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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, irradiation (photo-oxidation) of all six vitrain concentrates for three different time periods (10, 50 and 100 min) using the BLAK-RAY ultraviolet lamp was completed along with film flotation and surface luminescence measurements for each condition. Flotation results from photo-oxidized powdered vitrains appear to be contrary to earlier results obtained from contact angle measurements on polished surfaces. Some of the more strongly photo-oxidized powders, particularly for hvAb and mvb coals, exhibit greater hydrophobicity. The changes in hydrophobicity as well as a measured decrease in surface luminescence with increasing irradiation time, clearly shows that UV irradiation has had an influence on surface properties. The reasons for these observations are not yet entirely clear; however, several plausible explanations are offered which can be investigated during the remainder of this project.

There is some possibility that increasing exposure to the UV source may cause mobilization of aliphatic compounds (oils) from the fresh fracture surfaces of vitrain. These compounds, once exuded onto the surface could act like a natural flotation collector that would both increase particle hydrophobicity and may obscure the surface from further oxidation. Because most aliphatic compounds do not luminesce, their presence on the surface would reduce measured luminescence. A second possible explanation is that the types of oxygen functional groups which form during UV irradiation may inhibit or promote hydrophobicity depending upon their concentration.

In an attempt to resolve these issues several analytical tests will be undertaken.

Pyrolysis GC/MS will be used to investigate whether photo-oxidation of bulk vitrains was sufficiently severe with increasing UV irradiation. Reflectance-mode FTIR will be used to measure changes in surface chemistry for some of the irradiated powdered vitrains. Based upon our experiences with measurements on polished surfaces, this approach should provide information concerning not only the extent of surface oxidation, but also the possibility of any increase in the concentration of surface aliphatic CH_x groups resulting from exudations.

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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 photo-oxidation of six powdered vitrains were completed for periods of 10, 50 and 100 min using a longwave ultraviolet light source. These times correspond to irradiation periods of 1, 5 and 10 minutes, respectively, using our optical microscope system. Measurement of luminescence intensity and film flotation of the raw and photo-oxidized powders were completed. The following report summarizes our progress.

IRRADIATION AND FILM FLOTATION OF POWDERED VITRAIN

Introduction

A BLAK-RAY, 100 watt long wavelength ultraviolet spotlight (reported to be 366 nm) was evaluated in an earlier progress report for photo-oxidizing powdered vitrains (1). Empirical results suggested that the spotlight could be used effectively to photo-oxidize the polished surface of vitrinite in a manner similar to that induced under the optical microscope, except that, being weaker, longer irradiation times would be required. It was established that 10, 50 and 100 min of exposure under the UV source was equivalent to 1, 5 and 10 min, respectively under the blue-light flux of our optical microscope system.

Experimental Procedures

As discussed in previous progress reports (2,3), a monolayer of powdered vitrain ($<0.42 \text{ mm} > 0.15 \text{ mm}$) was spread out on the outside bottom half of a glass Petri dish and exposed to the UV-light for the desired time period. 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. For a typical 100 min irradiation this procedure required ≈ 29 h. A few milligrams of the original sample and of the irradiated materials were set aside for measurement of luminescence intensity of the particle surfaces as well as for pyrolysis GC/MS analysis.

Film flotation was conducted on the powdered samples by placing a monolayer of about 0.2 g of coal 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 were 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 (4). The surface tension of the liquid used was varied from 30 to 50 dynes/cm by the addition of anhydrous methanol to twice-distilled water.

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 (5). However, to obtain a level surface oriented perpendicular to the axis of the microscope a small amount of the powdered vitrain was gently pressed into modelling clay using a leveling press. A glass cover slip was placed between the press and the sample to avoid contamination. 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.

Results and Discussion

Film flotation distribution curves are shown in Figs. 1-6 for the six vitrinite concentrate samples prepared during this study and for all conditions of UV irradiation (0, 10, 50 and 100 min). Inspection of these flotation curves suggests some apparently erratic behavior with respect to anticipated results, i.e., some of the more strongly photo-oxidized powders appeared to exhibit greater hydrophobicity. This is contrary to earlier results of contact angle measurements on polished surfaces which showed diminished hydrophobicity with increasing photo-oxidation (6). Duplicate film flotation analyses performed on two of the concentrates (Fig. 7) suggests some moderate variability in the results, but generally the technique is repeatable and appears to be sensitive enough to show differences exceeding 5% flotation.

