Microporosity in Coal: Its Characterization and its Implications for Coal Utilization

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Microporosity in coal: its characterization and its implications for coal utilization

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The characterization of the microporosity in coals with the use of measurements of (i) non-steady-state diffusion of gases, (ii) gas adsorption and (iii) gas and liquid displacement is considered. Values of surface area and pore volumes are shown not to be unique but to depend upon the molecular probe used and measurement conditions. The importance of microporosity in coals to their utilization is considered.

1. Introduction

It is well accepted today that coals possess significant porosity and that a major fraction of this porosity for coals of most rank resides in micropores (that is, less than 2 nm in diameter or thickness) and, indeed, in ultra-micropores (that is, less than 0.8 nm in diameter). Because coals contain ultra-micropores, they behave as molecular sieve materials. That is, uptake of N_2 on coals increases with increasing temperature between 77 and 195 K (Maggs 1952), uptake of Ar continues for months at 77 K (Malherbe 1951), and CO_2 uptake at 195 K greatly exceeds N_2 uptake at 77 K (Walker & Geller 1956).

That coals contain significant microporosity would be predicted from our knowledge of their structure. X-ray diffraction studies, notably those of Cartz & Hirsch (1960), show that carbon atoms in coal are arranged in small aromatic layers linked to each other by aliphatic or alicyclic material or by five-membered rings to form large buckled sheets. From oxidation studies on coal, Deno *et al.* (1978; also Deno, personal communication, 1980) conclude that the main building blocks in bituminous coals are aromatic regions in which dihydrobenzene units are interspersed at frequent intervals such that the building blocks do not have overall planarity. Cross-linking of the building blocks by ether oxygen, methylene groups and sulphur also leads to their non-alignment. T. F. Yeh (personal communication, 1980) aptly describes coal as a cross-linked multipolymer.

In this paper the characterization of the microporosity in coals with the use of non-steady-state diffusion measurements, physical adsorption of gases to measure surface area, and displacement of liquids and gases to measure densities and pore volumes will be reviewed. Then the implications of the microporosity in coal for its ability to (i) hold methane underground, (ii) be transported in slurry form, (iii) be converted to gaseous and liquid fuels, and (iv) be used as a precursor of microporous carbons will be considered briefly.

2. Characterization of microporosity in coal

(*a*) *From diffusion measurements*

Flow of gas in ground coal is studied by using the non-steady-state diffusion of molecules either into or out of the particles. For small particles, since diffusion (or flow) in the larger pores is very rapid, the process that is experimentally followed over a period of time is diffusion in the smallest pores.

When the diffusion coefficient (D) is independent of concentration (C) and measurements are made at isothermal conditions, the equation of continuity for spherically symmetrical flow leads directly to Fick's second law in the form

$$\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D\frac{\partial C}{\partial r}\right), \tag{1}$$

where r is the radius and t is time. The non-steady-state diffusion process is remarkably insensitive to particle shape. Consequently, the radius of an equivalent sphere (r_0) may be used for coal particles of irregular shape.

Non-steady diffusion of gases into or out of coal particles can be measured experimentally. Consider diffusion out of particles. First, the coal particles are charged with the desired gas at the desired temperature and pressure. At the beginning of an experiment, the pressure outside the particles is quickly reduced to some value and held at that value during the diffusion run by increasing the volume of the collector into which the molecules that are slowly coming out of the micropores of the coal diffuse. Under these conditions for a spherical particle of volume V and area A, (1) has the following solution under conditions far removed from equilibrium:

$$\frac{V_t - V_0}{V_e - V_0} = \frac{6}{\pi^{\frac{1}{2}}}\left(\frac{Dt}{r_0^2}\right)^{\frac{1}{2}}, \tag{2}$$

where V_0, V_t, and V_e represent volumes of gas in the collector at times $t = 0$, $t = t$ and $t = \infty$ (this last being when the pressure inside and outside the coal particles is equal). Most workers studying gas diffusion in coal have used (2), that is have plotted $(V_t - V_0)/(V_e - V_0)$ against $t^{\frac{1}{2}}$, to obtain the diffusion parameter $D^{\frac{1}{2}}r_0^{-1}$. It is clear that r_0 is less than the particle radius for coals and that its exact value is unknown in all cases. Therefore, the diffusion coefficient D cannot be determined with any certainty by using the non-steady-state technique.

Nelson & Walker (1961) consider the advantages of using two complete solutions to (1): one that converges well for large values of $D^{\frac{1}{2}}t^{\frac{1}{2}}r_0^{-1}$ and the other that converges well for small values. Their use is also considered by Walker *et al.* (1966*a*) and Walker & Mahajan (1978).

Walker & Mahajan (1978) consider in detail experimental apparatus that can be used to measure diffusion in coal. They also consider what effects deviations from ideal diffusion behaviour, such as non-isothermal conditions, dependence of diffusion parameter on concentration, and a distribution in micropore size and particle size, can have on the diffusion parameters that are calculated. Since these deviations do not significantly alter conclusions about the microporosity in coals obtained from diffusion measurements, they will not be considered further in this paper.

A large number of studies on gas diffusion in coals have been made, as reviewed by Walker & Mahajan (1978). Several studies by Walker and coworkers can be summarised to demonstrate important principles. They have studied diffusion of N_2, CO_2, Ar and methane in coals of varying rank between about 295 and 373 K and over a pressure range from about 0.1 to 0.2 MPa. Before commencing a diffusion run, coals are outgassed at 383 K to remove most physically adsorbed water. For studies on 74 μm × 44 μm coal particles of varying rank from anthracite to high-volatile C (HVC), if it is assumed that r_0 does not change with temperature, Nandi

& Walker (1964) find that diffusion of N_2 and CO_2 into at least some of the micropores is activated and that the activation energy (E) for N_2 diffusion is always higher than that for CO_2. By contrast, the pre-exponential term in the Arrhenius expression is larger for N_2 than for CO_2, which results in the diffusion of N_2 into coal being more rapid than that of CO_2 above at least about room temperature. Results for a HVA Pittsburgh seam coal are shown in figure 1, where $D^{\frac{1}{2}} r_0^{-1}$ has units of $s^{-\frac{1}{2}}$.

