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SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

**Technical Progress Report for the Period
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by

Gareth Mitchell and Alan Davis

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PENNSTATE

Coal and Organic Petrology Laboratories

(814) 865-6544

Pennsylvania State University
University Park, PA 16802

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ABSTRACT

Five of the eight coals to be studied in this project have been selected on the basis of economic importance as well as geologic and chemical histories. Plans have been initiated to collect the first sample, a Pittsburgh seam coal from southwestern Pennsylvania. However, we have as yet not received permission from the mine to collect our working face sample. In addition, preliminary work was completed on development and testing of a procedure to photo-oxidize vitrinite containing coal blocks using the optical microscope.

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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 flotability 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 to 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 initial performance period progress was made in several important areas. Planning for some of the coals that will be needed for this study was initiated and attempts to collect the first fresh coal sample were made. Also, a preliminary procedure was developed and tested for the photo-oxidation of vitrinite. The following is a brief report of these investigations.

COAL SELECTION

An effort was made to identify bituminous coals that might generate few problems with regard to interpretation of results. It is well known that there are minor variations in the optical properties of vitrinite-group macerals. For example, desmocolinite typically provides a greater level of fluorescence emissions and lower reflectance values within any given coal than telocollinite. However, unlike desmocolinite, telocollinite is found in relatively broad bands that generally are free of other macerals. This is the primary reason that telocollinite was selected for this study. Coals that are associated with marine-influenced sedimentation also tend to show lower vitrinite reflectance and sometimes higher fluorescence emissions. Speculation as to the cause(s) of this phenomenon has centered on the hypothesis that "bitumens" or bacterial or algal lipids have accumulated in the vitrinite structure. The concentration of relatively low molecular weight materials from the degradation products of bacteria would have been favored under marine or anoxic conditions.

These considerations were factored into the process of selecting our initial coal

sample. As reported by Edmunds et al. (1979), Pennsylvanian age coals from the Monongahela Group are entirely nonmarine. One of these, the Pittsburgh seam, from southwestern Pennsylvania is an economically important coal that is being mined and beneficiated as a metallurgical product. It is also a coal that has been and is being studied world wide. Consequently, in late October we began discussions with U.S. Steel Mining Co., Inc. to obtain a fresh working-face sample of Pittsburgh seam coal from their Maple Creek Mine. Unfortunately, we are still waiting for notification of a specific date to collect the sample.

It is not our intention to eliminate marine-influenced coals from the study. In fact, our plan is to collect pairs of coals from seams of large lateral extent that may have been deposited under both marine and fresh water conditions in different areas. Two such pairs that we are investigating include the Lower Kittanning seam of the Allegheny Group coals in Pennsylvania and the Illinois No. 5 or No. 6 coals of the Kewanee Group (Carbondale formation) in Illinois. If it is possible to collect these samples, our intended sample set of eight coals will contain only three nonmarine bituminous coals from two different geologic basins. Although specific plans have not been made for three higher rank bituminous coals (medium and low volatile), it is likely that these samples will be taken from the marine-influenced New River or Pocahontas formations of southern West Virginia and/or the Allegheny Group of southern Pennsylvania. We believe that this plan will provide a diverse group of economically important coals that represent different geologic and chemical histories.

PHOTO-OXIDATION TECHNIQUE

Introduction

During this first quarter a technique for photo-oxidation of coal blocks containing large bands of telocollinite was investigated. One of the main concerns about using the optical microscope as a instrument to photo-oxidize coal surfaces, is the time that may be required to irradiate each 1 mm² area and the location of that area for the other surface characterization techniques. One to one-half square millimeter has been determined to be the effective area for most of the surface characterization techniques which will be employed in this study. Furthermore, all of the prior surface oxidation experiments conducted in this laboratory and the quantitative measurement of the alteration of fluorescence emissions have been performed by exposing relatively small areas (<50 µm diameter) of vitrinite to blue- or ultra-violet light irradiation. Therefore, our initial efforts will be directed at using the optical microscope as an instrument to photo-oxidize vitrinite. This will preserve the integrity of the relationship between quantitative measurement of fluorescence and surface alteration at the expense of sample (surface) preparation time. Once a clear relationship has been established between optical measurements and surface properties, we will begin to explore more efficient means of photo-oxidation.

Experimental

During the development of a preliminary procedure, small particles of coal (15x15x15 mm) were cut from the interior portion of a relatively large block of the Pittsburgh seam collected and stored under argon since 1990. These particles contained a 5 mm wide band of vitrain, and one surface was polished using 120, 400, 600 grit papers,

0.3 μm and 0.05 μm alumina slurries. The samples were gently wiped clean with distilled water and a cotton ball. No detergent was used. Samples were desiccated overnight under vacuum.

