SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

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Technical Progress Report for the Period January to March 1996

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ABSTRACT

During this report period, a vitrinite concentrate from the mvb Splash Dam seam (DECS-30) was prepared and analyzed. Results show that the concentrate was 91 vol % vitrinite and that the sample has been adequately protected from oxidation under refrigerated storage in argon. The 9% level of contamination within the vitrinite resulted from the extreme friability of the coal and to the dispersion of fine grains of semifusinite and micrinite.

Polished blocks containing vitrain bands that were prepared, irradiated in blue-light and employed in contact angle measurements were evaluated using specular reflectance-mode FT-ir for changes in functional group chemistry. Infrared spectra from unexposed areas of vitrinite and those irradiated for 1, 5 and 10 min for six coals ranging in rank from hvCb to mvb were obtained using a FTS 175 spectrometer with a Bio-Rad UMA 500 microscope accessory. Preliminary results demonstrate that photo-oxidation occurred during irradiation, becoming progressively more intense with increasing irradiation time; however, the magnitude of this change diminished with increasing rank. A relatively steady increase in the carbonyl region ($1800 - 1650 \text{ cm}^{-1}$) and a decrease in the aliphatic region ($2950 - 2850 \text{ cm}^{-1}$) of the spectra supports this observation and is similar to observations made in the past for natural weathering and laboratory oxidation of coals.

A series of tests was initiated to photo-oxidize powdered vitrains using the BLAK-RAY ultraviolet lamp evaluated last quarter. Samples of four vitrinite concentrates were exposed to UV light for 10 mins per side. These and the corresponding whole-seam

channel samples and raw vitrinite concentrates were submitted for initial microflotation tests which have not been completed at this time.

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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 a vitrinite concentrate was prepared from the medium volatile Splash Dam Seam (DECS-30) and analyzed. In addition, the series of polished coal blocks containing vitrain bands (≈ 3 mm wide) that were photo-oxidized in blue light for 1, 5 and 10 minutes and used for contact angle measurements (1,2) have now been evaluated using reflectance-mode FT-ir techniques. Also, whole seam samples corresponding to our vitrinite concentrates were prepared for microflotation testing and four vitrinite concentrates were photo-oxidized for 10 min duration using the longwave ultraviolet light source evaluated last quarter. The following report summarizes our progress.

COAL SAMPLING, PREPARATION AND ANALYSIS

A powdered vitrinite concentrate was prepared from the medium volatile Splash Dam seam (DECS-30) under a nitrogen atmosphere and divided into ≈ 1.5 g aliquots for microflotation testing. Analytical results were completed for the concentrate and are compared in Table 1 with information from its respective whole-seam channel sample.

The Splash Dam vitrinite concentrate (DECS-30-Vit) consists of greater than 91 vol. % vitrinite on a mineral-free basis (90% mineral containing). The process of hand picking vitrain was difficult because of this coal's extreme friability and, although a high concentration was obtained, about 9 vol. % of other macerals, mostly fine particles of semifusinite and micrinite, are also present. Concentration of the vitrinite has had a marginal effect on the chemical composition with decreased carbon, ash and pyritic sulfur

Table 1
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the mvb Splash Dam Seam, DECS-30

	Whole-Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	2.06	0.94
% Ash, dry	3.89	1.64
% Volatile Matter, daf	31.35	31.50
% Fixed Carbon, daf	68.65	68.50
<u>Ultimate Analysis, daf</u>		
% Carbon	87.83	87.44
% Hydrogen	5.36	5.42
% Nitrogen	1.57	1.65
% Total Sulfur	0.82	0.76
% Oxygen (diff.)	4.42	4.73
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	0.14	0.05
% Sulfate Sulfur	0.00	0.00
% Organic Sulfur (diff)	0.65	0.70
<u>Petrography</u>		
Vitrinite, % min.-free	76.8	91.2
Liptinite, % min.-free	3.6	1.2
Inertinite, % min.-free	19.6	7.6
Mean Maximum Vitrinite Reflectance, %	1.16	1.09
Vitrinite Luminescence Intensity in N ₂ (Uranyl Glass=10)	1.28	1.26
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpm	28188	-
Fluid Temperature Range °C	117	-
Free Swelling Index	8	-