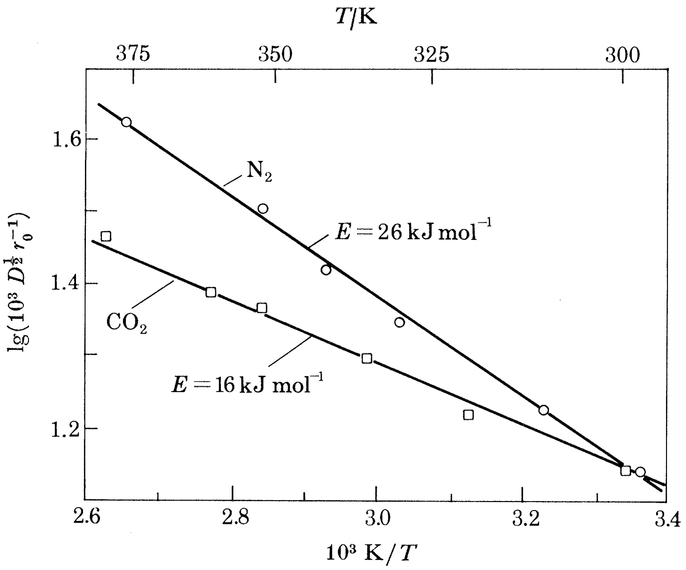

FIGURE 1. Arrhenius plots for the diffusion of N_2 and CO_2 from HVA Pittsburgh seam coal (Nandi & Walker 1964).

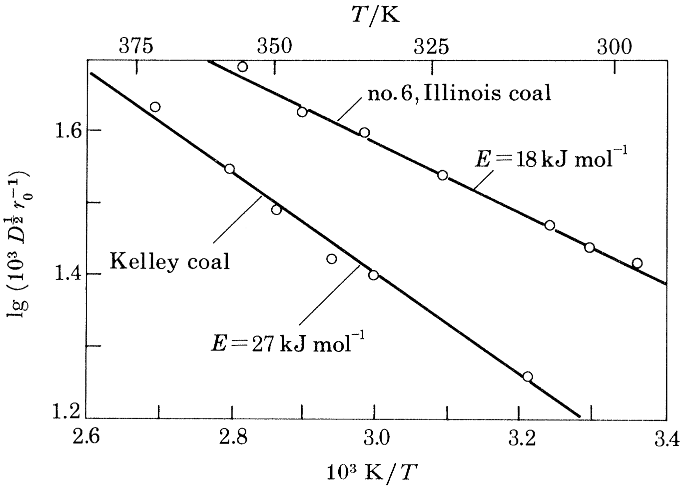

FIGURE 2. Arrhenius plots for the diffusion of Ar from bituminous coals (Nandi & Walker 1966).

Nandi & Walker (1966) also measured the diffusion of Ar in 74 μm × 44 μm coal particles of varying rank from anthracite to HVC bituminous. They find that diffusion is activated, as seen in figure 2 for Illinois no. 6 HVC coal and Kelley medium volatile bituminous coal from Pennsylvania. They further find that E for diffusion of Ar in coals goes through a sharp maximum at a carbon content (dry ash-free (d.a.f.) basis) of about 85 % (figure 3).

Nandi & Walker (1970, 1975) have also measured the diffusion of methane in coals of varying rank at pressures in the range 1.1–2.5 MPa. Diffusion in some of the micropores is again activated; for some of the coals studied the diffusion parameter is a function of pressure.

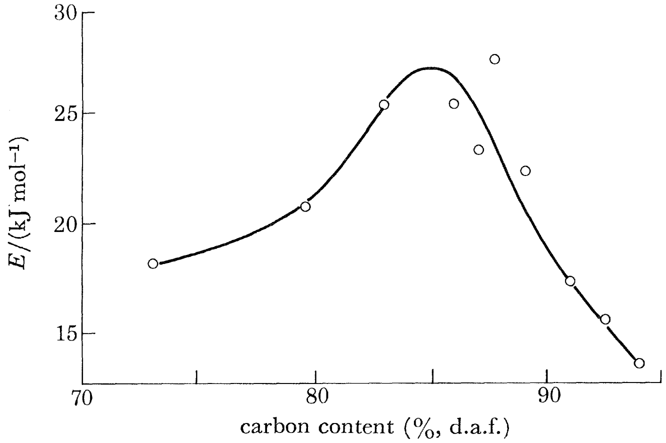

FIGURE 3. Relation between activation energy for diffusion of Ar in coals and their carbon content (dry-ash free) (Nandi & Walker 1966).

There have been discussions as to whether activation energies reported for diffusion in coal are real or apparent, that is whether they are large because of a contribution from the enthalpy of adsorption of the gas on the surface (Anderson & Hofer 1965). Walker *et al.* (1966*b*) consider this possibility and conclude that E is real for an occluded gas model but can be apparent for an adsorption-free model depending upon temperature and gas pressure. It is sufficient to say that the exact magnitude of E is not important in drawing a significant conclusion about the size of micropores in coal based on the findings of activated diffusion.

If the pores of molecular dimension in coal are assumed to be slit-shaped and formed by the closeness of approach of aromatic regions (or pseudo-graphitic basal planes), an estimate can be made of the energy of interaction between gas molecules and the basal surfaces at varying distances apart. That is, Walker *et al.* (1966*a*), using the Lennard–Jones (6-12) potential for dispersive and repulsive energies, conclude that activated diffusion of rare gases commences when basal planes approach each other more closely than the sum of the kinetic diameter of the diffusing species and about 0.16 nm.† Further, since the repulsive potential varies inversely with the twelfth power of distance, small decreases in slit thickness produce very large increases in activation energy for diffusion. Thus for Ar, with a kinetic diameter of 0.34 nm, it is estimated that activated diffusion will begin when basal planes approach each other more closely than about 0.50 nm. For asymmetrical N_2 and CO_2 molecules with minimum kinetic diameters of 0.36 and 0.33 nm, it is estimated that activated diffusion in coal will commence when basal planes approach each other more closely than about 0.52 and 0.49 nm.

