

SURFACE STRUCTURE OF COALS STUDIED BY IODINE AND WATER ADSORPTION

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1. Introduction

1.1 Iodine and carbon

The interaction of iodine with such carbonaceous materials as carbons and coals has been studied by adsorption both from the vapour phase (1-3) and from aqueous potassium iodide solution (1,3-6). Mechanisms of interactions have been studied using ESR (2,7) and related to the well-characterized formation of charge-transfer complexes of iodine with organic compounds (2). Thus, both classical physical adsorption theory and more specific chemical interactions have been proposed to model the adsorption of iodine by carbonaceous materials. Assessments of surface area and porosity in solid adsorbents are traditionally made from data of vapour phase adsorption (8). Although the technique is relatively elaborate, involving use of vacuum equipment, interpretation of a single component adsorbate is straight-forward. The alternative approach of adsorption from solution, a relatively simple experimental technique, is however much more difficult to interpret because of multi-component competitive adsorption processes (9). Adsorption of iodine from aqueous potassium iodide solution by carbons does however appear to be both relatively easy experimentally and to interpret. This study is concerned with the extension of the use of iodine as an adsorbate from carbons to coals. Kipling *et al.* (1) studied the adsorption of iodine, both from the vapour phase and organic solutions at 20°C on graphitized carbon blacks. Adsorption of iodine from organic solutions was solvent dependent and can be used to determine surface areas only under certain conditions mainly when solvent competition for the surface is minimized. Studies of the adsorption of iodine from aqueous potassium iodide solution on several porous carbons were carried out by Hill and Marsh (5). Iodine was not restricted to monolayer coverage and filling of meso-porosity occurred. The adsorption isotherm required the calculation of the concentration of free iodine (I_2) in equilibrium with the carbon surface. Surface area values were comparable to those from isotherms of nitrogen and carbon dioxide (5). Radioactive studies demonstrated that molecular iodine was physically adsorbed. Later, Juhola (3) using activated carbon reported similarly to Hill and Marsh (5). Meguro *et al.* (6) studied iodine adsorption on carbons from aqueous solution and concluded that iodine molecules were the only species adsorbed physically, in agreement with Hill and Marsh (5). Adsorption isotherms fitted the Langmuir equation over only part of the concentration range of free iodine whereas the Dubinin-Radushkevich (D-R) fitted the data much better over the whole range of concentration. Meguro *et al.* (6) therefore concluded that micropore filling rather than monolayer coverage occurred. To support this they showed that micropore volumes calculated from adsorption of carbon dioxide were in good agreement with values calculated from iodine adsorption using the D-R equation.

1.2 Iodine and coals

Although the interactions of iodine with carbons have been adequately studied, the literature of interactions with coals is scant. Aronson *et al.* (2) studied adsorption of iodine vapour on graphite, anthracite and bituminous coals at 70°C. Values of enthalpies of adsorption were in the range -44 to -60 kJ mol⁻¹, a value close to the enthalpies of complexing between model organic

compounds and iodine (10), indicating a relatively strong interaction when compared with, e.g. hydrogen bonding of -28 kJ mol^{-1} (11). Anthracite adsorbed more than the graphite from the vapour phase at equilibrium; the three bituminous coals and lignite all showed similar adsorption behaviour. The iodine/coal weight ratios had values of 2.5 (10 mmol g^{-1}) and 2.0 (8 mmol g^{-1}) for the three bituminous coals and lignite respectively. Such large extents of iodine adsorption by coals go far beyond extents of iodine adsorption by activated carbons and suggest a different form of iodine in equilibrium on coal surfaces.

It is established that iodine reacts reversibly with polynuclear aromatic hydrocarbons to form charge-transfer complexes in which several molecules of iodine are complexed with one hydrocarbon molecule (7,12). Aronson *et al.* (2) followed the reaction of iodine with polynuclear aromatic hydrocarbons from changes in vapour pressure and noted that the molecular ratio of iodine to hydrocarbon ranged from one to three. Perylene formed two complexes $\text{Pe}(\text{I}_2)_{1.5}$ and $\text{Pe}(\text{I}_2)_{2.9}$. Picene did not form a complex. Kim and Reiss (13) have studied adsorption of iodine vapour by films of polythiophene and shown it to be reversible, exhibiting Henry's law behaviour over a wide pressure range. They suggest that the number of iodine molecules adsorbed is comparable with the estimated number of thiophene monomer units in the polymer film.