contents and increased oxygen compared to the whole-seam channel. Mean maximum vitrinite reflectance was lower for the vitrinite concentrate whereas luminescence intensity was about the same. As shown in Fig. 1, the pattern of alteration in luminescence intensity during irradiation in air was similar for vitrinite in the whole-seam channel and the concentrate.

From these results, there does not appear to be any signs of deterioration resulting from storage under argon, no sulfate sulfur was observed and the alteration of luminescence in air (photo-oxidation) exhibits the same pattern, i.e., a negative response.

PHOTO-OXIDATION STUDIES

Introduction

Samples of polished coal blocks containing vitrain bands that were irradiated in blue light for 1, 5 and 10 mins and used for the measurement of contact angles (1,2) have been evaluated using specular reflectance-mode FT-ir. Following contact angle measurements, polished specimens of six coals (Illinois#6, Ohio#4a, Pittsburgh, Lower Kittanning (2 samples) and the Splash Dam seams) varying in rank from hvCb to mvb were immediately returned to storage under argon and refrigerated. Infrared interferograms were obtained in the reflectance mode using a Bio-Rad UMA 500 instrument.

Measurements were taken on areas of vitrinite that had been irradiated in blue light and adjacent non-irradiated areas to establish changes in functional group chemistry.

Sample Preparation History

Blocks containing one or more vitrain bands between 3 - 4 mm in height were employed. One surface of each block was polished using a sequence of grinding paper

Fig. 1 - Luminescence Alteration Patterns From Splash Dam, DECS-30 ∞

(600 grit) and alumina slurries (0.3 and 0.05 μm polishing compounds). Between each stage samples were cleaned in an ultrasonic bath containing distilled water. After the final polishing step, the surface was gently cleaned with cotton under a stream of distilled water, dried in a stream of filtered air and placed under vacuum for several hours to remove excess moisture from surface cracks and pores. Samples were then wrapped in cardboard rings to protect the polished surface and placed in a foil laminate bag, sealed in argon gas and refrigerated until needed.

Irradiation (Photo-Oxidation) of Vitrain Bands

Irradiation of the vitrain bands was conducted in the manner described in the last quarterly report (1). Briefly, the surface irradiation technique uses a light flux focused into a 200 μm diameter area with our optical microscope system. A single scribe mark had been cut across the vitrain band and, at approximately 200 μm from the scribe mark, successive 200 μm diameter areas of vitrinite were irradiated in a line parallel with the scribe mark until the full height of the vitrain band was traversed. A second line of irradiated areas placed immediately adjacent to the first provided a photo-oxidized area about 400 μm wide for the full height of the vitrain band. This procedure was followed for each period of irradiation, i.e., 1, 5 and 10 min. Usually, different vitrain bands in different blocks were irradiated for each time period as it was difficult to locate areas of vitrain free of fractures and inclusions of other macerals or minerals. Also, at regular intervals luminescence alteration patterns were recorded. Following irradiation, the samples were returned to storage in foil laminate bags under argon gas and refrigerated. Subsequently, contact angle measurements were made on all of these areas by advancing a

drop of distilled water across the surface (1,2) and then the samples were again returned to refrigerated storage in argon.

