LOW-TEMPERATURE COAL WEATHERING

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ABSTRACT

Illinois 6 coal (hvBb) was weathered for up to 330 days at 25 and 80°C with humid air. Its behavior was compared with Pittsburgh Seam (hvAb) and Horsepen Seam (mvb) coals weathered under the same conditions. The weathering rate showed a strong dependence on temperature and coal rank. At 25°C, the Illinois 6 coal showed much more substantial changes in chemical and physical properties upon weathering. Spectroscopic data indicate that the concentration of organic oxygen groups in the coal may eventually level off. Two potential causes of this behavior are proposed. Thermal (non-oxidative) treatment at 80°C has little effect on the chemical and physical properties of a fresh hvAb coal.

INTRODUCTION

Weathering can alter organic and mineral constituents of coal, change its chemical and physical properties and affect its utilization (1). Extensive laboratory research has been performed to study this important phenomenon. However, published studies have come to significantly different conclusions concerning the chemical nature of coal weathering (or oxidation). The rate of changes in coal properties induced by coal weathering or oxidation are dependent on temperature. Most reported coal weathering simulation experiments have been conducted at temperatures greater than 100°C to accelerate the oxidation rate. However, the reaction mechanism is reportedly different at temperatures above and below 70 to 80°C (2,3).

Three separate coal weathering reactions (two oxidative and one thermal) were recently proposed by Gethner (4,5) based on a coal oxidation study conducted at temperatures of 25 to 100°C. The rate of each reaction had a different temperature dependency. Gethner concluded, and we concur, that ill-defined or poorly controlled coal weathering or oxidation experiments can result in inaccurate conclusions (5). In addition to temperature, coal weathering is also known to depend on coal rank, humidity and oxygen partial pressure (1,3,6). The work reported here is a systematic study of coal weathering performed at realistic conditions. Different ranks of coal, including Illinois 6 (hvBb), Pittsburgh Seam (hvAb) and Horsepen Seam (mvb) coals, were weathered for up to 500 days at 25 to 80°C with humid air under well-controlled conditions. The work with Pittsburgh Seam and Horsepen Seam coals was reported previously (7). This paper includes the recent results of this study, most of which were obtained using the Illinois 6 coal. For present purposes, we will define oxidative weathering as the progressive changes in coal properties that occur as coal is exposed to humid air at temperatures of 80°C or less.

In addition to oxidative weathering, experiments were also performed with a different Pittsburgh Seam coal and a slightly weathered Illinois 6 coal under flowing humid N_2 at 80°C. The objective of these tests was to observe any non-oxidative, thermal effects on coal properties and chemical structural changes. This paper also includes recent results of this study.

EXPERIMENTAL

The experimental apparatus and procedures used in the weathering study were described previously (7). The non-oxidative experiment was carried out using N_2 instead of air at otherwise the same conditions. The Illinois 6 coal used in this study is the natural -28 mesh portion of fresh run-of-mine (ROM) coal from a deep mine in Jefferson County, Illinois. The Pittsburgh Seam coal used in the non-oxidative weathering study is the natural -28 mesh portion of fresh ROM coal from a deep mine in Monongalia County, West Virginia. Analyses of these two coals are listed in Table 1. Properties of the Pittsburgh Seam and Horsepen Seam coals used in the oxidative study were reported elsewhere (7).

RESULTS AND DISCUSSION

OXIDATIVE WEATHERING

Changes in elemental composition (H,C,O) observed upon weathering occurred more rapidly for the Illinois 6 coal (hvBb) than for the Pittsburgh Seam (hvAb) and Horsepen Seam (mvb) coals, as shown below.

	Illinois 6		Pittsburgh Seam		Horsepen Seam	
Weathering Time at 80°C, Days	0	46	0	45	0	51
Carbon, wt % MAF	81.8	78.6	82.9	81.1	89.3	87.7
Hydrogen, wt % MAF	5.2	4.7	5.5	5.2	5.0	4.9
Oxygen, wt % MAF (diff.)	9.9	14.0	7.2	9.5	3.1	4.9

These values indicate that rates of change in elemental compositions with weathering time are dependent on coal rank (6).

