coals to be as high as 10 m²/g, while the

Table 2 Nitrogen and carbon dioxide areas of coals

Sample	Surface area (m ² /g, mmcb)	
	Nitrogen	Carbon dioxide
PSOC-85	6.1	426
PSOC-80	7.0	408
PSOC-130	<1.0	231
PSOC-127	<1.0	253
PSOC-134	<1.0	197
PSOC-135	<1.0	214
PSOC-4	<1.0	213
PSOC-102	<1.0	141
PSOC-106	32.0	148
PSOC-95	<1.0	168
PSOC-105A	43.0	114
PSOC-215	1.6	179
PSOC-24	2.2	228
Rand	17.0	147
PSOC-213	27.3	160
PSOC-22	88.4	169
PSOC-26	35.0	133
PSOC-189	46.6	127
PSOC-190	83.0	96
PSOC-97	<1.0	359
PSOC-138	2.2	225
PSOC-100	2.6	308
PSOC-141	2.3	250
PSOC-90	2.0	264
PSOC-87	<1.0	268
PSOC-89	<1.0	238

cdmf Rank
 80.78 *Sub Bit A*
 77.56 *HVC*

specific area of the whole coal may be less than 1 m²/g¹³. It is probable, however, that the finely-divided mineral particles distributed in the organic matrix are not accessible to nitrogen at low temperature in these coals. Clearly, the reported carbon dioxide areas would not be too much affected by the surface area contributed by mineral matter since the total area, for all samples, was more than 100 m²/g.

Surface areas have been plotted against dry-ash-free-carbon content of the coals in Figure 1. Also included in this plot are the nitrogen area values of four samples taken from earlier work by Nandi and Walker¹⁴. It is seen that coals with more than 10 m²/g nitrogen area fall in the carbon content range 75.5 to 81.5%. In this range, also, fall some coals (two out of a total of fourteen) with negligible nitrogen area (< 1.0 m²/g). Sample PSOC-106 falls outside this range but still has a nitrogen

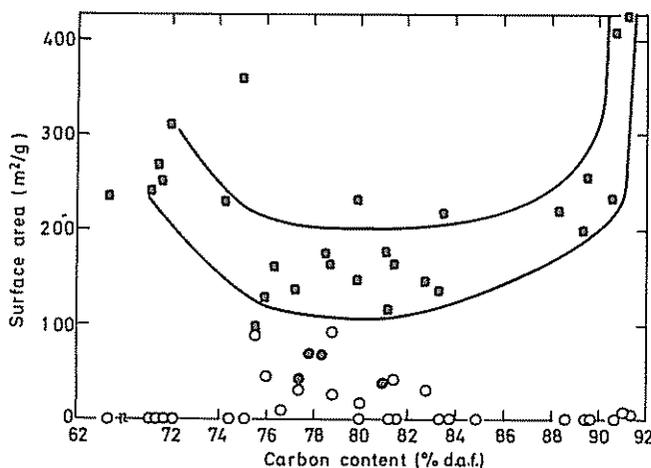


Figure 1 Variation of nitrogen and carbon dioxide surface areas of coals with carbon content
 ● N₂ (from reference 14), ○ N₂ (determined), ■ CO₂

area of 32 m²/g. However, this particular sample has a maceral composition radically different from the other coals. Its high fusinite content probably contributes to its rather high nitrogen area. Most coals on both sides of this range of carbon content (75.5 to 81.5%) have nitrogen areas less than 1 m²/g, exceptions being the anthracites which have surface areas of 5 to 8 m²/g. Carbon dioxide areas of the anthracites are high. There is a general decrease in area with decrease in carbon content to about 83%. The area then remains essentially constant down to a carbon content of 75.5% before rising again. Values fall within a band rather than on a line, differences in carbon dioxide area of coals of essentially the same carbon content being as great as 80 m²/g. It is seen that, generally, coals with higher nitrogen areas have lower carbon dioxide areas.

