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**OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
DE-FG22-90PC90287**

**Fiona M. Doyle
University of California at Berkeley
Dept. of Materials Science and Mineral Engineering**

TECHNICAL PROGRESS REPORT (6/30/93)

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RESEARCH OBJECTIVES

The objective of this research is to develop a mechanistic understanding of the oxidation of coal and coal pyrite, and to correlate the intrinsic physical and chemical properties of these minerals, along with changes resulting from oxidation, with those surface properties that influence the behavior in physical cleaning processes. The results will provide fundamental insight into oxidation, in terms of the bulk and surface chemistry, the microstructure, and the semiconductor properties of the pyrite.

During the eleventh quarter, dry thermal oxidation tests were done on coal samples from the Pennsylvania State Coal Bank. As-received and oxidized coal samples were studied by ion-exchange methods to determine the carboxylate and phenolic group concentrations. Film flotation tests were done to characterize the flotability of as-received and oxidized coals. In addition, electrokinetic tests were done on different coals, to obtain information pertinent to the selection of flotation reagents. DRIFT analysis was done to characterize the structure of coals.

EXPERIMENTAL METHODS AND RESULTS

a. - Sample Characterization

Coals with different rank and sulfur content obtained from the Pennsylvania State Coal Bank were studied. Table I shows the proximate and sulfur analysis of the coals studied.

b. - Dry Oxidation Studies

5 g samples of each coal were oxidized in a convection oven at 230°C for 1, 2, 4, 8 and 25 hours. The extent of oxidation was assessed by analyzing the concentration of carboxylic and phenolic groups by ion-exchange methods, as described in our December 1991 report.

Figure 1 shows the carboxylate and phenolic contents of sub-bituminous (PSOC-1442), HVA bituminous (DECS-12) and anthracite (PSOC-1461) coals. The sub-bituminous coal experienced the greatest increase in total acidity (carboxylic plus phenolic) in 24 hours. With the exception of the anthracite coal, oxidation was fastest in the first few hours. The sub-bituminous coal had a greater susceptibility to oxidation, consistent with the fact that lower rank coals are richer in aliphatic components that oxidize preferentially. The anthracite coal experienced negligible oxidation.

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Table I: Proximate and Sulfur Analysis of Coals Studied.

Penn State Coal Bank No	Origin	Rank	Proximate (dry, %)				Sulfur Forms (dry, %)			
			Ash	Volatile Matter	Fixed Carbon	Moisture (as rec'd)	Sulfatic	Org. Sulfur	Pyritic	Total
PSOC-1442	Darco Texas	Subbitu- inous C	11.27	67.39	21.34	32.60	0.02	0.65	0.11	0.78
PSOC-1494	Kentucky #9 Kentucky	HV3 Bituminous	11.81	38.51	49.58	7.12	0.02	1.69	3.14	4.85
PSOC-1481	Upper Clarion Penn.	HVA Bituminous	8.91	39.41	51.68	1.73	0.20	1.42	3.20	4.82
DECS-12	Pittsburgh #8 Penn.	HVA Bituminous	10.25	36.02	53.73	2.40	0.01	0.73	0.38	1.12
PSOC-1527	Upper Freeport Penn.	MV Bituminous	30.44	23.25	46.31	0.46	0.05	0.34	1.63	2.02
PSOC-1516	Lower Kittanning Penn.	LV Bituminous	10.31	17.73	71.96	1.97	0.01	0.78	0.61	1.40
PSOC-1461	Mammoth Penn.	Anthracite	24.18	4.01	71.81	3.06	0.02	0.65	0.11	0.78

Figure 2 shows the carboxylate and phenolic contents of LV bituminous (PSOC-1516), MV bituminous (PSOC-1527) and HVA bituminous (PSOC-1481) coals. The HVA bituminous coal (high S) underwent the highest increase in total acidity whereas the lowest was experienced by the LV bituminous coal. Again, the susceptibility of bituminous coals to oxidation is consistent with rank. Figures 1 and 2 show that PSOC-1481 was more susceptible to oxidation than DECS-12; this could be due to the higher sulfur content of the former HVA bituminous coal, or to its higher volatile matter content.

c. - Film Flotation Tests

Figure 3 shows film flotation curves of as-received and oxidized sub-bituminous (PSOC-1442), HVA bituminous (DECS-12) and anthracite (PSOC-1461) coals (the film flotation method was reported in our March 31, 1992 report). The hydrophobicity of the sub-bituminous and bituminous coals was markedly reduced after oxidation, by both the increase in surface acid groups and the loss of volatile matter on heating. As-received anthracite coal shows lower hydrophobicity, probably due to its high ash content. The decrease in hydrophobicity after thermal treatment is probably due to the loss of volatile matter.

