

On the Porous Structure of Coals: Evidence for an Interconnected but Constricted Micropore System and Implications for Coalbed Methane Recovery*

L.R. RADOVIC, V.C. MENON, C.A. LEON Y LEON AND T. KYOTANI[†]

Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

R.P. DANNER

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA

S. ANDERSON AND P.G. HATCHER

Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Received March 18, 1996; Revised June 24, 1996; Accepted July 10, 1996

Abstract. An experimental and theoretical study of adsorption and diffusion of carbon dioxide and methane in coals of widely varying rank was carried out. Low-pressure adsorption isotherms of CO₂ were obtained and analyzed using Dubinin's theory of volume filling of micropores. High-pressure adsorption isotherms of CH₄ were obtained and analyzed using tracer pulse chromatography in conjunction with an appropriate adsorption/diffusion model. A preliminary ¹²⁹Xe NMR analysis of chemical shifts experienced by xenon atoms in particles of different sizes is also reported.

The heretofore undocumented and/or underestimated effects of activated diffusion of CO₂ at 273–298 K complicate the elucidation of the true microporous structure of coals, especially its dependence on coal rank. Activated diffusion of both CO₂ and methane at room temperature does not allow reliable estimates of coalbed gas content to be made. A model of an interconnected network of pores which includes randomly distributed, numerous and ultramicroporous constrictions (at any size scale) is consistent with all these experimental and theoretical findings.

Keywords: coalbed methane, coal (porous structure, micropores), adsorption (of xenon, carbon dioxide, methane), Xe-129 NMR spectroscopy

Introduction

It is well documented in the literature that knowledge of the porous structure of coal is important for understanding and optimizing practically all coal utilization processes (Mahajan, 1982; Walker, 1981). In some

of these processes (e.g., gasification, combustion), the porous structure undergoes major changes before the onset of coal interaction with its environment. In others (e.g., coal liquefaction, beneficiation, methane recovery from coalbeds), the nature of the interaction itself is very much dependent on the initial surface area and pore size distribution of the coal. For example, these parameters determine the accessibility of a hydrogen-donor solvent to the liquefying coal in the critical early stages of the depolymerization process (Derbyshire, 1985). They also influence the storage capacity and

*Presented in part at the International Conference on Coal Science, Banff, Alberta, Canada, September 1993, and at the 21st Biennial Conference on Carbon, Buffalo, NY, June 1993.

[†]Permanent Address: Institute for Chemical Reaction Science Tohoku University, Sendai, Japan.

recoverability of methane from coalbeds (Eddy and Rightmire, 1982; Yee et al., 1993).

Since the pioneering work of Franklin (1949), Hirsch (1954) and Spencer and Bond (1966), many details of the complex porous structure of coal have been documented; the 'state of the art' has been summarized by Mahajan (1982), Walker (1981) and Marsh (1987). Coals have a more or less constricted, interconnected network of pores of widely varying sizes and thus exhibit molecular sieving properties. This view has been challenged recently by Larsen and coworkers (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992), who concluded that (the Argonne premium) coals contain "isolated pores which can be reached by diffusion through the coals and that an interconnected pore network which provides access to a large internal surface by pore diffusion does not exist" (Larsen and Wernett, 1992). Mahajan (1991) and Walker and Mahajan (1993) have drawn attention to some important facts that are difficult to reconcile with this model. For example, there is TEM evidence for the existence of interconnected pores; also, the production of activated carbon from coals would be very difficult indeed without the existence of an interconnected pore network.

Our interest in this topic is related to the possibility of predicting the recoverability of methane from coalbeds on the basis of knowledge of adsorption/diffusion properties of coals (Mavor et al., 1990; Smith and Williams, 1987; Yee et al., 1993). In the coalbed methane R&D community it is often stated that "[m]ethane is stored on [the coal's] surface, probably in a monolayer, by physical adsorption" (McElhiney et al., 1989). If this is indeed the case, then at least one apparent contradiction requires reconciliation: the gas content in coalbeds seems to increase monotonically with rank (Kim, 1977), while the coal's surface area seems to exhibit a minimum at intermediate rank (Mahajan, 1982). The pursuit of a relationship between the gas content and recovery rates, on one hand, and the microporous structure of coal, on the other, was thus the general objective of this study. More specifically, Dubinin's theory of volume filling of micropores (TVFM) (Dubinin, 1975; Dubinin, 1989; Kobayashi et al., 1993), which has proved to be successful in unraveling the porous structure of activated carbons (Carrasco-Marín et al., 1993; Marsh, 1987; Rodríguez-Reinoso and Linares-Solano, 1989) and zeolites (Dubinin, 1975), was employed in pursuit of a better understanding of the microporous structure of coals. In particular, the heretofore unexplored coal rank effects on the slope of the Dubinin-Radushkevich plots, which provides a

good measure of the average micropore size, were of interest. It was also of interest to confirm the suggestion (Smith and Williams, 1987) that the low-pressure adsorption of carbon dioxide may be used to predict the high-pressure methane storage capacity of coals. Finally, we employed ^{129}Xe NMR spectroscopy to assist our evaluation of micropore size and dimensionality.

Experimental

Volumetric Adsorption Experiments. Both low- and high-pressure adsorption studies were performed. Nitrogen (at 77 K) and carbon dioxide (at 273–298 K) were used at low pressure (≤ 1 atm) and methane (at 308 K) was used at high pressure (≤ 66 atm). Prior to each experiment, a size-graded coal sample (typically, 1 g in low-pressure studies and 10 g in the high-pressure work) was heated at 388 K overnight under continuous evacuation (< 0.01 torr).

The coals studied came from two sources. One was the Penn State/DOE Coal Sample and Data Bank (with PSOC and DECS designation); samples were selected to cover a wide range of coal rank, from lignites to anthracites. The other was a set of core samples primarily from the Valencia Canyon seam, San Juan Basin, Colorado (REI designation), site of a massive coalbed methane project in the recent past (Close et al., 1992), but also from the Warrior Basin, Alabama (Black Creek seam, S designation). All the samples were ground to different size fractions; no special precautions were taken to minimize coal oxidation, beyond storage in nitrogen-flushed containers and minimal air exposure during handling.

The low-pressure apparatus was a commercial static volumetric system (Carlo Erba Sorptomatic 1800). The equilibration criterion used was < 0.1 torr/3 min. While for microporous materials in general (e.g., activated carbons) this condition is typically satisfied within 30 min, for coals this was often not the case. Indeed, in many cases small pressure decreases continued for days at all relative pressures, particularly for higher-rank coals.

A schematic representation of the high-pressure system is shown in Fig. 1. It is a perturbation chromatography apparatus similar to the designs used in the past to characterize the porous structure of activated carbons and zeolites (Rolniak and Kobayashi, 1980), as well as the diffusivities of methane and nitrogen in coals (Olague and Smith, 1989). Methane (CH_4) was used as the carrier gas and deuterated methane (CD_4) was injected as the tracer pulse. Helium pulses were used

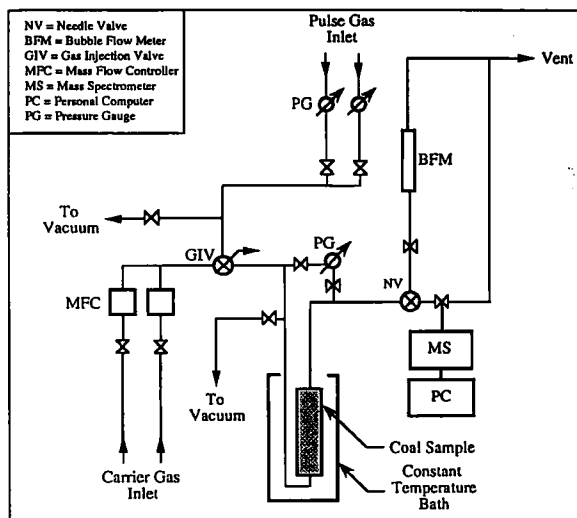


Figure 1. Schematic representation of the high-pressure perturbation chromatography adsorption/diffusion apparatus.

to determine the dead volume of the system. The peak analysis of CD_4 and He by mass spectroscopy provided the adsorption and diffusion parameters (Danner et al., 1980; Peterson et al., 1966). To the best of our knowledge, this is the first application of tracer pulse chromatography to the study of adsorption/diffusion properties of coals.