1.3 Water vapour and coals

The interpretation of water vapour adsorption isotherms of coals is complex (14,15). Water within coal, prior to the initial degassing, can form part of the structure of coal, in particular the low rank coals. Here, their significant oxygen contents bond water to coal material. The initial outgassing of coals can cause structural changes resulting in shrinkage, the coal swelling on re-adsorption of water. Isotherms may not be reproducible. Extents of water adsorption can be as high as 80 wt% (45 mmol g^{-1}) far in excess of extents of adsorption of carbon dioxide at 195 or 273 K and resulting from volume filling and coal swelling. Water isotherms are usually of Type III BET classification but extents of adsorption are critically dependent upon the oxygen content of surfaces (8). Adsorption of water is relatively high for low rank coals (high oxygen content), passing through a minimum for the coking bituminous coals because of development of closed porosity and rising again for the anthracites of enhanced microporous content (15).

1.4 Macromolecular structure of coal

Although coal is extremely heterogeneous in composition (16) attempts have been made to treat the vitrinite components of coals in terms of a macromolecular structure (17-19). As coals increase in rank so carbon-oxygen cross-links are replaced by hydrogen bonding (coking coals) and carbon-carbon cross-links in anthracites, a minimum in cross-link density occurring at about 87 wt% of carbon (17). Aromaticity in coals increases progressively with rank. Oxidation of coal, in air, is thought to remove both hydrogen from the surface and to chemisorb oxygen (20), both effects contributing to the loss of plasticity of bituminous coals on heating. The thermolysis of the fusing bituminous coals brings about breakage of cross-links in the initial coal.

The objectives of this study in general terms are to advance an understanding of coal substance and in specific terms to examine (a) the adsorption of iodine both from the vapour phase and from aqueous potassium iodide solution from a rank range of fresh coals, (b) the behaviour of oxidised coals, (c) the behaviour of coals after thermolysis pyrolysis.

2. Experimental

2.1 Materials used

Eleven coals of a rank range were used and from these coals three were selected for further oxidation studies, i.e. Gedling (NCB rank 801), Cortonwood (501) and Cwm (301). Analyses of the coals are in Table 1. An activated carbon cloth, No. 005 manufactured by Charcoal Cloth Ltd., U.K. was used as a comparison (nitrogen BET surface area $1300 \text{ m}^2\text{g}^{-1}$, pore volume $\sim 0.45 \text{ cm}^3\text{g}^{-1}$).

2.2 Techniques used

Coals were oxidised in an air oven at 100° , 150° , 200° and 250°C for 1 and 2 days. Iodine and water were adsorbed by dry coals from the vapour phase (no air) at 25°C over a two-week period. The amount of iodine and water adsorbed were determined gravimetrically using the silica springs of a McBain-type equipment (8). The coals were degassed at 100°C prior to an adsorption run. In determinations of extents of adsorption of iodine from aqueous solution, 100 mg of each fresh, oxidised and pyrolyzed coal was sealed with 50 ml of aqueous solution of iodine and iodide (0.07 mol of I_2 plus 0.15 mol of KI l^{-1}) at 25°C in a flask, with occasional shaking. After four weeks an aliquot of the solution was taken and the iodine concentration determined with a standard solution of sodium thiosulphate (5). Samples of fresh and oxidised charcoal cloth were similarly treated and analysed after seven days. Extents of adsorption corresponded to an equilibrium relative concentration of 0.45.

Fresh and oxidised coals were kept in iodine (aqueous) solution (0.056 mol I_2 plus 0.15 mol KI per litre) for periods ranging from 1 to 28 days. Values of kinetic constants were determined from the variation of extents of iodine adsorption with time. To study the swelling of coals by water and iodine solution, ground fresh and oxidised coals (~ 100 mesh) were placed in a 3.5 mm (int. diam) pyrex glass tube and packed carefully according to the procedure used by Larsen (21). The height of the coal bed was measured (average of four measurements after rotating the tube) before and after addition of $\text{I}_2/\text{KI}/\text{H}_2\text{O}$ (0.056 mol I_2 , 0.15 mol KI per litre) solution. The swelling ratio, Q , was calculated as ($Q = V_f/V_i = H_f/H_i$) where V_f and V_i are the final and initial volumes of the coal bed and H_f and H_i the corresponding heights. To study the effects of pyrolysis of coals, fresh and oxidised coals were carbonized under flowing nitrogen in a horizontal furnace to 200° , 300° , 400° , 500° , 600° and 700°C with a heating rate of 3°C min^{-1} and a soak time of 0.5 h.

