DOE/PC/93223--T8

SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

**Technical Progress Report for the Period
October to December 1995**

by

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Prepared for the United States
Department of Energy under
Grant No. DE-FG22-93PC93223

Date Published, February 1996

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ABSTRACT

During this report period, polished blocks of coal containing 3-4 mm wide vitrain bands were prepared for contact angle measurements of fresh and photo-oxidized surfaces using the advancing-drop technique. In this test a droplet of distilled water is grown initially on fresh surfaces and then moved across those irradiated in blue light for 1, 5, and 10 minutes. The sequence of growth was recorded on video tape, and the change in contact angle measured relative to position at the air/water/surface interface.

Contact angles were measured on two of the coals collected for this study, (the Ohio #4a (DECS-33) and Lower Kittanning (PSOC-1562) seams) and the results added to those presented in the last quarterly report. Although the new data give additional variation to the sample set, they are consistent with our original observations, i.e., that contact angle is influenced by irradiation time and coal rank. Using the maximum change in contact angle measured between fresh and photo-oxidized surfaces, a linear decrease is observed with increasing rank resulting from 5 and 10 minutes of irradiation. The magnitude of the decrease in contact angle diminishes with increasing rank.

Also during this period, an ultraviolet spotlight was evaluated as a means of irradiating powdered vitrain. This 100 watt, long wavelength (366 nm) ultraviolet lamp is to be used in place of our optical microscope system to establish the influence of surface photo-oxidation on the flotation characteristics of vitrain concentrates. A series of experiments was designed to determine the magnitude of change in the luminescence intensity (at 600 nm measured in the optical microscope) with exposure to the ultraviolet

light with time for vitrinite from different rank coals. We have established that there is a significant decrease in luminescence intensity with time of exposure which diminishes slightly as rank increases. The ultraviolet light appears to provide a level of photo-oxidation that is a factor of 10 lower than that obtained with our optical microscope system. In the coming quarter we will evaluate the influence of ultraviolet light irradiation on changes in floatability and surface oxygen functionality and content.

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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 ($\approx 1.0\text{g}$ 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 additional coal blocks containing vitrain bands (≈ 3 mm wide) were prepared into polished sections for photo-oxidation in blue light for 1, 5 and 10 minutes. Contact angle measurements using the advancing-drop technique were completed for the two remaining coals in our sample set (Lower Kittanning, PSOC-1562 and Ohio #4a, DECS-33). Further, an attempt was made to evaluate a second medium volatile coal (Sewell, DECS-13), but the samples fragmented during preparation and no measurements were made. In addition, preliminary evaluation of a longwave ultraviolet light source for irradiation of powdered vitrains was conducted. The following report summarizes our progress.

PHOTO-OXIDATION STUDIES

Introduction

To complete the measurement of contact angles with respect to irradiation time, polished blocks were prepared for the remaining coals in our samples set, including the Lower Kittanning (PSOC-1562) and Ohio #4a (DECS-33). Also, in an effort to substantiate the apparent rapid increase in surface wettability observed from photo-oxidation of the medium volatile Splash Dam (DECS-30) seam, blocks were prepared from another medium volatile coal (Sewell, DECS-13).

As described in the last quarterly report (1), polished specimens of each coal were subjected to blue-light irradiation at various time intervals corresponding to short, medium and long term photo-oxidation and then contact angle measurements were made using the

advancing-drop technique.

Sample Preparation

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 (600 grit) and alumina slurries (0.3 and 0.05 μm polishing compounds). Between each stage the 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 a cardboard ring 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 sequence described in the last quarterly report (1). Briefly, the surface irradiation technique uses a light flux focused into a 200 μm diameter area in our optical microscope system. A single scribe mark was cut across the vitrain band and, at approximately 200 μm from the scribe mark, successive 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 minutes. 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 until contact angles could be measured.

