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A direct measurement of expansion in coals and macerals induced by carbon dioxide and methanol

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Coals and macerals show a measurable extent of expansion in CO_2 at ambient temperature which is a function of CO_2 pressure. Equilibrium expansion is much more rapidly attained in CO_2 than in methanol. At similar relative pressures, expansion in methanol is significantly greater than in CO_2. Volume expansion of coals in CO_2 at temperatures and pressures used to measure surface areas from CO_2 uptake (<0.1 MPa, 298 K) is much less than the volume of CO_2 taken up under these conditions. Therefore, it is concluded that most of the CO_2 uptake is not due to imbibing of CO_2 within the coal structure but rather to CO_2 uptake in open and closed (to He) micropores. It is further concluded that the high surface areas of coals calculated from CO_2 uptake are at least semi-quantitatively correct and, thus, that coals have large microporosities.

(Keywords: macerals in coal; swelling; microporosity)

Early attempts at measuring surface areas of coals quantitatively using N_2 at 77 K led to the conclusion that the slow transport of N_2 within micropores results in its accessibility to only a limited fraction of the total area. A number of workers recognized the potential of using CO_2 as an adsorbate[1–4] in place of N_2, since it has a smaller minimum dimension and can be used at 298 K. Walker and Patel[2] reported that the areas of coals calculated from CO_2 adsorption at 298 K by the BET and Dubinin–Polanyi equations in their applicable pressure ranges showed excellent agreement. This has been accounted for by the suggestion that a large percentage of the total porosity in coals exists in micropores[5]. It is generally accepted that CO_2 adsorption at 298 K measures essentially the total surface area of coals[4,6]. However, it has been argued that adsorption of CO_2 may be influenced by the quadrupole moment of the adsorbate. Deitz *et al.*[7] reported that the amount of CO_2 adsorbed per unit of N_2 surface area increased with increase in the concentration of hydroxyl groups present on the coal surface. However, Ramsey[8] found that even upon substantially increasing the oxygen content of an anthracite by irradiation with γ-rays in air, the CO_2 area increased by only 5%. Walker and Kini[1] observed that the surface areas of coals measured using Xe at 273 K are in good agreement with those measured by CO_2 adsorption at 195 and 298 K. This indicates the absence of any significant chemical interaction of the CO_2 molecule with oxygen functionalities in coal.

Surface areas of coals calculated from CO_2 uptake at 298 K are, indeed, higher than those reported from N_2 uptake at 77 K, and in many cases considerably higher[5]. For some coals, pore volumes accessible to CO_2 exceed those accessible to He[9]. The greater CO_2 uptake is attributed to its accessibility to pores closed to He as well as to its imbibition into the solid structure of coal. It has been known for a long time that coals[10] and charcoals[11] expand when exposed to CO_2 at ambient temperatures. Recently, Reucroft and Patel[12] suggested that surface areas of coals measured by CO_2 adsorption at ambient temperatures are strongly influenced by swelling effects and, therefore, are much too high. They attributed this swelling to the closeness of the solubility parameters of CO_2 and many coals. More recently, Reucroft and Patel measured the CO_2-induced swelling in coals using a dilatometer[13], and found that volume increase due to swelling was substantially smaller than volume uptake of liquid CO_2 during adsorption measurements. The present authors interpret this to mean that most of the surface area in coals calculated from CO_2 adsorption measurements indeed exists and is not a result of CO_2 imbibition in the coal matrix.

Methanol has also been used for determining surface areas of coals. However, this approach has also been criticized owing to specific interactions of methanol with functional groups present on the coal surface[14]. Methanol, like many other organic solvents, imbibes in coal, thus producing extensive swelling and penetration into the volume where porosity and surface area did not originally exist. Recently, Nelson *et al.*[15] developed an indirect approach to determine the extent of this swelling from the pycnometric densities and the gravimetric uptake of the solvent at a relative vapour pressure (RVP) of 0.95. They reported that methanol-induced swelling in coals increases sharply with decreasing coal rank. In this study, expansion of coals in CO_2 and methanol at ambient temperature has been measured using a dilatometer. Expansion in CO_2 has been studied up to ≈ 5 MPa gas pressure (RVP ≈ 0.8). In the case of methanol, expansion was measured at an RVP ≈ 1.0.