3. Results

3.1 Adsorption of iodine by fresh coals

Figure 1 shows the variation of iodine adsorption from aqueous solution as a function of coal rank for fresh coals with carbon contents lying between 80 wt% C and 95 wt% C. Iodine adsorption increased from $\sim 4 \text{ mmol g}^{-1}$ for coal with carbon content of 80 wt% to a maximum value of 6 mmol g^{-1} for coals of ~ 84 wt% carbon content (dmmf). Iodine adsorption then fell with increasing carbon content to $\sim 2.3 \text{ mmol g}^{-1}$ for a coal with a carbon content of 95 wt%.

3.2 Adsorption of iodine by oxidised coals

Figures 2-4 illustrate the isotherms for adsorption of iodine by fresh and oxidised coals at 25°C . In all the coals a decrease in the amount of iodine uptake with extents of oxidation was observed. Changes in the shape of the isotherms were also observed as oxidation progresses. The isotherms are Type I and II, (BET classification) (8). Extents of iodine uptake (mmol g^{-1}) can be converted to an equivalent surface area by assuming a cross-sectional area of an iodine molecule of 0.4 nm^2 (5). Figure 5 shows the

isotherms for the adsorption of iodine by fresh and oxidised charcoal cloth. An increase in the amount of iodine adsorbed with extents of oxidation was observed. The isotherms are Type 1. The maximum of iodine adsorption was at $C/C_0 > 0.4$ (C/C_0 = relative free iodine concentration (5); C_0 is taken as 1.2 mmol l^{-1}). Extents of iodine adsorption observed for coals were much higher than those for charcoal cloth at similar C/C_0 values. Figure 6 summarises the changes in iodine adsorption following oxidation at different temperatures and times for the three coals at constant C/C_0 value ($C/C_0 = 0.6$).

3.3 Adsorption of iodine by pyrolysed coals

The adsorption of iodine as a function of heat treatment temperature (HTT) for Cwm (301), Cortonwood (501) and Gedling (801) coals is illustrated in Figure 7. An initial increase in amounts of adsorbed iodine was observed at the lower values of HTT reaching a maximum at $\sim 400^\circ\text{C}$ and decreasing sharply thereafter to low values. The effect of preoxidation and heat treatment on adsorption of iodine for the three coals is illustrated in Figures 8-10. Little change was observed when coals were oxidised at 100°C compared with the non-oxidised samples, but a marked decrease was observed when the coals were oxidised at the higher temperature of 200°C .

4. Discussion

4.1 Adsorption of iodine by fresh coals

Figure 1 shows that for a rank range of fresh coals, there is a clear rank dependence of iodine adsorption from aqueous solution. A maximum in iodine uptake ($\sim 6 \text{ mmol g}^{-1}$) occurs at 84 wt% C dmmf. The minimum value ($\sim 2.3 \text{ mmol g}^{-1}$) was obtained for coals with 95 wt% C. The variation of surface properties as a function of coal rank has been studied previously (22-24). Carbon dioxide surface areas measured at 195 K (-78°C) and 273 K (0°C) varied from 110 to about $310 \text{ m}^2\text{g}^{-1}$ and fell within a broad band with the minimum at about 85 wt% carbon.

The results obtained in this present study of iodine adsorption as a function of coal rank do not relate to those of carbon dioxide surface areas. The coal rank series shows a maximum in adsorption of iodine at about 85 wt% carbon; with carbon dioxide a minimum is observed. Further, the equivalent surface areas of coals with 86 and 95 wt% C, based on iodine adsorption are 1400 and $530 \text{ m}^2\text{g}^{-1}$ respectively. These values are extremely high compared with the carbon dioxide surface areas. This indicates that the mechanism of adsorption by iodine and carbon dioxide must be different.