A critical examination of the surface area values of lignite samples is necessary at this point. Both the nitrogen and carbon dioxide areas may be in significant error. Surface area determination involves heating the sample under vacuum at about 130°C. It has been reported that lignites, once dried very thoroughly, do not adsorb as much water as freshly mined samples¹⁵. The gel-like structure of lignites may be irreversibly altered upon drying and thus the low nitrogen areas may be apparent. In the case of carbon dioxide adsorption, the possibility of polar interaction with oxygen groups has been put forward by Anderson *et al*¹⁶. To check the possibility of irreversible carbon dioxide adsorption, two lignite samples PSOC-87 and 89 were degassed, after the initial carbon dioxide adsorption, at the adsorption temperature for 24 h and the adsorption runs repeated. The surface areas, calculated from the second adsorption runs, were 230 and 275 m²/g compared to 238 and 264 m²/g, obtained initially for PSOC-89 and 87. On the basis of these results, polar interaction of carbon dioxide with oxygen groups in lignites is not considered significant.

Helium and mercury densities

Helium densities. Densities of twelve samples were determined by helium displacement. Helium is the smallest atom available so that it would penetrate almost all pores. However, X-ray studies with anthracites have shown that there is some porosity in these high-rank coals which is closed to helium¹⁷. Therefore, the helium density of coal would be lower than the true density. The dispersion potential of helium is very small, yet adsorption of helium by coals and carbon, particularly at low temperature, has been reported^{18,19}. The results of Kini and Stacy¹⁹, however, indicate that adsorption of helium by vitrains is very low at room temperature. A temperature of 32.5°C was selected for the present measurements. On the basis of the mineral matter content of these samples, as determined by the low temperature ashing technique, a value of 2.7 g/cm³ can reasonably be assumed for the density of the mineral matter. Density data are given in Table 3. The variation of helium density (mineral-matter-free basis) with carbon content (dry, ash-free) is shown in Figure 2. The curve has a shallow minimum at about 81% carbon and rises very sharply as 90% carbon is approached. Franklin²⁰ also observed the same trend, though the minimum occurred at a somewhat higher carbon content for British coals.

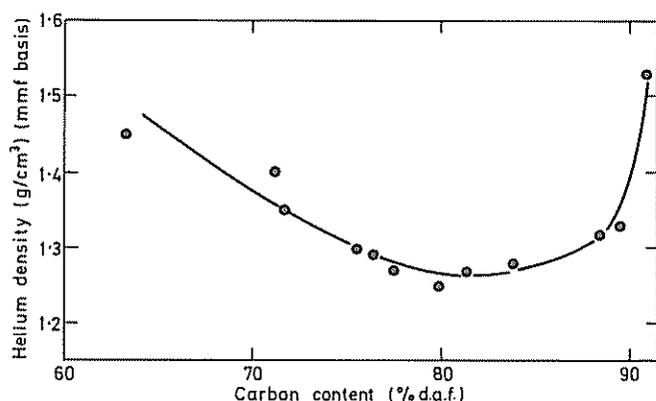
Mercury densities. The same twelve samples were used for mercury density determinations. In mercury density

Table 3 Helium and mercury densities and total open pore volume of coals

Sample	Carbon (% dry, ash-free)	LTA* mineral matter (%)	Helium density (g/cm ³ , mmcb)	Helium density (g/cm ³ , mmfb)**	Mercury density (g/cm ³ , mmcb)	Mercury density (g/cm ³ , mmfb)	Total open pore volume (cm ³ /g, mmfb)	Open porosity (%)
PSOC-80	90.8	19.2	1.67	1.53	1.51	1.37	0.076	10.4
PSOC-127	89.5	6.6	1.38	1.33	1.29	1.25	0.052	6.5
PSOC-135	88.3	5.4	1.36	1.32	1.29	1.25	0.042	5.3
PSOC-4	83.8	2.5	1.30	1.28	1.25	1.23	0.033	4.1
PSOC-105A	81.3	10.3	1.35	1.27	1.15	1.07	0.144	15.5
Rand	79.9	14.0	1.36	1.25	1.24	1.14	0.083	9.5
PSOC-26	77.2	18.2	1.41	1.27	1.19	1.06	0.158	16.7
POC-197	76.5	25.3	1.49	1.29	1.33	1.13	0.105	11.9
PSOC-190	75.5	10.9	1.38	1.30	1.07	1.00	0.232	23.2
PSOC-141	71.7	9.9	1.42	1.35	1.24	1.17	0.114	13.3
PSOC-87	71.2	9.0	1.46	1.40	1.28	1.22	0.105	12.8
PSOC-89	63.3	13.7	1.55	1.45	1.41	1.31	0.073	9.6