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Table 1 Analysis of coals and macerals

No.	ASTM rank	Proximate analysis: Mineral matter (wt %, dry)	Proximate analysis: Volatile matter (wt %, dmmf)	Ultimate analysis (wt %, dmmf): C	H	N	S_{org}	O^a	Pyritic sulphur (wt %, dry)	Vitrinite (vol %, dmmf)
Coal (PSOC)										
85	Anthracite	9.54	6.64	92.36	3.81	0.61	0.84	2.38	0.28	98
1197	lvb	11.76	16.80	91.01	4.92	1.81	0.74	2.22	0.38	95
1144	mvb	11.60	24.79	89.87	5.29	1.58	0.92	3.15	1.22	88
1192	mvb	14.55	25.53	89.64	5.30	1.67	0.89	3.30	3.14	87
1193	mvb	24.95	31.88	88.25	5.92	1.75	0.91	4.00	2.17	85
1201	mvb	9.79	17.87	89.33	4.65	1.73	0.55	4.23	0.22	91
1141	hvAb	11.60	34.21	86.93	5.70	1.53	0.71	5.80	0.75	79
1166	hvAb	6.82	35.42	84.36	5.56	1.73	0.98	8.25	0.23	86
1169	hvAb	14.17	39.94	84.69	5.81	1.68	0.86	7.71	1.27	83
1170	hvAb	10.41	38.46	85.71	5.54	1.81	0.75	6.84	0.26	86
1171	hvAb	12.45	43.60	86.06	6.11	1.71	1.58	6.00	3.35	78
223	hvBb	4.56	41.41	81.92	5.71	1.72	0.66	10.00	0.60	71
212	hvCb	3.05	39.74	79.33	5.38	1.46	0.73	13.10	0.11	73
248	subA	3.34	44.58	75.44	5.13	1.74	0.63	17.06	0.03	68
242	subB	6.72	46.04	74.45	5.43	1.68	0.46	17.98	0.11	77
1003	subC	8.28	46.05	74.32	4.90	1.12	0.81	19.65	0.03	73
246	Lignite	10.99	49.00	71.52	4.82	1.52	0.63	21.45	0.03	53
833	Lignite	13.39	45.25	70.43	5.17	1.05	0.45	23.32	0.10	72
Maceral (PSMC)										
63	hvAb	3.00	41.20	83.10	5.25	1.55	–	9.27	–	–
69	hvAb	5.64	29.22	85.18	5.25	1.58	–	7.72	–	–
71	hvAb	3.50	33.82	85.38	5.59	1.66	–	7.10	–	–
73	hvBb	2.63	41.11	79.00	5.40	1.21	1.89	13.24	–	–

[a] By difference

EXPERIMENTAL

Coal and maceral samples

In this study, coals and hand-picked macerals of varying rank were used. Unless otherwise indicated, measurements were made on −20 mesh material that had been stored under N_2 or Ar. The results for vitrinite macerals presented in this paper pertain only to telocollinite, the predominant vitrinite submaceral in coal. Vitrinite content of the macerals exceeded 96 vol % in all cases. Eighteen coals and four macerals were used, the chemical analyses of which are presented in *Table 1*.

Apparatus

A micro-dilatometer, designed and built in cooperation with the Leco Corporation, was used to measure expansion of coals and macerals at 298 K in the presence of controlled atmospheres. The dilatometer could be operated at elevated pressures if desired. Atmospheres used were CO_2 and methanol. A probe rod, positioned on top of the sample, could move up and down freely. The probe exerted a mechanical pressure of $10\,g\,cm^{-2}$ on to the bed of coal. This pressure could be increased by adding weights on top of the probe. The dilatometer was connected to a DuPont 990 thermal analyser. This assembly enables the recording of changes in the height of the coal bed. A complete description of the apparatus is given elsewhere[16].

The height of a known weight of sample in its holder was measured from the dilatometer output with and without a sample present. The pressure chamber was then purged with N_2 for ≈ 5 min, then pressurized with CO_2 at a rate of $\approx 0.68\,MPa\,min^{-1}$ to a desired level. Expansion was measured by the change in bed height. When using methanol, N_2 was passed through a column of the liquid to saturate it at an RVP of ≈ 1.0 at 298 K. The total pressure in this case was 0.1 MPa. Expansion of some samples in the presence of methanol was also measured using a Dupont 942 TMA dilatometer system, which operated at atmospheric pressure only. Expansion for all dilatometer measurements have been expressed on a dry mineral matter containing basis. As will be seen, expansion of coals at 298 K in methanol is slow. Expansion values, which are essentially at equilibrium, are reported.

RESULTS

Expansion in CO_2

The expansion of a bed of coal of known initial height was measured as a function of time upon the introduction of a pressure of CO_2. Attainment of equilibrium was reasonably rapid. The probe load was $10\,g\,cm^{-2}$ unless otherwise stated. *Figure 1* shows some preliminary results for samples of anthracite and lignite of 40 × 70 mesh particle size. Initial bed height was 0.78 cm. Pressure was raised gradually from 0.1 to 3.4 MPa over the first 5 min. Expansion of the bed was also checked for N_2 and He at similar pressures. Negligible bed expansion occurs upon the introduction of N_2 or He. However, in the case of CO_2, introduction of 3.4 MPa pressure (RVP = 0.54) results in significant expansion of both coals. Rates of expansion of the two coals are markedly different. Following the attainment of 3.4 MPa of CO_2 over the anthracite sample, expansion continues during the monitoring period (up to 31 min). In contrast, equilibrium expansion of the lignite occurs almost instantaneously upon the introduction of 3.4 MPa of CO_2.