Although the temperature of adsorption of iodine is high enough (25°C) to eliminate activated diffusion effects restricting adsorption (22-24) the larger size of the iodine molecule would be expected to result in a decreased adsorption compared with carbon dioxide. This does not occur. However, the iodine adsorption from the vapour phase is much less than from aqueous iodide solution (Table 2) indicating a co-operative effect between the water and the iodine. With adsorption from the vapour phase, three interacting factors may control the ultimate extents of iodine adsorption. The higher internal porosity and larger pore sizes of the lower rank coals will promote adsorption; the increase in aromaticity of coals with increasing rank will promote increased adsorption with rank; overall, extents of adsorption will decrease as the strength of cross-links and cross-link density increase. For adsorption of iodine and water from the vapour phase, the higher internal porosity of the lower rank coal appears to dominate.

Extents of iodine adsorption are much higher from aqueous solution (Table 2, Figure 1). It is possible that the water when in the coal, is able to expand the macromolecular structure of the coal sufficiently to allow a considerably larger amount of iodine to be adsorbed, but the water is not significantly competitive for the surface. The swelling data of Table 3 indicate that the Gedling coal can respond most to the co-operative effects of the water and iodine agreeing with the highest uptake of iodine from the vapour phase. Thus, as the cross-link density of the coals decreases with increasing rank to about 85 wt% carbon and then increases, so the iodine adsorption will increase to decrease subsequently beyond the 85 wt% carbon level. Thus, Figure 1 is indicative of the cross-link density of the coals of the rank range.

Figures 2-4 shows the isotherms of the fresh coals and indicate a change in isotherm shape, almost Type II for Gedling coal and Type III for Cortonwood and Cwm coals of higher rank. This is indicative of a lower enthalpy of adsorption between the iodine adsorbate and the coal adsorbent for the latter two coals.

The charcoal cloth behaves differently from the coals. The surface areas calculated from iodine adsorption are commensurate with nitrogen areas, i.e. about $1300 \text{ m}^2 \text{ g}^{-1}$. Oxidation causes an increase in iodine adsorption unlike the coals. Possibly oxidation enhances pore volume and with the rigid carbon-carbon cross-linked structure already established, it cannot be enhanced further and hence iodine adsorption is not diminished. Carbons and coals respond differently to iodine adsorption.

4.2 Adsorption of iodine by oxidized coals

The effects of increasing duration and temperature of oxidation in air of the Gedling, Cortonwood and Cwm coals are to decrease extents of iodine adsorption from both the vapour and aqueous phases. For coals of maximum oxidation treatment (2d at 200°C) extents of iodine adsorption from the vapour phase are equivalent to about $25 \text{ m}^2 \text{ g}^{-1}$. For the same coals extents of water adsorption increase with severity of oxidation, as anticipated (14,15). For all three coals progressive oxidation promotes swelling of the coals by water alone and by the iodine-water system, probably to equal extents. The isotherms of Figures 2-4 shows that the Gedling oxidized coals retain the Type II isotherm shape of the parent coal, whereas the isotherms of the Cortonwood and Cwm coals change from Type III to Type II with progressive oxidation.

In interpreting these findings, the influence of coal oxidation on iodine adsorption from the vapour phase operates in possibly three ways. Chemisorbed oxygen reduces the effective pore diameters and restricts iodine penetration; chemisorbed oxygen cross-links the coal so preventing the iodine being accommodated by some relaxation of the cross-linked network; chemisorbed oxygen is electronegative and this could reduce electron availability for charge transfer complexing (2).