* Remaining after low-temperature ashing of coal in an oxygen plasma at about 150°C

** Mineral-matter-free basis

**Figure 2** Variation of helium density of coals with carbon content

determinations of powders, there is some uncertainty regarding the minimum pressure at which the interparticle voids are completely filled. This threshold pressure has been experimentally determined with (40 X 70) mesh (the particle size used in the entire work) glass powders. Considerable amounts of mercury were forced into interparticle voids below 20 psia,* followed by much less mercury penetration between 20 and 60 psia, after which negligible further penetration occurred. To establish this point further, a similar run was made with the anthracite sample (PSOC-80). Mercury penetration occurred up to 60 psia; between 60 and 500 psia penetration was negligible. Since anthracite is known to have negligible macroporosity in the largest pores, it was concluded that at 60 psia the interparticle voids would be filled and any further mercury penetration at higher pressure would be due to the presence of pores. The mercury density values reported in *Table 4* are, therefore, calculated from measurements of mercury displaced by the samples at 60 psia. It is seen that a plot of variation of mercury density with rank would have a similar shape to that shown in *Figure 2* for helium density. Total open-pore volumes have been calculated from the differences of reciprocals of mercury and helium densities and are shown in *Table 3*. Also given are the percentages of the total volume of the coals which are contributed by the open porosity.

* 1 psia = 6.895 kN/m² (absolute)**Table 4** Comparison of pore volumes calculated in the overlap region*

Sample	Pore volume (cm ³ /g)	
	Isotherm method	Porosimetry method
PSOC-190	0.010	0.016
PSOC-26	0.006	0.008
PSOC-105A	0.008	0.010
POC-197	0.001	0.002
Rand	0.004	0.006
PSOC-80	0.002	0.003

* The pore diameter range (180–300 Å) where the porosimeter and the isotherm methods overlap

Pore size distributions

Calculated from nitrogen isotherms. Nitrogen isotherms at 77 K up to $p/p_0 = 0.93$ were measured on twelve of the samples. All isotherms have very similar shapes and may be classified as Type II or IV according to Brunauer²¹. A controversy arises as to which branch of the isotherm should be used in pore-size-distribution computations. Most of the investigators have used the desorption branch. The deciding factor in choosing a particular branch should be good agreement between the calculated cumulative pore wall area and the BET area and also between the calculated and experimental cumulative pore volume. Cranston and Inkley²², who have analysed both the adsorption and desorption branches of nitrogen isotherms for a wide variety of materials, have, in the majority of cases, found good agreement when using the adsorption branch. Mikhail, Copeland and Brunauer²³ also used the adsorption branch for the pore structure analysis of hardened Portland cement paste. In this investigation, pore size distributions in the diameter range 12 to 300 Å have been calculated from the adsorption branch of the isotherms, using the method of Cranston and Inkley²².

The pore-volume-distribution curve is obtained by plotting the incremental volume over the incremental diameter ($\Delta V/\Delta d$) against \bar{d} , the average diameter. Six of the coals studied showed significant nitrogen adsorption. The distribution curves fall into two types: those showing a single peak in the diameter range (300 to ≈ 12 Å) and those showing the superposition of two distributions.