Contact Angle Measurements

As described previously, contact angle measurements were carried out using a sessile-drop measurement technique in which a droplet of distilled water was grown or advanced across the polished surface of vitrain. The measurements were performed on fresh and photo-oxidized surfaces by placing a droplet on an unoxidized area of the coal and then grown across the irradiated area (1). The entire sequence of growth is recorded on video tape and, contact angle values are subsequently measured at different positions as the droplet advances from the fresh through the photo-oxidized surface.

Results and Discussions

Measurements of contact angle (Figs. 1 and 2) and the time-induced alteration of luminescence intensity during irradiation (Figs. 4 and 5) are reported for the vitrinite of two coals, i.e., Lower Kittanning (PSOC-1562) and Ohio #4a (DECS-33) seams, respectively. As in the case of contact angle results reported in the last quarterly report (1), the new data also show that contact angle values are influenced by coal rank and irradiation time. In general, a decrease in contact angle takes place when the droplet advances into the irradiated area, and the value remains lower than the initial value (unoxidized surface) throughout the 400 μm (0.4 mm) area. The magnitude of the decrease in contact angle increases with increasing time of irradiation. Combining the new data with those presented last quarter (1), Fig 3 illustrates the effect of both rank and irradiation

Fig. 1 - Advancing Contact Angle Measured on Polished Surfaces of Vitrain from the hvAb Lower Kittanning Seam (PSOC-1562)

Fig. 2 - Advancing Contact Angle Measured on Polished Surfaces of Vitrain from the hvBb Ohio #4a Seam (DECS-33)

Figure 1 is a scatter plot showing the relationship between the change in contact angle (ΔCA) and the percentage of carbon in the dry ash fraction ($\%C_{daf}$) for two different mineral separation methods: min10 (filled squares) and min5 (open circles). The y-axis represents ΔCA in degrees, ranging from 0 to 25. The x-axis represents $\%C_{daf}$, ranging from 72 to 90. Two regression lines are shown: a solid line for min10 with the equation $\Delta CA_{10} = -1.357(\%C_{daf}) + 123.47$, $r = -0.87$, and a dashed line for min5 with the equation $\Delta CA_5 = -0.727(\%C_{daf}) + 66.79$, $r = -0.67$. Both lines show a negative correlation between ΔCA and $\%C_{daf}$.

time for the complete sample set using the maximum change in contact angle (i.e., $\Delta CA = CA_{\text{fresh}} - CA_{\text{min}}$). As shown, there is a linear decrease in the change in contact angle with increasing rank resulting from 5 and 10 minute irradiation: The decrease with 10 minute irradiation is significantly greater, especially at lower rank.

Corresponding luminescence alteration patterns for a number of irradiated areas within each time interval for the new coal samples are given in Figs 4 and 5. Individual patterns identified as Area1, Area2, etc. on the graphs are keyed to maps of the irradiated regions (not shown). The alteration patterns for the Lower Kittanning seam and for the 5 minute irradiation sequence for the Ohio #4a seam show very little recovery in luminescence intensity at medium and long exposures (negative alteration) compared with similar rank coals reported last quarter (1). This may correspond to the relatively greater decrease in contact angle observed for these coals in Figs. 1 and 2.

All samples have been returned to refrigerated storage under an argon atmosphere until functional group analyses can be performed using reflectance-mode FTIR. In this regard, the new FTIR equipment has arrived and is being installed and evaluated.

IRRADIATION AND FILM FLOTATION OF POWDERED VITRAIN

The effort needed to photo-oxidize powdered vitrain using our optical microscope system was demonstrated to be prohibitive (2). Consequently, we have begun to evaluate the use of a BLAK-RAY, 100 watt ultraviolet spotlight. This lamp generates a brilliant spot of long wavelength ultraviolet light (reported to be 366 nm) which is slightly lower than the wavelength employed in our optical microscope system (390 - 490 nm). Because of the differences in luminous and thermal energies, a series of tests were conducted to

Fig. 4 - Luminescence Alteration Patterns From Areas Irradiated For the hvAb Lower Kittanning, PSOC-1562

Fig. 5 - Luminescence Alteration Patterns From Irradiated Areas For the hvBb Ohio #4a, DECS-33

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establish the effects of this irradiation on the luminescence intensity of polished surfaces of vitrain with time.