^{129}Xe NMR Experiments. Four size-graded samples of a vitrinite from an Upper Freeport bituminous coal were dried for 12–18 h at 100°C and 24 h at room temperature under vacuum. The samples are charged

with xenon gas in an NMR tube equipped with a Rototite valve (Wilmad). The samples were allowed to equilibrate for 40 min on a conventional volumetric manifold at 630–650 torr. The tubes were then sealed and removed from the manifold and NMR spectra were acquired. A Bruker AMX 360 NMR spectrometer operating at 99.61 MHz was used. A 90° pulse was employed with a 1.5 s delay and 3000–5000 scans. Xenon gas at 700 torr was used as an external chemical shift reference. Additional details of the spectroscopic measurements are provided by Anderson (1997).

Results

Table 1 summarizes the representative properties of some of the coals studied, covering a wide range of rank, from lignite ($\leq 75\%$ C) to anthracite ($> 90\%$ C). Included in the table are the conventionally obtained parameters of their micropore structure, whose values are seen to fall within expected ranges. Typical CO_2 adsorption isotherms and temperature-invariant Dubinin-Radushkevich (DR) plots are given in Figs. 2 and 3 for the Pittsburgh high-volatile A (hvA) bituminous coal. With the exception of the Smith-Roland and New Mexico #8 coals, all samples exhibited the thermodynamically inconsistent decreases in the quantities adsorbed as the temperature was decreased from 298 to 273 K. The magnitude of this activated diffusion problem for coals even at room temperature was surprising to us, but it is further documented in Figs. 4 and 5 for the Beulah lignite and the Mammoth anthracite. Both the rate of approach to (quasi)equilibrium and the

Table 1. Micropore structure characterization of coals (-20 Tyler mesh) of varying rank.

Coal	Seam	% C (daf) ^a	BET area (m^2/g) ^b	DR area (m^2/g) ^c	Micropore size (nm) ^c
DECS-10	Beulah	73.1	0.90	188	1.68
DECS-8	Smith-Roland	74.4	2.9	139	1.58
PSOC-1446	New Mexico #8	77.3	22	156	1.60
DECS-12	Pittsburgh	83.3	0.44	207	1.91
PSOC-1469	Mary Lee	84.9	1.5	173	1.85
PSOC-1516	Lower Kittanning	88.8	0.37	153	1.64
PSOC-1461	Mammoth	93.5	1.4	196	1.62

^aFrom ultimate analysis;

^bTotal surface area, determined from N_2 adsorption isotherm at 77 K using the BET model;

^cMicropore surface area and average micropore size, determined from CO_2 adsorption at 298 K, using the Dubinin-Radushkevich (DR) theory (Dubinin, 1989; Stoeckli et al., 1993).

Table 2. Effect of coal particle size on measured helium densities.

Particle size (Tyler mesh)	Coal	ASTM rank	He density ^a (g/cm ³)
20/28	DECS-10	Lignite	1.443
250/270	DECS-10	Lignite	1.506
20/28	PSOC-1461	Anthracite	1.809
250/270	PSOC-1461	Anthracite	2.008

^aThe samples were pre-dried *in situ* at 23°C and 1 atm in flowing He for 5–24 h (depending on how long it took to yield a stable pressure reading); the He densities were then determined at 23°C.

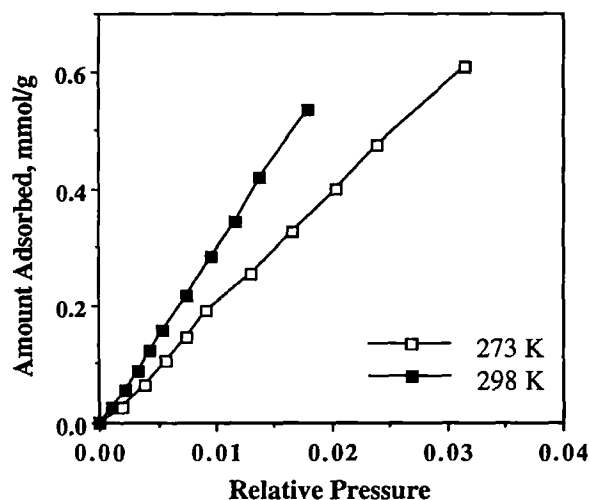


Figure 2. Effect of temperature on the CO₂ adsorption isotherm for the Pittsburgh high-volatile A (hvA) bituminous coal (–20 mesh).

quantity adsorbed (at a given relative pressure) increase with a decrease in the particle size of the coal. Helium density was also found to increase with decreasing particle size. This is illustrated in Table 2. Clearly, a straightforward application of TVFM to coals does not provide simple ‘take-home’ messages about their porous structure.

The results of our high-pressure studies are consistent with the observations at low pressure, as illustrated in Fig. 6 for an hvA bituminous coal from the Valencia Canyon seam. In contrast to the results obtained for an activated carbon (BPL, Calgon), the quantity of methane adsorbed (obtained from the first moment of the CD₄ pulse response peak) increases with decreasing flow rate of the CH₄ carrier gas (and with decreasing particle size), even after long equilibration of methane (typically, ~6 h) in the column.

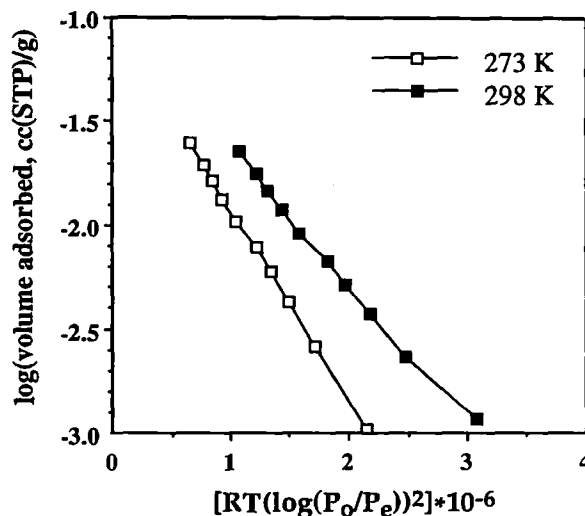


Figure 3. Effect of temperature on the Dubinin-Radushkevich (DR) plots for the Pittsburgh hvA bituminous coal (–20 mesh).

