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Uptake of bromine by anthracite

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It was found that when big chunks (1-in* cubes) of Pennsylvania anthracites (ranging in VM from about 4·5 to 9·0% on a daf basis) were exposed to bromine vapour at room temperature, they were reduced to −45 US-mesh material following a total exposure time of 24 h. This led to an attempt at preparing submicron-sized anthracite.

An anthracite (VM 5·6%, and ash 13·6%), previously ground in a fluid-energy mill to about 5 μm particle size, was exposed to bromine vapour at room temperature at a relative pressure close to 1·0 for 24 h. The bromine-loaded material was rapidly heated to about 800°C, in an attempt to develop a significant pressure of bromine vapour within the particle micropores — and, thereby, promote decrepitation to a still smaller particle size.

Size analysis by electron microscopy (transmission and scanning) before and after this shock treatment was inconclusive. However, some interesting features that were not present with the parent anthracite dispersion were found from transmission electron-microscopy observations of bromine-loaded and bromine-loaded—heat-treated dispersions, caught on a carbon film. First, there was a general reduction in the achievement of good contrast. Further, there were areas that collapsed, became spherical and finally evaporated away on increasing the beam intensity. Encounter with such areas on the bromine-loaded samples was more frequent than with the bromine-loaded—heat-treated samples. Possibly bromine in liquid form is trapped within the particles or some volatile bromides are formed upon interaction of the anthracite mineral matter with bromine during the sorption process.

Attempts to estimate particle size from a knowledge of nitrogen surface areas (measured at 77 K) were difficult owing to the highly microporous nature of anthracites. The nitrogen area of the fluid-energy-milled sample decreased sharply from its original value of 150 m²/g upon exposure to bromine for 24 h at 25°C. Under these adsorption conditions, 0·8 g of bromine was taken up per gram of anthracite. Bromine could be removed from the anthracite in flowing nitrogen or under vacuum in increasing amounts, by increasing the outgassing time at 25°C or by going to higher desorption temperatures, as seen in *Table 1*. Degassing at increasingly higher temperatures for 4 h also resulted in a recovery of the internal surface area of the anthracite, as shown in *Table 2*. Indeed, outgassing at 800°C resulted in a surface area (250 m²/g) which is significantly higher than that of the original sample. This suggests that exposure to bromine resulted in the elimination of some hydrogen from the anthracite and thus a subsequent increase in accessibility to the fine micropores of the treated anthracite (compared to the original material) upon complete removal of bromine. Similar results were reported by McDermot and Arnell[1] who exposed a carbon black,

* 1 in = 25·4 mm

Table 1 Removal of bromine from anthracite by treatment in flowing nitrogen

25°C		4 h	
Time (h)	Br₂ remaining (g/g)	Temp. (°C)	Br₂ remaining (g/g)
1	0·69	100	0·37
2	0·62	200	0·29
3	0·59	300	0·22
4	0·57	400	0·16
6	0·55	500	0·07
10	0·53	600	0·00
24	0·50		
68	0·48		

Table 2 Change in N₂ area upon heat treatment of bromine-loaded anthracite under vacuum

Temperature (°C)	Surface area (m²/g)
25	<1
100	8·0
200	13·4
300	22·8
400	56·4
600	158
≈800	250

Spheron 9, to saturated bromine vapour at room temperature. They then heated the black to various temperatures before measuring nitrogen surface areas (77 K). They found that up to 500°C the area was less than the original area (112 m²/g) of the black. However, after heating to 600°C, the area was larger — 121 m²/g.

In fact, it is well known that hydrogen present in coal is substituted in part by bromine upon exposure[2,3]. The extent of substitution is not well established. From the total uptake of bromine at room temperature by this anthracite, it is seen that the amount of bromine sorbed, although quite substantial, is much less than a 1:1 substitution of the hydrogen present in the anthracite. That is, on a dry basis, the anthracite contained 2·3 wt % hydrogen. Total substitution of this hydrogen by bromine would result in a pick-up of 1·8 g of bromine per gram of anthracite.

From data on mercury and helium densities for this anthracite, it is calculated that it has a total accessible pore volume of 0·063 cm³/g [4]. Taking the density of liquid bromine as 3·12 g/cm³, a maximum of about 0·2 g bromine/g of anthracite would be taken up. In fact, the anthracite took up four times this much bromine, which indicates that bromine had access to volume inaccessible to helium at room temperature. This could result from either imbibition into the anthracite or intercalation within some of the small trigonally bonded regions. Bromine intercalation is

extensive within highly graphitic forms of carbon[5].

