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SURFACE PROPERTIES OF PHOTO-OXIDIZED BITUMINOUS COALS

**Technical Progress Report for the Period
December 1993 to March 1994**

by

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ABSTRACT

During the report period, channel and block samples of the Pittsburgh seam (DECS-23) were collected from Consolidation Coal Company's Bailey Mine and were subsequently processed and partly analyzed. Powdered vitrinite concentrates were prepared from the block samples in a nitrogen-filled glovebox, and small coal blocks containing ≈ 5 mm thick vitrain bands were cut from the larger sections. Results of proximate, ultimate and petrographic analyses showed that the concentrate contained 97% (by volume, dmmf) vitrinite and about 3% (by weight) pyrite. On the basis of fluorescence intensity and alteration measurements, the coal and concentrate appeared to be extremely fresh, exhibiting no signs of oxidation or deterioration. A polished surface of one of the small coal blocks was prepared and photo-oxidized in order to evaluate reflectance-mode FTIR equipment and techniques, as well as for the measurement of contact angles. Photo-oxidation of this sample was accomplished by blue-light irradiation. In addition, arrangements are being made for the collection of two Lower Kittanning seam coal samples (marine- and freshwater- influenced) from northwestern Pennsylvania.

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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 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

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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 our first coal sample was collected, processed and partly analyzed. Powdered vitrinite concentrates were prepared and small coal blocks containing vitrain bands were cut from larger sections. One of these blocks was prepared and photo-oxidized under blue-light irradiation for evaluation and testing of the reflectance-mode FTIR equipment. Also, arrangements are being made for the collection of marine- and freshwater- influenced Lower Kittanning samples. These pairs are of interest because of the relative differences in reflectance, fluorescence and chemical properties of their vitrinites that may influence photo-oxidation. The following is a brief report of these investigations.

COAL SAMPLING, PREPARATION AND ANALYSIS

Sampling

Our attempt to collect a Pittsburgh seam sample from U.S. Steel Mining Co., Inc. was abandoned when it was learned in January that the Maple Creek Mine was closed. Instead, arrangements were made to collect a fresh working-face sample from Consolidation Coal Company's Bailey mine in Washington County, Pennsylvania. On February 2nd, 1994 a 227 kg (500 lb) channel sample and about 14 kg (30 lb) of coal blocks were collected from a working face exposed for less than 10 hr. The channel sample (DECS-23) was collected for a different project, but will provide characteristic information about the whole seam as background for the studies employing the vitrinite concentrates separated from the block samples. The latter samples were collected

specifically for this project. All samples were transported to the mine surface and placed under argon gas for initial storage. The block samples were placed in foil multilaminate bags with an excess of argon and stored at room temperature until manual separation of vitrinite could be undertaken.

As discussed in our first quarterly report (1), we are interested in collecting pairs of coals from seams of large lateral extent that may have been deposited under marine and freshwater conditions in different areas. To this end, we are attempting to locate active mines in which the Lower Kittanning seam may be freshly exposed in Lawrence, Butler or Venango counties. This geographic area contains a relatively sharp facies change between marine and freshwater shales associated with the Lower Kittanning coal. A site trip is being planned for early May to identify mines from which we may obtain fresh samples.

Sample Preparation

For the Pittsburgh seam sample, each bag of blocks was handled separately. One bag was placed in the glovebox which was successively evacuated and filled with nitrogen three times. Then, under a positive pressure of constantly-flowing nitrogen, the bag was opened, and each block inspected for vitrain bands greater than 3 mm in thickness. Small particles of vitrain were removed, inspected for purity and rejected if other lithotypes or minerals could be detected. Fine powder and particles were collected and placed into glass vials. This procedure required a minimum of a day for each bag. The vitrinite concentrate collected from each bag was sealed under nitrogen in a glass vial and sealed in a small foil bag in the glovebox before being removed and placed in refrigerated

storage. A total of about 40 g of powdered vitrinite concentrate was collected from the blocks. Also, several small blocks containing ≈ 5 mm vitrain bands were separated and preserved for preparation of polished surfaces.

The vitrinite concentrate was processed and subdivided in the glovebox in the following manner. The contents of all containers were combined, crushed by hand to pass a 40 mesh (420 μm) screen and homogenized using a micro-riffler. All further subsamples were obtained using the micro-riffler. Approximately 2 g of the concentrate was set aside for the preparation of a petrographic briquette (also performed inside the glovebox) and an 8 g sample was separated for proximate and ultimate analyses. The remaining concentrate was divided into two parts. Because microflotation and contact angle (by interface partitioning) measurements require a 1 g sample of limited particle size distribution, half of the concentrate was screened to remove the -100 mesh (<149 μm) fraction and then was subdivided into ≈ 1.5 g subsamples (40 X 100 mesh). The other half of the concentrate was divided into 2.0-2.5 g subsamples (-40 mesh). All subsamples were placed into separate glass vials, purged with nitrogen, sealed in nitrogen-filled foil laminate bags in the glovebox and are now stored under refrigeration.