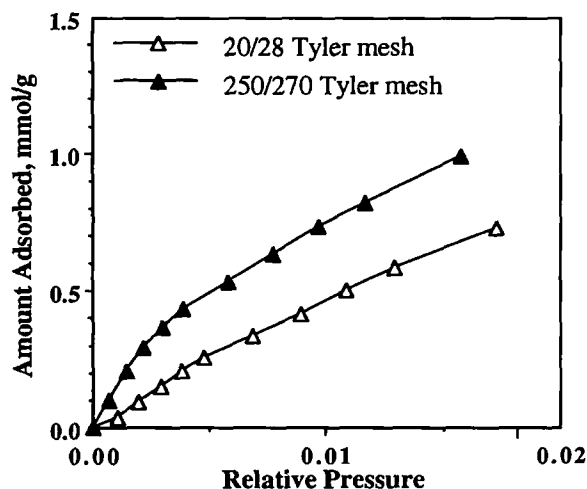


Figure 4. Effect of particle size on the CO₂ adsorption isotherm for the Beulah lignite.

Furthermore, as the methane flow rate increases the CD₄ pulse response peaks exhibit increasing tailing. These effects, consistently observed at all pressures, have been reported earlier for 4A molecular sieves (Oberholtzer and Rogers, 1969) using concentration-pulse chromatography. They complicate the applicability of the tracer pulse technique to coals but are helpful in providing further insights into the porous structure of coal, as discussed below. Similar complications due to “major (and somewhat unexpected) particle size dependence” on effective diffusivities of N₂ in coals were reported by Olague and Smith (1989).

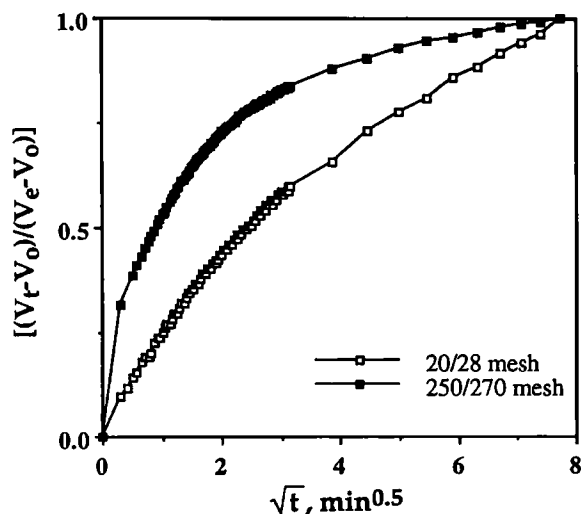


Figure 5. Effect of particle size on the rate of CO₂ diffusion for the Mammoth anthracite at 298 K. (The ordinate represents fractional adsorbate uptake; V = volume adsorbed, t = time.)

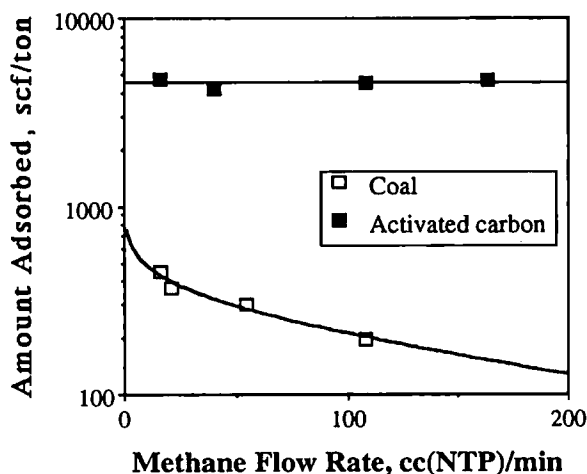


Figure 6. Carrier flow rate dependence of the quantity of methane adsorbed at 308 K, as determined using tracer pulse chromatography.

Discussion

The practical importance of the details of coal's pore size distribution depends on the application of interest. More specifically, the availability of surfaces in narrow micropores depends on the time available for adsorbates/reactants to reach them. Thus, for example, very narrow microporosity may indeed be 'closed', from a practical point of view, for large molecules that interact with coal during liquefaction (Larsen et al., 1995; Walker and Mahajan, 1993). When studying coalbed methane recovery, however, the issue of achievement

of true adsorption equilibrium in coal is of both practical and fundamental importance. It is believed that the coalification process released more methane than could be stored on the coal's surface and that, therefore, the coalbed should be "saturated" with methane (Eddy and Rightmire, 1982; Rightmire, 1984). The use of adsorption isotherms—in conjunction with the canister desorption data (McCulloch and Diamond, 1976; Yee et al., 1993)—to devise gas recovery strategies can be reliable only if the laboratory experiment is a reasonable simulation of the million-year-plus equilibration process in coalbeds. While the often reported 'undersaturation' of a coalbed (when the canister desorption datum falls below the adsorption isotherm) has a number of possible explanations (e.g., bed temperature decrease from the time of gas retention to that of gas recovery, effects of moisture in the coal and of higher-hydrocarbon constituents in the gas), the reasons for 'oversaturation' (Close et al., 1992) have not been apparent. One possibility is the presence of significant amounts of a higher-affinity adsorbate (e.g., CO₂) in the coalbed. The heretofore underestimated and undocumented activated diffusion effects of both CO₂ and methane near room temperature provide another straightforward explanation. These effects—together with the arguments of Mahajan (1991) and Walker and Mahajan (1993)—also support the classical physical model of coal: an extensive interconnected pore network with molecular sieving properties due to the presence of constricted pore openings. These issues are discussed in more detail below.

Relationship between the Porous Structure of Coal and Coal's Structural Properties. There is no question that the use of CO₂ adsorption at close to room temperature, as well as of Dubinin's TVFM, has improved our understanding of the porous structure of coal (Marsh, 1987; Walker and Mahajan, 1993). Nevertheless, it is somewhat surprising that, even when activated diffusion problems associated with N₂ adsorption at 77 K are resolved (Table 1 and Fig. 7(b)), no consistent trends emerge in the porous structure as a function of coal rank. This is illustrated in Figs. 7(a)–(c). In particular, the results in Fig. 7(c) do not support the intuitive expectation that higher-rank coals contain, on average, pores of smaller size because of better alignment of their more ordered and extended 'crystallites' (or basic structural units). This is thought to be due to the opposing effects of better crystallite alignment and decreasing oxygen content with increasing rank, as illustrated in

