CHARACTERIZATION OF COAL INTERFACIAL BEHAVIOR THROUGH FLOW MICROCALORIMETRY

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ABSTRACT

To assess factors that affect the surface behavior of coals, flow microcalorimetry studies were carried out to measure the heat evolved when methanol is displaced by water. This heat appears to be a function of coal rank and coal oxidation. In general, oxidized coals evolve less heat, which is ascribed to the increase of polar sites and the preferential adsorption of methanol over water on the coal. However, coals having a high moisture content behave oppositely in that during the initial stages of oxidation the coal becomes more hydrophobic. These factors are delineated through flow calorimetry, functional group analysis, and wettability studies.

INTRODUCTION

Interfacial properties of coal are important in a number of coal processing and utilization technologies. Although several experimental methods such as electrokinetic potentials, adsorption, contact angle, etc., are available to assess interfacial behavior, each method measures a somewhat different aspect of interfacial behavior. In this investigation, flow microcalorimetry studies were carried out to study the nature of surface groups on the surface of coal. The flow calorimetry results have been compared with functional group analysis and wettability measurements.

Coal surfaces are postulated to consist of several oxygen containing functional groups, which include -COOH, =CO, $-OCH_3$ and -OH (both alcoholic and phenolic) (1). Since these functional groups are expected to interact with water molecules, flow microcalorimetry has been used to measure the heat evolved when methanol, used as a carrier fluid, is displaced by water. Functional groups in coal samples were also determined by chemical analysis methods (2) and infrared spectroscopy (3).

Characterization of coal wettability by classical contact angle measurements requires careful sample selection to avoid cracks and other physical imperfections and a proper polishing procedure to avoid contamination. Furthermore, the large heterogeneity of coal may result in significant variation of measured contact angles from sample to sample. Therefore, in order to assess the wettability of fine coal particles and how it is influenced by coal rank and the degree of surface oxidation, the immersion time measurement technique has been employed (4,5).

Coal Samples:

The chemical analysis and surface areas of the four coal samples used in this investigation are given in Table 1. Four widely different samples were

Table 1 - Characteristics of Coal Samples

PROPERTY	COAL			
Proximate Analysis	BMC-A	BMC-B	GMC-B	DJM-SB
Moisture	3.56	2.31	2.67	27.65
Ash	5.06	5.99	8.22	6.26
Volatile	2.84	17.98	38.96	34.02
Fixed Carbon	88.54	73.72	50.15	32.07
Calorific Value (Btu/lb)	13,270	14,290	13,030	8,230
Ultimate Analysis (%, as-received)				
Moisture	3.56	2.31	2.67	27.65
Carbon	87.16	82.07	73.16	48.17
Hydrogen	1.45	4.19	4.98	3.56
Nitrogen	0.82	1.52	1.50	0.60
Chlorine	0.80	0.07	0.02	0.00
Sulfur	0.51	0.73	0.86	0.54
Ash	5.06	5.99	8.22	6.26
Oxygen (by diff.)	1.36	3.12	8.59	13.22
Surface Area, m^2/g (as-received)				
Nitrogen (B.E.T. analysis)		7.50	3.60	2.90
Carbon dioxide (D-P analysis)	274.42	130.00	132.00	219.00

BMC-A: Pennsylvania Anthracite
BMC-B: Pennsylvania Bituminous
GMC-B: Geneva Mine Coal, Utah, Bituminous
DJC-SB: Dave Johnston Coal, Wyoming, Subbituminous

selected to determine the effect of coal rank and genesis on the interfacial characteristics. Dave Johnston coal is particularly high in moisture - a factor that markedly affects the interfacial behavior as shown later in this paper. As can be seen from the results in Table 1, there is a considerable difference between the surface areas obtained by nitrogen adsorption and those obtained by carbon dioxide adsorption. Since micropores are essentially inaccessible to nitrogen molecules at liquid nitrogen temperatures, the surface areas obtained by nitrogen may be taken as a measure of the external surface. On the other hand, carbon dioxide molecules can adsorb in the micropores with no activation energy needed at room temperature (6). The carbon dioxide surface areas, therefore, represent the total surface area.

RESULTS AND DISCUSSION

Immersion Time Measurements:

In a previous study (5), the technique of immersion time measurements was employed to characterize coals of different rank and origin. In this technique, a small mass of 150 x 200 mesh coal is placed on the surface of aqueous methanol solutions in a test tube and the time for the particles to sink into the liquid is measured. The time, referred to as the immersion time, is a measure of the relative wettability. The immersion times for the Pennsylvania bituminous coal are given as a function of methanol concentration in Figure 1. The nature of the immersion time - vs - methanol concentration plots is typical of the various coals investigated. The surface tension of the methanol solutions is also given in Figure 1. The concentration of methanol where wetting behavior changes abruptly from wetting (short immersion time) to non-wetting (long immersion time) is defined as the critical wetting concentration, CWC, and the surface tension corresponding to the CWC is defined as the critical surface tension of the coal.

