

A CORRELATIVE INVESTIGATION OF THE EFFECTS OF OXIDATION ON THE MINERALS,
MACERALS AND TECHNOLOGICAL PROPERTIES OF COAL

By

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INTRODUCTION

The oxidation of coal by natural weathering processes is well known to degrade those properties important for cokemaking (1, 2). Conversely, the loss of fluidity and enhancement of char reactivity resulting from low-temperature coal oxidation are desirable properties for coal gasification (3). Thus, better understanding of the oxidation mechanisms of coal components and of the effect of such oxidation on technological processes is highly desirable.

⁵⁷Fe Mossbauer spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy were used to investigate the oxidation of minerals and macerals, respectively, and measurements of the Gieseler plasticity were made as representative of an important technological property, coal fluidity, that is affected by oxidation. The relative sensitivity of these techniques to coal oxidation were compared by correlating measurements made on a variety of bituminous coals.

SAMPLES AND EXPERIMENTAL TECHNIQUES

The naturally oxidized coal discussed in this paper is a low-volatile bituminous coal obtained from a strip mine on the Pocahontas No. 4 seam in West Virginia. Samples were collected from an outcrop (most oxidized) and the mine highwall (least oxidized), and at an intermediate location to obtain an oxidation profile across the strip pit.

Two high-volatile bituminous coals (Pittsburgh and Harlan seams) were used in long-term, room-temperature oxidation treatments. The -60 mesh coals were put into several 100-ml beakers and stored separately in dry, ambient and humid air atmospheres at room temperature in the laboratory for 950 days. The dry environment was simulated by placing the coals in a desiccator containing Drierite, whereas the humid environment was simulated by placing the coal in a similar desiccator vessel, but with water present. The ambient samples were stored in beakers open to the laboratory atmosphere.

Channel samples of two additional bituminous coals, one collected from the Pittsburgh seam in Pennsylvania and the other from the Pocahontas No. 3 seam in West Virginia, were used in two simulated weathering treatments. In one treatment, -40 mesh coal was placed in a gas-tight oven at 50°C. The moisture level of the air in the oven was maintained at approximately 65% RH (6.9 ± 0.2% H₂O). In the other treatment, stockpiled samples of -1/8-inch coal were exposed to the atmosphere in 20-pound aliquots in plywood boxes.

The iron-bearing minerals in the various coals were investigated by ⁵⁷Fe Mossbauer spectroscopy. Details of sample preparation and data reduction procedures can be found in previous papers (4, 5, 6). The diffuse reflectance infrared Fourier transform (DRIFT) spectra were measured on a Nicolet 7000 series FTIR spectrometer with data reduction capability. Samples for FTIR were either -60 mesh or -200 mesh coals without KBr dilution. Typical measurement times were 285 seconds and the resolution of the spectra was typically 4 cm⁻¹.

Standard ASTM methods were used for Gieseler plastometer measurements. The extent of coal oxidation was also monitored by an alkali extraction test (7).

RESULTS AND DISCUSSION

Gieseler Plastometer Measurements

Results of Gieseler plastometer measurements on the strip-mined coal samples are summarized in Table I. The thermal plasticity of the coal samples decreases markedly as a result of oxidation. The softening temperature increases and solidification temperature decreases by approximately 30°C, narrowing the plastic range from 90°C to 30°C. The maximum rate of rotation,

which corresponds to the maximum fluidity of coal samples, decreased by several orders of magnitude to the level of essentially no fluidity at all for the outcrop coal.

TABLE I

RESULTS OF LIGHT TRANSMISSION VALUES AND GIESELER PLASTOMETER MEASUREMENTS FOR POCAHONTAS NO. 4 SEAM

| Coal | Percent Transmission | Max. ddpm | Soft Temp. | °C | | |
|----------|----------------------|-----------|------------|------------------|--------------|---------------|
| | | | | Max. Fluid Temp. | Solid. Temp. | Plastic Range |
| Highwall | 97 | 3.5 | 401 | 461 | 491 | 90 |
| Middle | 58 | 2.3 | 412 | 457 | 481 | 71 |
| Outcrop | 28 | 0.2 | 413 | 448 | 463 | 30 |

The results of the alkali extraction test, also summarized in Table I, correlate fairly well with results of Gieseler plastometer measurements. This test is used in the metallurgical coal industry to detect coal oxidation prior to the coking operation. Usually, a coal with a light transmission value less than 80% is regarded as too oxidized for metallurgical usage (7). It is noted that the badly oxidized coal taken from the outcrop of the pit has a transmission value of only 30%, while the least oxidized highwall coal has a value of 97%.

