

Change in Surface Area of Anthracite on Heat Treatment

Maggs¹ and Malherbe², among others, have shown that coal behaves as a molecular sieve material. That is, the adsorption of nitrogen and argon at 77° K. is restricted because of activated diffusion into pores of molecular dimensions and gives data only on the readily accessible macropore area of coal. From heats of wetting and gas-adsorption data at higher temperatures, the macropore area is shown to represent an insignificant part of the total surface area of most coals.

The presence of a large micropore area in coal affects many of its properties. One property which is thought to be markedly affected is the thermal stability of anthracite on pyrolysis. Raw anthracite when used as a metallurgical fuel is susceptible to thermal shock, usually resulting in the lowering of its physical strength and subsequent size degradation. This phenomenon is thought to be primarily caused by the large increase in gas pressure in the micropores produced by the difficulty of releasing volatile matter from these pores upon heat treatment. It is with this thought in mind that a comprehensive programme has been initiated to study the nature of the micropore surface area in anthracites, its change with heat treatment, and its relation to decrepitation. An initial result of interest is being reported at this time.

The anthracite studied has the following proximate analysis on the as-received basis: water, 3.4 per cent; volatile matter, 2.9 per cent; ash, 7.1 per cent; fixed carbon, 86.6 per cent; and sulphur, 0.54 per cent. Adsorption studies were performed on minus-60 mesh samples (Tyler series) of raw and calcined anthracite. Calcination was conducted in a reducing atmosphere with samples heated to 1,200° C. in two hours and maintained at this temperature for two additional hours. Surface areas of the anthracite were determined from nitrogen adsorption at 77.2° K. and carbon dioxide adsorption at 194.6° K. using the procedure and Brunauer-Emmett-Teller equation discussed by Emmett³. Final adsorption pressures were read after 30 min. even though equilibrium was not completely attained.

Table 1 presents the surface area data. The nitrogen value can be considered essentially the macropore area, whereas the carbon dioxide value

can be considered essentially the total area. The nitrogen value would be expected to consist of some micropore area, and the carbon dioxide value would be expected to be somewhat less than the total area since equilibrium was not reached. Naturally, any arbitrary adsorption time of reasonable duration has the above limitations, and this fact must be kept in mind when interpreting the data. It should also be pointed out that good agreement of surface areas from nitrogen and carbon dioxide adsorption on carbons known to have an insignificant microporosity has been obtained⁴.

Table 1. SURFACE AREA OF RAW AND CALCINED ANTHRACITE

Treatment	N ₂ area, m. ² /gm.	CO ₂ area, m. ² /gm.
Raw	11.2	175
Calcined	0.78	2.8

It is seen that for the raw anthracite the micropore area represents at least 93 per cent of the total area, whereas for the calcined material only somewhat more than 72 per cent need be in micropores. Of greater significance is the marked decrease in the magnitude of micropore area upon calcination. At least 98 per cent of the micropore area has been destroyed or blocked from access to the exterior surface on calcination at 1,200° C.

Calcination of the anthracite produced approximately a 15 per cent volume-shrinkage. In the light of the area results, it appears that this shrinkage parallels the removal of the majority of micropore area from the anthracite. Indeed, anthracite which has been calcined at a very low heating rate⁵ shows good thermal stability when afterwards plunged rapidly into a hot zone, which is to be expected if the microporosity and occluded gases have been removed.

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¹ Maggs, F. A. P., *Nature*, **169**, 793 (1952).

² Malherbe, P. Le R., *Fuel*, **30**, 97 (1951).

³ Emmett, P. H., *A.S.T.M. Tech. Pub.*, **51**, 95 (1941).

⁴ Walker, jun., P. L., Foresti, jun., R. J., and Wright, C. C., *Indust. Eng. Chem.*, **45**, 1703 (1953).

⁵ Delvaux, Leon, M.S. thesis, Pennsylvania State University (1955).