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Surface Areas of Coals

S. P. NANDI and P. L. WALKER Jr have studied the activated diffusion of carbon dioxide and nitrogen in coals of various rank¹. They report that nitrogen has a higher activation energy for diffusion than does carbon dioxide. From these results, it is understandable why areas of coals reported from nitrogen adsorption at 77°K are small and represent primarily the sum of only the macropore and transitional pore surface areas. Later, P. L. WALKER Jr and K. A. KINI concluded that the surface area of coals calculated from carbon dioxide adsorption isotherms measured at 298°K most closely represent the total surface area, of any approach yet used². Walker and Kini also showed that carbon dioxide areas of coals go through a shallow minimum at a carbon (d.a.f.) content of *ca.* 84 to 90 per cent. In their study, they used coal of a 200 × 325 mesh particle size.

The purpose of the present study was to measure adsorption isotherms on varying particle sizes of coal of different rank. If adsorption is diffusion limited, uptake is expected to decrease with increasing particle size. Prior to adsorption measurements, samples were degassed at 150°C for at least four hours, down to a pressure of *ca.* 10⁻⁶ torr. Adsorption conditions used were: carbon dioxide at 298°K, nitrogen at 77°K, and neopentane at 273°K. Molecular areas taken were 25.3, 16.2 and 62 Å² respectively. Equilibration time in all cases was 30 min. Surface areas were calculated using the BET equation. Neopentane is a symmetrical molecule having a kinetic diameter³ of 6.2 Å. We thought that it might give a truer representation of the macropore plus transitional pore surface area than nitrogen, which has a kinetic diameter³ of 3.68 Å. That is, nitrogen may be getting into a small fraction of the micropore area, even at 77°K.

Table 1. Analyses of coals

Sample No.	Moisture %	Proximate analysis (moisture-free) %				Ultimate analysis (moisture-free) %			Carbon % d.a.f.
		Ash	VM	FC	S	C	H	N	
1	1.1	8.4	4.0	86.5	0.5	87.1	3.0	Nil	95.2
888	1.6	3.8	39.0	57.2	0.6	80.4	5.2	1.4	83.6
6	1.9	7.6	45.4	—	2.7	67.2	5.5	—	72.7

Table 1 presents analyses for the coals studied. Samples of these coals were used previously in the investigation of Walker and Kini². Surface area results are summarized in Table 2. Coal 888 has a carbon content which places it very close to the minimum in total surface area versus rank. Neopentane and nitrogen areas are nil (<1 m²/g) for all particle sizes of this coal studied. Obviously, even carbon dioxide adsorption has not reached equilibrium on this coal; the specific surface area increases with decreasing particle size. On the other hand, for the anthracite (No. 1) and high volatile C bituminous (No. 6) significant nitrogen and neopentane areas are measured. These areas do increase with decreasing particle size (down to 200 × 325 mesh), indicative

of slow diffusion occurring into some fraction of the micropores. Carbon dioxide diffusion is sufficiently rapid for the surface area to be essentially independent of particle size for the anthracite and for the No. 6 coal (in the latter case down to a size of 100×150 mesh).

Table 2. Surface area results

Sample No. and size	Surface area, m ² /g		
	CO ₂	N ₂	Neopentane
1			
42 × 65 mesh	234	8.0	1.0
65 × 100	231	12.5	1.3
100 × 150	226	22.6	3.7
200 × 325	224	34.0	—
888			
42 × 65 mesh	58.8	<1	<1
65 × 100	78.3	<1	<1
100 × 150	90.0	<1	<1
200 × 325	104	<1	<1
6			
42 × 65 mesh	160	10.3	11.9
65 × 100	156	11.1	12.9
100 × 150	158	18.1	20.3
200 × 325	139	22.0	—
—325	122	7.1	12.1

With No. 6 coal, there is a significant decrease in carbon dioxide surface area in going from the 100×150 to the 200×325 mesh size. This trend of decreasing surface area with decreasing particle size continues for all adsorbates when the size is further decreased to —325 mesh. It is suggested that during comminution of this coal to the finer sizes in a small hammer mill, sufficient heat was generated to produce some softening of the particles and, thus, some pore shrinkage and closure.

It is interesting to compare nitrogen and neopentane surface areas. With the anthracite, neopentane areas are significantly smaller than nitrogen areas. Obviously a smaller fraction of the microporosity has been entered. By contrast, for the high volatile C coal, neopentane areas are slightly higher than nitrogen areas. This suggests two possibilities: (1) imbibition of neopentane by the low rank coal and/or (2) the absence of a significant number of pores in the low rank coal lying in the size range from *ca.* 4 to 6 Å, that is, a size into which nitrogen could penetrate but neopentane could not.

These results again emphasize that when reporting the surface area (or the micropore volume) of coals, it is essential to indicate the adsorbate used, degassing conditions, adsorption temperature, equilibration time and coal particle size.

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