Searching the evidence for the intercalation of bromine in high-rank coal

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(Received 28 April 1986; revised 19 November 1986)

Similar to graphite, *meta*-anthracite absorbs bromine at room temperature to a concentration close to that of stage-2 graphite–bromine. Subsequent desorption at room temperature was incomplete, indicating that 88% of the bromine was loosely held and 12% was relatively strongly held in the *meta*-anthracite. The rate of bromine absorption and the amount and rate of bromine desorption were greater for *meta*-anthracite than for graphite. X-Ray diffraction, electron diffraction and differential scanning calorimetry showed the absence of intralayer or interlayer intercalate ordering in brominated *meta*-anthracite after desorption, hence yielding no evidence for intercalation. We conclude that the *meta*-anthracite was not intercalated. The ignition temperature of *meta*-anthracite was lowered by ≈80°C by the bromination.

(Keywords: coal; intercalation; bromine)

The reactions of coals with various reactants are technologically attractive for comminution, desulphurization and catalytic coal gasification. A number of workers have suggested the possibility of intercalating coals or cokes with K[1–6], Na[1–3], $FeCl_3$[7], $CuCl_2$[7] and $CrCl_2$[7]. This paper reports on a thorough experimental search for the evidence of intercalation using the most up-to-date intercalation science methods.

TESTS FOR INTERCALATION

'Intercalation' refers to the insertion of intercalate layers between carbon layers. This means that the intercalate is in the form of layers and is not simply trapped at defects.

Ideally the intercalate layers and the carbon layers are periodically stacked. The number of carbon layers between nearest intercalate layers is known as the 'stage' of the intercalation compound. The lower the stage, the higher the intercalate concentration. The 'staging' phenomenon is clearest in intercalation compounds with stage $\lesssim 4$. As the intercalate concentration decreases, the tendency for mixed staging (i.e., coexistence of more than one stage) increases. For example, it is rare to have a pure stage 7 occurring. Furthermore, as the intercalate concentration decreases, the intercalate layers occur farther apart and the tendency for staging therefore decreases. For example, it is inconceivable to have a stage 20! Therefore, in dilute compounds, staging is unclear and hence cannot be used as a test for the occurrence of intercalation.

In concentrated compounds, staging is clear and can be used as the test for intercalation. For probing the staging, X-ray diffraction is most commonly used. The $00l$ diffraction pattern includes (i) strong lines which are close to (but shifted from) the graphite 002, 004, 006, etc., lines, and (ii) weaker lines between the nearest strong lines. For example, in stage 2, there are two weak lines between the nearest strong lines. The observation of shifted 002, 004 and 006 graphite lines is a necessary but not sufficient test for staging. However, the observation of the superlattice lines is a sufficient test for staging.

Below the intercalate in-plane melting temperature (which is different from the intercalate bulk melting temperature), the intercalate is ordered within an intercalate layer, forming a superlattice perpendicular to the *c*-axis. This in-plane ordering is clear even when the intercalate concentration is low and staging is unclear. It has been shown that in-plane ordering exists in residue graphite–bromine with an intercalate concentration of only 0.2 mol % Br_2 (3 wt %)[8]. The observation of in-plane intercalate ordering implies the presence of intercalate layers. Therefore, in-plane ordering can be used as a test for intercalation, provided that the test is made below the intercalate in-plane melting temperature. In-plane ordering can be observed by either X-ray diffraction or electron diffraction. The $hk0$ diffraction pattern includes (i) strong graphitic lines, and (ii) weaker superlattice lines.

Since the intercalate in-plane melting temperature is a well-defined temperature which is different from the intercalate bulk melting temperature and is specific to the intercalate species, the observation of a phase transition at the appropriate intercalate in-plane melting temperature is an indication of the existence of in-plane intercalate ordering and thus can be used as a test for intercalation. Other phase transitions of the intercalation compound may also be used for this purpose. However, since melting is usually the dominant and most well-known phase transition, it can be observed most easily. The transition temperature may be conveniently determined by using differential scanning calorimetry (DSC) or differential thermal analysis (DTA).

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0016–2361/87/060799–04$3.00

Due to the charge transfer between the intercalate and the carbon, intercalation decreases the in-plane electrical resistivity of the carbon[9]. However, a decrease in the electrical resistivity does not necessarily mean that intercalation has taken place, since adsorption, for instance, might involve charge transfer and also might lead to a change in the electrical resistivity. As an example, the adsorption of bromine in anthracite decreases the electrical resistivity due to the polarization of the bromine molecules upon adsorption[10]. Therefore, a change in the electrical resistivity cannot be used as a confirmatory test for intercalation.

