SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

**Technical Progress Report for the Period
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by

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ABSTRACT

During this report period, two vitrinite concentrates were prepared and analyzed from the hvBb Ohio #4a (DECS-33) and hvAb Lower Kittanning (PSOC-1563) seams. Results show that concentrates of 97 and 96 vol % vitrinite were achieved for the respective samples, with the presence of other macerals being limited to those dispersed as fine grains within the vitrinite matrix. Both samples have relatively high concentrations of sulfate sulfur which is the only sign of deterioration. However, in the case of the Lower Kittanning sample the sulfate may have been part of the original sample.

Irradiation (photo-oxidation) of all six vitrinite concentrates for three different time periods (10, 50 and 100 min) using the BLAK-RAY ultraviolet lamp was continued during this report period. Our evaluation of the UV spotlight showed that these irradiation times provided a level of photo-oxidation that corresponded to the blue-light flux used in our optical microscope system for 1, 5 and 10 min irradiations, respectively. From evaluation of the surface luminescence of vitrain surfaces following exposure to UV light we have determined the intensity decreases with increasing irradiation time.

Film flotation results, although incomplete, show that there is some variability in flotation yield as a function of rank and of photo-oxidation time. As observed from contact angle and FTIR spectral measurements on polished surfaces, the hvCb Illinois #6 powdered vitrain (DECS-24-Vit) shows a significant loss in flotation yield with increasing irradiation time following 10 and 50 min of exposure to UV light. Also, a relative minor change in flotation yield was observed for the mvb Splash Dam vitrain powder (DECS-30-

Vit) after 10 and 50 min irradiation. However, contrary to earlier contact angle measurements, the Splash Dam vitrain gave a slight increase in flotation yield suggesting that the surface became somewhat more hydrophobic as a result of photo-oxidation. Results from the hvAb Lower Kittanning (PSOC-1562-Vit) sample appear to be intermediate, in that a significant increase in flotation yield occurs following 10 min of UV irradiation marked by a relatively large decrease after 50 min. Although the flotation response appears somewhat erratic with respect to earlier contact angle measurements, it may be providing important information about the effects of changing oxygen functionality on coal floatability.

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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 vitrinite concentrates were prepared and analyzed for the hvBb Ohio #4a seam (DECS-33) and the hvAb Lower Kittanning seam (PSOC-1563). This brings to six the total number of concentrates prepared for this study from coals ranging in rank from hvCb to mvb. A narrow size fraction (-40 +100 mesh) of all these powdered vitrains is currently being photo-oxidized for periods of 10, 50 and 100 min using a longwave ultraviolet light source. These time period correspond to irradiation periods of 1, 5 and 10 minutes, respectively, using our optical microscope system. Although some preliminary results are available, measurement of luminescence intensity and film flotation of the raw and photo-oxidized powders continues. The following report summarizes our progress.

COAL SAMPLING, PREPARATION AND ANALYSIS

Powdered vitrinite concentrates were prepared from the hvBb Ohio #4a seam (DECS-33) and the hvAb Lower Kittanning seam (PSOC-1563) under a nitrogen atmosphere and divided into ≈ 1.5 g aliquots for microflotation testing. Analytical results were completed for the concentrates and are compared in Tables 1 and 2 with information from their respective whole-seam channel samples.

The Ohio #4a vitrinite concentrate (DECS-33-Vit) consists of greater than 97 vol. % vitrinite on a mineral-free basis (95% mineral containing). Concentration of the vitrinite had some influence on the chemical composition with increases in carbon and oxygen contents and decreases in ash, volatile matter, hydrogen, sulfur and nitrogen

Table 1
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the hvBb Ohio #4a, Clarion Seam (DECS-33)