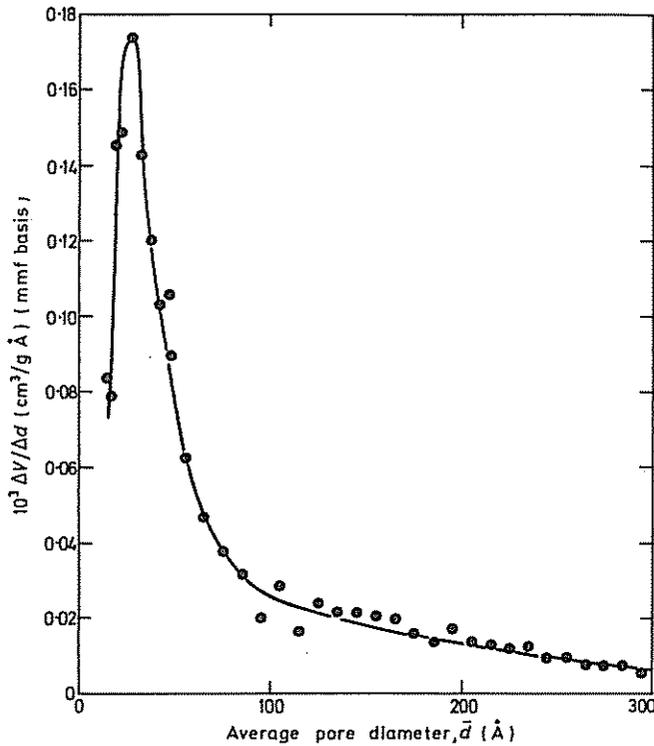


Figure 3 Pore-volume-distribution curve for coal PSOC-80, calculated from nitrogen adsorption isotherm at 77 K

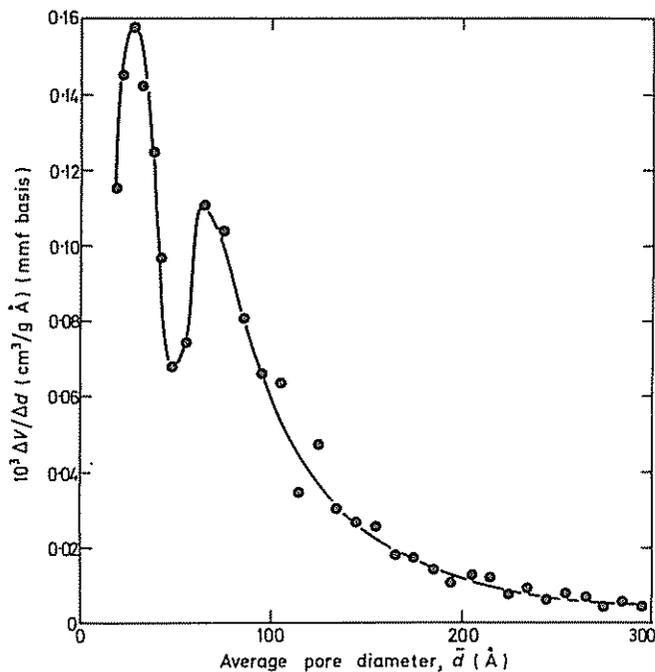


Figure 4 Pore-volume-distribution curve for coal POC-197, calculated from nitrogen adsorption isotherm at 77 K

Four samples belong to the first type and two to the second. Typical distribution curves are shown in Figures 3 and 4, which are representative of the first and second type, respectively. The width of the peak is narrowest for PSOC-80 (anthracite) and the position of the maximum is also located at the smallest diameter. Good agreement has been found between the nitrogen BET areas and the cumulative pore surface areas calculated by the Cranston and Inkley approach²⁴.

Calculated from porosimetry. The volume measured by the penetrometer of the porosimeter is the volume of all pores having a diameter greater than d . The diameter d is related to absolute pressure P , exerted in the porosimeter, by the Washburn equation²⁵.

$$d = \frac{-4\sigma \cos \theta}{P}$$

where σ is the surface tension of mercury and θ is the contact angle between mercury and the pore wall. A contact angle of 130° is used instead of 140° as suggested by Ritter and Drake²⁶. Barrett, Joyner and Skold²⁷ have found better agreement with a 130° contact angle, in comparing the distribution curves calculated from sorption isotherms with those calculated from porosimetry data in the overlap region. A maximum pressure of 10 000 psia was used, which corresponds to a pore diameter of 180 Å.

The overlap region

The upper limit in diameter for the isotherm method was 300 Å and the lower limit in diameter for the porosimetry method was 180 Å. The diameter range 180–300 Å is the overlap region in this study. In this range two independent computations of pore volumes are available. As can be seen from Table 4, pore volumes obtained by the porosimetry method are somewhat higher than those calculated from isotherms.

Total pore volume distribution

The cumulative pore volumes, in the pore diameter range 29 600 to ≈ 12 Å, plotted against $\ln d$ (where d is the pore diameter) for samples PSOC-190 and PSOC-26 are shown in Figures 5 and 6, respectively. In Figure 5, there are two principal rectilinear regions, indicating two distinct distributions of pore sizes. The upper limit of the first distribution is at about 280 Å. There is possibly a third group of pores starting at about 8000 Å in diameter. Figure 6 is similar in general shape, though the change of slope is more gradual. In this case, the upper limit of the first distribution could also be taken to occur at about 280 Å.