For comparison, expansion in 3.4 MPa of CO_2 was also measured for Saran char and a natural graphite. The

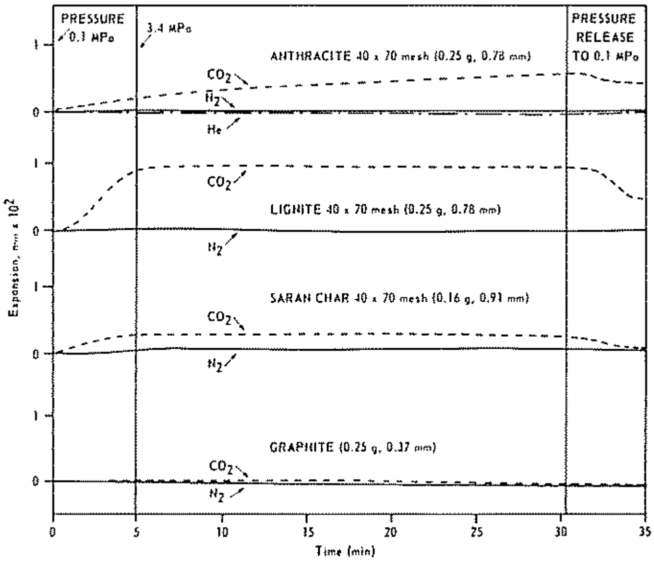

Figure 1 Expansion of selected samples in different atmospheres as measured by dilatometry

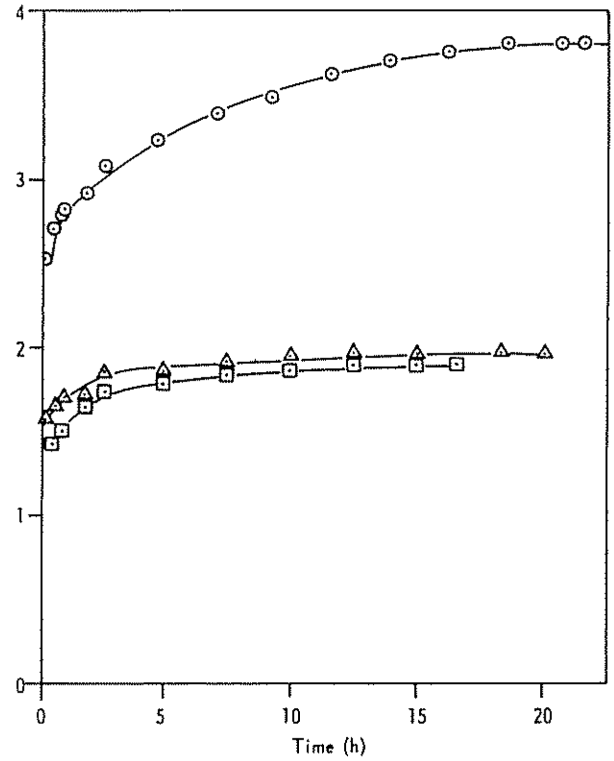

Figure 2 Expansion of vitrinite PSMC 73 as a function of time of exposure to CO_2 (RVP = 0.83) under different probe loads (g cm^{-2}): ○, 10; △, 90; □, 355

Saran char prepared at 1173 K resembles closely a coal char in having a small crystallite size and random crystallite alignment. It has a CO_2 surface area of 1224 m^2 g^{-1}, and very low hetero-atom and metal contents. Significant expansion can be measured on this char, with equilibrium being rapidly attained. A natural graphite of spectroscopic purity was also tested for swelling under similar conditions. It has negligible internal surface area, and as expected, expansion of the sample in CO_2, as well as N_2, is very small.

Following the holding of a sample at pressure for ≈30 min, pressure was gradually reduced back to atmospheric. As seen in *Figure 1*, the coal samples and Saran char do not return to their original height.

The effect of different loads placed on top of the probe rod was also examined. Variation from 10 to 126 g cm^{-2} has no significant effect on the swelling of coals in 0.1 MPa CO_2. By contrast, at a CO_2 pressure of 5.2 MPa (RVP = 0.83), there is an effect of load on expansion of a coal maceral, as seen in *Figure 2*. An increase in load from 10 to 90 g cm^{-2} decreased equilibrium expansion by 50%; a further increase in load to 355 g cm^{-2} has a negligible additional effect on reducing expansion. In subsequent tests, the load was maintained at 10 g cm^{-2} unless otherwise indicated.

The effects of bed density (ρ_{bed}) and pressure of CO_2 on expansion were examined for −20 mesh mv-bituminous coal PSOC 1192. Results are summarized in *Figure 3*. A large but somewhat erratic increase in expansion is seen with increasing pressure of CO_2. No systematic effect of bed density on extent of expansion is seen. Duplicability of results at equal bed densities was examined for coal PSOC 1192. As seen in *Table 2*, increase in expansion with increasing pressure is irregular, as previously noted. Further, at a given bed density, the pressure range over which the irregularities occur are not duplicated. This emphasizes that the dilatometer results should only be considered as semi-quantitative.

