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ADVANCED SPECTROSCOPIC ANALYSIS OF COAL SURFACES DURING BENEFICIATION

Fossil Energy Quarterly Report

July 1, 1989 - September 30, 1989

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Date Transmitted: October 1989

Prepared for: Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Project Monitor: J. Balzarini

*Operated for the U. S. Department of Energy by Iowa State University under
Contract No. W-7405-ENG-82.

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ABSTRACT

Preliminary FTIR spectra are reported on coals undergoing flotation where enhanced recovery was achieved by ultrasonic or chemical treatments. The spectra of sonicated coals indicate that ultrasonic treatment (10 kHz Swen Sonic) reduces the surface oxidation of heavily oxidized Illinois #6 coal but also increases slightly the oxidation of unoxidized coal. Spectra of chemically treated coal indicate that a higher mineral concentration is present on or near the surface of float coal suggesting that a slime might be present.

Spectra are reported for coal-, mineral-, and crystal-derived pyrite which show a strong absorbance band at 420 cm^{-1} . Spectra of eight Argonne Premium Coal Library specimens have been examined in the 420 cm^{-1} spectral region and are found to have numerous overlapping bands. This observation indicates that several advanced data processing methods will be required to quantitate pyrite concentrations in coal. One method has been explored which is likely to be useful. In this method, both magnitude and phase photoacoustic signals are processed in order to obtain more spectral contrast in coal data.

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Objective

The purpose of this project is to develop and test new FTIR and other spectroscopic methods for characterizing coal properties related to advanced coal cleaning processes.

Introduction

Collaboration began during the quarter with coal beneficiation projects of other groups where new infrared methods developed in this project can be applied to advantage. Preliminary spectra have been measured on coals undergoing flotation where either ultrasonic or chemical treatments are being applied to enhance recovery percentages and where the degree of surface oxidation is thought to play an important role in process behavior. FTIR spectroscopic analysis of pyrite, Argonne Premium Coals, coal slurries, and an improved data processing method have also been explored during the quarter.

Progress

An exploratory study investigated the use of FTIR photoacoustic spectroscopy to help understand the basis for enhanced flotation of sonicated Illinois #6 coal (1.30 float specific gravity fraction). The samples used were provided by W. H. Buttermore's group who are investigating sonic enhancement. The initial FTIR photoacoustic data suggested that, contrary to observations, sonication would not enhance flotation. Spectra of Figure 1 are contrary to the enhanced floatability observation because sonication is seen to increase the OH (3640 cm^{-1}) and carboxylate (1540 cm^{-1}) concentrations and decrease the aliphatic concentrations (2900 cm^{-1}) in both oxidized and unoxidized coals. These concentration changes are, however, expected to be more characteristic of the bulk than surface region of coal due to the penetration depth of infrared radiation ($\sim 1\mu\text{m}$) in coal and hence are not necessarily predictive of a surface-condition sensitive process such as flotation.

Figure 1. FTIR difference spectra of Illinois #6 coal for sonicated-
unsonicated samples which were oxidized (top) at 150°C in air for
150 hrs. and unoxidized (bottom).

In order to get more surface spectroscopic data, the FTIR/UV method was employed which probes just several hundred angstroms (Å) into the coal surface due to the short penetration distance of UV photons in coal. Figure 2 shows the UV-induced increases in the carbonyl band (1750 cm^{-1}) for fresh and oxidized sonicated and unsonicated coal. In the FTIR-UV analysis, a coal with a very low degree of surface oxidation is expected to produce a large increase in carbonyl after exposure to a fixed dose (30J) of UV radiation because there is more oxidizable material present relative to a

more aged coal. An arbitrary UV-induced carbonyl band height of 100 was assigned to the fresh unsonicated coal which, as expected, displayed the highest UV-induced carbonyl peak height. The other coals had peak heights of 86 (sonicated but unoxidized), 71 (sonicated after oxidation at 150°C for 150 hrs. in dry air) and 61 (same as 71 but not sonicated). The coals with carbonyl heights of 100, 71, and 61 displayed flotation behavior in Hallimond-tube recovery tests consistent with the FTIR/UV data in that the recovery percent rose fastest for the 100 peak height coal and progressively slower going down to 71 and to 61 peak height coal. The 86 peak height coal appears to have been slightly oxidized by sonication but was not run in the Hallimond tube. These results are very preliminary but suggest that analysis of surface oxidation by the FTIR/UV method may allow the time rate of recovery in coal flotation to be predicted in a situation where conventional infrared analysis lacks the needed surface specificity.