Experimental Procedure

The spotlight was fixed in a ring stand and leveled so that the area of maximum incident luminescence could be determined visually at different focal lengths by illuminating paper containing a phosphor. Following a two hour warm-up period small, freshly polished blocks of coal containing vitrain bands were exposed to the light for different time intervals up to a total of 40 minutes. After each exposure the luminescence intensity of the vitrain surface was measured under a nitrogen atmosphere using our standard microscope system and procedure (3). Two measurements were made on the surface, one from an irradiated area and the other from an adjacent area that was masked from exposure to the ultraviolet light (control). These measurements were made $\approx 400 \mu\text{m}$ apart along bedding and following an east-west scribe mark. A piece of card stock was used to mask off half the area above or below the scribe mark, while the other half was exposed to the ultraviolet light. In this manner, the effect of the ultraviolet irradiation on the vitrinite of different coals could be evaluated separately from normal variations of luminescence intensity within vitrinite.

Two experiments were conducted with distance between the coal surface and the lamp at 5.7 and 3.2 cm. These distances provide a surface area suitable for the irradiation of powdered vitrinite, with a minimum of light dispersion at the edges of the affected area. For each experiment, the coal blocks were mounted on a glass slide with modelling clay and the polished surface leveled to the same height in a mounting press. Luminescence

intensity was measured in what were to be the masked and unmasked areas under a flow of nitrogen. Then, with the mask in place, each sample was exposed for a set amount of time to the ultraviolet light, following which new intensity measurements were taken. Repeated exposures and luminescence intensity measurements were made on adjacent areas of the surface up to 40 minutes. Exposure times are cumulative with the maximum duration of any irradiation being 10 minutes.

Results and Discussion

In an initial experiment with a distance of 5.7 cm between coal surface and the lamp, polished blocks of the Ohio #4a (hvBb, DECS-33), Lower Kittanning (hvAb, PSOC-1563) and Splash Dam (mvb, DECS-30) were used to establish differences in coal rank. Fig. 6 shows the measured difference in luminescence intensity between the masked (control) versus irradiated surface for the three coals. Data points from the masked surface are provided with error bars based on standard deviation about their mean. As can be seen, there was significant variation in the measurements made on the Ohio #4a and some instances where the control surface was inadvertently exposed to ultraviolet light, making it difficult to determine whether changes in luminescence intensity with time are statistically important. However, measurements made on the Lower Kittanning and Splash Dam vitrain samples demonstrate that for these vitrains ultraviolet irradiation using the BLAK-RAY spotlight progressively decreases the measured luminescence intensity at 600 nm, particularly after 10 minutes of exposure.

In a second experiment, where the distance between the coal surface and lamp was reduced to 3.2 cm, the Illinois #6 (hvCb, DECS-24) was substituted for the Ohio #4a in

Fig. 6 - Influence of Exposing Various Coals to 366 nm Light From 5.7 cm on Luminescence Intensity Measured at 600 nm

the analysis set. It was anticipated that by reducing the distance an increase in luminous intensity might be experienced thereby intensifying the effect of photo-oxidation.

However, as seen in Fig. 7, little effective difference in the level of change in the luminescence intensity was obtained compared with the earlier experiment (Fig. 6). A significant decrease in luminescence intensity over time is found for the Illinois #6 and Lower Kittanning samples, whereas only a slight decrease was observed for the Splash Dam.

More variation was observed in the luminescence intensity measured from the control surface at closer range for the three coals (Fig. 7). This may be attributable to the experimental conditions. In the case of our microscope system, red and infrared wavelengths are filtered from the light source in order to reduce thermal damage. This is not the case with the ultraviolet lamp; the sample surface is close to the hot lamp and no wavelengths are filtered from the system. To determine the potential for thermal oxidation of the coal from the lamp, a fine unsheathed K-type thermocouple was fixed to the surface of coal and exposed to the ultraviolet light source at the two distances (i.e., 5.7 and 32. cm). Fig. 8 shows that within the first 2 to 3 minutes there is a very rapid temperature rise, followed by a steady low rate of increase out to 10 minutes (the longest period of exposure). The important observation is that there is a significantly lower temperature rise and maximum temperature at a greater distance from the lamp and, therefore to avoid the potential of thermal oxidation an increased distance from the lamp is desirable.