Intercalation gives rise to an increase in weight of the carbon sample. Again, however, an increase in weight does not necessarily mean that intercalation has taken place, since adsorption of any kind may cause an increase in weight. Therefore, weight uptake alone cannot be used as a test for the occurrence of intercalation.

The ease of intercalation decreases markedly with decreasing degree of carbon graphitization[11]. Therefore, the expected concentration of intercalate, if any, in coals or cokes is low. Under this situation, staging is not a good test for intercalation, but in-plane ordering is, as explained above. As previously mentioned, X-ray diffraction or electron diffraction may be used for probing the in-plane ordering. Alternatively, DSC or DTA may be used for determining the intercalate in-plane melting temperature.

REPORTED EVIDENCE FOR INTERCALATION

The only conclusive evidence for the intercalation of cokes with K and Na was given by the X-ray diffraction work of Berger *et al.*[1], who observed superlattice diffraction lines due to staging. Additional support for K intercalation in coal was given by the X-ray diffraction work of Kapteijn *et al.*[5].

For the intercalation of $FeCl_3$, $CuCl_2$ and $CrCl_2$ in coal, the evidence was insufficient, as it was based on the removal of the 002 graphite line rather than the appearance of superlattice lines in the X-ray diffraction pattern[7].

A SEARCH FOR EVIDENCE FOR INTERCALATION

Because of the high reactivity of the alkali metals and the insufficient evidence for the intercalation of coals with intercalates other than the alkali metals, the question of whether coals or cokes can in general be intercalated remains unanswered. To answer this question, a thorough experimental search for the evidence for intercalation was undertaken using the combination of Rhode Island *meta*-anthracite (94% fixed carbon) and bromine as a model system. Rhode Island *meta*-anthracite is a coal of very high rank and should have a higher tendency to intercalation compared with other types of coals; bromine is one of the most well-known intercalates. It had been reported that the exposure of Pennsylvania anthracite to bromine vapour at room temperature for 24 h caused a weight uptake of 80% and a reduction in the particle size of the anthracite[12]. This observed weight uptake was four times that calculated for bromine occupying the pore volume accessible to helium[11]. This was attributed to either imbibition into the anthracite or intercalation within some of the small trigonally bonded regions[12]. Subsequent removal of the bromine from the anthracite by treatment in flowing nitrogen reduced the weight uptake to 50% after 24 h at 25°C and 0% after 4 h at 600°C[12].

Weight uptake—absorption and desorption

Weight uptake measurement was performed by using a Cahn electrobalance. The sample was placed on a quartz pan which was suspended by a quartz hangwire. During bromination, the sample was exposed to bromine vapour in equilibrium with pure bromine liquid at room temperature. The bromine liquid level was ≈ 1 cm below the sample pan. To prevent corrosion of the balance by bromine, the balance was purged with dry air.

Before bromination, sample weights were typically ≈ 5 mg and during bromination the samples disintegrated.

After 6 h, the *meta*-anthracite had increased in weight by ≈ 81%. After this, further exposure to bromine did not cause any weight change. A simple calculation shows that this large amount of bromine in the *meta*-anthracite requires either multilayer adsorption (which most probably takes place in the pores) or intercalation. On the other hand, similar exposure of highly oriented pyrolytic graphite (HOPG) to bromine vapour caused a weight uptake of 85% after 192 h for a sample of size 6.0 × 6.0 × 0.1 mm and after 46 h for a sample of size 2.2 × 5.2 × 0.35 mm. Hence, the rate of weight increase was much higher for *meta*-anthracite than for HOPG.

When the Br_2 vapour was subsequently removed, the weight uptake of the *meta*-anthracite decreased rapidly during the first hour of desorption; after ≈ 20 h desorption, the weight uptake had decreased to ≈ 10% and, thereafter, became relatively constant. Hence, the desorption was incomplete at room temperature, indicating that 88% of the bromine was loosely held and 12% of the bromine was relatively strongly held.

Similar weight uptake measurements were made during the absorption and desorption of Br_2 by Pennsylvania anthracite (≈ 88% fixed carbon). The amounts of weight uptake after the completion of absorption and after the completion of desorption are listed in *Table 1*. The amount of bromine absorbed was smaller than that (80%) reported by Sinha and Walker[12], probably due to the difference in the anthracite material.

Included in *Table 1* are the results obtained for HOPG. The extent of bromine uptake was higher for *meta*-anthracite than anthracite. *Meta*-anthracite approached HOPG in its bromine absorption ability. The 85% weight uptake of bromine in HOPG corresponds to the formation of the second stage intercalation compound, which was confirmed by X-ray diffraction.