Expansion of single lumps of PSOC 1192 coal were followed with increasing CO_2 pressure. Apparently because of variations in orientation of the lumps with the

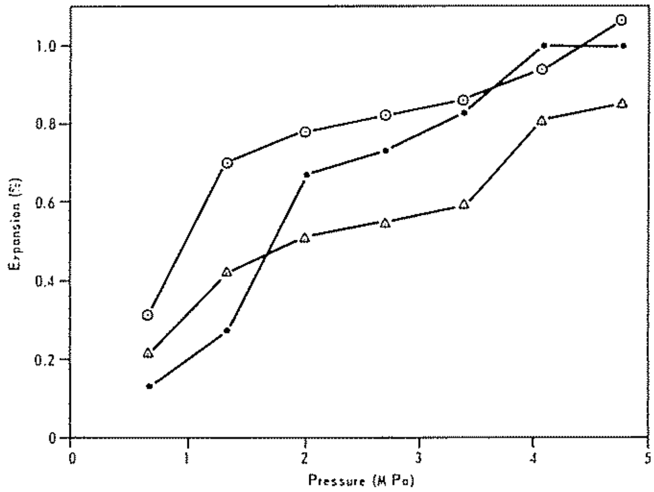

Figure 3 Expansion of particle beds of PSOC 1192 at various pressures of CO_2 at bed densities (g cm^{-3}): ●, 0.98; ○, 1.16; △, 1.26

Table 2 Expansion of PSOC 1192 in CO_2 as measured by dilatometry

Pressure (Mpa)	Expansion (%)^a ρ_{bed} = 1.16 g cm^{-3}		ρ_{bed} = 1.26 g cm^{-3}	
	1	2	1	2
0.68	0.31	0.31	0.21	0.21
1.4	0.70	0.74	0.42	0.38
2.0	0.78	0.94	0.51	0.55
2.7	0.82	0.98	0.55	0.59
3.4	0.86	1.02	0.59	0.62
4.1	0.94	1.06	0.81	0.66
4.8	1.06	1.08	0.85	0.89

^{a} Results reported in duplicate for both bed densities

Table 3 Expansion of PSOC 1192 and Saran char upon cycling of CO_2 pressure as measured by dilatometry

Sample	Cycle no.	Pressure (MPa)	Expansion (%)
Lump coal	1	3.4	1.11
		0.1	0.44
	2	3.4	1.16
		0.1	0.51
	3	3.4	1.27
		0.1	0.55
−20 Mesh coal	1	3.4	0.83
		0.1	0.65
	2	3.4	0.96
		0.1	0.65
	3	3.4	1.00
		0.1	0.69
Char	1	3.4	0.23
		4.8	0.36
		0.1	0.23
	2	3.4	0.43
		4.8	0.50
		0.1	0.30

Table 4 Expansion of selected coals in 0.1 MPa CO_2 as measured by dilatometry

Sample (PSOC no.)	Rank	Expansion (%)
85	an	0.028
1197	lvb	0.105
1192	mvb	0.095
1201	mvb	0.043
1141	hvAb	0.116
1166	hvAb	0.139
223	hvBb	0.093
212	hvCb	0.094
248	subA	0.069
242	subB	0.048
246	lig	0.099

bedding plane in the coal seam and the number of macrocracks, duplicability in three runs on three different lumps was poor. At a maximum CO_2 pressure of 4.8 MPa, expansions were 0.78, 1.06 and 1.47%. At the highest CO_2 pressure, expansions of the lumps were not radically different from those found for packed beds of −20 mesh particles.

As noted earlier, expansion of coal, when exposed to an elevated pressure of CO_2, is not reversible when pressure is reduced back to atmospheric. This is again seen in *Table 3* for −20 mesh powder and lump PSOC 1192, as well as for the Saran char. Further, with cycling to the same top pressure, expansion continues to increase, as does residual expansion, when the CO_2 pressure is reduced back to atmospheric.

Results for the expansion of coals of varying rank at 0.1 MPa CO_2 pressure are presented in *Table 4*. No regular trend of expansion with rank is seen. Even for coals of similar rank, substantial variation in expansion is present. Expansion of coals of varying rank as a function of CO_2 pressure was also investigated (*Table 5*). In each case, expansion increases with increasing pressure. At the higher CO_2 pressures, there is some trend of increasing expansion with decreasing coal rank.

Expansion in methanol

Expansion of −20 mesh coals and vitrinites in methanol at an RVP of 1.0 for methanol is much slower than expansion in CO_2 at all pressures studied. Expansion is also a function of load on the probe. *Figure 4* shows results for vitrinite PSMC 73. Expansion continues for up to 50 h. Increasing the probe load from 10 to 76 g cm^{-2} reduces expansion by over a factor of three. Further increases in load have little effect on further decreasing expansion. A probe load of 10 g cm^{-2} was selected for all additional studies to be reported.

