

WEATHERING STUDY OF ARGONNE PREMIUM COAL SAMPLES
BY FTIR AND MOSSBAUER SPECTROSCOPY

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INTRODUCTION

A considerable number of infrared studies have been done on the low-temperature oxidation of coal with conflicting results. Because the reactions occurring in coal are dependent on a number of factors such as coal rank, particle size, temperature and humidity, a consensus on the oxidation mechanism(s) has not been achieved. Oxidation has been found to produce ethers (1-4), carboxyl groups (2-6), and OH functionalities (5). The formation of a peroxide is generally considered to be the major pathway for the production of new oxygen-containing groups, while at the same time a decrease in the aliphatic CH stretching region is observed (1,5) corresponding to dehydrogenation. The present study is an attempt to use FTIR to follow the effects of mild weathering conditions on a series of standard coal samples. In one part of the study, the room temperature desorption of moisture from these coals was followed using diffuse reflectance spectroscopy (DRIFT), and in the other part, the coals were weathered at room temperature in water-saturated air and sampled at intervals over a three month period for FTIR and Mössbauer analysis.

EXPERIMENTAL

Eight Argonne premium coal samples (-100 mesh) were studied: Pennsylvania Upper Freeport, Wyodak, Illinois #6, Pittsburgh #8, Pocahontas #3, Utah Blind Canyon, West Virginia Stockton-Lewiston, and Beulah-Zap. After thorough mixing, each ampoule of PCSP coal was opened and about 300 mg of the neat sample was transferred to a DRIFT sample cup and enclosed in an environmental chamber in a stream of dry air (2 ml/sec). Infrared spectra were collected at intervals over an eight hour period and again after 24 hours with a Nicolet 60SXB FTIR using 300 scans at 4 cm^{-1} resolution. The same dried KBr reference was used for each series of spectra and, because difference spectra were obtained, the KBr did not contribute to the absorption in the OH region.

For the longer-term study, a second vial of the coal was opened and the coal transferred to a large petri dish which was placed in a large dessicator (without dessicant) through which water-saturated air at 22°C was flowed at a rate of approximately 1 ml/sec. Portions of the coal were removed at intervals of 0, 1, 4, 24, and 48 hours, 1 week, and 1 and 3 months. These samples were dried in a vacuum oven at 40°C for two hours to halt the weathering process and stored under vacuum prior to analysis. Each sample was divided into different portions for infrared, Mössbauer and elemental analysis. Another 0.5 g of the original coal was removed to make the low-temperature ash (International Plasma Machine 1101B, 130 Watts for several days). DRIFT spectra were obtained on the neat coal sample with an environmental chamber for the non-weathered coal and without an environmental chamber for all DRIFT samples. Transmission spectra were obtained on KBr

pellets (about 0.3% coal by weight). All spectra were collected at 4 cm^{-1} resolution using 500 scans for the DRIFT spectra and 128 scans on the KBr pellets. Samples for Mössbauer analysis were prepared by grinding 0.3-0.6 g of the coal with 0.8 g of SOMAR blend, an organic binding agent, and pressing the samples into 32 mm diameter pellets. Mössbauer spectra were obtained on a Ranger Scientific MS-900 spectrometer at room temperature for 1-3 days. Carbon, hydrogen and nitrogen analyses were performed with a LECO CHN-600 analyzer, and oxygen analyses were performed with a Carlo ERBA 1106 elemental analyzer.

RESULTS AND DISCUSSION

Moisture Desorption

The desorption of water from the fresh coal samples was followed by DRIFT in the region $3800\text{-}2800\text{ cm}^{-1}$. DRIFT is especially useful for this type of study because it eliminates the error associated with water which may be trapped in a KBr pellet. This method has been used previously to study water desorption at elevated temperatures (7). The decrease in the integrated area of the OH region from the fresh coal to the vacuum-dried coal can be directly related to the moisture content determined by a separate procedure. In this case, absorbance units were used rather than the Kubelka-Munk units normally used for DRIFT spectra with good results. Table 1 gives the moisture contents of the initial coals and the moisture contents remaining after 1/2 hour and 8 hours of exposure to a stream of dry air at room temperature. Eight hours was found to be sufficient to remove over 90% of the moisture in all but the Illinois and Pittsburgh coals. Between one-third to one-half of the water was removed within the first half-hour of drying with the rate of desorption proportional to the initial moisture level. Spectral subtraction revealed no other changes in the spectrum other than a negative band near 1640 cm^{-1} as water was removed.