Although we were not successful in producing submicron-sized anthracite by explosive shattering of particles filled with bromine, anthracite may be attractive for the removal of bromine vapours from gas streams and/or the production of hydrogen bromide.

ACKNOWLEDGEMENT

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Compound isolation from brown coal by low-temperature evacuation

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The compound 2,6-di-t-butyl-4-methylphenol has been isolated from brown coal during low-temperature evacuation. This discovery is important to all oxidation, hydration and distillation studies on brown coal.

The low-temperature oxidation of brown coal has been studied in this laboratory because of its importance in ignition, spontaneous combustion, and weathering properties, and because studies of brown-coal oxidation are few, relative to those of black-coal oxidation. The rate and extent of brown-coal oxidation has been shown to be far greater than that of black-coal oxidation (unpublished work, 1970, P. D. Swann and J. A. Harris). Bed-moist coal will not oxidize; consequently, the water must be removed from the coal before oxidation is performed. Considerable controversy exists concerning the state of the water in the coal. Common methods of moisture determination are: dehydration at uniform temperature[1], evacuation at $110°C$[2], and scavenging with nitrogen at $250°C$[3]. The work done by Allardice and Evans[4] on the brown-coal/water system employing vacuum desorption of water clarifies the situation for brown coal. They found that 'at least two classes of water exist in Yallourn brown coal at any particular temperature, firstly water which can be removed by evacuation at that temperature and secondly chemisorbed water which can be released only by raising the temperature to cause thermal decomposition of functional groups'. 'Above 60 degrees [C] significant quantities of carbon dioxide are also released from the evacuated coal.'

The method used here for removing the water from the coal was that used by Allardice and Evans, namely vacuum desorption at the oxidation temperature of $35°C$. Bed-moist brown coal which had been kept at all times under water was ground under water to −100 +200-mesh BS. It was then suspended in a bucket from a quartz spring in a water-jacketted glass reactor, and vacuum dried. Oxidation was performed by pure molecular oxygen at a pressure of 760 mmHg* and the extent of oxidation was measured by the weight increase of the coal which was followed by a cathetometer.

Experimental results showed that the amount of oxidation, as measured by the weight increase of the coal, was affected by the degree of drying. When the coal was evacuated to a pressure of 100 μmHg† the amount of

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* 760 mmHg = 1·013 bar
† 1 μmHg = 133 mN/m²

oxidation was far greater than when the coal was evacuated to a pressure of 10 μm Hg.

A possible explanation of this result was that volatile compounds were being removed from the coal when evacuation at $35°C$ was carried out at pressures lower than 100 μmHg. To investigate this, another apparatus was built. This apparatus made possible the collection of any gases removed from the coal during evacuation, and gas sampling of the reactor atmosphere during oxidation to investigate the production of carbon monoxide, carbon dioxide and water. The amount of oxidation was given by the volume of oxygen adsorbed and the moles of carbon dioxide, carbon monoxide and water produced. Two cold traps were used to protect the vacuum pump, with a tower of anhydrous magnesium perchlorate between them, so that no water collected in the trap nearest to the pump. In the experiments conducted, white crystals collected in the cold trap nearest to the pump, at liquid nitrogen temperature, during drying of the coal. As the trap was brought to room temperature some of the crystals sublimed. When the trap was opened, there was a very strong phenolic smell of lignite tar (like the smell of fresh rubber). Infra-red analysis of the atmosphere of the trap could detect only carbon dioxide; therefore some or all of the crystals which sublimed as the trap was brought to room temperature consisted of carbon dioxide. The white crystals which remained in solid form at room temperature and pressure were subjected to various treatments. An estimate of the amount of these crystals, expressed as a weight percentage of dry coal, is approximately 1%, and work is being done to determine the exact amount of the compound in the coal. A typical elemental analysis of these crystals is as follows: carbon 80%, hydrogen 11·6%, oxygen 8·4%. Mass spectrometric analysis of the white crystals showed that the exact molecular weight of the compound is 220. Mass and abundance Tables[5] show that, when the elemental analysis is considered, the only possible formula for the compound is $C_{15}H_{24}O$. The mass-spectrum fracture pattern is that of an aromatic compound. It shows the presence of methyl groups, but further definite identification of groups is doubtful because of the complex nature of the pattern. The compound melts with decomposition at $64–66°C$. Infra-red analysis of the compound[6,9] shows that the compound has identifiable peaks at the following wavenumbers: 3030 and 1600 cm⁻¹ (aromatic), 3625 cm⁻¹ (phenol), 2960, 2920 and 1430 cm⁻¹