From the general trend shown in Figures 5 and 6 and because the upper limit of the first distribution could not be determined accurately for all the samples, the different pore volumes in the indicated pore diameter range are being defined for convenience of classification as:

- (1) total open pore volume V_T , for pores accessible to helium at 32.5°C ;
- (2) pore volume V_1 , contained in pores greater in diameter than 300 Å;
- (3) pore volume V_2 , contained in pores in the diameter range 300 to ≈ 12 Å;
- (4) pore volume V_3 , contained in pores smaller in diameter than 12 Å, V_3 being equal to $V_T - (V_1 + V_2)$.

The pore volumes in different diameter ranges are given in Table 5. It can be seen that the anthracite sample (PSOC-80) has the highest proportion of V_3 and the lignite sample (PSOC-89) has the lowest. Even in a low-rank coal (PSOC-26) more than 40% of the pore volume is contributed by pores of diameter less than 12 Å. That is, almost all coals should show molecular sieve properties.

Table 5 Gross pore distributions in coals

Sample	Rank	V_T (cm ³ /g)	V_1 (cm ³ /g)	V_2 (cm ³ /g)	V_3 (cm ³ /g)	V_3 (%)	V_2 (%)	V_1 (%)
PSOC-80	Anthracite	0.076	0.009	0.010	0.057	75.0	13.1	11.9
PSOC-127	LV Bit.	0.052	0.014	0.000	0.038	73.0	nil	27.0
PSOC-135	MV Bit.	0.042	0.016	0.000	0.026	61.9	nil	38.1
PSOC-4	HVA Bit.	0.033	0.017	0.000	0.016	48.5	nil	51.5
PSOC-105A	HVB Bit.	0.144	0.036	0.065	0.043	29.9	45.1	25.0
Rand	HVC Bit.	0.083	0.017	0.027	0.039	47.0	32.5	20.5
PSOC-26	HVC Bit.	0.158	0.031	0.061	0.066	41.8	38.6	19.6
POC-197	HVB Bit.	0.105	0.022	0.013	0.070	66.7	12.4	20.9
PSOC-190	HVC Bit.	0.232	0.040	0.122	0.070	30.2	52.6	17.2
PSOC-141	Lignite	0.114	0.088	0.004	0.022	19.3	3.5	77.2
PSOC-87	Lignite	0.105	0.062	0.000	0.043	40.9	nil	59.1
PSOC-89	Lignite	0.073	0.064	0.000	0.009	12.3	nil	87.7