	Whole-Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	5.97	6.03
% Ash, dry	12.02	2.97
% Volatile Matter, daf	48.94	45.02
% Fixed Carbon, daf	51.06	54.98
<u>Ultimate Analysis, daf</u>		
% Carbon	79.01	80.01
% Hydrogen	5.81	5.62
% Nitrogen	1.35	1.21
% Total Sulfur	4.25	2.29
% Oxygen (diff.)	9.58	10.88
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	1.41	0.30
% Sulfate Sulfur	0.01	0.04
% Organic Sulfur (diff)	2.32	1.88
<u>Petrography</u>		
Vitrinite, % min.-free	76.7	97.3
Liptinite, % min.-free	8.3	0.9
Inertinite, % min.-free	15.0	1.8
Mean Maximum Vitrinite Reflectance, %	0.51	0.56
Vitrinite Luminescence Intensity in N ₂ (Uranyl Glass=10)	2.45	2.13
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpm	86	-
Fluid Temperature Range °C	75	-
Free Swelling Index	4	-

Table 2
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the hvAb Lower Kittanning Seam Samples, PSOC-1563

	Whole-Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	3.49	3.57
% Ash, dry	6.62	1.27
% Volatile Matter, daf	41.50	37.88
% Fixed Carbon, daf	58.50	62.12
<u>Ultimate Analysis, daf</u>		
% Carbon	81.31	82.93
% Hydrogen	5.90	5.60
% Nitrogen	1.77	1.40
% Total Sulfur	4.08	0.69
% Oxygen (diff.)	7.94	9.38
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	3.32	0.11
% Sulfate Sulfur	0.03	0.04
% Organic Sulfur (diff)	0.46	0.53
<u>Petrography</u>		
Vitrinite, % min.-free	85.5	96.4
Liptinite, % min.-free	5.7	1.2
Inertinite, % min.-free	8.8	2.4
Mean Maximum Vitrinite Reflectance, %	0.77	0.81
Vitrinite Fluorescence Intensity in N ₂ (Uranyl Glass=10)	1.91	1.12
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpm	2,592	-
Fluid Temperature Range °C	73	-
Free Swelling Index	5	-

compared to the whole-seam channel. Macerals other than vitrinite found in the concentrate included fine-grained dispersed sporinite, cutinite, micrinite, semifusinite, fusinite and inertodetrinite. Mean maximum vitrinite reflectance was slightly higher and luminescence intensity at 600 nm was lower for the concentrate. 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.

The vitrinite concentrate of the Lower Kittanning (PSOC-1563-Vit) contained nearly 96 vol.% vitrinite on a mineral-free basis (96% mineral containing). As with the other sample carbon and oxygen contents were increased compared to the whole seam channel and contents of ash, volatile matter, hydrogen, sulfur and nitrogen were diminished. Other macerals included within the vitrinite were fine-sized sporinite, resinite, cutinite, semifusinite, fusinite and micrinite. Also, the mean maximum vitrinite reflectance was slightly higher and luminescence intensity at 600 nm was lower for the vitrinite concentrate. Patterns of the alteration of luminescence intensity were similar for vitrinite in the whole-seam channel and the concentrate, as shown in Fig. 2.

For both concentrates there was a significant decrease in mineral matter; in particular, a large decrease in pyritic sulfur was observed. However, there was a small increase in the sulfate sulfur, which could represent a minor amount of deterioration during storage. Sulfate crystals and some desiccation were observed on blocks of the Lower Kittanning (PSOC-1563) during hand picking. Judging from the relatively high concentration of sulfate sulfur in the whole-seam channel (Table 2) it is likely that the sulfate was present at the time of collecting the Lower Kittanning sample. The Ohio #4a

Fig. 1 - Luminescence Alteration Patterns From the hvCb Ohio #4a (DECS-33)
Comparison of Whole Seam Channel Sample and Vitrain Concentrate

Fig. 2 - Luminescence Alteration Patterns From the hvAb Lower Kittanning (PSOC-1563)
Comparison of Whole Seam Channel Sample and Vitrinite Concentrate

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sample shows a much larger increase in sulfate (Table 1) as the vitrinite concentrate has 0.03 % more than the whole-seam channel. However, no sulfate crystals were observed during hand picking. No other signs of deterioration were observed for either sample.

IRRADIATION AND FILM FLOTATION OF POWDERED VITRAIN

Introduction

A BLAK-RAY, 100 watt ultraviolet spotlight was evaluated in an earlier 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 be used effectively 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, it was established that 10, 50 and 100 min of exposure under the UV spotlight was equivalent to 1, 5 and 10 min under the blue-light flux of our optical microscope system, respectively.