The FTIR oxidation index is defined as the ratio of the integrated intensity of the carbonyl band (1635-1850 cm^{-1}) to that of the C-H stretching band (2745-3194 cm^{-1}) in the diffuse reflectance FTIR spectrum of coal (7,8). Increases in the oxidation index upon weathering can be attributed to the progressive oxidation of C-H groups to carbonyl groups as the coal weathers (8,9). The oxidation index is plotted in Figure 1 as a function of weathering time at 80°C for the three coals. The oxidation index of Illinois 6 coal not only increases more rapidly with weathering time, but it also has a higher initial value than Pittsburgh Seam and Horsepen Seam coals. This indicates that both the initial value and the rate of change with time of the oxidation index are rank dependent.

The rate of change with time of the oxidation index also depends on weathering temperature. In Figure 2, the oxidation index of Illinois 6 coal is plotted as functions of weathering time and temperature. Changes are rapid at 80°C, and slow, but experimentally significant, at 25°C. Significant changes in the oxidation index of coals weathered at 25°C were observable for the Illinois 6 coal but, as reported previously (7,10), not for the Pittsburgh Seam and Horsepen Seam coals.

Gieseler maximum fluidity was found to be one of the most sensitive indicators of oxidation for the higher rank coals (7,8). However, the lower rank Illinois 6 coal has essentially no fluidity, even when fresh. Though free swelling index (FSI) measurements are less sensitive to weathering than Gieseler fluidity, they do provide an indication of the effect of weathering on the thermoplastic properties (7,8). Figure 3 shows that the rate of change with weathering time of the free swelling index (FSI) of Illinois 6 coal is much greater at 80°C than at 25°C; however, even at 25°C, changes were significant. In contrast, there was very little change in the FSI of Pittsburgh Seam (7) and Horsepen Seam (10) coals weathered at 25°C. This again demonstrates the rank dependency of coal weathering. The FSI and oxidation index of weathered Illinois 6 coal are compared in Figure 4. Figure 4 shows that there is a general linear relationship between the oxidation index and FSI of Illinois 6 coal weathered at both 25 and 80°C, as also noted previously by Huffman et al. (9). The alkali extraction test (11) also shows a general linear relationship with oxidation index for the weathered Illinois 6 coal (Figure 5). Alkali extraction test results are expressed as percent transmittance at 520 nm.

As shown in Figure 1, the oxidation index of Illinois 6 coal weathered at 80°C appears to level off after about 46 days weathering. Results of X-ray photoelectron spectroscopic (XPS) characterizations of the coal weathered at 80°C are consistent with this observation. Table 2 lists the surface elemental compositions of the Illinois 6 coal weathered at 80°C for 0, 46 and 80 days. Organic oxygen was calculated by the method of Perry and Grint (12) in which inorganic oxygen is subtracted from total oxygen assuming inorganic oxygen is associated with Si and Al in oxide forms (12). The organic O/C ratio increased from 0.15 to 0.23 after 46 days weathering at 80°C (Table 2). As shown in Figure 6, an asymmetric C_{1s} peak with a shoulder at high binding energy (287-292 eV) was observed by XPS, indicating that carbon-oxygen functional groups were generated upon weathering for 46 days at 80°C. This is in agreement with FTIR results that show production of carbonyl groups. As weathering time increased from 46 to 80 days, only a slight increase in organic O/C ratio, from 0.23 to 0.24, was observed (Table 2). In addition, there was no significant change in XPS C_{1s} spectrum of the coal between 46 and 80 days (Figure 6).

There are at least two possible explanations for this observation. First, it may be that after 46 days at 80°C, most of the active sites originally available for oxidation had reacted, i.e., few active sites were available for further oxidation at these conditions. Painter et al. (13) reported that coal oxidation is indeed site selective. They concluded that benzylic sites are most easily oxidized to carbonyl groups. Low-temperature weathering work by Larsen et al. (2) supported this concept.