Similar plasticity behavior as a result of oxidation was also found for the Pittsburgh and Harlan seam coals stored in dry, ambient and wet atmospheres for over 950 days at room temperature, as summarized in Table II. These results indicate that the extent of oxidation depends greatly on the humidity of the coal environment, with high humidity accelerating coal oxidation.

TABLE II

GIESELER PLASTOMETER RESULTS OF COALS "WEATHERED" FOR 950 DAYS AT ROOM TEMPERATURE

| Sample | Max. ddpm | Soft Temp. | Max. Fluid Temp. | Solid. Temp. | Plastic Range |
|----------------------|-----------|------------|------------------|--------------|---------------|
| Pittsburgh (dry) | 22400.0 | 347 | 410 | 464 | 117 |
| Pittsburgh (ambient) | 1600.0 | 365 | 422 | 467 | 102 |
| Pittsburgh (wet) | 580.0 | 366 | 420 | 459 | 93 |
| Harlan (dry) | 18.0 | 365 | 410 | 440 | 75 |
| Harlan (ambient) | 9.0 | 387 | 432 | 459 | 72 |
| Harlan (wet) | 5.0 | 391 | 427 | 454 | 63 |

An extremely rapid decrease of Gieseler plasticity due to oxidation is shown in Figure 1, where the maximum fluidity is plotted versus time of oxidation treatment for coals treated at 65% RH and 50°C. Accompanying this rapid reduction of fluidity, there is also a significant decrease of the plastic range. The -1/8-inch stockpiled samples of the same coals show similar but less rapid changes.

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Fe Mossbauer Spectroscopy

The distribution of iron among minerals obtained by low-temperature Mossbauer spectroscopy is summarized in Table III for the strip-mined Pocahontas No. 4 samples. The data indicate that the pyrite has been completely converted to iron oxyhydroxide in both the middle and outcrop coals. Additionally, with increasing oxidation, a decrease in the percentage of iron contained in clay minerals and an increase in the percentage of iron present as an unidentified ferric phase (Fe^{3+}) are observed. This Fe^{3+} phase is most probably either a ferric sulfate or Fe^{3+} in clays.

TABLE III

MOSSBAUER DATA ON DISTRIBUTION OF IRON AMONG MINERALS FOR
POCAHONTAS NO. 4 COAL SAMPLES

| Sample | Percentage of the Total Sample Iron Contained in: | | | | | |
|----------|---|----------|--------|----------|----------------------|------------------|
| | Clay | Siderite | Pyrite | Jarosite | Iron Oxyhydroxide | Fe ⁺³ |
| Highwall | 76 | 13 | 6 | 1 | - | 4 |
| Middle | 64 | 14 | - | 1 | 10 | 12 |
| Outcrop | 51 | 11 | - | - | 21 | 17 |

Results of Mossbauer spectroscopy investigations on the room-temperature oxidation of Pittsburgh and Harlan coals are summarized in Tables IV and V. The data indicate that in Harlan coal, the clay and siderite are apparently little affected by oxidation, whereas the pyrite is extensively oxidized and transformed to jarosite, iron oxyhydroxide and a ferric iron phase. For the Pittsburgh coal, the pyrite was transformed to ferrous sulfate initially and then to ferric sulfates and iron oxyhydroxide. As discussed elsewhere (8), this and other differences in mineral oxidation reflect the significantly different sulfur content and mineralogies of the two coals.

TABLE IV

MOSSBAUER DATA ON THE DISTRIBUTION OF IRON AMONG MINERALS FOR
PITTSBURGH COAL SAMPLES

| Sample | Phases | % Fe ^a |
|---------|-------------------------------|-------------------|
| Fresh | Pyrite | 100 |
| Dry | Pyrite | 96 |
| | Szomolnokite | 4 |
| Ambient | Pyrite | 76 |
| | Szomolnokite | 20 |
| | Rozenite | 4 |
| Wet | Pyrite | 26 |
| | α -FeOOH | 23 |
| | Jarosite | 4 |
| | Fe ³⁺ | 25 |
| | Unidentified Fe ⁺² | 22 |

a. Percentage of the total iron in the sample contained in the indicated phase.