The adsorption of iodine from aqueous solution by oxidized coals is much less affected by the oxidation process than adsorption from the vapour phase. What is possibly happening here is that the water, by association with the chemisorbed oxygen, causes the coal to swell giving greater access to the iodine, and this effect enhances with progressive oxidation. Competition between adsorbed iodine and the water molecules becomes stronger and presumably the hydrogen bonding and clustering of water molecules (14,15) in the coal material prevents access of iodine to the macromolecular structure of coal and the balance is a diminished adsorption of iodine with increased oxidation at high relative concentrations of the isotherms (Figures 2-4). For the Cortonwood and Cwm coals, 230

the effects of oxidation are to enhance iodine adsorption at values of $C/C_0 < 0.2$. The Gedling coal, with its 9.4 wt% of oxygen has a Type II isotherm when fresh. Oxidation of the Cortonwood (5.9 wt% O) and Cwm (3.2 wt% O) coals changes these coal surfaces in a way comparable to the Gedling coal. The large extents of iodine adsorbed by the fresh coals, in the order of 6 mmol g^{-1} (equivalent surface area of $1,500 \text{ m}^2 \text{ g}^{-1}$ (25)) may also involve clustering of iodine molecules (7, 12). The presence of oxygen in the coal (either rank or oxidation related) creates sites of high adsorption potential which are covered at the lower values of relative concentration. Karsner and Perlmutter (26), in studies of coal drying and oxidation, report changes in the macro-molecular and microporosity of coals. Hence for the Cortonwood and Cwm coals the drying process associated with oxidation at e.g. 200°C could cause decreases in size of micro-porosity so enhancing the adsorption potential and shifting isotherm shape to a Type II. The studies of Oda *et al.* (27) on methanol and hexane densities of oxidised coals showed that coal density increased during the initial stages of oxidation. How this affects pore sizes remains to be clarified.

The variation of extent of iodine adsorption with time for fresh and oxidized Cortonwood and Cwm coals is illustrated in Table 4. The rate data approximate to first-order kinetics and what is clear is that rates of iodine adsorption decrease with severity of oxidation, more so for the Cortonwood coal. This suggests a diffusional limitation to adsorption with a possible pore narrowing as drying and oxidation proceed.

4.3 Adsorption of iodine by pyrolyzed coals

The findings of this aspect of the study (Figures 7-10) are that for the three fresh Gedling, Cortonwood and Cwm coals the effect of increasing heat treatment temperature (HTT) is to enhance iodine adsorption to a minimum of HTT of 400°C followed by a rapid decrease to 600°C (Figure 7). The chars (HTT 700°C) of Gedling and Cwm coals are able to adsorb iodine (equivalent to about $300 \text{ m}^2 \text{ g}^{-1}$) whereas the Cortonwood coke adsorbs no iodine.

The effects of oxidation for the Gedling coal (Figure 8) are to reduce the overall extent of iodine adsorption, to promote a minimum in adsorption at an HTT of 300°C but with still a maximum at 400°C and to decrease the HTT of closure of the porosity. This latter effect is very pronounced for the Cortonwood and Cwm coals (Figures 9,10). The rise in adsorption capacity with increasing HTT (Figure 8) is also found using nitrogen and carbon dioxide as adsorbates (28-30) but the magnitude of iodine adsorption (equivalent to $1750 \text{ m}^2 \text{ g}^{-1}$) must not be overlooked. The effect of pyrolysis could be to reduce, thermally, the cross-link density of coals and this allows greater access of iodine into the macromolecular system. Increasing HTT causes loss of volatile with considerable enhancement of cross-link density so reducing the ability of iodine to adsorb from an equivalent of 1750 to $300 \text{ m}^2 \text{ g}^{-1}$. The effect of oxidation of coals on their carbonization behaviour is to promote further the development of cross-links with increasing HTT (Figures 8-10). The evidence available from the water adsorption data is to suggest that oxygen cross-links are not formed during the oxidation process.

5. Conclusions

5.1 Adsorption of iodine by fresh coals

Adsorption of iodine by coals differs in mechanism from adsorption of nitrogen and carbon dioxide. Complexing of iodine with the molecular components of coal to the extent of an equivalent $1750 \text{ m}^2 \text{ g}^{-1}$ probably involves molecular clustering of iodine. Iodine adsorption by coals, at constant relative concentrations, is indicative of cross-link density of coals and is rank dependent. Extents of adsorption of iodine from the vapour phase are

significantly lower than from aqueous solution. The adsorption of iodine from the aqueous phase is dependent upon a co-operative effect with adsorbed water.

5.2 Adsorption of iodine by oxidized coals

Oxidation and associated drying of coal changes coal structure, removes hydrogen, introduced chemisorbed oxygen but probably does not create oxygen cross-links. Oxidation of coal reduces its capability for iodine adsorption from vapour and aqueous phases but water vapour adsorption is enhanced. Isotherm shape is changed and is indicative of structural change.