Figure 4 shows film flotation curves of as-received and oxidized LV bituminous (PSOC-1516), MV bituminous (PSOC-1527) and HVA bituminous (PSOC-1481) coals. The hydrophobicity of each coal was reduced appreciably by the increase of acidic groups and the loss of volatile matter. The MV bituminous coal underwent a dramatic reduction in hydrophobicity, for reasons that are not well understood.

d. - Electrokinetic Studies

3g samples (-400 mesh) of as-received sub-bituminous (PSOC-1442), HVA bituminous (DECS-12) and anthracite (PSOC-1461) coals were oxidized in a convection oven

at 230°C for 24 hours. Raw samples of each coal were freshly prepared by grinding to -400 mesh with a ceramic mortar and pestle under argon. A 0.002 M sodium nitrate solution was used as the electrolyte. Sodium hydroxide and nitric acid solution were used for pH adjustment. Samples containing 0.02 grams of coal in 100 ml of electrolyte solution were conditioned for 17 hours. The zeta potential of each sample was measured in a Model 501 Lazer Zee Meter, using 25.0 ml of coal suspension and a potential of 100 mV. Measurements were made in triplicate for each coal sample. Figures 5, 6 and 7 show the average of three measurements versus the final pH after conditioning.

Figure 5 shows that oxidation at 230°C slightly increased the negative zeta potential of PSOC-1441 coal at pH values above 3.0. Also, the PZC decreased from about 2.1 (for as-received) to about 1.8 after oxidation and the zeta potential remain relatively insensitive to pH in the range 3 to 10. Figure 6 shows that oxidation strongly affected the zeta potential of DECS-12 coal over the whole pH range; the PZC decreased from about 3.1 (for as-received) to about 2.3 after oxidation. Figure 7 shows that the zeta potential of anthracite (PSOC-1461) was unaffected by 24 hours at 230°C; this is in agreement with the fact that this coal was not appreciably oxidized at 230°C for 24 hours. The PZC was found to lie at about 2.7; the strongly negative zeta potential observed is probably due to the high ash content of this coal, which had a high silica content. Figures 5, 6 and 7 show that the coal surfaces are negatively charged except under strongly acidic conditions. This is consistent with the presence of acidic functional groups which are ionized, except at low values of pH. The reduction in the magnitude of the zeta potential at pH greater than 10 is probably due to the bulk dissolution of dissociated humic acids at high pH values.

e. - Diffuse Reflectance Infrared Fourier Transform Spectroscopy Analysis (DRIFT)

Coal samples were prepared for DRIFT analysis by grinding a small amount of coal in an argon atmosphere to -400 mesh. Spectra were obtained using a computer controlled Perkin Elmer 1700 Fourier transform infrared spectrometer, employing a liquid nitrogen-cooled MCT (Hg-Cd-Te) detector and operated at nominal resolution of 4 cm^{-1} . Prior to each analysis, coal samples were thoroughly mixed with KBr powder and transferred into a 10 mm aluminum cup. This cup was mounted in a beam condensing accessory. Typically 400 interferogram scans were combined to obtain each spectrum. Each spectrum was referred to the spectrum of finely powered KBr.

Figures 8, 9 and 10 show the spectra of as-received and oxidized sub-bituminous (PSOC-1442), HVA bituminous (DECS-12) and anthracite (PSOC-1461) coals respectively. The peaks at about 2900 cm^{-1} observed in the spectra of as-received PSOC-1442 and DECS-12 coals are characteristic of aliphatic C-H and CH_2 groups. A significant decrease in the peak intensity was observed after thermal oxidation, indicating that the aliphatic structure was either severely oxidized or volatilized. Figure 10 shows no peak at 2900 cm^{-1} for anthracite (PSOC-1461), which is consistent with the highly aromatic structure of high rank coals.