(*b*) *From physical adsorption measurements*

Despite the objections of Spencer & Bond (1966) and others that the concept of surface area in microporous solids like coal, calculated from physical adsorption measurements, has little

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† As Walker *et al.* (1966*a*) discuss, there is some uncertainty in this figure since it depends upon what expression is used to calculate the constant in the dispersive energy term. Activated diffusion could begin for distances some 0.08 nm greater than the values that will now be given.

meaning, surface areas continue to be reported and are of utility, at least from a relative standpoint. They can, however, be converted to monolayer volumes (by using the B.E.T. equation) or micropore volumes (by using the Dubinin–Polanyi (D.P.) equation) if desired.

What is now understood is that there is no such thing as one surface area for a coal, or for that matter any other molecular sieve material. The area measured is affected by such parameters as adsorbate used, adsorption temperature, outgassing temperature and time before adsorption, particle size, and time allowed for adsorption. How changing these parameters affects the surface area measured gives information on the nature of the microporosity in coals.

Consider the dilemma of selecting an outgassing temperature before an adsorption run. As will be seen later, water covers, to some extent, the hydrophilic sites in coal, that is oxygen functional groups and mineral matter; and it therefore blocks entrances to some of the finer micropores. Selection of a temperature of 383 K and outgassing overnight is probably the best compromise in that most of the water is removed from most hydrophilic sites and yet heating to this temperature has a negligible effect on thermally changing the structure of coals.

It is obvious that the time allowed for adsorption can affect surface area values if equilibrium is not reached. Prime examples are the use of N_2 and Ar adsorption at 77 K. Workers found early on that surface areas reported from the use of these systems continued to increase with increasing time allowed for adsorption. It is now clear, from diffusion parameters measured on coals for N_2 and Ar at room temperature (like figures 1 and 2) and then their extrapolation to 77 K, that very long (impracticable) times are required to reach equilibrium adsorption or a fractional uptake close to 1.0.

Recognizing the limitations of using N_2 and Ar at 77 K, workers began to explore the possibilities of using adsorbates having higher critical temperatures. In this way, surface areas could be determined from adsorption at higher temperatures where activated diffusion could be better overcome. Systems of particular interest are CO_2 at 195 K (Walker & Geller 1956), Kr at 195 K, Xe at 273 K, and CO_2 at 298 K (Walker & Kini 1965). The latter system is of particular interest since CO_2 has the smallest minimum dimension of the above adsorbates and measurements can be made at room temperature (critical temperature of CO_2, 304 K). It is concluded that surface area measurements made below room temperature are not only affected by activated diffusion limitations but also by some decrease in the size of the micropores. The latter conclusion is based on surface areas of coals accessible to *n*-butane at 273 K being considerably larger than areas accessible to N_2 at 77 K (Anderson *et al.* 1956) and surface areas accessible to Xe at 273 K being considerably larger than areas accessible to Kr at 195 K (Walker & Kini 1965), that is, the additional kinetic energy imparted to the larger molecules by conducting adsorption at higher temperatures would not be sufficient to compensate for their larger size in either case.†

Because the vapour pressure of CO_2 at 298 K is 6.4 MPa, if the B.E.T. equation (Brunauer *et al.* 1938) is to be used to calculate surface areas from adsorption isotherms, it is necessary to work at pressures up to about 1.3 MPa (or a relative pressure of about 0.2). Thus Kini & Walker 1965) used a stainless steel pressure adsorption apparatus for their studies. Later Walker & Patel (1970), using a conventional glass adsorption apparatus, were able to determine the micropore volumes (surface areas) of 74 μm × 44 μm diameter coals from adsorption of CO_2 at 298 K and pressures between about 1.5 and 65 kPa by using the D.P. equation (Marsh &

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† These results could also possibly be explained by significant imbibing of *n*-butane and Xe into the coal structure, as discussed later.

Siemieniewska 1965). D.P. plots for CO_2 at 298 K on coals generally give one straight line over the pressure range from about 2.5 to 52 kPa, as seen in figure 4 for anthracite and bituminous coals. An equilibration time of 30 min was allowed for each adsorption point. The intercepts of the straight lines on the ordinate in figure 4 are taken as the volumes of CO_2 adsorbed in the micropores. Interestingly, because almost all the surface area in coals is located in the micropores, there is good agreement between areas calculated by using the B.E.T. equation (high-pressure adsorption apparatus) and the D.P. equation (by using the vacuum apparatus) as seen in table 1. A molecular area for CO_2 at 298 K of 0.253 nm^2 is taken based on calibration with non-porous carbons with known surface areas as measured by N_2 at 77 K (Walker & Kini 1965). It is concluded that this agreement obviates the necessity of constructing an expensive pressure adsorption apparatus to measure the surface area of coal by using CO_2 at 298 K. Gan *et al.* (1972) report the surface areas of coals of varying rank by using CO_2 at 298 K (D.P. equation) and N_2 at 77 K (B.E.T. equation). The coals were sieved to 420 µm × 210 µm, oven dried at 378 K for 1 h and outgassed at 403 K for 12 h. The equilibrium time for each

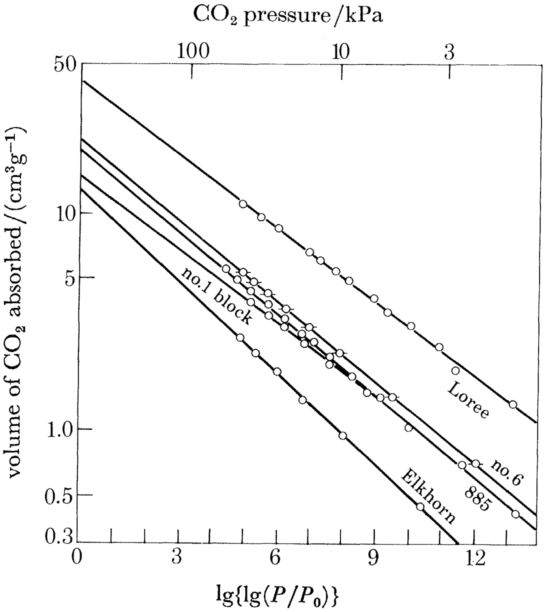

FIGURE 4. Dubinin–Polanyi plots for CO_2 adsorption (at s.t.p.) at 298 K on selected coals (Walker & Patel 1970).