A Leitz Orthoplan MPV-II microscope photometer system was used for photo-oxidation of the coal as well as for the measurement of fluorescence intensity. This system generates excitation energy from a 100-watt high-pressure mercury-arc lamp which is passed through a heat filter (suppressing red and infrared wavelengths) and then through a series of interference filters. The excitation light of wavelengths between 390-490 nm is reflected by a 510 nm reflection short-pass dichromatic beam splitter and condensed onto the sample through a 50X NPL FLUOTAR air objective. Part of the absorbed excitation energy is released as fluorescence emission at longer wavelengths than the absorbed light. The fluorescence emission is passed back through the dichromatic beam splitter, and a 515 nm long-pass barrier filter blocks any remaining reflected excitation light. The emitted fluorescence passes through the measurement filter of 600 nm with a 60 nm halfwidth. The optical signal is transformed into an electronic signal by an EMI 9558 photomultiplier and amplified.

Calibration of the photoelectric system is accomplished using a masked uranyl glass standard and a neutral density filter of 9.3% transmittance to reduce the intensity of the standard to a level comparable to vitrinite. The photomultiplier reading obtained from the uranyl glass is adjusted to a voltage output of 1.000 ± 0.002 v before any measurements are made.

Two types of fluorometric measurements are made on each sample, i.e., mean

fluorescence intensity and alteration. Before each measurement, an area of vitrinite is moved under the measuring spot using white-light illumination. Then, with all light blocked from the surface, the filter block and mercury-arc illumination is introduced into the light path. At the moment irradiation commences, a photometric reading of emitted fluorescence intensity is taken. Mean fluorescence intensity values are determined by taking the mean of 100 separate readings, whereas fluorescence alteration represents the accumulation of readings from the same area at regular intervals over a period of time (generally 2-10 min) during which photo-oxidation is occurring. Thus, intensity measurements result in a single value, whereas alteration results in a curve.

Results and Discussion

Tests were performed to determine the influence of enlarging the field diaphragm to 100 μm from 50 μm . Using a masked uranyl glass standard of stable fluorescence emission, this change in diaphragm diameter resulted in no significant change in the photoelectron current. Unfortunately, the uranyl glass only has an effective diameter of about 10 μm so the influence of re-absorption of fluorescent emissions from a large area can not be evaluated. Instead, a similar test was performed using areas of vitrinite in one of the coal blocks. The photomultiplier aperture (measuring spot-size) was kept constant at 8 μm diameter. Measurements of fluorescence intensity from adjacent areas of vitrinite using a 100 μm field diaphragm size compared well with measurements made with a 50 μm diaphragm. This enlargement of the field diaphragm will result in a significant time savings during photo-oxidation.

Inspection of the samples in white and blue light using an air objective revealed that

the vitrain band was nearly pure telocollinite. Fluorescence alteration and intensity measurements were made on the test block to determine the suitability of the sample for irradiation. Initial intensity values measured in air showed that the band had an intensity of about 7.9%. This is relatively low compared to the fresh coal value of 14.3% which was measured on all vitrinite types shortly after the sample was collected. However, telocollinite typically gives lower fluorescence values. Alteration tests showed that this Pittsburgh seam coal gave a dual alteration pattern in which fluorescence intensity first decreased and then increased with duration of irradiation. Fluorescence intensity decreased to a minimum value within 3 mins (from 7.0% to 4.6%) and was accompanied by a very faint decrease in surface reflectance.

Another coal blocks was oriented using perpendicular scribe marks cut into the polished surface with a razor blade. An arrowhead was cut into one of these scribe marks to identify the up or north position. An east-west scribe mark was cut into the vitrain band to identify the location of the area to be photo-oxidized. A grid was established in the lower right-hand quadrant beginning 100 μm down (south) from the east-west scribe and 100 μm to the right (east) of the north-south scribe. This was done to eliminate potential interference with the uneven surface created by the scribe marks. Beginning at the upper left hand corner of the grid, the surface was photo-oxidized using blue light and quantitative measurements of emission intensity were made. Initially, it was determined that 2.5 min of irradiation time would be sufficient to reach a minimum fluorescence intensity value. Adjoining fresh areas were moved under the field diaphragm and the new surface was irradiated for 2.5 mins. In this way over a five hour period a 1000 x 1000

µm area was irradiated.

During the process of irradiation some surface features were noted (fractures and the presence of liptinite macerals) and drawn on a diagram of the grid. Initial intensity values were measured in several grid squares, as well. In general, initial fluorescence intensity values were somewhat variable over the irradiated area and tended to be greater toward the south east (lower right-hand corner). Because of the relatively low initial fluorescence intensity values, alteration did not create the noticeable reflectance decrease that was found using the first test section. This response could be due to the age of the sample, and indicates the importance of collecting fresh samples and making the required measurements promptly.

Summary

From these preliminary tests a procedure for the irradiation and photo-oxidation of the surface of vitrinite was developed. Although the present technique is laborious, we believe that it will provide the desired alteration of the surface properties of vitrinite and generate detailed fluorometric information. This initial work seems to confirm our supposition that absolutely fresh and well prepared samples must be utilized in order to achieve the ultimate goal of this project.

References

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