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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, vitrinite concentrate samples were prepared from the Illinois #6 (DECS-24) and Lower Kittanning (PSOC-1562) seam samples that were collected last year. Some of the analytical information on these concentrates are provided. In addition, preparation of a surface-oxidized powdered vitrinite concentrate of the Pittsburgh seam (DECS-23) sample for microflotation experiments and pyrolysis GC/MS was initiated following development of a procedure for the irradiation sequence for this sample.

Our collaborative efforts with Dr. Pigram of the University of New South Wales and Dr. Cody of Argonne National Laboratory have continued. As a result of problems in relocating the irradiated areas prepared for Scanning Ion Mass Spectroscopy (SIMS), a new sample preparation technique was developed. This procedure involves the use of a finder grid that is attached to the coal surface allowing Dr Pigram's group to positively identify the affected area.

A new ultrathinned section of the medium volatile Sewell seam (DECS-13) was prepared for Scanning Transmission X-ray Microscopy (STXM) and analyzed. Preliminary findings suggest the changes in oxygen functionality on the irradiated surfaces (1, 5 and 10 mins) of this coal compare well with that previously reported for the subbituminous Wyodak and high volatile Pittsburgh seam discussed in the last quarterly report. Kinetic data from evaluation of carbon near-edge x-ray adsorption fluorescence spectroscopy (C-NEXAFS) has yet to be completed.

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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 preparation of vitrinite concentrates and blocks from two of the coals collected in June and July, 1994 was completed. Some analytical results have been obtained and are reported here. In addition, the process of irradiating powdered vitrinite concentrate from the Pittsburgh seam sample (DECS-23) has begun. These samples will be used for microflotation and pyrolysis GC/MS experiments.

The last sample supplied to Dr. Paul Pigram of University of New South Wales, Australia was not successfully analyzed because the areas irradiated could not be located. Furthermore, another sample was prepared for STXM (C-NEXAFS) from which results are not yet available. The following report summarizes our progress.

COAL SAMPLING, PREPARATION AND ANALYSIS

Powdered vitrinite concentrates and blocks containing relatively thick vitrinite bands were separated by the technique established and reported in an earlier progress report (1). Briefly, the separation and processing of the vitrinite concentrate is performed under a flow of nitrogen in a glovebox, where all separation, particle size classification and packaging are performed. Samples of the Lower Kittanning seam (PSOC-1562, marine-influenced) and the Illinois#6 (DECS-24) were prepared and are currently being stored in a refrigerator under argon in individual 1 to 2 g lots. Analytical results, although incomplete, are provided in Tables 1 and 2, respectively and are compared with the results from whole seam channel samples.

Further, plans have been made to collect three additional samples in mid-June,

Table 1
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the Lower Kittanning Seam Samples, PSOC-1562

	Whole Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	1.88	1.99
% Ash, dry	13.04	3.60
% Volatile Matter, daf	43.95	40.31
% Fixed Carbon, daf	56.05	59.69
<u>Ultimate Analysis, daf</u>		
% Carbon	81.77	82.31
% Hydrogen	5.98	5.56
% Nitrogen	1.73	1.63
% Total Sulfur	4.45	1.61
% Oxygen (diff.)	6.07	8.89
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	3.54	0.72
% Sulfate Sulfur	0.02	0.08
% Organic Sulfur (diff)	0.31	0.75
<u>Petrography</u>		
Vitrinite, % min.-free	83.6	
Liptinite, % min.-free	6.6	
Inertinite, % min.-free	9.8	
Mean Maximum Vitrinite Reflectance, %	0.77	
Vitrinite Fluorescence Intensity in N ₂ (Uranyl Glass=10)	2.35	
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpm	26,620	
Fluid Temperature Range °C	88	
Free Swelling Index	6	

Table 2
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the Illinois #6 Seam Samples, DECS-24

	Whole Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	13.20	12.87
% Ash, dry	13.39	2.77
% Volatile Matter, daf	47.15	42.98
% Fixed Carbon, daf	52.85	57.02
<u>Ultimate Analysis, daf</u>		
% Carbon	76.27	78.12
% Hydrogen	5.30	5.32
% Nitrogen	1.32	1.26
% Total Sulfur	6.38	3.36
% Oxygen (diff.)	10.73	11.94
<u>Forms of Sulfur, dry</u>		
% Pyritic Sulfur	3.05	0.50
% Sulfate Sulfur	0.29	0.03
% Organic Sulfur (diff)	3.05	2.73
<u>Petrography</u>		
Vitrinite, % min.-free	90.2	
Liptinite, % min.-free	3.0	
Inertinite, % min.-free	6.8	
Mean Maximum Vitrinite Reflectance, %	0.49	
Vitrinite Fluorescence Intensity in N ₂ (Uranyl Glass=10)		
<u>Thermoplastic Properties</u>		
Maximum Fluidity, ddpm	49	
Fluid Temperature Range °C	78	
Free Swelling Index	3	