Figure 2. FTIR-UV difference spectra (after-before irradiation) for (from top to bottom) sonicated unoxidized, oxidized, sonicated after oxidation, and fresh wet-sieved coal. The coal used was a 1.30 specific gravity float fraction of Illinois #6. Oxidation was at 150°C for 150 hrs. in air.

Exploratory spectra were measured on two types of eastern coals in the forms of float, float oxidized, and sink materials so that a manufacturer of coal flotation treatment chemicals could evaluate FTIR photoacoustic spectroscopy as an analytical method with the possibility of a research collaboration. Spectra were measured on chunks of 1-2 mm size and with shallow and deep sensing. Expected differences in mineral concentrations and oxidation were observed. Clay concentration appeared to be higher nearer to the surface in the float coals suggesting that a slime may have formed. The manufacturer's name and spectra are not reported here because they are considered confidential until the spectra have been analyzed by the firm and opportunities for collaboration have been discussed.

Spectra were measured of pyrite derived from coal, mineral, and crystal sources and are shown in Figure 3. The sharp band at 420 cm^{-1} is the primary pyrite absorbance band in the mid-infrared spectral region while the other bands are due mostly to impurities. The spectra of eight Argonne Premium coal samples were measured as received (except for a 24 hr. vacuum drying cycle) and examined in the 420 cm^{-1} spectra region for evidence of the pyrite band. This spectral region was found to contain numerous overlapping absorbance bands which will probably require some spectral deconvolution before the pyrite contribution can be identified.

The Argonne Premium coal spectra are of interest to many coal researchers and were sent to the Center for Microanalysis and Reaction Chemistry at the University of Utah where efforts will be made to correlate the FTIR spectral data with the Center's NMR spectroscopic and other measurement results on these important coals.

The use of photoacoustic signal magnitude and phase rather than just magnitude information was discussed in the last quarterly report as a means to extend the linearity of photoacoustic spectra to higher absorbance values. This linearization procedure also enhances the spectral contrast of spectra (makes the spectral peaks sharper and valleys deeper) and thereby reveals more spectral detail. Figure 4 illustrates the enhancement of detail going from the low modulation-frequency magnitude-calculated spectrum at the bottom, to the high modulation-frequency, magnitude-calculated

Figure 3. Spectra of pyrite derived from coal (top), mineral (middle), and pure crystal (bottom). The primary pyrite band is at 420 cm^{-1} .

spectrum in the middle, and finally to the high modulation-frequency, magnitude- and phase-calculated spectrum at the top. It is hoped that this approach combined with other data processing methods such as factor analysis and spectral deconvolution will allow determinations of substances such as pyrite in coal.

Figure 4. Spectra of Illinois #6 coal measured under different conditions as described in the text.

A measurement was also made during the quarter on a moist coal from a slurry by Attenuated Total Reflectance (ATR Circle Cell) but only a water spectrum was observed. This result suggests that ATR is not a promising method for studying coal surface/liquid interfaces.

Future Work

Progress is expected next quarter in applying Transient Infrared Emission Spectroscopy (TIRES) to on-line analysis of coal oxidation and in collaboration with researchers developing beneficiation processes where coal oxidation is important.

Professor Siquan Luo of the Chemistry Department at the University of Science and Technology of China will begin work on the project in December as a Visiting Scientist. Professor Luo was a researcher at the Ames Laboratory previously in the position of a visiting scholar.

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