A second possibility is that after 46 days at 80°C, the rate of carbonyl production is matched by the rate of carbonyl destruction, e.g., by decarbonylation and decarboxylation. Gethner (4,5) noted the importance of decarbonylation and decarboxylation reactions during coal oxidation. The rate of carbonyl destruction must depend on the concentration of carbonyl groups. As oxidation proceeds, carbonyl concentrations increase and thus, the rate of carbonyl destruction should increase as well. Eventually, a state may be reached in which the rates of carbonyl production and destruction are equal.

At this point, our data do not confirm or refute either explanation. Additional work is under way to gain a better understanding of this.

NON-OXIDATIVE WEATHERING

A reaction mechanism involving thermal decomposition of carbon-oxygen functional groups (e.g., decarboxylation) was proposed by Gethner (4,5). He noted that this reaction was independent of the oxidative reactions that occur during low-temperature oxidation (4,5). Non-oxidative thermal effects on coal properties and chemical structural changes were examined by treating a Pittsburgh Seam coal under flowing humid nitrogen at 80°C for 48.4 days. No significant changes in elemental compositions were observed over the duration of the test. In addition, Gieseler maximum fluidity, Audibert-Arnu dilitation, FTIR oxidation index and alkali extraction measurements all show little or no change. The Gieseler maximum fluidity and the oxidation index of the Pittsburgh Seam coal treated at 80°C in flowing humid N_2 are plotted as functions of time in Figure 7. These data show that the changes in coal properties that were noted in the oxidative weathering tests with Pittsburgh Seam coal are dependent on the presence of oxygen. Purely thermal effects, except perhaps those involving newly formed oxidized components, were negligible. Since thermal (non-oxidative) effects may be rank dependent, a similar test is now being performed with a slightly weathered Illinois 6 coal.

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TABLE 1

ANALYSES OF ILLINOIS 6 AND PITTSBURGH SEAM COALS

	Illinois 6	Pittsburgh Seam (a)
Moisture, wt % as received	2.76	0.64
Proximate Analysis, wt % dry basis		
Volatile Matter	35.74	37.24
Ash	5.30	12.07
Fixed Carbon (Diff)	58.96	50.69
Ultimate Analysis, wt % MAF basis		
Carbon	81.76	84.22
Hydrogen	5.23	5.74
Nitrogen	1.96	1.62
Sulfur, Total	1.19	3.54
Pyritic	0.51	1.97
Sulfate	0.03	0.05
Organic (Diff)	0.65	1.52
Oxygen (Diff)	9.86	4.88
Heating Value, Btu/lb, MAF basis	14,560	15,031
Wet Screen Analysis, wt %		
Tyler Mesh		
28 x 48 mesh	37.8	26.4
48 x 100 mesh	31.0	32.0
100 x 200 mesh	17.8	19.1
-200 mesh	13.4	22.5

(a) This coal used only in the non-oxidative test.

TABLE 2

FTIR OXIDATION INDEX AND SURFACE COMPOSITION BY XPS OF ILLINOIS 6 COAL WEATHERED AT 80°C

Weathering Time, Days	FTIR Oxidation Index	Atomic Percentage C	O Total	O Organic	S	N	Na	Si	Al	Organic O/C Ratio
0	1.26	75.0	19.3	11.2	0.1	0.8	0.3	2.7	1.8	0.15
46	2.76	68.0	24.6	15.9	0.3	1.1	0.4	3.0	1.8	0.23
80	3.26	68.3	25.3	16.7	0.3	1.1	0.3	3.0	1.7	0.24

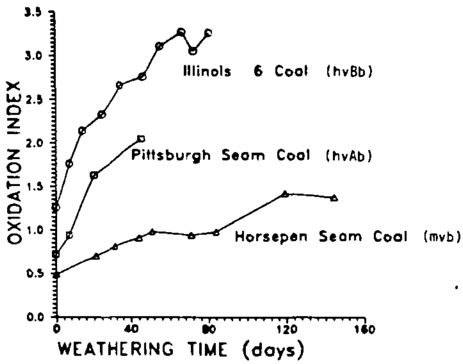

Figure 1. Oxidation Index vs Weathering Time for Coals Weathered at 80°C.