namely the Banner (hvAb) and Splashdam (mv) seams from Virginia and the Ohio #4a (hvBb) seam from Ohio. These coals, of diverse ranks and deposited under marine-influenced sedimentation, will round out the rank series necessary for this project.

PHOTO-OXIDATION STUDIES

Introduction

During the past performance period the long process of irradiating a powdered vitrinite concentrate of the Pittsburgh seam (DECS-23) was initiated. Also, collaborative work was continued with two external research groups on blue-light irradiated coal samples. Information was provided by Dr. Paul Pigram of the University of New South Wales in Australia following evaluation with Secondary Ion Mass Spectrometry (SIMS), and from Dr. George Cody of Argonne National Laboratory following evaluation using Scanning Transmission X-ray Microscopy (STXM) and Carbon Near-Edge X-ray Absorption Fluorescence Spectroscopy (C-NEXAFS) microanalysis and imaging.

Irradiation of Powdered Vitrinite

A 1.4 g sample of powdered vitrinite from the Pittsburgh seam (DECS-23) and size classified between 40 and 100 mesh (0.42 to 0.15 mm) was selected for preliminary photo-oxidation by irradiation under blue-light for 10, 5 and 1 minutes. Irradiation of such a large sample for 10 minutes was found to be prohibitively time consuming under a light flux focused at 100-200 μm diameter. Consequently, the photo-oxidation procedure has been altered by increasing the diameter of the area of irradiation for a longer time sequence, i.e., 5 mm for 30 minutes. Therefore, the current procedure being employed for the long duration photo-oxidation is to place a single layer of vitrinite particles on a 2.5

cm dish and expose successive ≈ 5 mm diameter areas to blue light for 30 minutes until the total surface area of the vitrinite particles has been irradiated. Even with this change, the procedure remains very time consuming. As yet, the first sample irradiated to 10 mins has not been completed.

Secondary Ion Mass Spectrometry (SIMS) Samples

Information about the sample of Pittsburgh seam vitrinite (DECS-23) prepared for Dr. Pigram (2) and having areas of $100\ \mu\text{m}$ irradiated at different times (1, 5 and 10 mins) for SIMS analysis, was obtained during this quarter. Unfortunately, his laboratory was unable to find the irradiated areas on the surface, because of the weak photo-oxidation and the difficulty in locating $100\ \mu\text{m}$ diameter size spots. In future the technique will be altered by affixing an Alltech (Agar) finder grid directly to the polished coal surface. These copper grids will provide clear markings for $100\ \mu\text{m}$ square areas of coal so that locating the irradiated areas should be improved.

Scanning Transmission X-ray Microscopy (STXM)

In a continuation of work reported in the last progress report (2), a sample of vitrinite from the medium volatile Sewell seam (DECS-13, from West Virginia) was prepared for STXM and C-NEXAFS analysis. This particular sample was selected because block samples had been stored under argon since the time of collection (1990) and it was closest in rank and geography to the medium volatile coal we have selected for this project (Splashdam seam). Along with the high volatile Pittsburgh seam (DECS-23) and subbituminous Wyodak (DECS-26) evaluated earlier (2), the addition of the medium volatile coal will complete our evaluation of this technique as a means of measuring

surface oxidation induced by blue-light irradiation. These three ranks of coal possess different fluorescence alteration patterns (i.e., positive, dual and negative with increasing rank) during photo-oxidation and presumably interact with oxygen in different manners.

A new ultrathinned section of the medium volatile Sewell seam vitrinite (DECS-13) was prepared and irradiated for Scanning Transmission X-ray Microscopy (STXM). Preliminary findings suggest that the change in oxygen functionality on the irradiated surfaces (1, 5 and 10 mins) of this coal compared with that previously reported for the subbituminous Wyodak and high volatile Pittsburgh seam, i.e., hydroxyl and carbonyl functionalities increase whereas methyl group concentration decrease (2). However, the kinetic data from evaluation of carbon near-edge x-ray adsorption fluorescence spectroscopy (C-NEXAFS) has yet to be completed.

REFERENCES

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