

# Adsorption of Halogens by Activated Carbon and Fresh and Oxidized Coals

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**Abstract.** Studies of adsorption of iodine from the vapour phase and solution can contribute to the understanding of coal structure and coal oxidation. An activated carbon cloth and three coals, fresh and oxidised, were used as adsorbents for the adsorption of iodine and water vapours and for iodine from aqueous KI/I<sub>2</sub>. Extents of adsorption of iodine decreased with increasing severity of oxidation of the coals. Despite enhanced adsorption of water vapour by oxidised coals, the availability to iodine decreased. Extents of iodine adsorption exceeded the pore volumes of the coals.

## Introduction

**Adsorption of iodine.** Hill and Marsh (1) studied the adsorption of iodine (I<sub>2</sub>) from aqueous solution of KI(I<sub>3</sub>) and related extents of adsorption to the free iodine concentration (I<sub>2</sub>)<sub>free</sub> for a series of activated charcoals. Juhola (2) made similar studies. Kipling *et al.* (3) adsorbed iodine from several solvents on carbon blacks and recommended the use of aqueous systems for assessments of surface areas. Puri *et al.* (4) made similar observations. Aronson *et al.* (5) assessed, qualitatively, adsorption isotherms of iodine on coal and lignite from measurements of vapour pressure of iodine in equilibrium with iodine/coal mixtures. It appeared that the isotherms were Type III (BET classification) with extensive iodine up-take at the saturation vapour pressure of iodine (P<sub>0</sub>=1.08 kPa at 343 K). Uptake of iodine by graphite and anthracite obeyed Henry's Law. The extensive up-take by coals was attributed to complexing by the iodine possibly via charge-transfer complex formation (6).

**Swelling of coal.** Coals imbibe certain solvents and consequently swell, the volume of solvent taken up by the coal far exceeding the pore-volume of the coal when assessed from mercury and helium densities. Thus the swelling characteristics of coal afford a method of examining coal structure. Nelson *et al.* (7) monitored the swelling behaviour of a rank range of coals by methanol, benzene and tetralin and noted that swelling by methanol decreased rectilinearly with increasing coal rank, the swelling by benzene and tetralin showing a maximum with coals of 75 wt% of C. Pre-adsorption of tetralin caused the maximum in swelling to be displaced to 85 wt% of C as a result of breakage of hydrogen bonding within the polymeric structures of coal. Reugnot *et al.* (8) related measured surface areas of coals to the solubility parameters of the

adsorbate used. Marzec and Kisielow (9) explained swelling of coals in terms of electron-donor, electron-acceptor characteristics of solvents. Green *et al.* (10, 11) measured swelling in coals from binary solvent mixtures.

## Objectives

This paper is concerned with aspects of coal and carbon oxidation, e.g. the removal of hydrogen and of possible cross-linkages by ether bridges within the structures. It is considered that studies of adsorption of iodine and water-vapour from the vapour phase and of iodine from solution could contribute to the understanding of coal structure and oxidation.

**Materials Used.** Three coals were used, Gedling (NCB rank 801), Cortonwood 501 and Cwm 301, of surface areas (m<sup>2</sup>g<sup>-1</sup>); 225, 140 and 160 respectively. An activated carbon cloth, No. 005, manufactured by Charcoal Cloth Ltd, U.K. was used, nitrogen BET surface area of 1300 m<sup>2</sup>g<sup>-1</sup> (pore volume of -0.45 cm<sup>3</sup>g<sup>-1</sup>). In conversions of mmol g<sup>-1</sup> adsorbed to cm<sup>3</sup>g<sup>-1</sup> of liquid adsorbate, the following molar volumes (cm<sup>3</sup>mol<sup>-1</sup>) were used: H<sub>2</sub>O 18.0; I<sub>2</sub>, 38.1 (ref 2); CO<sub>2</sub>, 44.0; N<sub>2</sub>, 34.6.

**Experimental.** (A) Coals and the carbon cloth were oxidised in air at 373, 423, 473, 523 K for known periods of time. (B) Iodine was adsorbed by dry coals from the vapour phase (no air) at 298 K over a 2 week period by a gravimetric method. (C) Iodine was adsorbed by coals and the carbon cloth (fresh and oxidised) from aqueous KI solution and from methanol over a 4 week period. (D) The swelling of coals was measured directly in aqueous KI/I<sub>2</sub> solution, and by water itself. (E) Adsorption of CO<sub>2</sub> at 273 K by coals was measured and surface areas calculated.

**Results.** The principal results are contained in Table 1. The adsorption of iodine from aqueous solution ( $I_2/KI$ ) and from methanol by fresh and oxidised activated carbon cloth showed only small changes for the oxidised cloth.