TABLE 1. SURFACE AREAS OF COALS FROM CO_2 ADSORPTION AT 298 K

(After Walker and Patel (1970).)

		surface area/($m^2 g^{-1}$)	
coal	rank	D.P.	B.E.T.
St Nicholas, Pennsylvania	anthracite	238	226
Loree, Pennsylvania	anthracite	274	273
Elkhorn, Kentucky	HVA bit.	86	80
C Seam, Kentucky	HVA bit.	89	85
885, Pennsylvania	HVC bit.	133	132
no. 6, Illinois	HVC bit.	144	139
no. 1 block, Indiana	HVC bit.	100	97

adsorption point was 30 min. As seen in figure 5, surface areas as measured by CO_2 adsorption are all greater than 100 $m^2\,g^{-1}$. Even though there is considerable spread in these areas as a function of carbon content (rank), they go through a broad minimum for the bituminous coals. Values for the anthracites increase very sharply. By contrast, N_2 surface areas (from a molecular area for N_2 of 0.162 nm^2) are very low for most coals; they only show substantial values for the HVC and HVB bituminous coals.

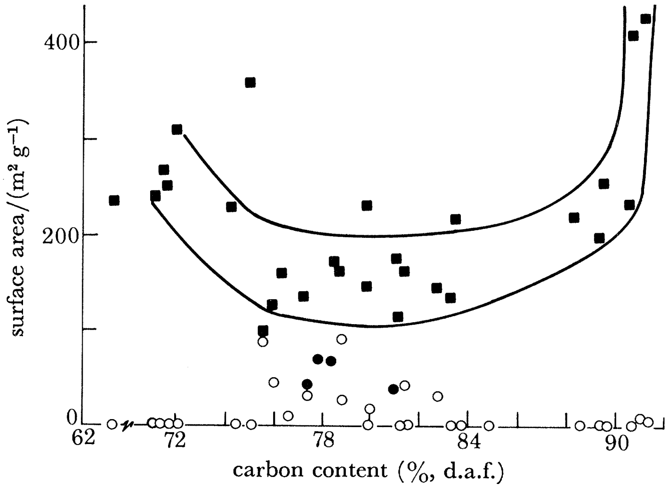

FIGURE 5. Variation of N_2 and CO_2 surface areas of coals with carbon content, ●, N_2 (Nandi & Walker 1971); ○, N_2; ■, CO_2 (Gan *et al.* 1972).

TABLE 2. SELECTED SURFACE AREA RESULTS ON COALS

(After Walker *et al.* (1968).)

size/μm	surface area/($m^2\,g^{-1}$) CO_2	N_2	neopentane
	1 (anth.)		
420 × 250	234	8.0	1.0
230 × 149	231	12.5	1.3
149 × 100	226	22.6	3.7
74 × 44	224	34.0	
	888 (HVA bit.)		
420 × 250	58.8	< 1	< 1
230 × 149	78.3	< 1	< 1
149 × 100	90.0	< 1	< 1
74 × 44	104	< 1	< 1
	6 (HVC bit.)		
420 × 250	160	10.3	11.9
230 × 149	156	11.1	12.9
149 × 100	158	18.1	20.3
74 × 44	139	22.0	—
< 44	122	7.1	12.1

Studies by Walker *et al.* (1968) show some additional factors that complicate the interpretation of the surface areas of coal. Results are presented in table 2 for an anthracite (no. 1), an HVA bituminous (no. 888) and an HVC bituminous (no. 6). The time allowed was 30 min for each adsorption point. For the anthracite, equilibrium was essentially reached for CO_2 uptake in 30 min for each particle size; that is, there was a negligible change of surface area with particle size. On the other hand, equilibrium was not reached for N_2 or neopentane adsorption; that is, surface area increased with decreasing particle size (shorter diffusion distance). As expected, for a particular particle size N_2 areas were larger than the neopentane areas. Even though neopentane was adsorbed at 273 K compared with 77 K for N_2, this temperature difference is not expected to compensate for differences in size of the molecules: neopentane (0.62 nm) as against N_2 (0.36 nm). For the HVA coal, activated diffusion restricts the attainment of equilibrium for all adsorbates.

TABLE 3. SURFACE AREAS OF COALS

(After Mahajan & Walker (1971).)

		surface area/($m^2\ g^{-1}$)		
	sample	CO_2 (D.P., 298 K)	water (B.E.T., 293 K)	f
anthracite	1	224	33	0.15
LV bit.	912	146	17	0.12
MV bit.	956	125	24	0.19
HVA bit.	888	104	38	0.37
HVA bit.	885	132	42	0.32
HVC bit.	6	139	82	0.59

For the HVC coal, equilibrium in CO_2 uptake is essentially reached for the three largest particle size fractions; that is, CO_2 surface areas are the same. As seen in table 2, a further reduction in particle size leads to a reduction in CO_2 surface areas. Surface areas, as calculated from both N_2 and neopentane uptake go through a maximum as particle size is decreased. It is concluded that the grinding of this coal in air to finer sizes resulted in the closure of some micropores due to overheating and plastic flow during grinding. For each particle size of the HVC coal, the neopentane area is larger than the N_2 area. This is attributed to the imbibing of neopentane in a coal of HVC bituminous rank, resulting in the creation of new pore volume and surface area. These results emphasize that the surface areas of some coals, calculated from uptake of organic compounds, must be suspect because of imbibition.

As shown by Mahajan & Walker (1971), water adsorption onto coals at 293 K gives useful information; that is, water has a smaller minimum dimension than CO_2, and diffusional limitations to adsorption in the micropores are therefore at a minimum. However, in the monolayer, water only adsorbs on hydrophilic sites. Table 3 summarizes results for six coals ranging in rank from anthracite (no. 1) to HVC bituminous (no. 6). Studies were made on $74\ \mu m \times 44\ \mu m$ particles outgassed at 383 K. An equilibrium time of 90 min was allowed for each adsorption point. The fraction (f) of the total surface area that consists of hydrophilic sites (based on a molecular area for water of 0.106 nm^2) increases sharply as the rank of the coal decreases.