The effect of surface oxidation on the critical surface tension of wetting of the various coals was determined by the above procedure and the results are plotted in Figure 2. For the "as-received" samples, a minimum is observed in the critical surface tension vs. the carbon content at about 80% carbon. These results are in general agreement with the contact angle measurements of Gutierrez-Rodriguez et al. (7). Brown (8) had also observed a similar variation of contact angle with carbon content, but the maximum in contact angle occurred at somewhat higher values of the carbon content. The effect of coal rank on immersion time can, therefore, be explained in terms of the variation of the hydrophobic sites (paraffinic and graphitic) and the hydrophilic sites (oxygen containing functional groups), as has been done to explain contact angle results (9). Except for the Dave Johnston coal, oxidation increases the critical surface tension of wetting, which is expected because oxidation is likely to increase the number of hydrophilic oxygen containing functional groups, thereby, increasing wettability of coals. The increase in oxygen functional groups is confirmed by the results given in Table 2. The concentration of oxygen functional groups was determined by chemical titration methods (2) and infrared spectroscopy (which gives only a relative measure. The critical surface tension of wetting of the "as-received" sample of Dave Johnston coal is greater than the same coal oxidized at 150°C. Although the results appear to be puzzling at first, they may be explained in terms of the higher moisture content of this coal. When the coal is heated to 150°C, the moisture content is decreased and the unfilled pore sites act as hydrophobic sites. In the "as-received" sample, the pores filled with water would behave as hydrophilic sites. At higher oxidation temperatures, this coal also becomes more hydrophilic as expected on the basis of the increase in oxygen-containing functional groups. The effect of high moisture content on coal is also observed in the flow microcalorimeter results, as discussed in a later section. Figure 2 also shows that the critical surface tension is lowered when an oxidized coal sample is washed with water, that is, the coal becomes more hydrophobic. This observation is in agreement with previously reported studies that soluble components are formed when coals oxidize (10). After the removal of water-soluble products from the oxidized surface, the coal becomes more hydrophobic. The increase in hydrophobicity of coal after the oxidation-washing treatment is greater for higher rank coals. In fact, the anthracite became considerably more hydrophobic than the "as-received" sample after such a treatment.

Table 2 - Concentration of Oxygen Functional Groups in Two Pennsylvania Coals by Titration and Infrared Spectroscopy

PRETREATMENT	WEIGHT % OXYGEN Carboxylic	Phenolic	Total	$\left(\frac{I_{1690}}{I_{1600}}\right)$
Anthracite (BMC-A)				
None	0.023	0.029	0.052	---
Oxidized				
at 150°C in air	0.031	0.075	0.106	---
at 200°C in air	0.073	0.109	0.182	---
at 244°C in air	0.073	0.393	0.466	---
in 30% H_2O_2	0.015	0.075	0.090	---
Bituminous (BMC-B)				
None	0.012	0.047	0.059	0.11
Oxidized				
at 100°C in air	---	---	---	0.13
at 150°C in air	0.016	0.065	0.081	0.71
at 200°C in air	0.100	1.905	2.005	0.91
at 244°C in air	5.074	6.185	11.259	1.00
in 30% H_2O_2	0.024	0.156	0.180	---

Flow Microcalorimetric Measurements:

Calorimetry has been used in the past to study coal chemistry and to elucidate the structure of coal (11). Traditionally, calorimetric measurements involve heat of immersion measurements. Information about the application of flow calorimetry on coal chemistry is meager (12). In this investigation, and adiabatic flow microcalorimeter (Microscal Ltd., London) was used to measure the heat of displacement of a carrier fluid (methanol) by water. A water-methanol system was selected because the results could then be correlated with the wettability results. A known amount of aqueous methanol solution was injected into a bed of 150 x 200 mesh coal particles and the heat evolved was measured. The heat evolved increased linearly with the amount of water injected as shown in Figure 3 and is independent of the composition of the injected solution. The slope of the line is a measure of the heat evolved in units of millicalories per gram coal per microliter water. The heat evolved for the various coals and their pretreatment is given in Table 3. Except for Dave Johnston coal, the heat evolved is less when the coal is oxidized. At the start of the experiment, the strongly hydrophilic oxidized sites are already covered by water molecules and methanol as a carrier fluid does not displace them. Therefore, the contribution from strongly hydrophilic sites to the measured heat is nil. The heat of dissolution of soluble oxidation products could be endothermic, which would also contribute to an overall decrease in the amount of heat evolved. The calorimetric behavior of Dave Johnston, which also behaved differently in immersion time measurements, is different because of its high moisture content. When this coal is heated, the moisture is driven off, making the coal effectively more hydrophobic.