As seen in *Figure 5*, expansion of coals and vitrinites in methanol vary widely. High-rank coals PSOC 1193 and PSOC 1197 expand much less than lower-rank coals PSOC 1166 and PSOC 1170 and vitrinite PSMC 71. *Table 6* summarizes equilibrium expansion results for coals and vitrinites of different rank in methanol. On average, expansion increases with decreasing coal rank. However, variations in expansion are also seen for coals and vitrinites of similar rank. These variations cannot be correlated with variations in mineral matter content, even though a coal of higher mineral matter content would be expected to expand less, assuming a constant behaviour of the organic matter phase.

Table 5 Expansion of selected coals in elevated pressures of CO_2 as measured by dilatometry

Pressure (MPa)	Expansion (%) for coal (PSOC no.)					
	1197	1201	1166	1170	248	246
0.68	0.59	0.78	0.64	0.90	0.86	1.03
1.4	0.78	0.98	0.83	0.98	1.05	1.38
2.0	0.86	1.18	0.94	1.80	1.24	2.07
2.7	0.98	1.29	1.40	1.92	2.06	2.41
3.4	1.06	1.84	1.51	1.92	2.22	3.10
4.1	1.18	1.88	1.73	1.96	2.60	3.17
4.8	1.57	1.92	1.85	2.00	3.11	3.79

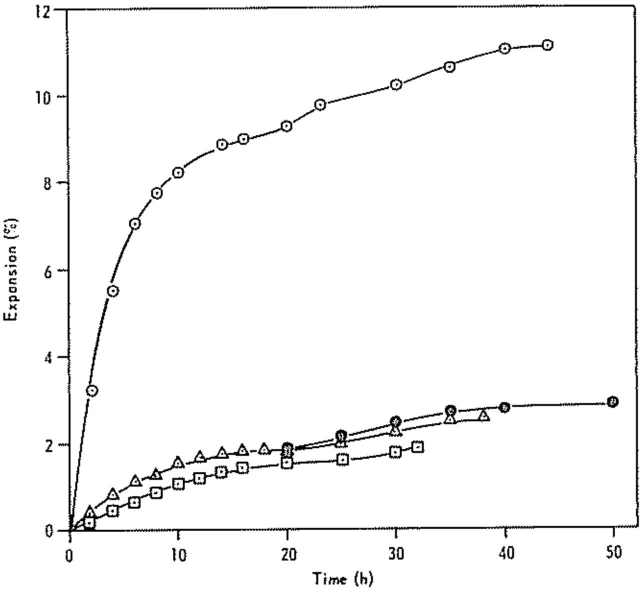

Figure 4 Expansion of vitrinite PSMC 73 as a function of time of exposure to methanol (RVP = 1.0) under different probe load (g cm^{-3}): ○, 10; ◉, 76; △, 95; □, 330

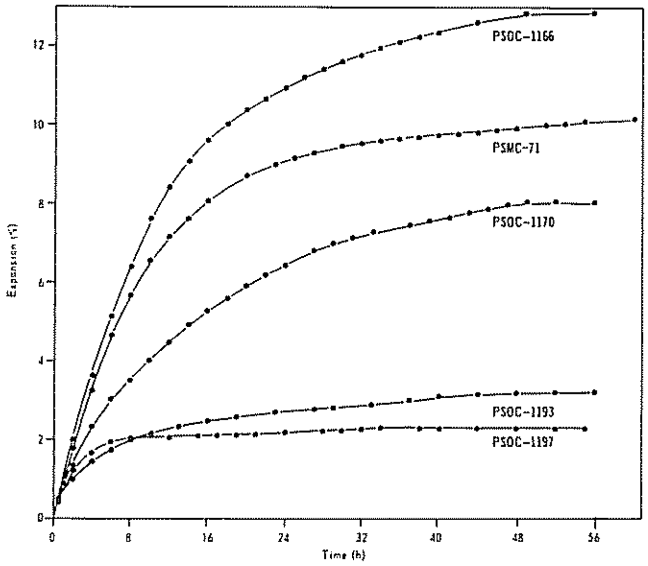

Figure 5 Expansion of selected samples as a function of time of exposure to methanol (RVP = 1.0)

Table 6 Expansion and swelling of selected coals and vitrinites in methanol (RVP = 1.0)

Sample	Rank	Dilatometer expansion (%)
PSOC coals		
85	an	2.00
1197	lvb	2.32
1144	mvb	2.38
1192	mvb	2.54
1193	mvb	3.20
1201	mvb	2.50
1166	hvAb	12.9
1169	hvAb	6.92
1170	hvAb	8.08
1171	hvAb	5.43
1003	subC	5.70
833	lig	12.9
PSMC vitrinites		
63	hvAb	17.7
69	hvAb	3.54
71	hvAb	10.2
73	hvBb	11.2