(c) *From measurements of displacement of liquids and gases*

Displacement of liquids and gases at room temperatures enables us to measure densities and, in turn, pore volumes. Gan *et al.* (1972) among others (Franklin 1949; van Krevelen & Chermin 1954) show that helium densities go through a broad minimum for coals with carbon contents between 80–90 % (figure 6). Helium densities rise slowly as carbon content is decreased below 80 % and rise rapidly as carbon content is increased above 90 %. Even though it is not possible to precisely determine true densities for the solid phase in coals from X-ray diffraction, it is thought that the helium densities are significantly less than the true densities. This would mean that helium is displaced not only by the solid phase but also by cavities closed to helium, that is those with openings or existing behind apertures with openings less than about 0.42 nm. The premise that significant closed-pore volume exists in coals is based on a number of findings: (i) helium densities increase upon reduction of coal particle size (Franklin 1949); (ii) the specific volume of coals calculated from helium densities is a linear function of hydrogen content but extrapolates to give a density of 1.85 g cm^{-3} at zero hydrogen, not 2.26 g cm^{-3}, the true density of graphite (Franklin 1948); and (iii) X-ray diffraction studies give an interlayer spacing for the building blocks in anthracite of about 0.35 nm (Cartz & Hirsch 1960), corresponding to an estimate of its true density being in excess of 2.0 g cm^{-3} compared with a helium density of about 1.5 g cm^{-3}.

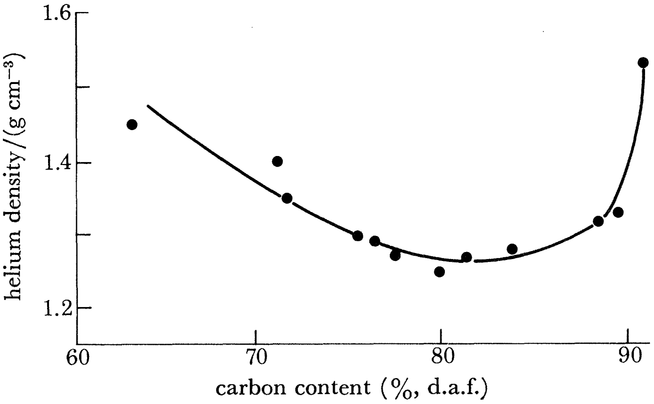

FIGURE 6. Variation in helium density for 420 µm × 210 µm coals with carbon content (Gan *et al.* 1972). Densities placed on a mineral matter free basis by assuming a mineral matter density of 2.7 g cm^{-3}.

TABLE 4. DENSITIES (GRAMS PER CUBIC CENTIMETRE; DRY, MINERAL MATTER FREE) OF SELECTED COALS AT 298 K

(After Nelson (1979).)

rank	P.S.O.C. no.	helium	mercury	methanol	benzene	tetralin
anthracite	177	1.565	1.391	1.598	1.521	1.395
LV bit.	318	1.326	1.256	1.402	1.340	1.295
MV bit.	254W	1.294	1.233	1.326	1.286	1.264
HVA bit.	268	1.282	1.255	1.348	1.283	1.262
HVB bit.	223	1.292	1.157	1.409	1.355	1.285
HVC bit.	212	1.323	1.213	1.465	1.372	1.274
Sbb-A	248	1.340	1.206	1.497	1.392	1.312
Sbb-B	242	1.334	1.232	1.512	1.348	1.305
lignite	246	1.364	1.136	1.564	1.379	1.350

In this laboratory, Nelson (1979) measured the densities of coals of 420 µm × 210 µm particle size by displacement of different fluids at 298 K. Assuming that the density of the inorganic phase in coal is 2.7 g cm^{-3}, Nelson gives densities (table 4) and pore volumes accessible to the different fluids (table 5). As previously reported by numerous workers including Franklin (1949) and Bond & Spencer (1958), volumes in coals that are accessible to organic molecules frequently exceed volumes accessible to helium because of imbibition.

As discussed by Nelson (1979), volumes of liquid taken up, from pycnometric measurements, represent closely liquid filling of the open and closed porosity ($V_{0,\,c}$) in the coals. Total volumes of liquids taken up (including the volume imbibed), that is V_t, were also determined gravimetrically by Nelson (1979). Results, normalized to the volume accessible to helium in the coals, are given in table 6. It is concluded that imbibing of organic molecules not only creates pore volume that did not exist in some of the original coals (causing swelling) but also enables these molecules to fill at least some of the pore volume closed to helium in the coals. The extent to which a coal swells is thought to depend upon the amount of cross-linking in the structure and the closeness of match of the solubility parameters of the organic compound and the coal (van Krevelen 1965; Sanada & Honda 1966).

TABLE 5. VOLUMES (CUBIC CENTIMETRES PER GRAM) IN SELECTED COALS ACCESSIBLE TO DIFFERENT FLUIDS AT 298 K

(After Nelson (1979).)

sample P.S.O.C. no.	mercury†	helium	methanol	benzene	tetralin
177	0.003_3	0.080	0.094	0.062	0.002
318	0.016_9	0.049	0.090	0.058	0.031
254W	0.012_9	0.039	0.056	0.033	0.019
268	0.010_9	0.017	0.055	0.017	0.004
223	0.013_8	0.090	0.154	0.126	0.086
212	0.009_5	0.069	0.142	0.096	0.040
248	0.014_8	0.083	0.161	0.111	0.067
242	0.016_9	0.062	0.150	0.070	0.045
246	0.086_2	0.147	0.242	0.155	0.139

† Macropore volume (that is V_m, in pores greater than 50 nm in diameter) as measured by mercury penetration.