Table 3 - Heat Evolved in Millicalories/gμl Water for Displacement of Methanol by Water in a Flow Microcalorimeter

PRETREATMENT PROCEDURE	COAL SAMPLE			
	BMC-A	BMC-B	GMC-B	DJC-SB
None	42	41	44	17
Oxidized at 200°C	33	15	23	48
Oxidized at 200°C and leached in H_2O	51	42	57	64

This is the reason for the evolution of more heat when this particular coal is oxidized. As postulated above, water soluble products form when coals oxidize. This is observed in the microcalorimetric results also. From the results summarized in Table 3, it is clear that more heat is evolved when the coal is oxidized at 200°C and is leached with water (the washed coal was dried in vacuum at 36°C prior to microcalorimetric measurements). The oxygen groups present on the surface of oxidized and washed coal contribute substantially to the heat evolved when water molecules displace methanol molecules, as shown in last row of Table 3.

SUMMARY

The immersion time measurement technique was used to determine the effect of coal rank and the degree of oxidation on the critical surface tension of wetting. Heat of displacement of methanol by water molecules, measured by flow calorimetry, generally correlates very well with the wetting measurements. The coal surface is considered to consist of hydrophobic sites (paraffinic and graphitic) and hydrophilic sites (oxygen functional groups). All oxygen functional groups are not similar, however. Methanol is able to displace water molecules from weakly hydrophilic groups, but not from the strongly hydrophilic groups. In addition, the state of filling of micropores strongly influences both the immersion time and heat measurements. Empty pores behave as hydrophobic sites (or patches), whereas pores filled with water as hydrophilic sites (or patches). The above model of coal surface can be used to explain the effect of coal rank and state of oxidation on the interfacial properties of various coals.

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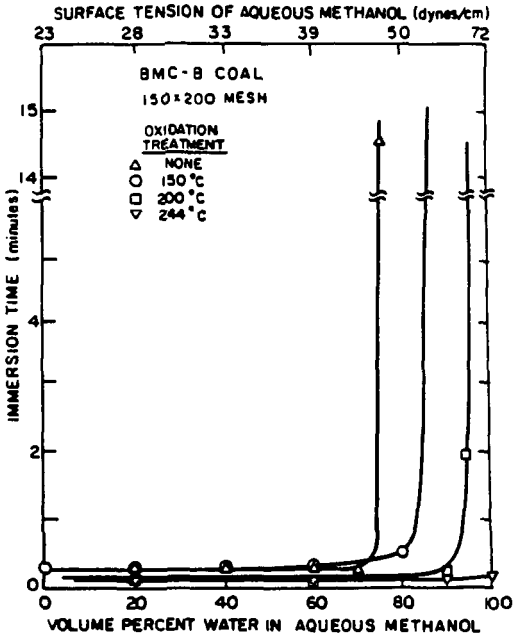

Fig. 1 - Representative immersion-time curves for Pennsylvania bituminous coal that had been oxidized in air at different temperatures along with the behavior of as-received coal.

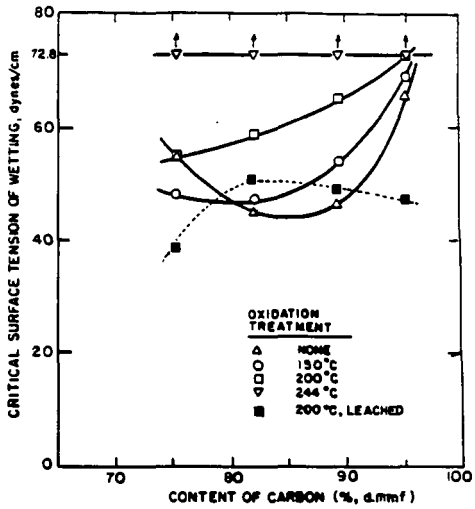

Fig. 2 - The critical surface tension of wetting as a function of coal rank and oxidation treatment.

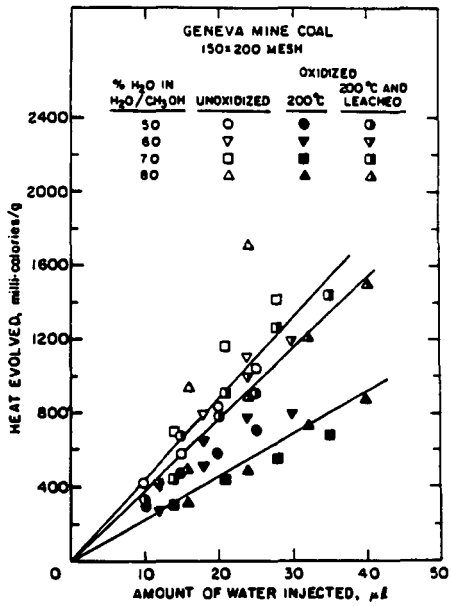

Fig. 3 - Heat of displacement of methanol by water on BMC-A coal as determined by a flow microcalorimeter.