DISCUSSION

Upon exposing a porous solid to a fluid, swelling can be produced by at least two phenomena: (1) adsorption of a liquid-like layer on the surface of the pores[17–20]; and (2) imbibition or intercalation of the fluid into the solid structure itself[21]. In the first instance, if the solid structure has a high surface area (i.e., an abundance of micropores), adsorption results in the creation of pressure gradients sufficiently large ($\approx 10^6$ g cm^{-2}) to cause measurable deformation of the solid[17]. In the second instance, chemical interactions of the fluid with the solid through hydrogen bonding and/or electron transfer can prompt the building blocks in the solid to move apart, allowing the fluid to enter. Swelling due to adsorption, even in solids of high surface area, is relatively small. Swelling due to imbibition can range from negligible to large, depending upon the extent of chemical and/or physical interaction of the fluid with the solid.

Since He is the smallest molecule, if pore volumes reported[9] to be accessible to other fluids are larger than those accessible to He, it is clear that the interactions of those fluids with coal have altered the coal structure resulting, probably, in swelling. Higher pore volumes are frequently, but not always, seen to be the case when coals and macerals are exposed to CO_2, methanol and some other fluids at 298 K. These fluids are, therefore, penetrating the porosity and/or the coal structure that is closed to He.

Briggs and Sinha[10] in 1933 reported that pieces of anthracite and hvC bituminous coals, when exposed to 2 MPa CO_2, expanded at equilibrium by 0.58 and 0.53%, respectively. In the present study, most coals investigated at a CO_2 pressure of 0.1 MPa expand between 0.05 and 0.1%, and show no trend with rank. However, as expected, the expansion in CO_2 increases with increasing CO_2 pressure (activity). At a pressure of 4.8 MPa (RVP = 0.76), the coals studied expand between 0.9 and 3.8% and show some rough increase in expansion with decreasing rank. Increasing CO_2 pressure from 0.1 MPa (RVP = 0.016) to 4.8 MPa results in ratios of expansion at the two pressures ranging from 13 to 45 for the coals studied.

As seen in *Table 3*, expansion of coal in CO_2 is not reversible when an elevated pressure is reduced to atmospheric. Furthermore, with cycling from a low to a high pressure, expansion both at the high pressure and upon return to atmospheric increases. This same irreversibility of expansion and increasing residual expansion upon cycling is found for the Saran char, where negligible imbibition of CO_2 should be present. These results are expected since, as discussed elsewhere, uptake of molecules in pores of molecular dimension and/or their imbibition leads to irreversible changes in the structure of the solid[22]. The amount of expansion when a fluid is brought into contact with the solid thus depends upon the previous history of the solid. The extent of irreversibility of expansion is also expected to be dependent upon the starting density of the packed bed of particles. This effect was not investigated in this study.

As seen in *Figure 2*, the amount of expansion of vitrinite PSMC 73 (hvBb) in the presence of 5.2 MPa CO_2 is dependent upon the mechanical load applied to the bed of coal particles via the probe at low loads but is independent of load at higher loads. That is, the pressure (load) effect saturates. As previously discussed, sorption of a fluid in pores of molecular dimension produces very large pressure gradients ($\approx 10^5$ g cm^{-2}). It would, therefore, be expected that increasing the load on the sample from 10 to 90 g cm^{-2} would have an insignificant effect on expansion produced by sorption. By contrast, it is suggested that expansion due to imbibition is quite sensitive to small changes in load, probably owing to two phenomena. First, a small load may squeeze some fluid out between the structural units in the solid, thereby reducing expansion. Second, imbibition will 'plasticize' the coal, reduce its glass transition temperature, and thus make it more susceptible to flow under load. This flow will reduce bed volumes between coal particles and, thus, linear expansion of the bed. For CO_2 uptake on PSMC 73 under a CO_2 gas pressure of 5.2 MPa, it is concluded that an expansion of $\approx 1.9\%$ is due to CO_2 sorption within the pore system (both pores open and closed to He). At a load of 10 g cm^{-2}, it is concluded that the additional expansion of $\approx 1.9\%$ is due to imbibed CO_2. If the load

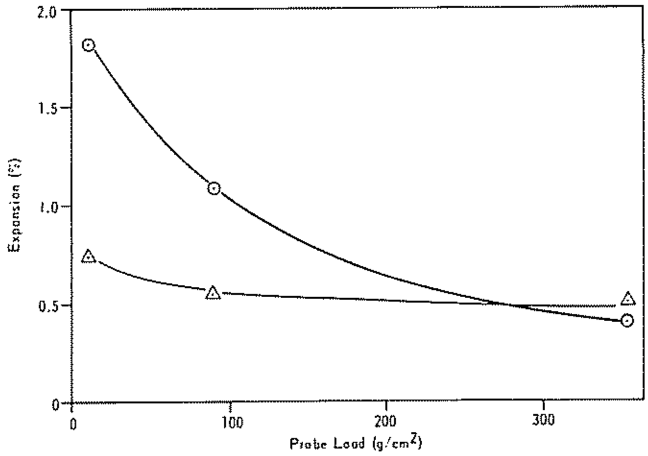

Figure 6 Effect of probe load on maximum expansion of macroporous polymer (○) and Saran char (△) in methanol (RVP = 1.0)

were reduced below 10 g cm^{-2}, it is possible that additional imbibition of CO_2 and accompanying expansion would occur. It was not possible to check this point in this study, since the probe alone created the pressure of 10 g cm^{-2}.