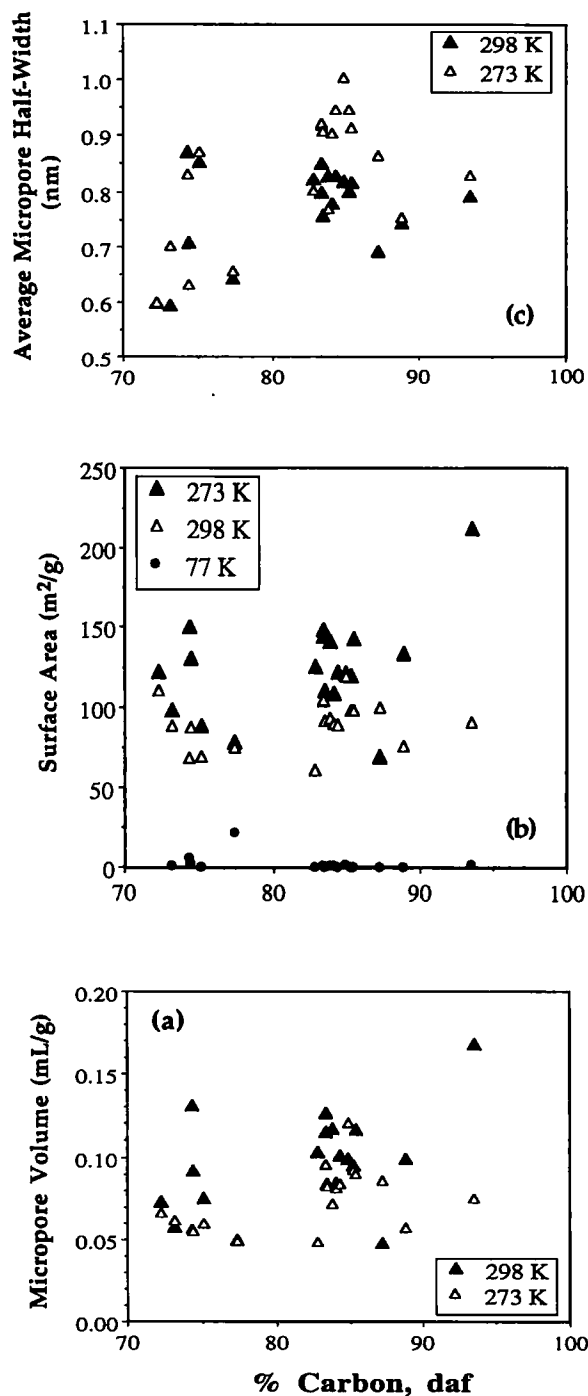


Figure 7. Variations in micropore volume (a), surface area (b) and average micropore size (c) with coal rank (expressed as % C, on dry, ash-free basis). Micropore volume was determined from the intercept of the DR plot. Surface area was determined using either Dubinin's approach (Stoeckli et al., 1993) from the slope and intercept of the DR plot (for CO₂ at 273 or 298 K) or BET theory (for N₂ at 77 K). Average micropore size was determined from the slope of the DR plot.

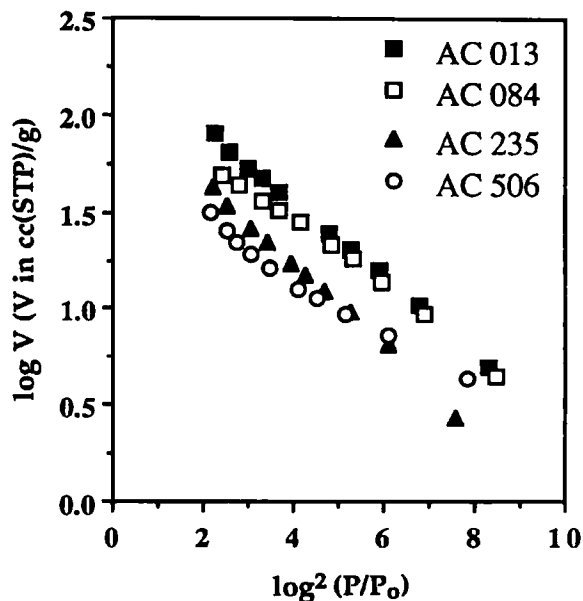


Figure 8. Effect of oxidation on the DR plots for Norit RX3 Extra activated carbon. (The numbers shown in the legend correspond to the wt.% oxygen in the carbon; see Table 3.)

Table 3 and Fig. 8. The former trend (better crystallite alignment with increasing coal rank) contributes to the formation of smaller pores, while the latter (decreasing oxygen content with increasing rank) contributes to the detection of pores of larger effective size.

The case of an activated carbon (RX3 Extra, Norit) is shown for its simplicity (Table 3). The parent carbon AC 013 (mean particle size, $\sim 100 \mu\text{m}$) has a high CO₂ surface area. Furthermore, its N₂ surface area is higher than its Dubinin-Polanyi (DP) CO₂ surface area. This indicates the presence of both narrow and wide micropores. At the other extreme, the N₂ surface area of AC 506 is very low (in spite of the potentially enhanced quadrupole interaction between N₂ and oxygen functionalities on the carbon surface); this indicates the absence of wide micropores (Garrido et al., 1987). Hence, narrow pores are responsible for the microporosity of this carbon. An increase in the oxygen content (as a consequence of a higher population of carboxyl groups at the edges of the 'crystallites') leads therefore to the eventual decrease in the effective width of the micropores. (A practical application of this concept, and indeed a new method for the preparation of carbon molecular sieves, has been described recently by Lizzio et al. (1994).) As a result, the wide micropores are converted to narrow micropores and the narrow micropores become more or less closed to CO₂. A similar effect has been

Table 3. Effect of oxidation on the pore structure of the RX3 extra activated carbon.

Sample	Oxidative treatment ^a	Oxygen content ^b	Diffusion parameter ^c	DR micropore volume ^d	DR micropore surface area ^e	BET surface area ^f	DP surface area ^g
AC 013	None	0.13	0.27	0.35	456	1441	964
AC 084	0.2	0.84	0.10	0.19	287	1328	512
AC 235	2.0	2.35	0.14	0.17	218	706	462
AC 506	10	5.06	0.03	0.07	119	6	205

^aConcentration of nitric acid (M) used during oxidation;^bWeight %, from desorption of CO and CO₂ up to 950°C;^cFrom kinetics of CO₂ adsorption for the first equilibrium data point at 273 K, in min^{-0.5};^dFrom intercept of CO₂ Dubinin-Radushkevich (DR) plot at 273 K, in cm³/g;^eFrom slope and intercept of CO₂ DR plot at 273 K, in m²/g;^fFrom N₂ adsorption at 77 K using the BET theory, in m²/g;^gFrom CO₂ adsorption at 273 K using the so-called Dubinin-Polanyi (DP) approach, i.e., assuming that micropore volume (from DR plot) is equivalent to the monolayer coverage, in m²/g.

reported by Boehm et al. (1982) as a result of chlorine and sulfur chemisorption on active charcoals. The unsteady-state diffusion data (Walker and Mahajan, 1978) for CO₂ at 273 K (Table 3) are in agreement with this interpretation: at high oxygen loadings, there is a very significant decrease in the diffusion parameter.

The particle size and temperature effects shown in Figs. 2–5 and Table 2, as well as the equilibration time and moisture effects (Menon, 1996), are also consistent with the above interpretation. For example, in many cases, though not always, as the particle size decreased and temperature was raised (quasi)equilibrium was reached faster and the adsorption equilibrium values were typically higher. Also—and contrary to what seems to have become “conventional wisdom”, that at 298 K adsorption equilibrium is attained within ~30 min (Mahajan, 1982)—the shape of the CO₂ adsorption isotherm can be quite sensitive to the equilibration time (Tomita et al., 1979), even when the formal equilibration criterion (e.g., <0.1 torr/3 min) is satisfied. It is suggested that the results of such a sensitivity analysis are mandatory for unraveling the porous structure of complex microporous materials such as coals.

