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SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

**Technical Progress Report for the Period
April to June 1995**

by

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ABSTRACT

During this report period, analysis of the vitrinite concentrate samples of the Lower Kittanning (PSOC-1562) and Illinois #6 (DECS-24) seams were completed. These results show that the concentrates are in excess of 97 vol. % vitrinite and that the sample remains in good shape for microflotation and GC/MS experiments. Two new coal samples, the hvAb Banner seam (DECS-29) and the mvb Splashdam seam (DECS-30) were collected in mid-June. Preliminary processing of the channel samples suggests that the Banner seam sample is severely weathered and may need to be replaced. Collection of a third sample, the hvBb Ohio #4a seam, was delayed until next quarter.

Surface oxidation of a powdered vitrinite concentrate sample of the Pittsburgh seam (DECS-23) was completed during this quarter. The technique of photo-oxidizing vitrain samples using our optical microscope was laborious and time consuming. Even after the procedure was streamlined the procedure of irradiating 1.4 g of vitrinite required 29 days. A limited number of samples will be irradiated in this manner in order to maintain continuity between our fluorometric measurements and microflotation experiments, but other methods of surface oxidation will be explored.

Presentations were made at the DOE Contractor's Review and Peer Review meetings held in Nashville, TN on June 13-14, 1995.

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PROGRAM OBJECTIVES

The general objectives of this research are 1) to measure the changes in functional group concentration as a function of the duration of photo-oxidation using FTIR and flash pyrolysis GC/MS techniques, 2) to identify the influence of photo-oxidation on coal floatability by measuring contact angles from polished surfaces and powders as well as by microflotation, and 3) to correlate the changes in surface chemistry with measurements of luminescence intensity and alteration. The ultimate objective is to develop new luminescence techniques that will measure quantitatively changes in surface properties as a function of oxidation and relate them to coal cleanability.

PROGRAM OUTLINE

Coal Sampling and Characterization

Vitrinite concentrates and individual particles containing vitrinite will be obtained from eight coals ranging in rank from high volatile B to low volatile bituminous. Every effort will be made to collect fresh coals from the field and to maintain them under conditions that limit their exposure to atmospheric oxygen, to drastic changes in temperature and relative humidity, and exposure to direct sunlight. Moreover, where practical, samples of coal which have been exposed and naturally weathered in outcrop will be collected for comparative studies. Powdered vitrinite concentrates will be generated in a controlled atmosphere glove box under nitrogen, whereas the large particles will have to be sized and polished in air. Vitrinite concentrates will be characterized by proximate, ultimate and petrographic analyses. In some cases, whole seam channel samples may be available from the same vicinity as the blocks removed for concentrates

affording comparisons with whole seam coal samples.

Photo-oxidation and Luminescence Analysis

Luminescence spectral analysis, measurement of emission intensity at a given wavelength (600 nm) and photo-oxidation will be performed initially using a Leitz Orthoplan MPV-II microscope. Basic luminescence properties of the vitrinite from each coal will be measured under a nitrogen atmosphere. Corresponding areas on the same polished surface will be irradiated in air (photo-oxidized) for different periods of time (5, 10 and 15 min) and profiles of the emissions will be measured. Construction of the time-resolved alteration process across the visible frequency range will be necessary to determine the relationship between the change in luminescence and the chemistry associated with photo-oxidation.

Infrared Analysis and Contact Angle Measurements

Once the optimum time intervals of irradiation are determined, separate 1 mm² areas of the polished surface will be photo-oxidized and analyzed by FTIR. We will use a Digilab 60 FTIR with a microspectrophotometric system in the reflectance mode for the FTIR analysis. We expect to have excellent resolution in detecting the changes in functional group chemistry within the top few layers of molecules. Functionalities of interest will be C=O (1710 cm⁻¹), aryl ether (1260 cm⁻¹), alkyl ether (1030-1090 cm⁻¹), C-O (1300-1100 cm⁻¹), C=C (1600-1500 cm⁻¹), δ CH₃ (1400-1320 cm⁻¹), δ CH₂+CH₃ (1480-1400 cm⁻¹), and ar γ CH (920-720 cm⁻¹). The data obtained will be integrated into a set of rate expressions describing the photochemistry for each coal.

These same irradiated areas will be used to measure the sessile-drop contact angle

using a Ramé-Hart Model A-100 contact-angle goniometer. Although the sessile-drop method with water results in slightly more data scattering than captive-bubble measurements, the better control over drop placement afforded by the technique is necessary. Use of pure vitrains ensures that a true rank-related effect will be measured, and that the wide variability introduced into wettability experiments by variation in maceral and mineral composition is avoided.