TABLE 6. COMPARISON OF SORBATE UPTAKE ON COALS AS MEASURED BY PYCNOMETRIC AND GRAVIMETRIC METHODS TO TOTAL PORE VOLUME ACCESSIBLE TO HELIUM

(After Nelson (1979).)

sample P.S.O.C. no.	$V_{0,c}/V_{He}$			V_t/V_{He}		
	methanol	benzene	tetralin	methanol	benzene	tetralin
177	1.18	0.78	0.03	—	—	—
318	1.84	1.18	0.63	2.00	1.32	—
254W	1.44	0.85	0.49	1.94	1.13	—
268	3.24	1.00	0.24	5.52	2.25	—
223	1.71	1.40	0.96	3.34	2.51	1.21
212	2.06	1.39	0.58	5.22	3.38	1.21
248	1.94	1.34	0.81	5.03	3.42	1.60
242	2.42	1.13	0.73	7.04	2.40	0.81
246	1.65	1.05	0.95	3.55	1.40	—

As previously discussed, the micropore volume in coals can be estimated from D.P. plots of CO_2 adsorption results. The question is what molar volume should be used for CO_2 when it is in ultra-micropores. It is expected that the CO_2 interacting with two pore walls will be under a large energy of interaction or, effectively, a large pressure (W. A. Steele, private communication, 1980). If the molar volume is assumed to be that for liquid CO_2 at 298 K under a pressure of 50 MPa (42.7 $cm^3\ mol^{-1}$), micropore volumes from the adsorption studies of Nelson (1979) can be calculated; these are given in table 7. Also given are the pore volumes in the coals for pores between 50 nm in diameter and the smallest size entered by helium at 298 K (about 0.42 nm).

These latter pore volumes were calculated by subtracting the macropore volumes of the coals (V_m), as measured by mercury penetration down to a pore size of 50 nm, from the total pore volume (V_{He}). It is seen that for a number of the coals calculated micropore volumes are larger than the ($V_{He} - V_m$) pore volumes. Obviously this should not be so and raises interesting questions about the state of CO_2 in ultra-micropores in coal. It suggests that CO_2 has a still smaller molar volume than that taken for the liquid under a pressure of 50 MPa and that it is possibly approaching the molar volume of solid CO_2, that is 28.1 $cm^3\ mol^{-1}$. It further brings into question what molecular area to use for CO_2 at 298 K when it is adsorbed in ultramicropores. Indeed, van der Sommen *et al.* (1955) conclude that methane sorbed on a bituminous coal at 298 K has a density well above its liquid density.

TABLE 7. COMPARISON OF MICROPORE VOLUME AS ESTIMATED FROM CO_2 ADSORPTION ON COALS AT 298 K WITH (V_{He}–V_m)

(After Nelson (1979).)

sample P.S.O.C. no.	$V_{CO_2}/(cm^3\ g^{-1})$	$(V_{He} - V_m)/(cm^3\ g^{-1})$
177	0.106	0.077
318	0.057	0.033
254W	0.016	0.027
268	0.018	0.007
223	0.067	0.076
212	0.073	0.059
248	0.056	0.068
242	0.065	0.045
246	0.063	0.061

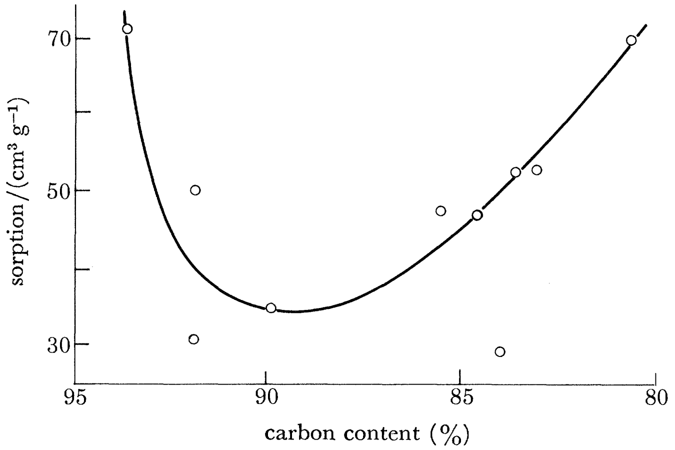

FIGURE 7. Methane sorption (at s.t.p.) on coals at 298 K and 100 MPa (Moffat & Weale 1956).

3. IMPLICATIONS OF THE MICROPOROSITY IN COAL FOR ITS USE

(a) *Methane in coal seams*

The ability of coal seams to hold methane is important from the standpoint of its release during mining (safety implications) and the possibility of its recovery as a fuel gas before mining. van der Sommen *et al.* (1955) show that the amount of methane adsorbed in a bituminous coal at 298 K and elevated pressures (greater than 10 MPa) is in agreement with the volume of ultra-micropores. Moffat & Weale (1956) measured the uptake of methane on British coals at 298 K up to 100 MPa pressure. They find that methane uptake goes through a minimum for a coal of about 90% carbon (figure 7). At the minimum in methane uptake, assuming that the methane had a density of the bulk liquid (about 0.42 g cm^{-3}), the pore volume occupied is 0.060 cm^3 g^{-1}. This volume is larger than the total pore volume accessible to helium in American coals of equivalent rank, and suggests that either the density of sorbed methane is higher than that for the bulk liquid and/or some imbibing of methane and consequent swelling of the coal occurs.

TABLE 8. DENSITIES OF SELECTED COALS IN WATER AT 298 K AND VOLUMES OF WATER TAKEN UP

coal P.S.O.C. No.	density / g cm^{-3}	V_{H_2O} / cm^3 g^{-1}
318	1.526	0.141
254W	1.465	0.128
268	1.371	0.068
223	1.400	0.150
212	1.432	0.126
248	1.556	0.186
242	1.648	0.205
246	1.563	0.240

(b) *Coal–water slurries*

Transport of coal in slurry form with water over long distances from mine to power plant or over short distances for feed into gasifiers operating at elevated pressures promises to become increasingly important. In both instances it is generally desired to use a minimum amount of water consistent with the attainment of a pumpable slurry. Excess water means a reduction in thermal efficiency of the combustion or gasification process. Unfortunately, water taken up in the pore system of coal when slurries are prepared is, in essence, 'excess baggage'; it does not lead to a more pumpable slurry. Table 8 presents results for the densities of coals measured by water displacement at 298 K over 5 days (A. Youssef, O. P. Mahajan & P. L. Walker, Jr, unpublished, 1976). Densities are higher in water than the corresponding helium densities (table 4) in all cases, suggesting that some imbibition of water into the coals occurred. From values for the pore volumes filled with water (V_{H_2O}), it is estimated that at least from 160 to 580 J g^{-1} coal of energy would be consumed in subsequent vaporization of water from the coals during their use in combustion and gasification processes.