At a CO_2 pressure of 0.1 MPa it is recalled that increasing the load on the coal bed has no significant effect on bed expansion. In line with the previous discussion, it is concluded that at this low RVP of CO_2, negligible expansion of coals due to imbibition of CO_2 occurs.

If one compares the dilatometer results for PSMC 73 in CO_2 (RVP = 0.83) with those in methanol (RVP = 1.0) in *Figures 2* and *4*, respectively, some significant differences are noted. First, most of the expansion in CO_2 is rapid. At a load of 10 g cm^{-2}, $\approx$60% of the expansion had occurred in 7.5 min. By contrast, $\approx$6 h was required for 60% of the total expansion to occur in methanol. Second, at a load of 10 g cm^{-2}, equilibrium expansion in methanol is roughly three times that in CO_2, but at a load of $\approx$340 g cm^{-2}, expansions are comparable. It is concluded that expansion of $\approx$1.9% in CO_2 and methanol (at roughly equivalent relative pressures) is due to sorption. It follows that expansion due to imbibition of methanol exceeds that due to imbibition of CO_2 by a factor of about five. This large difference in expansion in methanol (9.4%) compared with that in CO_2 (1.9%) is thought to parallel much greater imbibition of methanol in PSMC 73 than imbibition of CO_2. Indeed, total uptake of methanol ($\approx$0.47 cm^3 g^{-1}) greatly exceeds that of CO_2 (0.0498 cm^3 g^{-1}) in PSMC 73 at an RVP of 1.0, with no mechanical load on the bed[23].

It is instructive to look at the behaviour of two diverse samples, a macroporous polymer and a microporous Saran char, when exposed to methanol at an RVP of 1.0. The polymer [actually a tripolymer of styrene (88%), divinylbenzene (4%), and ethylene glycol dimethacrylate (8%)] had an estimated molecular weight between cross-links of 1240 and a negligible microporosity[15]. *Figure 6* presents results for the effect of probe load on expansion of a bed of polymer particles in methanol. As expected for the polymer, which has an essential absence of micropores, there is a continuous decrease in expansion with increasing load. Presumably, expansion would become negligible at still higher loads than those used in this study. By contrast, the effect of load on expansion of the Saran char is much less marked, with little effect being seen at a load >90 g cm^{-2}, even though expansion is still significant. This is consistent with little imbibing of methanol being expected for the Saran sample.

As seen in *Table 6*, a considerable spread of values for expansion in methanol exists for coals and vitrinites of equal rank. Values are expected to be a complex function of surface area, pore volume, extent of imbibition, mineral matter content, small differences in extent of uncontrolled preoxidation, compressibility of the coal, and extent to which the coal is plasticized. A higher surface area will result in more expansion due to adsorption. A higher pore volume will provide more space for the swollen solid to expand into, thus reducing particle (bed) expansion. Increasing amounts of mineral matter will reduce expansion. Expansion of bituminous coals is reduced dramatically by small amounts of coal oxidation. Lastly, as the compressibility of a coal changes (it is thought to go through a maximum at $\approx$75% carbon content[15]), expansion due to adsorption will change. Swelling of coals in methanol shows a general increase with decrease in coal rank[15]. From much limited data, dilatometric expansion of coals in methanol also shows a general increase with decreasing coal rank.

Validity of reported surface areas as measured by CO_2 uptake

Since it has been known for some time that coals swell in CO_2 at high pressures, the question has frequently been raised as to the validity of surface areas of coals deduced from CO_2 uptake. For example, in 1983 Reucroft and Patel concluded that CO_2 imbibition by coals accounts for most of its uptake and high surface area reported[12]. They concluded that N_2 (77 K) surface areas are closer to the true surface areas than are CO_2 (195 K or 298 K) surface areas. The question is not one of a small difference in surface area but of a difference of two orders of magnitude for most coals. Reported surface areas of most coals, as measured by N_2 (77 K), are < 1 m^2 g^{-1}, whereas CO_2 surface areas are reported to exceed 100 m^2 g^{-1} for all coals and in some cases (anthracites) to exceed 400 m^2 g^{-1} (Ref. 5). Surface areas of the magnitude reported from CO_2 uptake could be accounted for if coals contain a significant microporosity (that is, area in pores <2.0 nm in diameter). On the other hand, reported surface areas of < 1 m^2 g^{-1} would mean that coals contain negligible microporosity. The ultimate question, therefore, is whether coals are microporous materials or not.