Pyrolysis GC/MS and Wettability Analysis

Small amounts of powdered coal samples (≈ 1.0 g at ≈ 0.25 mm) will be irradiated in air using the same conditions, optical equipment and time intervals as with the polished-surface samples. A small subsample will be prepared for luminescence spectral analysis for comparison with the polished samples; the remainder will be employed for pyrolysis GC/MS and wettability studies.

Pyrolysis GC/MS will be performed using a DuPont 490B GC/MS with a temperature-programmed furnace which fits directly into the injection port. The temperature program we intend to use involves ramping up to 610°C at $5^{\circ}\text{C}/\text{msec}$ and holding at 610°C for 10 secs; this program compares well with Curie-point pyrolysis methods. The capillary column employed is a low polarity, DB-17 column, which provides excellent resolution of the oxygen-containing molecules. The mass detector employs a magnetic sector mass separator which achieves a resolution of 1 amu at mass 500.

Contact angles will be measured for the powdered vitrinite samples by using the interface partitioning method developed at Penn State. The technique involves placing a

fine coal particle, with its natural irregular surfaces, at the water/air interface. The position of the particle at the interface depends on the particle wettability and its aspect ratio (size and shape). From this analysis contact angles of many naturally shaped particles can be determined. Both fresh and photo-oxidized samples will be tested and, provided that significant differences are found from photo-oxidation, a number of microflotation tests will be conducted.

DESCRIPTION OF TECHNICAL PROGRESS

INTRODUCTION

During this performance period analytical results were obtained for vitrinite concentrates prepared from the PSOC-1562 (Lower Kittanning) and DECS-24 (Illinois #6) samples. Further, two new samples, the Banner (DECS-29) and Splashdam (DECS-30) seams from Virginia, were collected for this project in mid-June. Also, the process of irradiating a powdered vitrinite concentrate of the Pittsburgh seam sample (DECS-23) to be used for microflotation and pyrolysis GC/MS experiments was completed. Finally, presentations were prepared for the Contractor's Review and Peer Review meetings held June 13-14, 1995 in Nashville, Tn. The following report summarizes our progress.

COAL SAMPLING, PREPARATION AND ANALYSIS

As reported in the last quarterly report (1), powdered vitrinite concentrates and blocks of the Lower Kittanning (PSOC-1562, marine-influenced) and the Illinois #6 (DECS-24) seams were prepared. Analytical results were completed for the vitrinite concentrates and are compared in Tables 1 and 2 with information from whole-seam channel samples taken at the time of collection.

The Lower Kittanning vitrinite concentrate (PSOC-1562-Vit) consisted of greater than 97 vol. % vitrinite on a mineral-free basis (95% mineral containing). The forms of sulfur analysis indicated that most of the pyrite was removed during the process of hand picking the vitrain; the predominant mineral components observed under the microscope were dispersed clays and pyrite. Macerals other than vitrinite found in the concentrate included fine-grained dispersed sporinite, micrinite and inertodetrinite. As was found with

Table 1
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the Lower Kittanning Seam Samples, PSOC-1562

	Whole-Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	1.88	1.99
% Ash, dry	13.04	3.60
% Volatile Matter, daf	43.95	40.31
% Fixed Carbon, daf	56.05	59.69
<u>Ultimate Analysis, daf</u>		
% Carbon	81.77	82.31
% Hydrogen	5.98	5.56
% Nitrogen	1.73	1.63
% Total Sulfur	4.45	1.61
% Oxygen (diff.)	6.07	8.89
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	3.54	0.72
% Sulfate Sulfur	0.02	0.08
% Organic Sulfur (diff)	0.31	0.75
<u>Petrography</u>		
Vitrinite, % min.-free	83.6	97.4
Liptinite, % min.-free	6.6	0.9
Inertinite, % min.-free	9.8	1.7
Mean Maximum Vitrinite Reflectance, %	0.77	0.80
Vitrinite Fluorescence Intensity in N ₂ (Uranyl Glass=10)	2.35	2.01
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpm	26,620	-
Fluid Temperature Range °C	88	-
Free Swelling Index	6	-

Table 2
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the Illinois #6 Seam Samples, DECS-24

	Whole-Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	13.20	12.87
% Ash, dry	13.39	2.77
% Volatile Matter, daf	47.15	42.98
% Fixed Carbon, daf	52.85	57.02
<u>Ultimate Analysis, daf</u>		
% Carbon	76.27	78.12
% Hydrogen	5.30	5.32
% Nitrogen	1.32	1.26
% Total Sulfur	6.38	3.36
% Oxygen (diff.)	10.73	11.94
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	3.05	0.50
% Sulfate Sulfur	0.29	0.03
% Organic Sulfur (diff)	3.05	2.73
<u>Petrography</u>		
Vitrinite, % min.-free	90.2	98.7
Liptinite, % min.-free	3.0	0.6
Inertinite, % min.-free	6.8	0.7
Mean Maximum Vitrinite Reflectance, %	0.49	0.44
Vitrinite Fluorescence Intensity in N ₂ (Uranyl Glass=10)	-	2.21
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpn	49	-
Fluid Temperature Range °C	78	-
Free Swelling Index	3	-

the Pittsburgh seam concentrate (DECS-23-Vit, ref. 2), the mean maximum reflectance was higher and the vitrinite fluorescence intensity was lower for the Lower Kittanning vitrinite concentrate compared to the channel sample because of a high concentration of telocollinite.