The low-temperature Mossbauer spectra of Pittsburgh coal, treated in the experimental oven (50°C, 65% RH) and coal stockpiled out of doors, are shown in Figure 2. For both Pittsburgh and Pocahontas No. 3 coals treated in the oven, the iron sulfate, szomolnokite, was detected after 40 and 124 days of treatment, respectively. As the oxidation proceeds, the iron sulfate content continues to increase at the expense of pyrite. However, for the coals stockpiled out of doors, iron oxyhydroxide is the oxidation product of pyrite and no iron sulfate has yet been detected. This indicates that different oxidation processes or different rate-determining steps are involved in the oxidation of pyrite in the two environments.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

The infrared spectra of the strip-mined coal samples are shown in Figure 3. The most obvious trend with increasing oxidation is increases in intensity of various carbonyl bands between 1600 cm⁻¹ and 1800 cm⁻¹. These increases in intensity were also accompanied by an increase in intensity of the region between 1100 cm⁻¹ and 1300 cm⁻¹, which is associated with the C-O stretching vibration and O-H bending modes of phenols, ethers and esters (9, 10). Similar increases in intensity can also be found in the absorption bands of hydroxyl groups ranging from 3200 cm⁻¹ to

3600 cm^{-1} . However, the intensity of absorption bands at 2860, 2920 and 2950 cm^{-1} , which correspond to the aliphatic C-H stretching modes, show systematic decreases from the least oxidized to the most oxidized coal samples. Similar decreases in intensity also occur for the aromatic C-H stretching mode at 3040 cm^{-1} , and the absorption bands between 700 and 900 cm^{-1} , which correspond to the aromatic C-H out-of-plane bending modes.

TABLE V

MOSSBAUER DATA ON THE DISTRIBUTION OF IRON AMONG MINERALS FOR HARLAN COAL SAMPLES

| Sample | Phases | % Fe ^a |
|---------|-------------------|-------------------|
| Fresh | Pyrite | 53 |
| | Clays | 43 |
| | Siderite | 4 |
| Dry | Pyrite | 46 |
| | Clays | 43 |
| | Siderite | 5 |
| | Jarosite | 6 |
| Ambient | Pyrite | 42 |
| | Clays | 43 |
| | Siderite | 6 |
| | Jarosite | 9 |
| Wet | Pyrite | 12 |
| | Clays | 42 |
| | Siderite | 6 |
| | Jarosite | 20 |
| | Iron Oxyhydroxide | 7 |
| | Fe ⁺³ | 13 |

a. Percentage of the total iron in the sample contained in the indicated phase.

For the laboratory-oxidized Pittsburgh and Harlan coal samples, the carbonyl and carboxylic-acid absorption bands between 1600 cm^{-1} and 1800 cm^{-1} , which are found in naturally oxidized coals from strip-mines and are closely associated with effects of coal oxidation, were not detected. This suggests that the oxidation of these coal samples is still at a relatively early stage, although both Mossbauer spectroscopy and Gieseler plastometer measurements clearly show changes due to oxidation. This observation is further supported by the DRIFT results obtained after severely oxidizing the dry and wet Pittsburgh coal samples in air at 110°C for seven days. Figure 4 shows that, in addition to the 1650 cm^{-1} and 1735 cm^{-1} bands observed before, carbonyl and carboxyl bands near 1585, 1680, 1690, 1710 and 1765 cm^{-1} also appear after this rather severe oxidation treatment.

DRIFT spectra were also obtained from all oven-oxidized and stockpiled coal samples. No significant difference between the treated and fresh coals was found. This indicates that DRIFT spectroscopy is not sufficiently sensitive to detect the early stages of oxidation that cause the large decreases observed in plasticity.

CONCLUSIONS

Mossbauer spectroscopy shows that pyrite in coal is readily altered by low-temperature coal oxidation. The oxidation of pyrite in coals subjected to simulated weathering treatments at constant temperature and humidity in the laboratory gives rise to a variety of iron sulfates. This is in contrast to coal samples stockpiled out-of-doors and strip-mined coals, in which the principal pyrite oxidation product is iron oxyhydroxide.

A reduction in intensity of aliphatic and aromatic bands with increasing oxidation of a strip-mined coal is detected in DRIFT spectra. These changes accompany the enhancement in intensity of certain carbonyl and carboxyl bands. However, these carbonyl bands are not detected in spectra of laboratory oxidized coals until oxidation is quite extensive.