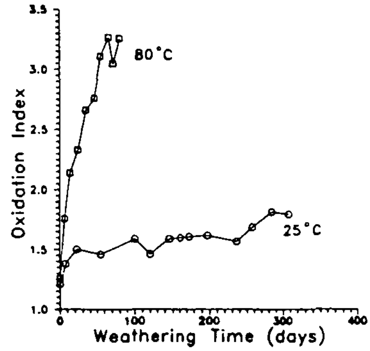

Figure 2. Oxidation Index of Ill. 6 Coal vs Weathering Time and Temperature.

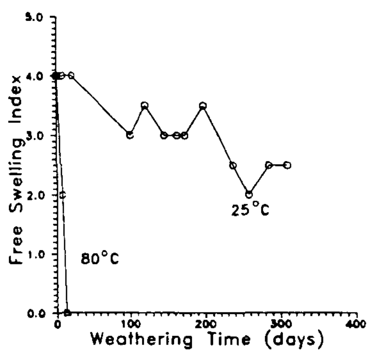

Figure 3. Free Swelling Index of Ill. 6 Coal vs Weathering Time and Temperature.

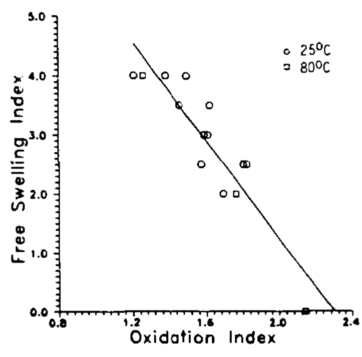

Figure 4. Free Swelling Index of Ill. 6 Coal vs Oxidation Index.

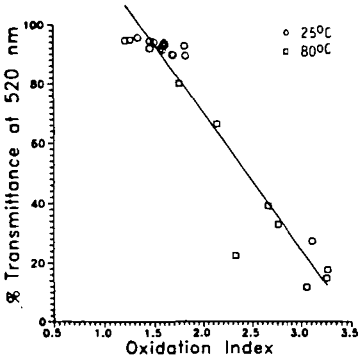

Figure 5. Alkali Extraction Test Results for Weathered Ill. 6 Coal vs Oxidation Index.

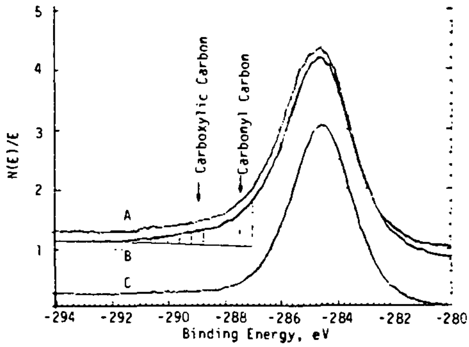

Figure 6. XPS C_{1s} Spectra of Ill. 6

A) Coal weathered at 80°C for 46 days.

B) Coal weathered at 80°C for 80 days.

C) Fresh Coal.

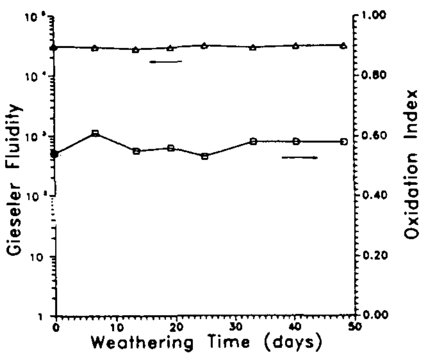

Figure 7. Gieseler Fluidity and Oxidative Index vs Time for Pittsburgh Seam Coal in the 80°C Non-Oxidative Weathering Test.

△ Gieseler Fluidity

☐ Oxidation Index