The vitrinite concentrate of the Illinois #6 (DECS-24-Vit) contained nearly 99 vol. % vitrinite on a mineral-free basis (96% mineral containing). As with the other samples most of the pyrite was removed by hand picking leaving only the dispersed forms of clay and pyrite and some cleat carbonate. The minor macerals are the dispersed forms of sporinite, micrinite and inertodetrinite. In contrast to the previous samples, the Illinois #6 concentrate has a lower mean maximum reflectance than the channel sample.

There does not appear to be any signs of deterioration of these two samples resulting from storage under argon, although slightly more sulfate sulfur was observed in the Lower Kittanning sample (PSOC-1562-Vit). However, the alteration of fluorescence in air (photo-oxidation) for the Lower Kittanning and Illinois #6 concentrates given in Figs. 1 and 2, shows a strong dual pattern, which supports the conclusion that there has been no deterioration.

During this reporting period two new samples were collected in mid-June, namely the Banner (DECS-29) and Splashdam (DECS-30) seams from Virginia. These coals, of hvAb and mvb rank (respectively) were obtained to round out our rank series of samples for the project. Preliminary processing and petrographic analyses have been completed on the whole-seam channels showing that the coals collected were of the expected ranks. However, there was difficulty in getting a fresh working-face sample of the Banner seam

Fig. 1 - Alteration of Fluorescence Intensity of Vitrinite
for PSOC-1562 and Vitrinite Concentrate

Fig. 2 - Alteration of Fluorescence Intensity for
DECS-24 Vitrinite Concentrate

and our analyses suggest that the Banner seam is severely weathered. Once the samples have been completely characterized a decision will be made whether to replace the Banner seam with another sample. Plans to collect a sample of the Ohio #4a seam of hvBb rank have been delayed. This sample will be collected during the next quarter.

PHOTO-OXIDATION STUDIES

Irradiation of Powdered Vitrinite

During the past performance period the first powdered vitrain concentrate of the Pittsburgh seam (DECS-23) was irradiated. As discussed in the last progress report, a 1.4 g sample of powdered vitrinite from the Pittsburgh seam (DECS-23), size classified between 40 and 100 mesh (0.42 to 0.15 mm), was selected for preliminary photo-oxidation by irradiation under blue light. Irradiation of such a large sample for 10 minutes was found to be prohibitively time consuming under a light flux focused at 100-200 μm diameter, so the procedure was altered by increasing the diameter of the area of irradiation for a longer time sequence, i.e., 5 mm for 30 minutes. Even with this procedural change, 29 days were required to irradiate the full 1.4 g sample using the optical microscope. Following irradiation, the sample was returned to storage under argon and refrigerated. Although this preliminary evaluation suggests that another, more efficient technique for irradiation vitrain samples needs to be employed, we are hopeful that a limited number of vitrains can be irradiated using the optical microscope so that continuity may be maintained between our fluorometric analyses and microflotation measurements.

DOE CONTRACTOR'S REVIEW AND PEER REVIEW MEETINGS

Laboratory work on this project was suspended between May and June, 1995 in order to prepare our Peer Review assessment documentation and two oral presentations, one for the DOE Contractor's Review meeting and the other for the Peer Review Meeting that was held in Nashville, TN, June 13-14, 1995. These reviews provided us with a useful opportunity to reflect on the project accomplishments, goals and problems.

Fig. 3 shows our project schedule and the tasks that remain to be completed in this project. The schedule reflects the fact that, for the most part, we have concentrated our previous work on collection and characterization of an excellent set of coals as well as developing a set of analytical techniques and procedures that will allow us to characterize the photo-oxidized surface of coal. As this project deals with surface properties that can change or can alter rapidly, the timing and sequence of analysis is important to the success of the work. It was, and is our intent to photo-oxidize the surface of a number of coal blocks, evaluate the surface functional group chemistry using reflectance-mode FTIR, then immediately evaluate the wettability of these surfaces with contact angle measurements followed by measurements of near-surface oxygen concentration using electron-optical X-ray mapping techniques. In March FTIR equipment we had planned to use was totally destroyed by an electrical fire. New equipment has been ordered, but may not be in service until January 1996. We are currently investigating alternative options.

Fig. 3 - Project Schedule

REFERENCES

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