Infrared Microspectroscopy

Specular reflectance FT-ir spectra were obtained from an FTS 175 spectrometer with a Bio-Rad UMA 500 infrared microscope accessory fitted with a 250 μm diameter narrow-band MCT (mercury-cadmium-telluride) detector cooled to 77°K. The polished blocks were mounted level on a slide with modelling clay. An area on the surface was identified in white light (40 X total magnification in air) and masked to include only the irradiated area. Then, the infrared objective (150 X total magnification) was placed in the optical path. Before measurements were made an environmental chamber was placed around the sample and a rapid flow of nitrogen was begun. The flow of nitrogen helped to reduce moisture levels within the chamber and at the coal surface. Preliminary interferograms were taken to monitor moisture levels; depending upon the coal, 10-60 min were required before analysis could commence. The analytical conditions used were: single beam accumulation of 2000 scans; 4000-650 cm^{-1} spectral range; spectral resolution of 2-4 cm^{-1} . An infrared background spectrum was collected from a gold-coated plate at the beginning of each session and was subtracted from spectra derived from the coal surfaces. Correction of the reflectance spectra for distortions caused by specular reflection was carried out using a Kramers-Krönig formulation provided with the Bio-Rad software.

Results and Discussions

Examples of complete infrared spectra (with some pertinent regions identified) for fresh and 10 min irradiated surfaces of the Illinois #6 (DECS-24) are compared in Fig. 2.

Fig. 2 - FT- i.r. Spectra From Adjacent Areas of Illinois #6 (DECS-24) 11
Vitrinite for Fresh and 10 min Irradiated Surfaces

The diffuse nature and relative absorbance of reflectance mode spectra are demonstrated in Fig. 2 and are fairly characteristic of most spectra collected in this portion of the study.

Specific regions of spectra (between 2000 - 1200 cm^{-1} and 3800 - 2700 cm^{-1}) collected on each irradiated area are placed together on the same plot in Figs. 3 - 8 for comparison of results from the six coals. After close inspection, it appears that a number of the spectra will need to be rerun before a complete evaluation of the FT-ir technique can be made.

The presence of water caused distortion of spectra collected from the surface of the Ohio #4a (DECS-33) and Lower Kittanning (PSOC-1562) specimens irradiated for 1 and 5 min, as seen from the periodic noise in the 3800 - 3600 cm^{-1} regions of Figs. 4 and 6, respectively. Also, the apparent lack of change in the carbonyl region (1800 - 1650 cm^{-1}) of the Pittsburgh seam (DECS-23) following 10 mins of irradiation (Fig 5) compared to a strong change observed following 5 mins, suggests that the irradiated area may not have been located properly. Once these analyses have been repeated a more comprehensive evaluation of the spectra will be performed.

Even preliminary comparison of the spectra suggests that as irradiation time increases there is a significant increase in the carbonyl region located between 1800 - 1650 cm^{-1} and a decrease in the aliphatic CH stretching region between 2950 - 2850 cm^{-1} . Furthermore, the magnitude of these changes decreases with increasing rank. Also, there is some indication of an increase in the intensity of the O-H band near 3450 cm^{-1} , although this region is rather diffuse. These observations correspond with earlier evidence from Scanning Transmission X-ray Microscopy (STXM) and Carbon Near-Edge X-ray Adsorption Fluorescence Spectroscopic (C-NEXAFS) analyses of the Pittsburgh seam

Fig. 3 - Comparison of FT-i.r. Spectral Regions for Fresh (0 min) and Irradiated Surfaces (1, 5 and 10 min) of the hvCb Illinois #6, DECS-24 13

¹⁴ Fig. 4 - Comparison of FT-i.r. Spectral Regions for Fresh (0 min) and Irradiated Surfaces (1, 5 and 10 min) of the hvBb Ohio #4a, DECS-33

Fig. 5 - Comparison of FT-i.r. Spectral Regions for Fresh (0 min) and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Pittsburgh Seam, DECS-23

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16 Fig. 6 - Comparison of FT-i.r. Spectral Regions for Fresh (0 min) and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Lower Kittanning, PSOC-1562

Fig. 7 - Comparison of FT-i.r. Spectral Regions for Fresh (0 min) and Irradiated Surfaces (1, 5 and 10 min) of the hvAb Lower Kittanning Seam, PSOC-1563

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¹⁸ Fig. 8 - Comparison of FT-i.r. Spectral Regions for Fresh (0 min) and Irradiated Surfaces (1, 5 and 10 min) of the mvb Splash Dam, DECS-30

vitronite which show increases in aromatic-ring associated OH and carbonyl concentration with decreasing CH_3 with increasing irradiation time (3).