For some time this laboratory has claimed that the surface areas of coals obtained from CO_2 uptake are at least semi-quantitatively correct, and thus that coal is a microporous material[1,2,5,6,9]. The much lower surface areas reported from N_2 uptake (77 K) have been attributed to two factors: (1) N_2 has a larger minimum dimension than CO_2 and thus cannot enter some of the finer micropores; and (2) diffusion into the fine micropores is activated and occurs at a much slower rate at 77 K for N_2 than at 298 K, where CO_2 uptake is measured[9]. Thus we have claimed that coal is a molecular sieve material as well as being microporous.

After reviewing the available evidence, the authors continue to conclude that CO_2 surface areas of coals are at least semi-quantitatively correct.

1. Surface areas are reported from CO_2 uptake measured at CO_2 pressures <0.1 MPa. At these pressures, dilatometric studies show volume swelling of coals to be much smaller than measured volume uptake of CO_2. Volume increases of $<0.5\%$ are found for all coals studied (*Table 4*), whereas Reucroft and Patel note that volume increases of the order of 9% are necessary to account for the surface areas usually found by CO_2 adsorption on coal[13]. If, as just discussed, essentially all of the swelling measured by the dilatometer can be attributed to sorption of CO_2 on open and closed (to He) micropores and not to CO_2 imbibition at pressures <0.1 MPa, then the conclusion is made even stronger that the majority of CO_2 uptake by coals can be attributed to the presence of micropores.
2. In a very recent study, Stacy and Jones measured the swelling of brown coals in CO_2 up to pressures of 0.1 MPa by a novel technique using displacement of mercury[24]. They conclude that 'CO_2, at the maximum pressure used in a surface area measurement, causes no detectable swelling of coal. There is, therefore, on the basis of these results, no reason to believe that the adsorbate is changing the internal structure of the coal and thereby causing spurious values for the surface area.'
3. CO_2 uptake shows a maximum on anthracite coals[5]. However, expansion of anthracites in CO_2, as measured by the dilatometer, is at a minimum (*Table 4*).
4. It has been suggested that surface areas reported from CO_2 uptake are large because of a close match between the solubility parameters of CO_2 and coal[12], which is thought to maximize the imbibing of CO_2 into the coal structure. However, it has generally been overlooked that reported CO_2 surface areas (298 K) are not significantly higher than those deduced from N_2 uptake (77 K) for coals of all rank[5]. There is a narrow band of hvC bituminous coals around 77–81 wt% carbon content (daf) where the N_2 surface areas are reported to go through a rather sharp maximum ($100\ m^2\ g^{-1}$) and to approach closely CO_2 surface areas. It would not be consistent to attribute this high value of surface area primarily to imbibition since the solubility parameters of CO_2 ($22.7\ MPa^{1/2}$) and N_2 ($12.7\ MPa^{1/2}$) are sharply different. Rather, the authors have suggested previously that the close agreement between N_2 and CO_2 areas for coals of this rank means that they contain a minimum of fine micropores (≈ 0.4–0.5 nm) which would exhibit molecular sieving between N_2 and CO_2.
5. Some SAXS results support the conclusion that coals contain significant microporosity. Results of Spitzer and Ulicky[25] on 20 Czechoslovakian coals varying in carbon content from 64 to 91 wt%, as well as a Pennsylvania anthracite and an Illinois hvC bituminous coal, show surface area values comparable to those measured by CO_2 adsorption. It is true that it is difficult to use SAXS to determine the surface areas in the micropores of coals quantitatively because of weak X-ray intensities at the higher angles, where scattering from micropores occurs, and uncertainty as to the shape of the pores[26]. If disc-shaped pores are assumed, which seems reasonable for coal, surface areas of $100\ m^2\ g^{-1}$ are reported for an Australian brown coal[26].
6. Spiro and co-workers have constructed space-filling models for coal composed of four proposed coal molecules[27,28]. Packing of the space-filling models results in porosity, some of micropore size and some closed (to the smallest molecules).

Even though it is concluded that surface areas of coals measured by CO_2 uptake are at least semi-quantitatively correct, it is to be emphasized that there is not one correct surface area for a coal. The value obtained will be different for each sorbate used. It will depend upon the extent to which the sorbate: (1) imbibes into the coal structure; (2) gets into closed (to He) pore volume (surface area) because of swelling; and (3) overcomes activated diffusion into small micropores which are open to He. The uncertainty in surface area is further compounded by the uncertainty as to what area to assign to the sorbate molecule when filling the small micropores. Under this circumstance, each sorbate molecule can, on average, cover more than one pore wall.

Perhaps it is time simply to agree that coals are microporous materials and to discontinue reporting their surface areas. A more precise characterization of the porosity in coal appears to be the use of: (1) helium and mercury densities to determine the total pore volume accessible to He; and (2) mercury porosimetry to determine pore size distributions. Negligible volume change of coal occurs in He or even in mercury as long as the pressure used to make measurements in the porosimeter is not too high[15].

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