A technique that should prove to be more powerful (and more efficient) than volumetric adsorption in illustrating (and perhaps quantifying) the severity of some of the above problems is ¹²⁹Xe NMR spectroscopy (Dybowski et al., 1991; Gallegos et al., 1987; Moudrakovski et al., 1995; Ripmeester and Ratcliffe, 1990; Ripmeester and Ratcliffe, 1993; Suh et al., 1991; Tsiao and Botto, 1991; Wernett et al., 1990). We have initiated recently a detailed study of coal porosity using ¹²⁹Xe NMR (Anderson, 1997). One virtue of this technique is that chemical shifts allow us to

distinguish between Xe atoms in different local environments. Figure 9 shows the effects of particle size for a low-volatile bituminous coal (vitrinite). Each particle size was examined using the same approximate quantity of coal and the same approximate Xe pressure. Pressure was consistent for each sample to avoid chemical shift variations due to the well known pressure dependence of the ¹²⁹Xe chemical shift (Dybowski et al., 1991). The peak at ~0 ppm, with a resonance frequency very close to that of free Xe gas, corresponds to Xe gas interacting with an open surface (e.g., external surface of particles), while the other very broad peak corresponds to adsorbed xenon. The magnitude of the observed chemical shift (~200 ppm) indicates that the latter peak corresponds to Xe adsorbed in micropores (Demarquay and Fraissard, 1987). If exchange between Xe atoms in the two environments occurred within the time scale of the NMR experiment (~0.2 s), the two signals would shift toward the location of their weighted average value; in the limit of fast exchange, a single averaged peak would be observed (Kaplan and Fraenkel, 1980). No significant differences in the spectra for the large and intermediate-size particles are seen. In contrast, the displacement of the two peaks toward each other in the -400 mesh sample could be interpreted as preliminary evidence that intra-/extra-particle exchange of Xe is occurring. While these results are also thought to be consistent with the existence of an open (albeit very constricted) porous structure of coal, additional experiments are in progress to evaluate whether this interpretation is consistent with the intraparticle diffusion rates.

Activated diffusion of CO₂ at 273–298 K through an open but highly constricted pore network is thus

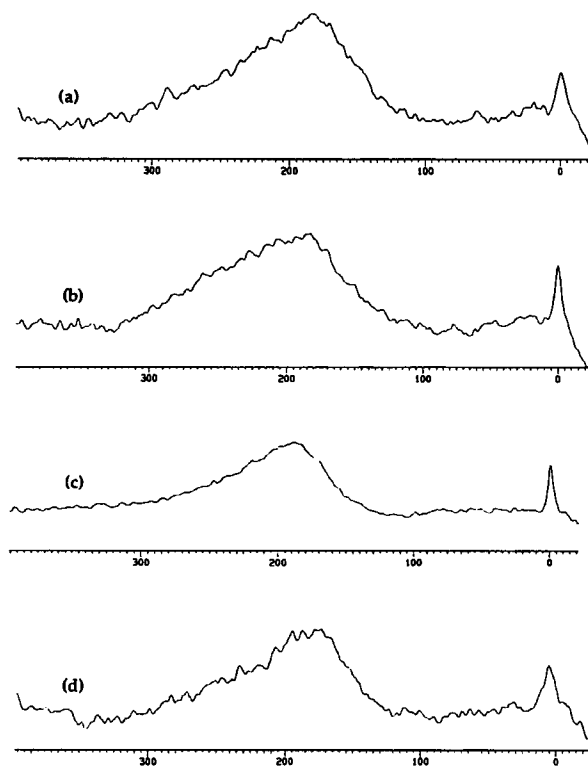


Figure 9. ^{129}Xe NMR spectra for the vitrinite maceral obtained from an Upper Freeport low-volatile bituminous coal: (a) +60 mesh; (b) 60–100 mesh; (c) 100–200 mesh; (d) –400 mesh. (The units on the abscissa are ppm.)

concluded to complicate the elucidation of the true microporous structure of coal. The related implications for methane storage in coals are discussed in the next section.

Relationship between Methane Storage/Adsorption Capacity and Porous Structure of Coal. Methane in coalbeds has been equilibrating in the micropores for millions of years. Hence, the high pressure adsorption/diffusion data, to be most meaningful, must be obtained under conditions that are as close to equilibrium as possible. For this, a key requirement, when using the perturbation chromatography technique, is the invariance of the amount adsorbed with changes in carrier gas flow rate; this condition was shown to be satisfied for an activated carbon, but not for coals (Fig. 6). Obviously, the sizes of micropore openings in the two materials are responsible for this difference in behavior. In activated carbons, the wide openings allow the methane molecules to enter the micropores, adsorb and desorb at all carrier gas flow rates. For coals, on the other hand, the narrow constrictions (gateways to the micropores)

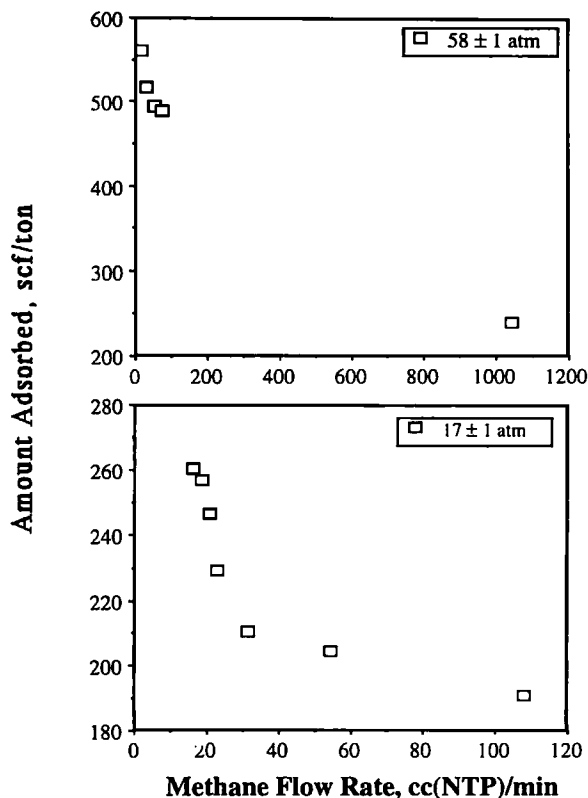


Figure 10. Effect of carrier gas flow rate on the amount of methane adsorbed on a Valencia Canyon coal (REI#34-3, 7.2 g, 250/270 mesh) at 308 K (as determined by tracer pulse chromatography).

are comparable in size to methane molecules. Thus methane needs a longer equilibration time to reach all the adsorption sites; this is provided by decreasing the carrier gas flow rate. Additional dramatic illustrations of this effect are summarized in Fig. 10.

The extent of activated diffusion of methane in coal (Nandi and Walker, 1970; Nandi and Walker, 1975; Patel et al., 1972) is reflected in the degree of tailing of the chromatographic peaks. This is illustrated in Fig. 11. For the activated carbon, both methane and helium peaks have negligible tailing. For coal samples, helium peaks have negligible tailings, consistent with the smaller size of the helium atoms. On the other hand, the methane peak at the highest flow rate exhibits significant tailing; furthermore, the degree of tailing decreases as the methane flow rate decreases.

These findings were shown to be consistent with the predictions of a mathematical model for this adsorption/diffusion process (Menon, 1996). The details of the model, which considers a packed bed of monodispersed non-pelletized adsorbent particles and includes

Table 4. High-pressure adsorption data for methane on coals at 308 K obtained using the perturbation chromatography technique in conjunction with the Langmuir isotherm.

Coal sample	Langmuir volume (scf/ton) ^a	Langmuir pressure (psia)	Correlation coefficient	Particle size (Tyler mesh)	Carrier gas flow rate (cc(NTP)/min)	Quantity of sample used (g)
REI#34-1	400	374	0.989	250/270	16	9.4
REI#34-2	597	831	0.807	—100	16	1.8
REI#34-3	892	480	0.956	250/270	16	7.2
REI#34-4	703	827	0.810	—100	16	1.8
REI#34-5	680	442	0.986	250/270	16	9.5
S#47	725	525	0.933	—100	21	4.9

^aTo convert from scf/ton to cc(STP)/g, divide by 32.