Analysis

Table 1 presents the proximate, ultimate and petrographic analyses of the whole-seam channel sample and vitrinite concentrate. About 60% of the total sulfur of the channel sample is pyritic, occurring either finely dispersed throughout the organic matrix or as cleat fillings. As a result of hand picking the vitrinite concentrate, the cleat pyrite was avoided, but the dispersed form was not. Pyrite accounts for most of the ash (3.3%)

Table 1
Comparison of Whole Seam Channel and Vitrinite Concentrate
from the Pittsburgh Seam Sample, DECS-23

	Whole Seam Channel	Vitrinite Concentrate
<u>Proximate Analysis</u>		
% Moisture, as-received	2.00	1.58
% Ash, dry	9.44	3.33
% Volatile Matter, daf	43.53	41.38
% Fixed Carbon, daf	56.47	58.62
<u>Ultimate Analysis, daf</u>		
% Carbon	81.95	82.67
% Hydrogen	5.63	5.57
% Nitrogen	1.49	1.54
% Total Sulfur	4.27	2.49
% Oxygen (diff.)	6.66	7.73
<u>Petrography, dmmf Vol. %</u>		
% Vitrinite	79.4	96.7
% Liptinite	6.9	1.1
% Inertinite	13.7	2.2
Mean Maximum Vitrinite Reflectance	0.73	0.77
Vitrinite Fluorescence Intensity in N ₂	3.18	2.78

yield from the concentrate. In terms of the maceral analysis, the concentrate contained 97% (by volume, dmmf) vitrinite.

The mean maximum vitrinite reflectance is slightly higher for the concentrate as compared to the channel sample. This resulted from the selection of only the thicker vitrain bands, which are composed of telocollinite (Fig. 1).

Measurement of fluorescence properties of the whole-seam channel and of the vitrinite concentrate have been completed. As described in the previous quarterly report (1), measurement of vitrinite fluorescence intensity represents the mean of 100 individual readings. As shown in Table 1, the fluorescence intensity of the whole-seam channel (measured in a nitrogen atmosphere to avoid photo-oxidation) was slightly higher than that of the vitrinite concentrate. The reason for this difference is that fluorescence properties of different vitrinite types within a given coal also are different. This is illustrated in Fig. 2, which shows the alteration of fluorescence intensity in air for two types of vitrinite (telocollinite and desmocollinite). Telocollinite has a lower initial intensity at time zero, takes longer to reach a minimum fluorescence and does not recover to as high a level as desmocollinite. Thus, readings taken on desmocollinite would increase the overall fluorescence intensity of the whole-seam channel sample compared with the vitrinite concentrate.

Compared with fluorometric results from other Pittsburgh seam samples (2), the high level of vitrinite fluorescence intensities observed for DECS-23 channel sample and concentrate suggests that the sampling and preparation techniques employed were successful in avoiding coal deterioration.

Fig. 1 - Comparison of Mean Maximum Vitrinite Reflectance Distributions of Whole Seam and Vitrinite Concentrate of DECS-23

Fig. 2 - Fluorescence Alteration in Air of Vitrinite Types in
Whole Seam and Vitrinite Concentrate of DECS-23

PHOTO-OXIDATION

Introduction

A polished sample of DECS-23 was prepared and irradiated (photo-oxidized) using blue light (390-490 nm) in order to evaluate our methods for reflectance-mode FTIR and contact angle measurement. However, initial testing of the Bio-Rad/Digilab FTIR spectrometer which supports the UMA 300A infrared microscope accessory we will be using demonstrated that a significant alignment problem existed between the laser and the area of measurement in the specimen plain. Arrangements have been made for the equipment to be serviced. In the meantime, the DECS-23 sample has been submitted to Dr. Rui Lin of UNOCAL along with another Pittsburgh seam sample (DECS-12, sampled in 1990) for initial evaluation of functional-group chemistry of areas photo-oxidized by various techniques in our and UNOCAL's laboratories.

Procedures

Polished samples were cut from the interior of relatively large blocks of two Pittsburgh seam samples collected and stored under argon since 1990 (DECS-12) and 2/1994 (DECS-23). Approximately 5 mm wide bands of vitrain were located and cut into small blocks $\approx 14 \times 20$ mm. Surfaces were polished by hand using 320, 400, 600 grit papers, 0.3 μm and 0.05 μm alumina slurries. The samples were cleaned and then desiccated overnight under vacuum.

Each vitrain block was oriented using thin scribe marks cut into the polished surface. An arrow head was cut to identify the up or north position placement relative to the microscope. An east-west scribe mark was cut into each vitrain band so as to identify

the location of irradiated areas by quadrant. A map of the surface including imperfections, minerals, fractures, etc. near the areas of irradiation was generated by microscopic examination.

Two areas were irradiated on each sample using different protocols, 1) with the field diaphragm fully open at $\approx 280\text{ }\mu\text{m}$, and 2) a 3 by 3 matrix of $100\text{ }\mu\text{m}$ diameter areas. The reason for this, is to understand and measure the relative difference in extent of photo-oxidation by these methods. Irradiation of the larger area, although more efficient in terms of time, requires that the light energy be dispersed, possibly resulting in less effective photo-oxidation.

Irradiation, in all cases, was performed using blue light (390-490 nm) in air for at least 10 minutes per area. During the course of irradiating some of these areas, fluorescence intensity values (at 600 nm) were recorded. Following irradiation, a visible darkening of the surface of the 3 by 3 matrices was observed under white-light illumination using an air objective, whereas for the large, single areas discoloration was barely visible.

After irradiation, the small coal blocks were packaged separately so that the surfaces were protected. Samples were sealed in foil laminate bags under argon for shipment to UNOCAL, Brea, CA. When Dr. Lin's analyses have been completed, the samples will be returned for reflectance-mode FTIR and contact angle measurements in our laboratory.

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