(c) *Coal gasification*

The preservation of the microporosity in coal at elevated temperatures where gasification reactions occur depends upon a balance between different factors. For coals that behave as thermosetting precursors, that is those that do not soften significantly upon heating to temperatures of about 1273 K or below, removal of volatiles results in an increase in average pore size of the open microporosity that existed in the coals and an opening up of previously closed porosity (Nandi *et al.* 1964; Nsakala *et al.* 1978). However, for coals that behave as thermoplastic precursors (this includes most of the bituminous coals), much of the open microporosity is lost upon heating to gasification temperatures. Figure 8 summarizes the relation between the CO_2 surface areas of chars and cokes prepared by heating to 1273 K for 1 h in N_2 and the carbon content of the precursor coals (Soledade 1976). Even though there is considerable scatter to the

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data in the plot, it is clearly seen that chars produced from sub-bituminous and lignitic coals (thermosetting precursors) have much higher CO_2 surface areas than the cokes produced from bituminous coals. It is interesting that chars produced from anthracites at 1273 K also have low surface areas, even though they behave as thermosetting precursors. This is attributed to the small amount of volatile matter released from these coals, accompanied by enhanced crystallite growth and alignment.

Figure 9 summarizes results for the reactivity of the chars and cokes to 0.1 MPa of CO_2 at 1173 K and 0.1 MPa of air at 773 K. Even though there is a spread in reactivity as a function of carbon content of the parent coal due primarily to differences in amount and dispersion of inorganic species present that act as catalysts, a large increase in reactivity occurs for chars

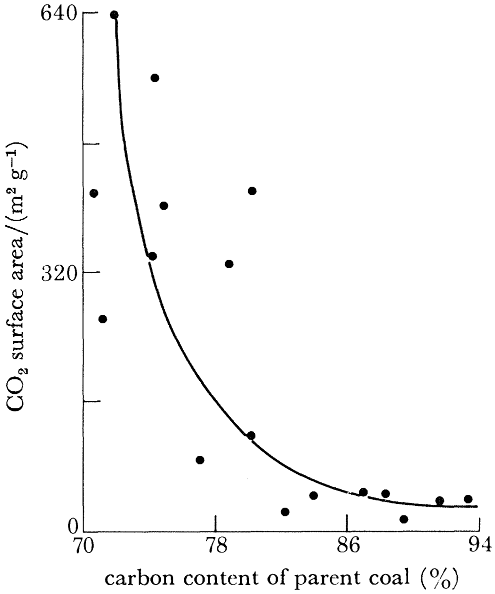

FIGURE 8. CO_2 surface area of chars and cokes produced by heating coals of varying rank to 1273 K in N_2 (Soledade 1976).

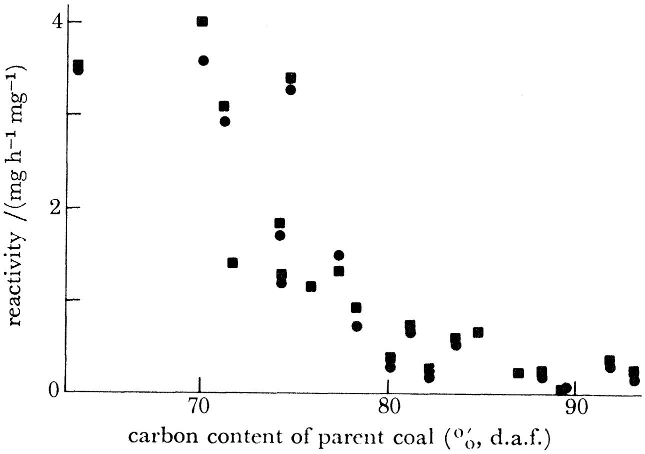

FIGURE 9. Variation of reactivity of 1273 K chars and cokes produced from coals of different rank, ●, CO_2 at 1173 K; ■, air at 773 K (Walker 1978).

produced from coals with carbon contents below about 78%. This suggests that the preservation of microporosity in coals as they are converted to chars and cokes is important to achieving high reactivity to gasification reactions.

Substantiation of the importance of microporosity to reactivity has been confirmed recently for low-volatile bituminous coal PSOC 127. The coke produced from this coal has the lowest CO_2 surface area, given in figure 8 (12 $m^2\ g^{-1}$), and the lowest reactivity, given in figure 9. As increasing amounts of oxygen were added to this coal by exposure to air at temperatures between 453 and 523 K, the thermoplasticity of the coal was progressively reduced. This is attributed to an increasing number of ether cross links being formed as the coal is subsequently heated between about 600 and 800 K. The result (Mahajan *et al.* 1980) was the production of 1273 K cokes of increasing CO_2 surface areas and reactivity (figure 10). Addition of 3.0% oxygen to the coal subsequently led to about a 30-fold increase in carbon reactivity in air over that found for the coke produced from the untreated coal.