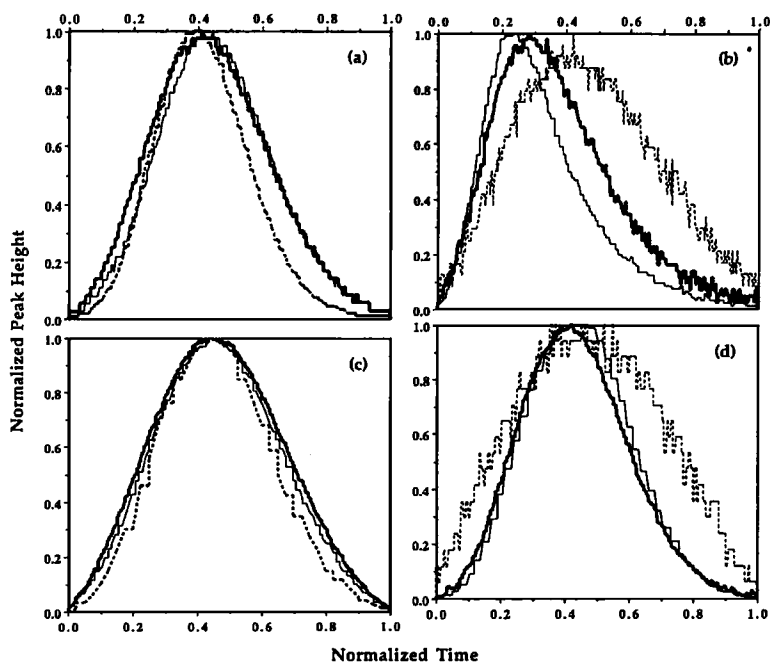


Figure 11. Normalized responses to CD_4 ((a) and (b)) and He ((c) and (d)) pulses introduced through a column ($1/4''$ stainless steel tubing, 2.4' long) packed with an activated carbon (BPL, Calgon, 0.5 g, 12/30 mesh) ((a) and (c)) or coal (Valencia Canyon REI#34-3, 7.2 g, 250/270 mesh) ((b) and (d)) into CH_4 carrier gas flowing at three different flow rates at 308 K and 58 ± 1 atm. Dotted lines are for 16.2 cc(NTP)/min, bold solid lines are for 31.6 cc(NTP)/min, and solid lines are for 76.0 cc(NTP)/min.

the effects of micropore diffusion and axial dispersion, are provided elsewhere (Hufton, 1992). From the first and second moments of the experimental tracer peaks such as those shown in Fig. 11, adsorption equilibrium constants and micropore diffusivities were obtained. Only the results that are relevant for the microporous structure of coal are summarized briefly here. For example, a decrease in carrier gas velocity from 10 to 5 cm/s, in a packed bed characterized by a micropore diffusivity of 3.8×10^{-8} cm^2/s , produced a delay in the appearance of the eluted peak but no increase in

peak tailing. In contrast, when the micropore diffusion coefficient was decreased by three orders of magnitude, while maintaining constant the adsorption equilibrium constant, significant peak tailing was observed at comparable carrier gas velocities. This result suggests in turn that micropore diffusivities for methane, at least in the coals studied here, are closer to the lower limit of the typically reported range of 10^{-6} – 10^{-11} cm^2/s (Bojan et al., 1992).

Table 4 summarizes the estimates of methane content for coals of interest to the coalbed methane community

(Close et al., 1992; Mavor et al., 1990). The reliability of these results increases as the particle size and carrier gas flow rate decrease and as the amount of sample used increases. Under favorable conditions they are seen to be in the same range as those typically reported in the literature (Joubert et al., 1973; Joubert et al., 1974; Ruppel et al., 1974; van der Sommen et al., 1955; Yang and Saunders, 1985). Furthermore, some of the data reflect the findings from the field (using core samples and a canister desorption technique) that gas content increases with increasing coal burial depth. However, they are not true equilibrium values and estimates of gas content based either on conventional static volumetric measurements or the perturbation chromatography technique should thus be viewed with caution. Levine has recently presented additional reasons for caution when performing coalbed gas reservoir analyses (Levine, 1992).

Model of Porous Structure of Coal. Figure 12 illustrates schematically (i.e., not to scale) the key features of the porous structure of a coal particle that is consistent with most (if not all) experimental observations. Because of their relatively small aspect ratio (e.g., length/width <10), the conical and slit-shaped micropores are thought to be dominant throughout the particle, at any size scale. Such systems have been modeled recently by Steele and coworkers (Bojan et al., 1994). The points of closest approach of the polyaromatic hydrocarbon units (which have a natural tendency to align parallel to each other but may be prevented from doing so by the heteroatoms at their peripheries) are the constrictions that lead to the activated diffusion effects for both CO_2 and methane at room temperature. These constricted pore openings, which have been known to give rise to the molecular sieving properties of coals (Nandi and Walker, 1970; Nandi and Walker, 1975), are both numerous and ultramicroporous. Whether their concentration is uniform at all size scales, as the observed particle size effects suggest, remains to be determined in more detailed studies. If the pores were isolated and He, CO_2 and CH_4 were dissolving into the coal matrix, as Larsen and coworkers have argued recently (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992), the equilibrium criterion being the same, gas uptakes would be independent of particle size. On the contrary, both the observed particle size effects and the influence of temperature support the notion that the degree of

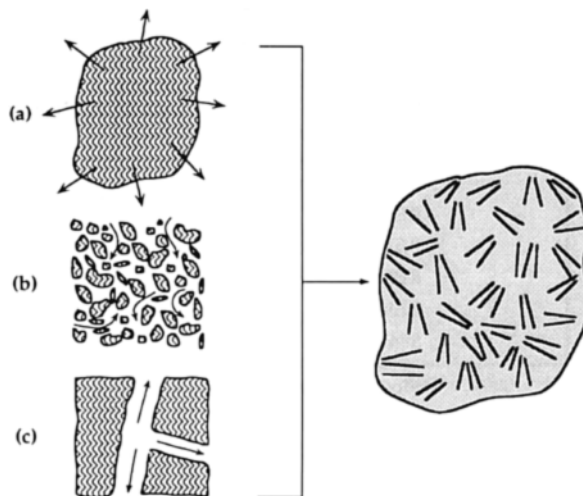


Figure 12. A simplified two-dimensional schematic representation of the porous structure of a coal particle is shown on the right. Each 'line' represents a polyaromatic structural unit of coal. The ångström-size constrictions are highlighted; they are distributed randomly throughout the coal matrix at all magnification levels. On the left is shown the porous structure commonly envisioned in the coalbed methane R&D community (King and Ertekin, 1989). Magnification decreases from (a) to (c): (a) desorption from internal coal surfaces; (b) diffusion through the matrix and micropores; (c) fluid flow in the natural fracture network.

achievement of equilibrium is dependent on adsorbate's ability to overcome the energy barrier associated with diffusion through ultramicroporous constrictions ($<0.6\text{--}0.7\text{ nm}$): (a) the relatively high activation energy of this process and its high sensitivity to adsorbate molecular size (Walker and Mahajan, 1993) are consistent with the abnormally high values of (apparent) fractal dimension of coals (Larsen et al., 1995; Larsen and Wernett, 1988; Larsen and Wernett, 1992); (b) as the particle size decreases, many constricted pore openings are widened and some 'closed' porosity becomes accessible to the adsorbates. Preliminary ^{129}Xe NMR results support this view: slow diffusion of xenon through coal particles suggests that the constrictions are of the order of the diameter of the xenon atom (4.4 Å).