Upon removal of the *meta*-anthracite from the bromine vapour, a total of 88% of the absorbed bromine was

Table 1 Weight uptake in carbons due to bromination and subsequent desorption at room temperature

Type of carbon material	Weight uptake after absorption (%)	Weight uptake after desorption (%)
Meta-anthracite	81	10
Anthracite	50	20
Highly oriented pyrolytic graphite	85	30

desorbed at room temperature. After 70 min desorption, the weight uptake had dropped to 20%. After 20 h desorption, the weight uptake had dropped to 10%. In contrast, for an initially stage-2 graphite–bromine sample, the weight uptake dropped to 70% after 8 h, 66% after 20 h, 46% after 6 days and 41% after 14 days. Hence, the desorption was much faster for *meta*-anthracite than for HOPG. Similarly, the absorption of bromine was much faster for *meta*-anthracite than for HOPG. This indicates that the bromine absorption in *meta*-anthracite was a different process from that in HOPG. This difference between *meta*-anthracite and HOPG suggests that the bromine was adsorbed in *meta*-anthracite and was intercalated in HOPG.

Table 1 indicates that the amount of retained bromine at the end of the desorption was higher in anthracite than *meta*-anthracite, even though the amount of bromine before the desorption was lower for the former. This suggests that the retained bromine might be trapped at defects, dangling bonds, or pores, which are more abundant in lower rank coals. On the other hand, the amount of retained bromine was smaller in *meta*-anthracite than in HOPG, even though the amounts of bromine before the desorption were comparable for *meta*-anthracite and HOPG, and HOPG had fewer defects, dangling bonds or pores than *meta*-anthracite. This suggests that the difference between *meta*-anthracite and HOPG in their bromine trapping capability after desorption was not due to the difference in defect or pore structure, but was due to the fact that the bromine was more loosely bound in the *meta*-anthracite than in HOPG. This again suggests that bromine was adsorbed in *meta*-anthracite and was intercalated in HOPG. It had been reported that the amount of retained bromine intercalate at the end of the desorption increased with decreasing degree of graphitization[13]. Hence, if the *meta*-anthracite were intercalated, as for HOPG, the amount of retained bromine would have to be higher for *meta*-anthracite than HOPG. That the contrary situation was observed again points to the absence of intercalation in the *meta*-anthracite.

Although the amount of weight increase due to bromine absorption in *meta*-anthracite might suggest intercalation, the rate of weight uptake and the amount and rate of decrease due to subsequent bromine desorption all suggest that adsorption rather than intercalation occurred.

Diffraction—superlattice formation

Both X-ray diffraction and electron diffraction characterization were performed at room temperature on *meta*-anthracite and HOPG after bromination and subsequent desorption. The in-plane intercalate melting temperature in graphite–bromine is 100°C[14–17]. Hence, at room temperature, in-plane intercalate ordering exists in graphite–bromine.

Because of the low bromine concentration in the brominated HOPG after desorption and the low intensities of $00l$ superlattice lines of graphite–bromine, the $00l$ superlattice diffraction lines due to staging were not observed in the HOPG. However, the $00l$ graphitic lines were slightly shifted from the ideal graphite values; the amount of the shift suggested a stage of 6. Although the evidence for staging was weak, intercalation was clearly indicated in HOPG by the presence of the in-plane superlattice lines, which were clearly observed by electron diffraction with the electron beam along the c-axis. This electron diffraction pattern was observed even for graphite–bromine containing as little as 3 wt% bromine[8].

For the *meta*-anthracite after desorption, neither X-ray nor electron diffraction gave any evidence for staging or in-plane intercalate ordering.

Calorimetry—phase transition

The in-plane intercalate melting transition at 100°C in graphite–bromine can be readily observed by differential scanning calorimetry (DSC) as an endothermic peak during heating and an exothermic peak during cooling[14–17], and this observation serves as good evidence for intercalation.

Calorimetry was performed using Perkin-Elmer DSC-2 and DSC-7 differential scanning calorimeters. The DSC peak due to the melting transition was reversibly observed even in residue graphite–bromine (HOPG). However, no such peak was observed in brominated *meta*-anthracite after desorption.

Combustion

The DSC technique was used to measure the combustion temperature of *meta*-anthracite and anthracite before and after bromination to investigate the effect of bromination on the chemistry of the coals. Measurement on the brominated *meta*-anthracite was made after most of the desorption had occurred.

A Perkin-Elmer DSC-2 differential scanning calorimeter was used. During the DSC measurement, the sample was mounted in an unsealed platinum pan with a platinum cover. For combustion, the sample holder was purged with oxygen at 0.14 MPa (20 psi).