5.3 Adsorption of iodine by pyrolysed coals

Pyrolysis of fresh coals to 400°C enhances extents of iodine adsorption probably because of breakage of cross-links. Further pyrolysis severely enhances cross-link density. For all oxidised coals, in particular Cortonwood and Cwm heat treatment causes marked reductions in iodine adsorption, probably due to formation of oxygen cross-links.

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Table 1

Elemental Analyses of Coals (wt% dmmf)

Coal	%C	%H	%O	%N
Siemenowice	80.3	4.7	12.1	2.3
Gedling	81.6	5.2	9.4	1.7
Cresswell	82.3	4.6	10.1	1.8
Markham D.H.	82.3	5.7	7.9	1.5
Cortonwood	84.2	5.6	5.9	1.7
Manif. Lip	84.5	5.5	5.9	1.9
Horden	86.3	5.4	4.1	1.8
Cwm	90.0	5.0	3.2	1.6
Oakdale L.C.	91.7	4.8	2.0	1.6
Taft Merthyr	92.4	4.2	1.6	1.5
Cynheidre	95.2	2.9	0.9	1.0

Table 2

Adsorption of Iodine from Vapour and Solution and of Water Vapour

Coal Treatment Oxid. in days (d)	Adsorption of Iodine from Vapour $P/P_0 = 1.0$		Adsorption of Iodine from Solution $C/C_0 = 0.6$		Adsorption of Water Vapour $P/P_0 = 1.0$	
	mmol g^{-1}	$\text{cm}^3 \text{g}^{-1}$	mmol g^{-1}	$\text{cm}^3 \text{g}^{-1}$	mmol g^{-1}	$\text{cm}^3 \text{g}^{-1}$
<u>Cedling</u>						
Fresh	2.7	0.10	5.8	0.22	6.3	0.11
Oxid. 1d 100°C	2.5	0.10	5.6	0.21	7.0	0.13
2d 100°C	2.3	0.09	5.3	0.20	6.8	0.12
1d 150°C	1.1	0.04	5.0	0.19	7.3	0.13
1d 200°C	0.13	0.005	3.8	0.14	8.4	0.15
2d 200°C	0.09	0.003	3.6	0.14	8.2	0.15
<u>Coronwood</u>						
Fresh	1.4	0.05	6.8	0.26	0.6	0.014
oxid. 1d 100°C	1.2	0.04	6.7	0.25	1.1	0.020
2d 100°C	1.1	0.04	6.4	0.24	1.2	0.022
1d 150°C	0.7	0.03	6.2	0.23	2.1	0.038
1d 200°C	0.07	0.003	5.4	0.13	5.1	0.092
2d 200°C	0.06	0.003	3.5	0.13	6.4	0.115
<u>Canb</u>						
Fresh	1.5	0.06	4.6	0.17	0.8	0.014
Oxid. 1d 100°C	1.2	0.04	4.4	0.17	0.9	0.016
2d 100°C	1.2	0.04	3.9	0.15	1.0	0.018
1d 100°C	0.8	0.03	3.6	0.14	1.4	0.025
1d 200°C	0.16	0.006	3.3	0.13	3.2	0.058
2d 200°C	0.09	0.003	2.5	0.10	4.5	0.081
<u>Activated Charcoal</u>						
Fresh	-	-	3.8	0.15	-	-
Oxid.	-	-	4.3	0.19	-	-

Table 3

Swelling Ratio for Coals in Water and Iodine Aqueous Solution

Oxidation State	Coal: H ₂ O Q = Vf/Vi			Coal: I ₂ /I ₃ /H ₂ O Q = Vf/Vi		
	Gedling	Cortonwood	Cwm	Gedling	Cortonwood	Cwm
Fresh	1.00	1.00	1.00	1.06	1.00	1.00
Oxid. 1D 100°C	1.02	1.05	1.02	1.05	1.01	1.01
2D 100°C	1.04	1.07	1.02	1.09	1.00	1.02
1D 150°C	1.10	1.07	1.07	1.10	1.03	1.00
2D 150°C	1.14	1.07	1.03	1.12	1.03	1.02
1D 200°C	1.17	1.17	1.02	1.16	1.06	1.00
2D 200°C	1.25	1.17	1.03	1.17	1.15	1.09
1D 250°C	-	1.27	1.19	1.23	1.19	1.16
2D 250°C	-	1.31	1.17	1.20	1.23	1.16