Summary and Conclusions

Application of Dubinin's theory of volume filling of micropores to coals of widely varying rank, using CO_2 as the adsorbate at $273\text{--}298\text{ K}$, leads to a perhaps surprising conclusion: not only are there no clear trends in surface area with rank, but no correlation appears to

exist between coal rank and the average size of the slit-shaped micropores. The latter conclusion is counter-intuitive; it is proposed to be a consequence of several opposing effects. On one hand, as coal rank increases micropores of smaller size do develop. On the other hand, however, as coal rank increases so does the inability of the adsorbate to probe the highly constricted microporous structure (using conventional adsorbates, equilibration times and adsorption temperatures); this leads to the detection of pores of larger effective size for higher-rank coals. Furthermore, the increase in the population of oxygen surface groups with decreasing coal rank contributes to the detection of pores of smaller effective size in lower-rank coals.

The existence of an interconnected but highly constricted pore system imposes severe limitations on our current ability to use adsorption data to predict coalbed methane content and recovery rates. Neither static volumetric techniques nor dynamic perturbation chromatography methods allow the achievement of true adsorption equilibrium using ordinary procedures. Until a method is developed to overcome the activated diffusion problems discussed in this paper, the coalbed methane community will have to rely on expensive but more reliable canister desorption experiments for evaluating recovery strategies and profitability of this unconventional gas resource.

Acknowledgments

Partial support for this study was provided by the U.S. Department of Energy (Grant #DE-FG22-94-PC94216). Discussions with J.R. Hufton, J.L. Duda and I. Hadj Romdhane are gratefully acknowledged. The coal samples from the Penn State/DOE Sample and Data Bank, as well as core samples from the Valencia Canyon (REI series) and Black Creek (S series) seams, were kindly provided by Gareth Mitchell. The vitrinite sample was donated by Jonathan Mathews.

References

- Anderson, S., Ph.D. Thesis, The Pennsylvania State University, 1997.
- Boehm, H.P., B. Tereczki, and K. Schanz, "Blocking of Pores in Porous Carbons by Chemisorption," in *Adsorption at the Gas-Solid and Liquid-Solid Interface*, J. Rouquerol and K.S.W. Sing (Eds.), pp. 395-401, Elsevier, Amsterdam, 1982.
- Bojan, M.J., R.P. Danner, C.V. Menon, G. Mitchell, L.R. Radovic, and W.A. Steele, "Adsorption and Transport in Coalbed Reservoirs," Gas Research Institute, Final Report, 1994.
- Bojan, M.J., G. Mitchell, L.R. Radovic, and W.A. Steele, "Adsorption and Transport in Coalbed Reservoirs," Gas Research Institute, Report # GRI-91/0375, 1992.
- Carrasco-Marín, F., M.V. López-Ramón, and C. Moreno-Castilla, "Applicability of the Dubinin-Radushkevich Equation to CO₂ Adsorption on Activated Carbons," *Langmuir*, **9**, 2758-2760 (1993).
- Close, J.C., T.J. Pratt, and M.J. Mavor, "Evaluation of the Cooperative Research Well Valencia Canyon 32-1," Gas Research Institute, Report #GRI-92/0016, 1992.
- Danner, R.P., M.P. Nicoletti, and R.S. Al-Almeeri, "Determination of Gas Mixture Adsorption Equilibria by the Tracer-Pulse Technique," *Chem. Eng. Sci.*, **35**, 2129-2133 (1980).
- Demarquay, J. and J. Fraissard, "¹²⁹Xe NMR of Xenon Adsorbed on Zeolites. Relationship Between the Chemical Shift and the Void Space," *Chem. Phys. Lett.*, **136**, 314-318 (1987).
- Derbyshire, F.J., "Catalysis in Coal Liquefaction," International Energy Agency Report, IEACR/08, 1985.
- Dubinin, M.M., "Physical Adsorption of Gases and Vapors in Micropores," in *Progress in Surface and Membrane Science*, D.A. Cadenhead, J.F. Danielli, and M.D. Rosenberg (Eds.), pp. 1-70, Academic Press, New York, 1975.
- Dubinin, M.M., "Fundamentals of the Theory of Adsorption in Micropores of Carbon Adsorbents: Characteristics of Their Adsorption Properties and Microporous Structures," *Pure Appl. Chem.*, **61**, 1841-1843 (1989).
- Dybowski, C., N. Bansal, and T.M. Duncan, "NMR Spectroscopy of Xenon in Confined Spaces: Clathrates, Intercalates, and Zeolites," in *Annual Review of Physical Chemistry*, H.L. Strauss, G.T. Babcock, and S.R. Leone (Eds.), pp. 433-464, Annual Reviews Inc., Palo Alto, CA, 1991.
- Eddy, G.E. and C.T. Rightmire, "Relationship of Methane Content of Coal Rank and Depth: Theoretical vs. Observed," in *SPE/DOE Unconventional Gas Recovery Symposium*, pp. 117-122, Pittsburgh, PA, 1982.
- Franklin, R., "A Study of the Fine Structure of Carbonaceous Solids by Measurements of True and Apparent Densities," *Trans. Faraday Soc.*, **45**, 274-286 (1949).
- Gallegos, D.P., K. Munn, D.M. Smith, and D.L. Stermer, "A NMR Technique for the Analysis of Pore Structure: Application to Materials with Well-Defined Pore Structure," *J. Colloid Interf. Sci.*, **119**, 127-140 (1987).
- Garrido, J., A. Linares-Solano, J.M. Martín-Martínez, M. Molina-Sabio, F. Rodríguez-Reinoso, and R. Torregrosa, "Use of N₂ vs. CO₂ in the Characterization of Activated Carbons," *Langmuir*, **3**, 76-81 (1987).
- Hirsch, P.B., "X-ray Scattering from Coals," *Proc. Roy. Soc. (London)*, **A226**, 143-169 (1954).
- Hufton, J.R., Ph.D. Thesis, The Pennsylvania State University, 1992.
- Joubert, J.I., C.T. Grein, and D. Bienstock, "Sorption of Methane in Moist Coal," *Fuel*, **52**, 181-185 (1973).
- Joubert, J.I., C.T. Grein, and D. Bienstock, "Effect of Moisture on the Methane Capacity of American Coals," *Fuel*, **53**, 186-191 (1974).
- Kaplan, J.I. and G. Fraenkel, *NMR of Chemically Exchanging Systems*, Academic Press, New York, 1980.
- Kim, A.G., "Estimating Methane Content of Bituminous Coalbeds from Adsorption Data," Bureau of Mines Report #8245, 1977.
- King, G.R. and T. Ertekin, "State-of-the-Art in Modeling of Unconventional Gas Recovery," in *SPE Joint Rocky Mountain Regional/Low Permeability Reservoir Symposium*, pp. 173-191, Denver, CO, 1989.