**Analysis of results.** 1. Extents of iodine up-take from the vapour decreased with increasing severity of oxidation of the coal until only fractional coverage of coal surface occurred ( $\sim 10\%$ ) for coals oxid. 2d at 473 K. Pore blockage by oxygen may be a contributory factor.

2. Extents of iodine up-take from solution also decreased with increasing severity of oxidation of the coals, but always exceeded the pore volume of the coals (See Ref. 12). For fresh Gedling coal, iodine adsorption =  $6.6 \text{ mmol g}^{-1} \equiv 0.25 \text{ cm}^3 \text{ g}^{-1} \equiv 1600 \text{ m}^2 \text{ g}^{-1}$ . Swelling of the coal must have occurred.

3. Extents of water vapour up-take, however, increased with increasing severity of oxidation of the coals.

4. The total volume of iodine and water adsorbed for each coal decreased only slightly with increasing severity of oxidation, the iodine dominantly occupying the volume of swelling for fresh coals and the water for oxidised coals. The presence of water facilitates the extensive up-take of iodine for fresh coals from solution, i.e. on average  $\sim 3.5$  times that of adsorption from the vapour.

5. For Cortonwood and Cwm coals, the isotherm shape changed from Type III (fresh) to Type II (oxidised). The isotherms of the low rank Gedling coal were of Type II.

6. Rates of iodine adsorption from solution decreased with increasing severity of oxidation of the coals.

7. The swelling indices (not included) indicate a greater contribution from the iodine for fresh coals than from water.

8. Extents of iodine up-take by the charcoal cloth from methanol decreased marginally with severity of oxidation and did not exceed the pore volume of the charcoal (maximum up-take  $\sim 3.0 \text{ mmol g}^{-1} \equiv 0.114 \text{ cm}^3 \text{ g}^{-1} \equiv 730 \text{ m}^2 \text{ g}^{-1}$ ). Extents of up-take from aqueous solution increased with oxidation (maximum  $\sim 4.5 \text{ mmol g}^{-1} \equiv 0.17 \text{ cm}^3 \text{ g}^{-1} \equiv 1100 \text{ m}^2 \text{ g}^{-1}$ ).

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Table 1

#### Adsorption of Iodine from Vapour and Solution and of Water Vapour

Coal Treatment Oxid. in days (d)	Adsorption of Iodine from Vapour $P/P_0 = 1.0$ $\text{mmol g}^{-1}$ $\text{cm}^3 \text{ g}^{-1}$		Adsorption of Iodine from Solution $C/C_0 = 0.6$ $\text{mmol g}^{-1}$ $\text{cm}^3 \text{ g}^{-1}$		Adsorption of Water Vapour $P/P_0 = 1.0$ $\text{mmol g}^{-1}$ $\text{cm}^3 \text{ g}^{-1}$		Vol. of $I_2 + H_2O$ $\text{cm}^3 \text{ g}^{-1}$
<b>Gedling</b>							
Fresh	2.7	0.10	6.6	0.25	6.3	0.11	0.36
Oxid. 1d 373 K	2.5	0.10	5.6	0.21	7.0	0.13	0.34
2d 373 K	2.3	0.09	5.3	0.20	6.8	0.12	0.32
1d 423 K	1.1	0.04	5.0	0.19	7.3	0.13	0.32
1d 473 K	0.13	0.005	3.8	0.14	8.4	0.15	0.29
2d 473 K	0.09	0.003	3.6	0.14	8.2	0.15	0.29
<b>Cortonwood</b>							
Fresh	1.4	0.05	6.8	0.26	0.8	0.014	0.27
Oxid. 1d 373 K	1.2	0.04	6.7	0.25	1.1	0.020	0.27
2d 373 K	1.1	0.04	6.4	0.24	1.2	0.022	0.26
1d 423 K	0.7	0.03	6.2	0.23	2.1	0.038	0.27
1d 473 K	0.07	0.003	3.4	0.13	5.1	0.092	0.22
2d 473 K	0.06	0.003	3.5	0.13	6.4	0.115	0.25
<b>Cwm</b>							
Fresh	1.5	0.06	4.6	0.17	0.8	0.014	0.18
Oxid. 1d 373 K	1.2	0.04	4.4	0.17	0.9	0.016	0.19
2d 373 K	1.2	0.04	3.9	0.15	1.0	0.018	0.17
1d 423 K	0.8	0.03	3.6	0.14	-	-	-
1d 473 K	0.16	0.006	3.3	0.13	3.2	0.058	0.19
2d 473 K	0.09	0.003	2.5	0.10	4.5	0.081	0.18
<b>Activated Charcoal</b>							
Fresh	-	-	3.8	0.15	-	-	-
Oxid.	-	-	4.3	0.19	-	-	-