Combustion resulted in an exothermic DSC response during heating. After combustion, less than 1 wt% of the original sample remained. As shown in *Table 2*, bromination decreased the ignition temperature of *meta*-anthracite by $\approx$80°C and that of antracite by $\approx$30°C. The ignition temperature of *meta*-anthracite was higher than that of anthracite, but the ignition temperatures of both were decreased by bromination. For the same bromination time, the ignition temperature decreased with decreasing desorption time. This indicated that a higher bromine concentration was favourable for a lower ignition temperature. This observation is probably due to the polarization of the adsorbed bromine in the *meta*-anthracite and the anthracite[10].

CONCLUSION

In order to test the general possibility of intercalating coal, a thorough experimental search for the evidence for the intercalation of bromine in *meta*-anthracite was

Table 2 Effect of bromination on the combustion temperature

Coal type	Bromine absorption time	Bromine desorption time	Combustion temperature (°C)
Meta-anthracite	0	—	649
	4 days	3 days	582
	4 days	1 h	563
Anthracite	0	—	568
	5 days	2.5 h	537

undertaken. Similar to HOPG, the amount of bromine absorption in *meta*-anthracite was significant and gave rise to a bromine concentration close to that of stage-2 graphite–bromine. However, the rate of bromine absorption and the amount (88%) and rate of subsequent bromine desorption were greater for *meta*-anthracite than for graphite. That desorption did not occur to completion at room temperature indicates the presence of at least two types of bromine in the *meta*-anthracite before desorption. One type (88%) was loosely held; the other type (12%) was relatively strongly held. X-ray and electron diffraction indicated the absence of any intralayer or interlayer ordering in brominated *meta*-anthracite after desorption. Differential scanning calorimetry showed the absence of the intercalate in-plane melting transition in brominated *meta*-anthracite after desorption. No evidence for intercalation was found. Therefore, it can be concluded that the *meta*-anthracite was not intercalated, but rather contained adsorbed bromine both before and after desorption. On the other hand, the bromination and subsequent desorption decreased the ignition temperature of *meta*-anthracite from 650 to 570°C.

ACKNOWLEDGEMENT

This work was supported in part by the Benedum Foundation. The X-ray diffraction equipment grant from the Division of Materials Research of the National Science Foundation under Grant DMR-8005380 is appreciated. Equipment support from the Materials Research Laboratory Section, Division of Materials Research, National Science Foundation, under Grant DMR 76-81561 A01 is also acknowledged.

REFERENCES

1 Berger, D., Carton, B., Metrot, A. and Herold, A. 'Chemistry and Physics of Carbon' (Eds. P. L. Walker, Jr. and P. A. Thrower), Vol. 12, 1975
2 Hawkins, R. J., Monte, L. and Waters, J. J. *Ironmaking and Steelmaking* 1974, **1**, 151
3 Krol, L., Dankmeyer-Laczny, J. and Buzek, J. *Arch. Eisenhuettenwes.* 1981, **52**, 341
4 Lu, W-K., Samaan, G. and Uribe, M. *Iron Steelmaker* 1981, **8**, 24
5 Kapteijn, F., Jurriaans, J. and Moulijn, J. A. *Fuel* 1983, **62**, 249
6 Murdie, N., Marsh, H. and Lin, M-F. *Ext. Abstr. Prog.—Bienn. Conf. Carbon* 1985, **17**, 55
7 Beall, H. *Fuel* 1980, **59**, 140
8 Chung, D. D. L. *J. Electron. Mater.* 1978, **7**, 89
9 Hennig, G. R., in 'Progress in Inorganic Chemistry' (Ed. F. A. Cotton), Wiley Interscience, New York, 1959, pp. 125–205
10 Zubkova, Yu. N. and Lopanov, A. N. *Sov. Progr. Chem.* 1980, **46**, 23
11 Dowell, M. B. *Mater. Sci. Eng.* 1977, **31**, 129
12 Sinha, R. K. and Walker, Jr., P. L. *Fuel* 1973, **52**, 153
13 J. Maire and J. Mering, *Proc. 3rd Conf. Carbon*, Buffalo, New York, 1957; Pergamon Press, New York, 1959
14 Bardhan, K. K., Wu, J. C. and Chung, D. D. L. *Synth. Met.* 1980, **2**, 109
15 Culik, J. S. and Chung, D. D. L. *Mater. Sci. Eng.* 1979, **37**, 213
16 Culik, J. S. and Chung, D. D. L. *Carbon* 1985, **23**, 459
17 Erbil, A., Kortan, A. R., Birgeneau, R. J. and Dresselhaus, M. S. *Mat. Res. Soc. Symp. Proc.* Vol. 20, pp. 21–26, Elsevier, 1983; *Phys. Rev. B* 1983, **28**, 6329