Of the film flotation tests performed, only those obtained from the hvCb, Illinois #6 (DECS-24-Vit) show a decrease in floatability with increasing photo-oxidation (Fig. 1), but only for powders irradiated for 0, 10 and 50 min. Following 100 min of photo-oxidation, floatability increased to a point intermediate between the raw flotation curve and those produced after irradiation at 10 and 50 min. The hvBb Ohio #4a (DECS-33-Vit) exhibited a similar relationship but only at higher surface tension (>40 dynes/cm, Fig. 2); at lower surface tensions little variability in percent float is observed. For the powdered vitrains from hvAb and mvb coals (Figs. 3 - 6), increased levels of hydrophobicity were recorded

Fig. 1 - Film Flotation of hvCb Illinois #6 Vitrinite Concentrate (DECS-24-Vit)⁸
Following 0, 10, 50 and 100 min UV Irradiation

Fig. 2 - Film Flotation of hvBb Ohio #4a Vitrinite Concentrate (DECS-33-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Fig. 3 - Film Flotation of hvAb Lower Kittanning Vitrinite Concentrate (PSOC-1562-Vit)

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Following 0, 10, 50 and 100 min UV Irradiation

Fig. 4 - Film Flotation of hvAb Lower Kittanning Vitrinite Concentrate (PSOC-1563-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Fig. 5 - Film Flotation of hvAb Pittsburgh Vitrinite Concentrate (DECS-23-Vit)

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Following 0, 10, 50 and 100 min UV Irradiation

Fig. 6 - Film Flotation of mvb Splash Dam Vitrinite Concentrate (DECS-30-Vit)
Following 0, 10, 50 and 100 min UV Irradiation

Fig. 7 - Repeatability of Film Flotation for Illinois #6 and Splash Dam Samples

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for all of the 100 min irradiated concentrate samples and even for some of the 10 and 50 min irradiated samples.

Clearly, UV irradiation of powdered samples does not produce results corresponding to those obtained from photo-oxidation of polished surfaces. However, it can not be argued that irradiation has had no effect because significant changes in surface hydrophobicity are observed, although in an unexpected direction. In addition, measurements of surface luminescence (Fig. 8) demonstrate that some change in surface properties has occurred that tends to decrease luminescence intensity (3).

One explanation for these results involves is that aliphatic compounds (oils) within the coals have been mobilized as a result of irradiation. Mobile "bitumens" can be observed as surface films on the mined faces of coal exposed to sunlight and have been observed during blue-light irradiation under the optical microscope (7). If oils are exuded from the fracture surfaces during UV irradiation of powdered vitrains they would act very much like a natural flotation collector by providing a more hydrophobic surface and may, to some extent counter any surface oxidation. Because most aliphatic compounds have little or no luminescence, these exudations could also reduce the surface luminescence. Presumably, the longer the exposure, the greater would be the amount of exudation and the lower the luminescence intensity. The natural fracture surfaces present in the powdered vitrain samples are different from polished surfaces which have been closed or obscured during the polishing process, thus explaining the different observations between polished and natural fracture surfaces.

Another explanation for the observed results was presented in the last quarterly

Fig. 8 - Change in Surface Luminescence Intensity of
Vitrinite Following UV (366 nm) Irradiation

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report (3) in which we suggested 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 also the type of oxygen functionality (i.e., alcohols, ketones, aldehydes, esters, carboxylic acid, or anhydrides) created at the surface and changes in their relative concentrations with irradiation time. In other words, although photo-oxidation increases overall with increasing severity of irradiation, some oxygen functionalities may inhibit whereas others may promote hydrophobicity.

It is likely that one or both of these explanations has some merit. However, the question is whether remaining planned analyses, which includes pyrolysis GC/MS, will be able to address this problem. The likelihood of pyrolysis GC/MS providing an answer is uncertain because the technique is really a bulk analytical technique. Surface oxidation would need to be relatively severe with respect to the total mass for significant changes to be detected. To test this premise, three of the powdered vitrains [Illinois#6 (DECS-24-Vit), Lower Kittanning (PSOC-1562-Vit) and Splash Dam (DECS-30-Vit)] await irradiation and pyrolysis. If the photo-oxidation of powdered vitrain has been inhibited by a minor, uneven film resulting from exudation, then the pyrolysis technique probably will not show any significant differences resulting from the duration of UV irradiation.

To address the possible variability of oxygen functionality resulting from irradiation, two approaches will be used. The first will involve the evaluation of reflectance FTIR subtraction spectra and their derivative forms in an attempt to resolve the component oxygen functionalities. These will be obtained from polished surfaces irradiated by blue-light. Then, the reflectance-mode FTIR will be used to evaluate the

fracture surfaces of some irradiated powdered vitreins. As has been demonstrated during this project, this technique should be able to provide information on the relative change in surface concentration of not only the oxygen functional groups but also any change in the aliphatic CH_x group concentration.

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