Weathering

Weathering under humid conditions over a longer period of time showed other changes in the OH region. DRIFT spectra of the vacuum-dried coals show an increase in the OH band over periods of 1 week and 1 month (Figure 1) with the largest increases found in the Pittsburgh, Illinois, Beulah-Zap and Blind Canyon coals and the least increase in the Pocahontas coal. Simultaneously, a slight increase in absorption centered around 1100 cm^{-1} is observed in all of the KBr pellet coal spectra after 1 week and after 1 month of weathering. An increase in this region after weathering is usually attributed to ethers but may also be due to alcohol groups. Other increases were apparent in the carbonyl region $1800\text{-}1500\text{ cm}^{-1}$ after 1 month (Figure 2). A weak band at 1710 cm^{-1} , not very apparent in the compressed spectra of Figure 2, appears in the subtraction spectra of the Pocahontas and Wyodak coals. All of the coals show an increase near $1660\text{-}1630\text{ cm}^{-1}$, which may be due to highly hydrogen-bonded carbonyls or to water bending modes from water of hydration which is not removed by vacuum. All of the coals except Pennsylvania and Pocahontas show a slight increase in the region $1560\text{-}1540\text{ cm}^{-1}$, which may arise from the formation of carboxylate groups.

In contrast to previous studies which found ether formation the dominant reaction under low temperature oxidation conditions (1-2), these results indicate the formation of an OH group, from either a hydroxyl functionality or water of hydration. This formation is only slightly dependent on coal rank, as the Pennsylvania and Pocahontas coals form the least amount of OH, but the other coals form OH in a manner independent of rank. The formation of ether groups and/or alcohol groups is indicated by the increase near 1100 cm^{-1} . The new bands near 1650 cm^{-1} may be due to water or to a shift in carboxyl group frequency due to increased hydrogen bonding, as might occur with the formation of OH groups, or to oxidation to new carbonyl groups. Carboxylate groups appear to form for all but the highest rank coals. In conclusion, new functional groups are formed on coal after weathering under humid conditions at room temperature for as little as 1 week. These include carboxylate groups on all but the Pennsylvania and Pocahontas coals, carbonyl groups on the Pocahontas and Wyodak coals, and chemisorbed water, alcoholic or ether groups.

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Table 1. Moisture Content of Coals After Room Temperature Air-Drying

	Initial Moisture, %	Moisture Remaining After 1/2 Hour, %	Moisture Remaining After 8 Hours, %
Pocahontas	0.84	0.42	0
Pennsylvania	1.41	1.01	0
Pittsburgh	2.54	1.31	0.32
Lewiston-Stockton	2.70	1.69	0.27
Blind Canyon	5.04	2.38	0
Illinois	8.65	5.83	1.41
Wyodak	24.23*	15.00	0.24
Beulah-Zap	32.84*	25.45	0.92

*From PCSP provided data.

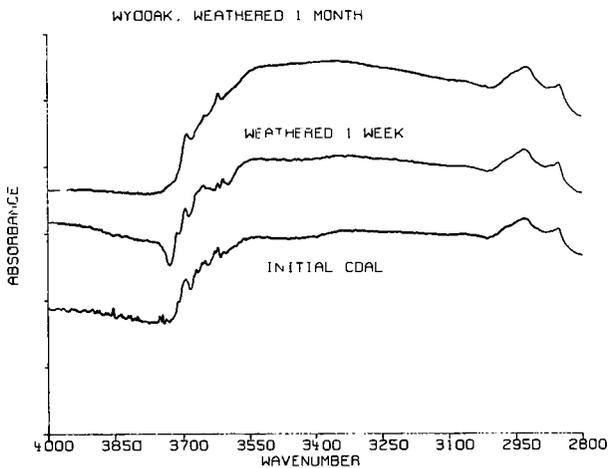


Figure 1. Increase in OH region over one month (Wyodak coal).

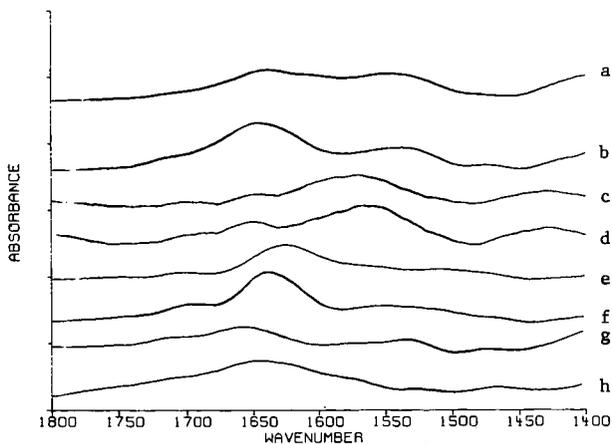


Figure 2. Change in carbonyl region over one month (a = Pittsburgh, b = Illinois, c = Lewiston-Stockton, d = Blind Canyon, e = Pennsylvania, f = Pocahontas, g = Wyodak, h = Beulah-Zap).