Table 4

Kinetics of Adsorption of Iodine from
Solution

Oxidation State	-k values * x 10 ⁻³ days ⁻¹	
	Cortonwood	Cwm
Fresh	9.4	6.6
Oxid. 1D 100°C	8.1	6.6
Oxid. 2D 100°C	6.3	5.6
Oxid. 1D 150°C	6.3	5.8
Oxid. 2D 150°C	6.5	-
Oxid. 1D 200°C	3.8	3.5
Oxid. 2D 200°C	3.7	3.8

* 1st order kinetics in $\left\{ \frac{I_2}{I_2} \right\} = -kt$

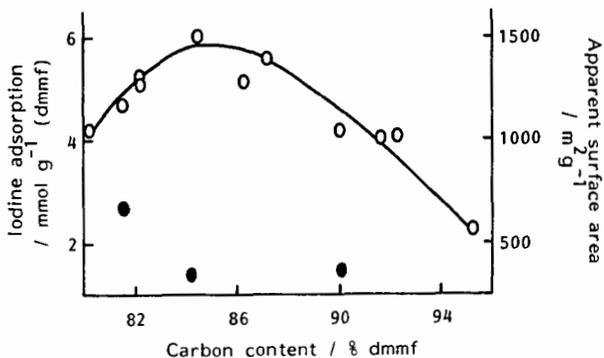
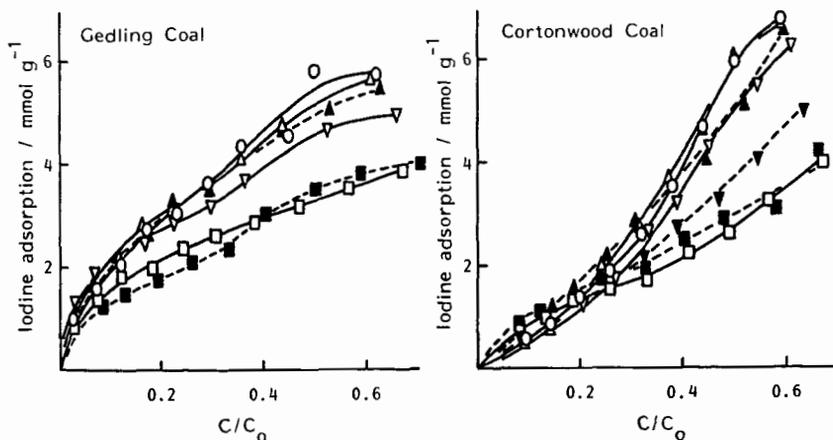


Figure 1. Variation of iodine adsorption with coal rank from vapour and aqueous phases ($I_3^-/I^-/H_2O$). ($t_{eq} = 28$ days).

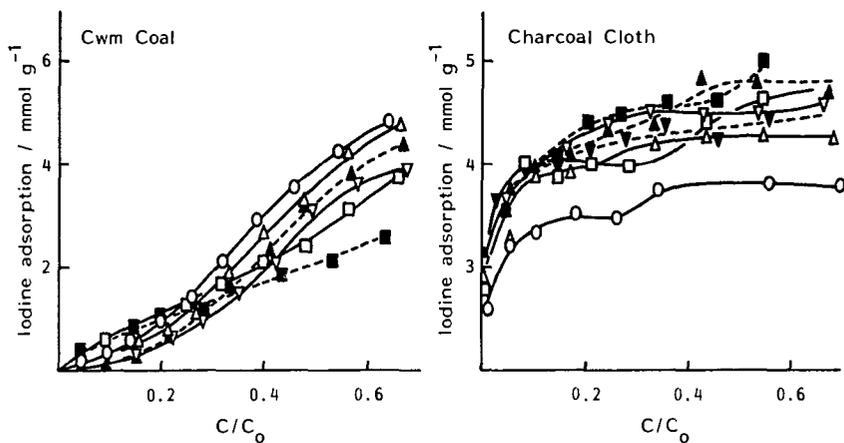
Iodine adsorbed from the vapour phase.