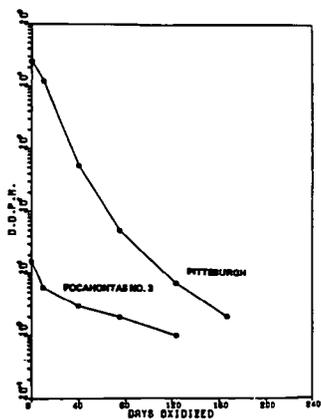


Fig. 1 Variations of maximum fluidity as measured by Gieseler plastometer with days of oxidation at 50°C, 65% RH.

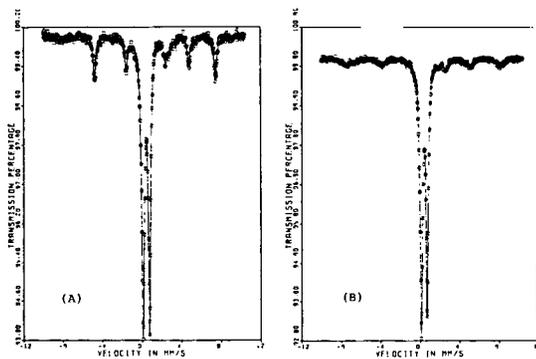


Fig. 2 Low-temperature Mossbauer spectra of Pittsburgh coals: (A) treated in 50°C, 65% RH for 167 days; (C) stockpiled out of doors for 139 days.

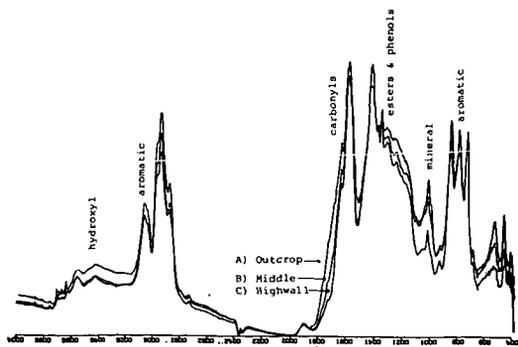


Fig. 3 FTIR spectra of Pocahontas No. 4 seam coals: (A) outcrop, (B) middle, (C) highwall.

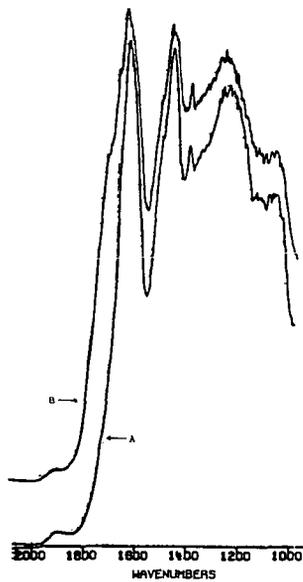


Fig. 4 FTIR spectra of (A) Pittsburgh coals oxidized for over 30 months in wet air atmosphere at room temperature; (B) wet Pittsburgh coal oxidized in air at 110°C for seven days.

The plastic properties of coal, as determined by Gieseler plastometer measurements, are extremely sensitive to oxidation. The maximum fluidity shows a very rapid reduction with oxidation. There is also a significant narrowing of the plastic range. Of the three techniques, the Gieseler plasticity measurement is the most sensitive and DRIFT spectroscopy the least sensitive to the initial stages of coal oxidation. This order of sensitivity is inverse to their applicability to coals as the Gieseler measurements are restricted to coking bituminous coals and Mossbauer techniques are best applied to high pyrite coals, whereas DRIFT spectroscopy can be applied to all coals with little or no modification.

The extreme sensitivity of the thermoplastic behavior of coal to initial oxidation as determined by the Gieseler measurements is in contrast to the insensitivity of DRIFT spectroscopy and the relative minor oxidation of pyrite detected by Mossbauer spectroscopy, both of which are bulk-oriented techniques. The explanation must be attributed to the fact that the first stages of coal oxidation are surface controlled, as are most oxidation processes. Even though plasticity is determined by a macroscopic measurement, it is dependent upon the fusing together of separate coal particles. Consequently, it is likely to be highly sensitive to very thin surface layers on the coal particles. Further investigations involving the characterization of oxidized coal surfaces are currently underway.

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