Experimental Procedures

As discussed in the last progress report (2), following a warm-up period, the BLAK-RAY UV spotlight is 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 the desired period of time. Then, the top half of the petri dish was placed over the bottom half to secure the particles while they were inverted. Then the undersides of the particles were irradiated for the same time period. 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 particle surfaces as well as for pyrolysis GC/MS analysis.

Measurement of luminescence intensity of the raw and irradiated (photo-oxidized) surfaces of vitrinite used the same microscope instrumentation and general procedure as employed for analysis of polished surfaces (3). However, in order to obtain a sample surface oriented perpendicular to the optical axis of the microscope a small amount of the powdered vitrain was spread onto a level surface of modelling clay and gently pressed into the clay using a leveling press. To avoid contamination, a glass cover slip was placed between the press and the sample. The sample was placed in the environmental cell of the microscope under a rapid flow of dry nitrogen for 5 min before measurements commenced. The surface of individual particles was brought into focus in white light and then luminescence intensity was measured at 600 nm. The mean intensity of twenty different particles is reported.

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 (4), 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 involves separating the material into lyophilic and lyophobic fractions which are then dried and weighed to provide a distribution of wettable coal particles that is analogous to a density distribution (5). The surface tension of the liquid used is varied from 30 to 50

dynes/cm by the addition of anhydrous methanol to twice distilled water.

Results and Discussion

Film flotation distribution curves are shown in Figs. 3-5 for the hvCb Illinois #6 (DECS-24-Vit), hvAb Lower Kittanning (PSOC-1562-Vit) and mvb Splash Dam (DECS-30-Vit) samples irradiated for 10 and 50 min. These preliminary results show that, compared with the unexposed powders, the photo-oxidized particles give flotation results which vary with rank. As anticipated from contact angle measurements (6), the hvCb Illinois #6 shows a decrease in floatability with increasing oxidation (Fig. 3). However, as rank increases, flotation yield of the hvAb Lower Kittanning vitrain after 10 min of irradiation exhibits greater floatability than the unexposed sample, before diminishing significantly after the 50 min irradiation (Fig. 4). For the mvb Splash Dam (Fig. 5), a minor increase in floatability is observed after 10 and 50 min of irradiation. This corresponds to the magnitude of change observed in contact angle and the IR spectrum measurements (6), except that hydrophobicity as measured by film flotation appears to increase rather than decrease. These early results suggest that more may be involved at or near the vitrain surface than a simple increase in oxygen concentration and functionality during photo-oxidation. It may be more important to consider further the type of oxygen functionality (i.e., alcohols, ketones, aldehydes, esters, carboxylic acid, or anhydrides) occurring at the surface and how their relative concentrations may change with irradiation time.

In terms of the surface luminescence measurements shown in Fig. 6, intensity for all the vitrains decrease with increasing level of UV irradiation. However, the degree of

Fig. 3 - Film Flotation of hvCb Illinois #6 (DECS-24-Vit)
Following 10 and 50 min UV Irradiation

Fig. 4 - Film Flotation of hvAb Lower Kittanning (PSOC-1562-Vit)
Following 10 and 50 min UV Irradiation

Fig. 5 - Film Flotation of mvb Splash Dam (DECS-30-Vit)
Following 10 and 50 min UV Irradiation

Fig. 6 - Change in Surface Luminescence Intensity of Vitrinite
Following UV (366 nm) Irradiation

change is quite variable among the vitrains. The Pittsburgh and Ohio #4a seam vitrains show the greatest loss in luminescence intensity with irradiation time, whereas the Illinois #6 and Splash Dam show the least. The two Lower Kittanning vitrains show fairly similar intermediate responses.

These preliminary results suggest that photo-oxidation of powdered samples has a more varied response to measurements of hydrophobicity (film flotation) and luminescence intensity than results from polished surfaces. The reasons for this are not yet entirely clear and may be addressed further when the data set is complete.

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