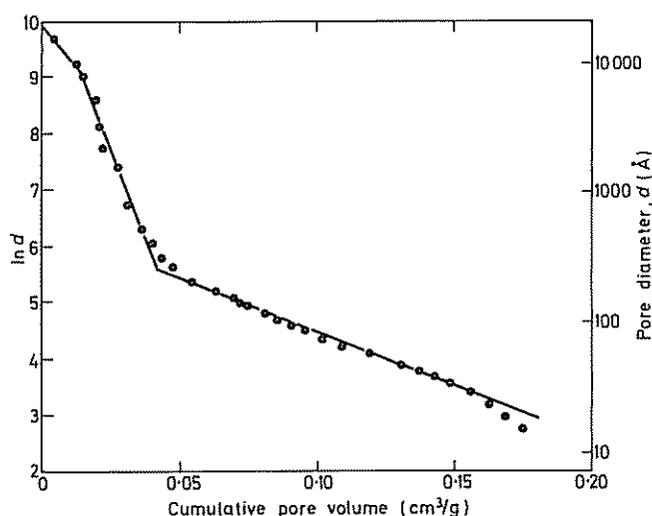


Figure 5 Pore volume distribution for coal PSOC-190

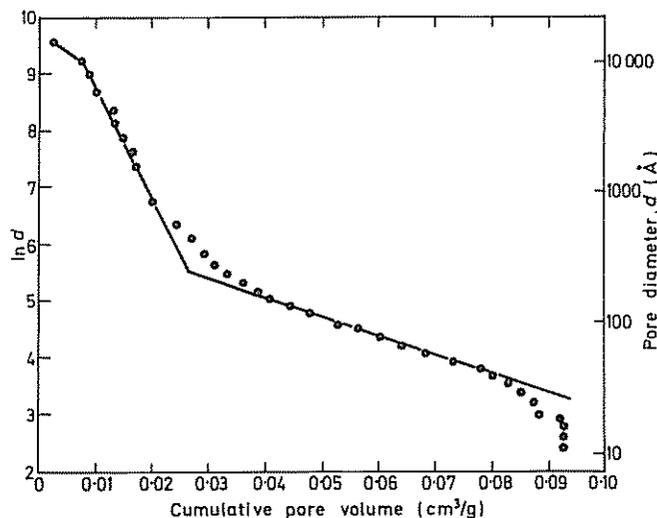


Figure 6 Pore volume distribution for coal PSOC-26

The three lignite samples have only 41% or less of their pore volumes in pores less than 300 Å in diameter. But at the same time, their carbon dioxide areas are higher, compared to those for the HVC samples, which have about 80% of their pore volume in pores smaller in diameter than 300 Å. Since smaller pores are primarily responsible for contributing surface area, the carbon dioxide areas of lignites seem too high; but at present we cannot give an explanation for the apparent anomaly.

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REFERENCES

- Hirsch, P. B. *Proc. R. Soc.* 1954, A226, 143
- Anderson, R. B., Hall, W. K., Lecky, J. A. and Stein, K. C. *J. phys. Chem.* 1956, 60, 1548
- Carlton, S. S., Marr, C. M. Jr., Foye, C. W., Owens, C. K., Chiancone, R. A. and Raynes, B. C. *US Dept of Interior, Office of Coal Res., Res. and Dev. Rep. No.12*, 1965
- Emmett, P. H. *A.S.T.M. Tech. Publ.* No.15, 1941, p 95
- Winslow, N. M. and Shipiro, J. J. *A.S.T.M. Bull.* No.236, 1954, p 39
- Bessant, G. A. R. M.S. Thesis, Penn. State Univ. 1964
- Gluskoter, H. *J. Fuel, Lond.* 1965, 44, 285
- Marsh, H. *Fuel, Lond.* 1965, 44, 253
- Spencer, D. H. T. 'Porous Carbon Solids' (Ed. R. L. Bond), Academic Press, London and New York, 1967, pp 87-154
- Walker, P. L., Jr. and Kini, K. A. *Fuel, Lond.* 1965, 44, 453
- Marsh, H. and Siemieniowska, T. *Fuel, Lond.* 1965, 44, 355
- Walker, P. L., Jr. and Patel, R. L. *Fuel, Lond.* 1970, 49, 91
- O'Gorman, J. V. Ph.D. Thesis, Penn. State Univ. 1971
- Nandi, S. P. and Walker, P. L., Jr. *Fuel, Lond.* 1971, 50, 345
- Gauger, A. W. 'Chemistry of Coal Utilization', Vol.1 (Ed. H. H. Lowry), John Wiley & Sons Inc., New York, and Chapman and Hall Ltd, London, 1945, p 613
- Anderson, R. B., Bayer, J. and Hofer, L. J. E. *Fuel, Lond.* 1965, 44, 443
- Kotlensky, W. V. and Walker, P. L., Jr. *Proc. 4th Conf. on Carbon*, Pergamon Press, 1960, p 423
- Maggs, F. A. P., Schwabe, P. H. and Williams, J. H. *Nature, Lond.* 1960, 186, 956
- Kini, K. A. and Stacy, W. O. *Carbon*, 1963, 1, 17
- Franklin, R. E. *Fuel, Lond.* 1948, 27, 46
- Brunauer, S. 'Adsorption of Gases and Vapors', Princeton University Press, New Jersey, 1943, Ch.11
- Cranston, R. W. and Inkley, F. A. 'Advances in Catalysis', Vol.9, Academic Press, New York, 1957, p 143
- Mikhail, R. S., Copeland, L. E. and Brunauer, S. *Can. J. Chem.* 1964, 42, 426
- Gan, H. M.S. Thesis, Penn. State Univ. 1970
- Washburn, E. W. *Proc. natn. Acad. Sci.* 1921, 7, 115
- Ritter, H. L. and Drake, L. C. *Ind. Engng Chem. analyt. Edn.* 1945, 17, 782
- Barrett, E. P., Joyner, L. G. and Skold, R. *J. Am. chem. Soc.* 1951, 73, 3155