The progressive decrease in luminescence intensity suggests that exposure to this ultraviolet light may indeed be photo-oxidizing the coal surface. Diminished luminescence

Fig. 7 - Influence of Exposing Various Coals to 366 nm Light From 3.2 cm on Luminescence Intensity Measured at 600 nm

Fig. 8 - Temperature Increase Measured on Coal Surfaces During Irradiation With
the BLAK-RAY Longwave (366 nm) Ultraviolet Spot Light

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intensity is a consequence of both natural weathering and storage deterioration of coals (4). However, for this study it is important to correlate the degree of photo-oxidation that is occurring from the spotlight with respect to our optical microscope system, because it is luminescence intensity as measured under the optical microscope that will form the bases of our correlation with oxidation, contact angle measurements and flotation yields. In comparing the degree of change in luminescence observed from these experiments with the changes found during luminescence alteration measurement using the microscope system, we have determined that (on average) there is approximately a factor of 10 less change in intensity with the BLAK-RAY UV lamp. Thus, to obtain a comparable level of surface photo-oxidation, irradiation times may need to be increased ten times using the ultraviolet spotlight. Although additional comparative test must be made to substantiate the influence of the ultraviolet lamp, current results look promising and will be pursued.

PUBLICATIONS

The following abstract was submitted to and received by the program secretary of the Pittsburgh Coal Conference to be held September 3-7, 1996 in Pittsburgh, Pennsylvania.

THE INFLUENCE OF PHOTO-OXIDATION ON THE WETTABILITY OF VITRINITE FROM BITUMINOUS RANK COALS

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Luminescence photometric techniques were employed to alter the surface chemistry of vitrinite from bituminous coals in order to determine the kinetic effects of surface oxidation on coal wettability/cleanability. Blocks and particulate concentrates of vitrinite were prepared from six coals ranging in rank from high volatile C to medium volatile bituminous. Block samples were photo-oxidized under light of 390-490 nm wavelength for various time intervals and examined for specific changes in surface chemistry and wettability. Particulate samples were irradiated under ultraviolet light (366 nm) and then tested for changes in bulk flotation. Analytical results from reflectance-mode FTIR, Scanning Transmission X-ray Microscopy and Secondary Ion Mass Spectrometry show that blue-light irradiation of the vitrinite surfaces results in a photo-oxidation, with increasing aromatic carbonyl and hydroxyl groups and decreasing methyl group concentration with irradiation time. Contact angle measurements on fresh and photo-oxidized vitrinites show that increasing irradiation time increases surface wettability, but the magnitude of change decreases with increasing coal rank.

REFERENCES

1. Mitchell, G.D., Polat, H., Davis A. and Chander, S. (1995). Surface Properties of Photo-Oxidized Bituminous Coals, DOE Technical Progress Report for the Period July to September, 1995, No. DOE/PC/93223--8.
2. Mitchell, G.D., Davis A. and Chander, S. (1995). Surface Properties of Photo-Oxidized Bituminous Coals, DOE Technical Progress Report for the Period April to June, 1995, No. DOE/PC/93223--7.
3. Mitchell, G.D. and Davis A. (1993). Surface Properties of Photo-Oxidized Bituminous Coals, DOE Technical Progress Report for the Period September to November, 1993 No. DOE/PC/93223--1.
4. Mitchell, G.D., Davis, A. and Rathbone, R. (1991). The Use of Vitrinite Fluorescence as a Measure of Changes in Coal Thermoplasticity and Weathering. Proc. 50th Ironmaking Conf., Washington, D.C., Iron & steel Soc. AIME, pp. 199-206.