- Kobayashi, M., E. Ishikawa, and Y. Toda, "Experimental Relation Between DR Equation and Langmuir Equation for Various Adsorbates on Many Carbons," *Carbon*, **31**, 990-992 (1993).
- Larsen, J.W., P. Hall, and P.C. Wernett, "Pore Structure of the Argonne Premium Coals," *Energy Fuels*, **9**, 324-330 (1995).
- Larsen, J.W. and P. Wernett, "Pore Structure of Illinois No. 6 Coal," *Energy Fuels*, **2**, 719-720 (1988).
- Larsen, J.W. and P.C. Wernett, "The Argonne Coals Do Not Have an Extended Inter-Connected Pore Network," in *American Chemical Society Preprints (Division of Fuel Chemistry)*, pp. 849-855, San Francisco, 1992.
- Levine, J.R., "Oversimplifications Can Lead to Faulty Coalbed Gas Reservoir Analysis," *Oil and Gas Journal*, pp. 63-69, Nov. 23, 1992.
- Lizzio, A.A., S.N. Vyas, and M. Rostam-Abadi, "Synthesis of Carbon Molecular Sieves From Illinois Coal: Carbon vs. Oxygen Deposition," in *Carbon '94*, Granada, Spain, pp. 530-531.
- Mahajan, O.P., "Coal Porosity," in *Coal Structure*, R.A. Meyers (Ed.), pp. 51-86, Academic Press, New York, 1982.
- Mahajan, O.P., "CO₂ Surface Area of Coals: The 25-year Paradox," *Carbon*, **29**, 735-742 (1991).
- Marsh, H., "Adsorption Methods to Study Microporosity in Coals and Carbons—A Critique," *Carbon*, **25**, 49-58 (1987).
- Mavor, M.J., L.B. Owen, and T.J. Pratt, "Measurement and Evaluation of Coal Sorption Isotherm Data," in *65th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers*, New Orleans, LA, SPE #20728, 1990.
- McCulloch, C.M. and W.P. Diamond, "Inexpensive Method Helps Predict Methane Content of Coal Beds," *Coal Age*, pp. 102-106, June 1976.
- McElhiney, J.E., R.A. Koenig, and R.A. Schraufnagel, "Evaluation of Coalbed-Methane Reserves Involves Different Techniques," *Oil and Gas Journal*, pp. 63-72, Oct. 30, 1989.
- Menon, V.C., The Pennsylvania State University, unpublished work (1996).
- Moudrakovski, I.L., C.I. Ratcliffe, and J.A. Ripmeester, "Application of ¹²⁹Xe 2D-EXSY NMR to Intra- and Interparticle Exchange in Zeolites," *Appl. Magn. Reson.*, **8**, 385-399 (1995).
- Nandi, S.P. and P.L. Walker, Jr., "Activated Diffusion of Methane in Coal," *Fuel*, **49**, 309-323 (1970).
- Nandi, S.P. and P.L. Walker, Jr., "Activated Diffusion of Methane From Coals at Elevated Pressures," *Fuel*, **54**, 81-86 (1975).
- Oberholtzer, J.E. and L.B. Rogers, "Effects of Micropores on Peak Shape and Retention Volume in Gas-Solid Chromatography," *Anal. Chem.*, **41**, 1590-1594 (1969).
- Olague, N.E. and D.M. Smith, "Diffusion of Gases in American Coals," *Fuel*, **68**, 1381-1387 (1989).
- Patel, R.L., S.P. Nandi, and P.L. Walker, Jr., "Molecular Sieve Characteristics of Slightly Activated Anthracite," *Fuel*, **51**, 47-51 (1972).
- Peterson, D.L., F. Helfferich, and R.J. Carr, "Measurement of Phase Equilibria at High Pressures by Tracer-Pulse Chromatography," *AIChE J.*, **12**, 903-905 (1966).
- Rightmire, C.T., "Coalbed Methane Resource," in *Coalbed Methane Resources of the United States*, C.T. Rightmire, G.E. Eddy, and J.N. Kirr (Eds.), pp. 1-13, The American Association of Petroleum Geologists, Tulsa, OK, 1984.
- Ripmeester, J.A. and C.I. Ratcliffe, "On the Application of ¹²⁹Xe NMR to the Study of Microporous Solids," *J. Phys. Chem.*, **94**, 7652-7656 (1990).
- Ripmeester, J.A. and C.I. Ratcliffe, "¹²⁹Xe NMR Spectroscopy in Microporous Solids: The Effect of Bulk Properties," *Anal. Chimica Acta*, **283**, 1103-1112 (1993).
- Rodríguez-Reinoso, F. and A. Linares-Solano, "Microporous Structure of Activated Carbons as Revealed by Adsorption Methods," in *Chemistry and Physics of Carbon*, P.A. Thrower (Ed.), vol. 21, pp. 1-146, Marcel Dekker, New York, 1989.
- Rolniak, P.D. and R. Kobayashi, "Adsorption of Methane and Several Mixtures of Methane and Carbon Dioxide at Elevated Pressures and Near Ambient Temperatures on 5A and 13X Molecular Sieves by Tracer Perturbation Chromatography," *AIChE J.*, **26**, 616-625 (1980).
- Ruppel, T.C., C.T. Grein, and D. Bienstock, "Adsorption of Methane on Dry Coal at Elevated Pressure," *Fuel*, **53**, 152-162 (1974).
- Smith, D.M. and F.L. Williams, "Adsorption and Diffusion in Western United States Coals," in *Coal Science and Chemistry*, A. Volborth, (Ed.), pp. 381-403, Elsevier, Amsterdam, 1987.
- Spencer, D.H.T. and R.L. Bond, "The Determination and Use of Specific Surface Values for Coals," *Adv. Chem. Ser.*, **55**, 724-730 (1966).
- Stoeckli, F., D. Huguenin, A. Greppi, T. Jakubov, A. Pribylov, S. Kalashnikov, A. Fomkin, A. Pulin, N. Regent, and V. Serpinski, "On the Adsorption of CO₂ by Active Carbons," *Chimia*, **47**, 213-214 (1993).
- Suh, D.J., T.-J. Park, S.-K. Ihm, and R. Ryoo, "¹²⁹Xe NMR Spectroscopy of Xenon Gas Adsorbed on Amorphous Carbons," *J. Phys. Chem.*, **95**, 3767-3771 (1991).
- Tomita, A., T. Tano, Y. Oikawa, and Y. Tamai, "Gasification of Coals Treated with Non-Aqueous Solvents. 5. Properties of Coals Treated with Liquid Ammonia," *Fuel*, **58**, 609-613 (1979).
- Tsiao, C. and R.E. Botto, "¹²⁹Xe NMR Investigation of Coal Micropores," *Energy Fuels*, **5**, 87-92 (1991).
- van der Sommen, J., P. Zwietering, B.J.M. Eillebrecht, and D.W. van Krevelen, "Chemical Structure and Properties of Coal. XII. Sorption Capacity for Methane," *Fuel*, **34**, 444-448 (1955).
- Walker, P.L., "Microporosity in Coal: Its Characterization and Implications for Coal Utilization," *Phil Trans. R. Soc. Lond. A*, **300**, 65-81 (1981).
- Walker, P.L., Jr. and O.P. Mahajan, "Methane Diffusion in Coals and Chars," in *Analytical Methods for Coal and Coal Products*, C. Karr (Ed.), pp. 163-188, Academic Press, 1978.
- Walker, P.L. and O.P. Mahajan, "Pore Structure in Coals," *Energy Fuels*, **7**, 559-560 (1993).
- Wernett, P.C., J.W. Larsen, O. Yamada, and H.J. Yue, "Determination of the Average Micropore Diameter of an Illinois No. 6 Coal by Xe-129 NMR," *Energy Fuels*, **4**, 412-413 (1990).
- Yang, R.T. and J.T. Saunders, "Adsorption of Gases on Coals and Heat-Treated Coals at Elevated Temperature and Pressure. 1. Adsorption from Hydrogen and Methane as Single Gases," *Fuel*, **64**, 616-620 (1985).
- Yee, D., J.P. Seidle, and W.B. Hanson, "Gas Sorption on Coal and Measurement of Gas Content," in *Hydrocarbons from Coal*, B.E. Law and D.D. Rice (Eds.), pp. 203-218, The American Association of Petroleum Geologists, Tulsa, OK, 1993.