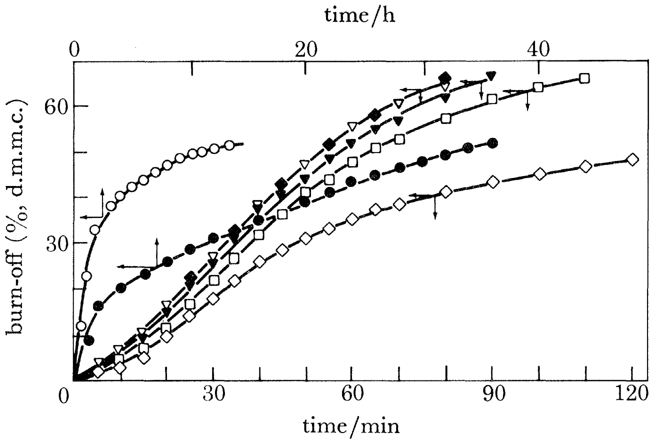

FIGURE 10. Effect of different levels of preoxidation on burn-off curves at 743 K in air for cokes and chars produced from an LV bituminous coal of 74 μm × 57 μm particle size. Percentage mass gain during preoxidation: ●, none; ○, 0.45; ◇, 0.67; □, 1.4; ▼, 1.9; ▽, 3.0; ◆, 4.5 (Mahajan *et al.* 1980).

(*d*) *Coal liquefaction*

Unlike with its gasification, the question of whether the microporosity in coal is important in enhancing rates of its liquefaction is more subtle. In coal liquefaction, as Neavel (1976) has noted, development of plasticity is desirable since it indicates the breakage of cross links in the coal, the reduction of molecular mass, and enhanced solubility in benzene. Concurrent with the appearance of plasticity is the disappearance of the microporosity in coal. In contrast to the enhancement of rate of gasification of caking coals by their low temperature preoxidation, oxidation of bituminous coal preceding liquefaction at 673 K can be deleterious to liquid yield (Neavel 1976).

When coal is taken to liquefaction temperatures (673–723 K), it is important that the donor solvent be in intimate contact with free radical species being produced as a result of the thermal breakage of chemical bonds so that they can be capped off, preventing retrogressive polymerization reactions from occurring. The donor solvent would be imbibed into the solid regions of the coal at some rate even if the coal contained no porosity, but clearly the time required for the completion of this imbibition and concurrent swelling of the coal will be reduced substantially by the presence of porosity and, more particularly, microporosity within the coal. From studies on the rate of uptake of tetralin into bituminous coal particles of 420 μm × 210 μm size over the temperature range 303–343 K, Nelson (1979) concluded that equilibrium sorption should be completed within 2 min at 673 K. Therefore, it is suggested that because all coals contain microporosity, it is possible for the donor solvent to thoroughly penetrate the coal structure before a significant production of free radical species and breakage of cross links commences. Without the presence, initially, of this microporosity within the coal, it is suggested that coals would have to be ground to much smaller particle sizes than now practised if substantial liquefaction yields were to be realized.

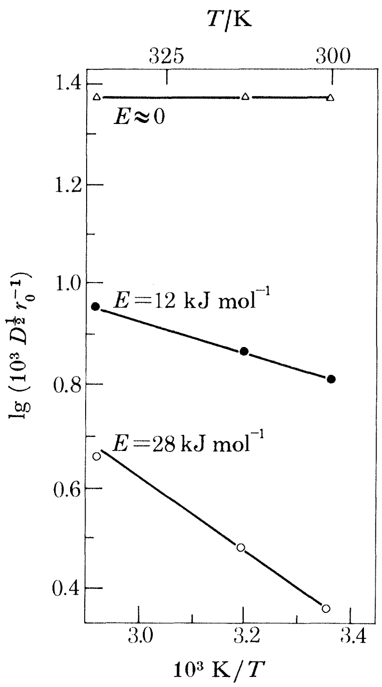

FIGURE 11. Diffusion parameters for methane diffusion into 400 μm × 230 μm anthracite char as a function of diffusion temperature and char burn-off (percentages): ○, 6.9; ●, 8.0; △, 9.1 (Walker & Mahajan 1978).

(e) *Microporous carbons*

Coal is the most important precursor for the production of activated carbons of large surface area. Clearly, for this to be successful, coals must have microporosity and this porosity must be preserved and, in fact, increased as coals are heated in reacting gases during their activation. To preserve the microporosity, only coals that behave as thermosetting precursors can be used. This necessitates the low-temperature preoxidation of bituminous coals before their activation in steam, CO_2 and/or air at elevated temperatures.

Recently, interest has developed in the production of narrow-pore carbon molecular sieves from coal (Juntgen *et al.* 1976) that can be used in the separation of gases. Their production requires very careful control of changes in the micropore size in coal chars with extent of carbon gasification, carbon deposition from hydrocarbons, and heat treatment as possible variables. Considering that the repulsive potential between a molecule and a surface varies inversely with the twelfth power of the distance in the Lennard-Jones potential, it is obvious that small changes in slit thickness produce very large changes in activation energy for diffusion and, hence, in the magnitude of the diffusion coefficient. This principle is clearly seen in figure 11 for the diffusion of methane in anthracite char. Activation of the char in air between 6.9 and 9.1% burn-off enlarged the average micropore size sufficiently to change methane diffusion from being highly activated to having only a small temperature dependence (Knudsen).

4. SUMMARY

All coals contain microporosity (that is, voids less than 2 nm in size), with much of this porosity in or behind voids about 0.5–0.6 nm in size. Thus all coals exhibit molecular sieve behaviour to gases, vapours and liquids which interact with them during important coal conversion processes. The characterization of the microporosity can best be achieved by use of molecular probes. The accessibility of various probes into the microporosity is a function of coal rank, temperature and molecular size, shape and functionality. Accessibility is enhanced for some probes because of the swelling of the coal. Of particular utility in characterizing microporosity are: (i) adsorption of CO_2 at 289 K and N_2 at 77 K, (ii) displacement of He and Hg at 298 K, (iii) non-steady-state diffusion of CO_2, N_2 and Ar into or out of coals around 298 K, and (iv) uptake of liquids at 298 K.

The microporosity in coal is of importance in determining: (i) quantities of methane held in coal seams, (ii) water uptake in coal–water slurries, (iii) reactivity of coal chars during their gasification, (iv) rapidity of penetration of particles by donor solvents during the initial stages of coal liquefaction, and (v) nature of microporous carbons produced from coal.

I am very grateful for the help given in research and discussions by my students and academic colleagues over the years in our pursuit of an understanding of the microporosity in coal. Financial support of the United States Department of Energy for research on coal is particularly appreciated.

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