Once re-analysis of some of the spectra have been completed, a more detailed evaluation can be performed, including taking difference and derivative spectra (4). An aim of this further analysis will be to resolve more details concerning the carbonyl region in order to identify the sources of carbonyl associated with carboxylic acid, aldehydes, ketones, esters or perhaps anhydride groups that may be present and changing in relative concentration with irradiation time. Likewise similar analyses can be performed for the aliphatic regions to establish changes that may be taking place relative to concentrations of CH_3 , CH_2 and CH groups.

Conclusions

Preliminary evaluation of reflectance-mode FT-ir spectra from irradiated and non-irradiated surfaces of vitronite show that as time of exposure to blue light increases there is an increasing level of photo-oxidation. The photo-oxidized surfaces show an increase in the carbonyl region and a decrease in the aliphatic region of the spectra similar to what has been reported in the literature for natural weathering and laboratory oxidation of coals. It is hoped that a further analysis of the data will enable some of the chemical mechanisms that may be involved to be understood.

IRRADIATION AND FILM FLOTATION OF POWDERED VITRAIN

A BLAK-RAY, 100 watt ultraviolet spotlight was evaluated in the last progress report for photo-oxidizing powdered vitrains (1). This device provides a brilliant spot of long wavelength ultraviolet light (reported to be 366 nm). Our preliminary tests suggested

that the spotlight could effectively be used to reduce luminescence intensity (presumably through photo-oxidation) of the polished surface of vitrinite in a manner similar to that induced under the optical microscope except that, being weaker, more irradiation time would be required. Thus, during this reporting period, ≈ 1.0 g samples of the four vitrinite concentrates were irradiated for a period of 10 min for evaluation of luminescence intensity and for microflotation measurements. It was established that 10 min of exposure under the UV spotlight was equivalent to 1 min under the blue-light flux of our optical microscope system. In addition, raw coal samples were prepared from six of the coals collected for this study for initial evaluation of the film flotation technique.

Experimental Procedure

Following a warm-up period, the BLAK-RAY spotlight was ready for use. A monolayer of powdered vitrain was spread out on the outside bottom half of a glass petri dish and exposed to the UV-light for a period of 10 min at a distance of 5 cm from the lamp. Then, the top half of the petri dish was placed over the bottom half so as to secure the particles while they were inverted. Then the undersides of the particles were irradiated for 10 min. These steps were repeated on successive layers until approximately a gram of irradiated vitrain was produced. A few milligrams of the original sample and the irradiated materials were set aside for measurement of luminescence intensity of the surface as well as for pyrolysis GC/MS analysis.

Microflotation tests are to be conducted on the irradiated samples. However, the technique is yet to be perfected. To do this through some initial testing, samples of the whole seam channel samples reduced to the particle size range (-40 +100 mesh) and mass

(≈ 1.0 g) that will be used for the vitrinite concentrates. Samples of the Illinois#6, Ohio#4a, Pittsburgh, Lower Kittanning (2 samples) and the Splash Dam seams were provided. At this time the work has not been fully completed.

Film flotation will be carried out on the powdered samples using an approach to immersion-time tests for defining their lyophobic-lyophilic characteristics. As discussed in a previous report (5), a monolayer of about 0.3g of coal is placed on the surface of a liquid in a shallow vessel (a funnel was used in this case) of about 75 mm diameter at the top and a height of about 20 to 30 mm. In general, the particles either remained on the liquid surface (lyophobic) or are imbibed into the liquid (lyophilic). Thus, film flotation of the solids involve separating the solid material into lyophilic and lyophobic fractions which are then dried and weighed. The surface tension of the liquid used is varied from 30 to 55 dynes/cm by the addition of anhydrous methanol to twice distilled water.

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