$1 \text{ mmol } I_2 = 250 \text{ m}^2 \text{ g}^{-1}$ of surface. $\sigma = 0.40 \text{ nm}^2$.



Figures 2 and 3. Variation of iodine adsorption from aqueous phase with iodine relative concentration for fresh and oxidized Gedling and Cortonwood coal ($T = 298 \text{ K}$; $t_{eq} = 28$ days).

○ Fresh; ▲ 1 day, 100°C; ▲ 2 days, 100°C; ▼ 1 day, 150°C;
 ▼ 2 days, 150°C; □ 1 day, 200°C; ■ 2 days, 200°C



Figures 4 and 5. Variation of iodine adsorption from aqueous phase with iodine relative concentration for fresh and oxidized Cwm coal and activated charcoal cloth ($T = 298 \text{ K}$; $t_{\text{eq}} = 28 \text{ days}$ and 7 days respectively).

○ Fresh; △ 1 day, 100°C; ▲ 2 days, 100°C; ▽ 1 day, 150°C;
 ▼ 2 days, 150°C; □ 1 day, 200°C; ■ 2 days, 200°C

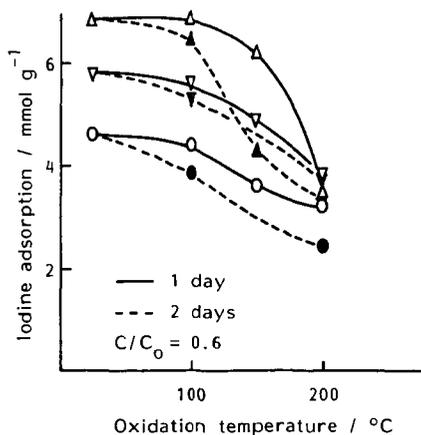


Figure 6. Variation of iodine adsorption from aqueous phase with oxidation temperature for three coals.

△ Cortonwood Coal ▽ Gedling Coal ○ Cwm coal

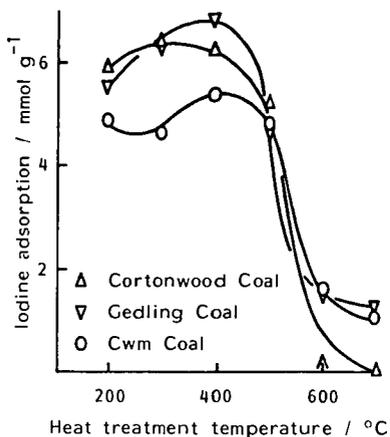


Figure 7. Variation of iodine adsorption from aqueous phase with heat treatment temperature for three fresh coals.

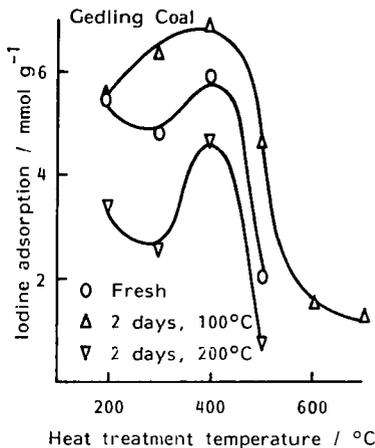
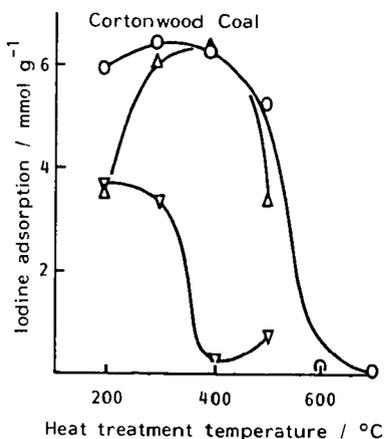


Figure 8. Variation of iodine adsorption from aqueous phase with heat treatment temperature for fresh and oxidized Gedling coal.



Figures 9 and 10. Variation of iodine adsorption from aqueous phase with heat treatment temperature for fresh and oxidized Cortonwood and Cwm coal.

○ Fresh; △ 2 days, 100°C; ▽ 2 days, 200°C