The 1900-1400 cm^{-1} region is of interest in oxidation studies because most of the oxygen functional groups absorb infrared radiation in this region. A medium intensity peak at about 1726 cm^{-1} -1720 cm^{-1} , corresponding to carboxylic acids, was observed in the spectra of oxidized PSOC-1442 and DECS-12 coals. The peak at about 1600 cm^{-1} probably corresponds to aromatic rings. The peak at about 1450 cm^{-1} is characteristic of aliphatic bending modes; this peak was less intense in the spectrum of oxidized DECS-12 coal than for the as-received coal, reflecting a loss of CH_2 and CH_3 groups with thermal oxidation. The broad band at 3300-3400 cm^{-1} in the spectra of as-received and oxidized PSOC-1442 and DECS-12 coals probably reflects the presence of phenolic groups. The spectra of as-received and oxidized anthracite coal in Figure 10 are distinguished by weak aliphatic stretching bands at about 2900 cm^{-1} and the weakness of the peaks in the 1900-1400 cm^{-1} region. The

peak at about 1430 cm^{-1} decreased with oxidation. The peak at about 1013 cm^{-1} is due to aromatic structures.

In the case of sub-bituminous and bituminous coals, the organic structural changes caused by thermal oxidation are very similar, except for a few minor differences. Anthracite coal shows more uniform adsorption in the $3000\text{-}1500\text{ cm}^{-1}$ region.

PLANS FOR THE NEXT QUARTER

During the next quarter, we will study the oxidation behavior of coal samples from the Pennsylvania State Coal Bank by wet oxidation tests using different oxidants. These studies will include analysis by diffuse reflectance infrared fourier transform analysis (DRIFT) to observe the change in type and relative concentration of surface functional groups, as a function of both time, and nature of oxidant. Wettability, functional group analysis, surface area, porosimetry and electrokinetic measurements are also planned. Contact angle measurements on coal pyrite samples and cyclic voltammetry experiments with coal pyrite electrodes will be done over broader potential ranges than hitherto studied, and different scan rates. Flotation tests under controlled potential and pH conditions are planned for different coals.

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Figure 1: Wt% carboxylate and phenolic oxygen of coals oxidized at 230°C. PSOC-1442 (Sub-bitum C):□: phenolic, ■: carboxylic; DECS-12 (HVA Bituminous):○: phenolic, ●: carboxylic; PSOC-1461 (Anthracite):△: phenolic, ▲: carboxylic.

Figure 2: Wt% carboxylate and phenolic oxygen of coals oxidized at 230°C. PSOC-1481 (HVA Bituminous):□: phenolic, ■: carboxylic; PSOC-1527 (MV Bituminous):△: phenolic, ▲: carboxylic; PSOC-1516 (LV Bituminous):○: phenolic, ●: carboxylic.

Figure 3: Film flotation curves of raw and after oxidation at 230°C for 24 hours. PSOC-1442 (Sub-bitum C): □: oxidized, ■: raw; DECS-12 (HVA Bituminous): ○: oxidized, ●: raw; PSOC-1461 (Anthracite): △: oxidized, ▲: raw.

Figure 4 : Film flotation curves of raw and after oxidation at 230°C for 24 hours. PSOC-1481 (HVA Bituminous): △: oxidized, ▲: raw; PSOC-1527 (MV Bituminous): □: oxidized, ■: raw; PSOC-1516 (LV Bituminous): ○: oxidized, ●: raw.

Figure 5: Electrokinetic measurements on Sub-bituminous C coal PSOC-1442; ■: as-received; +: oxidized at 230°C for 24 hours.

Figure 6: Electrokinetic measurements on HVA bituminous coal DECS-12; *: as-received; □: oxidized at 230°C for 24 hours.

Figure 7 : Electrokinetics measurements on anthracite coal PSOC-1461; x: as-received; ▲: oxidized at 230°C for 24 hours.

Figure 8: DRIFT spectra of Sub-bituminous C coal PSOC-1442;
 (A): as-received; (B): oxidized at 230°C for 24 hours.

Figure 9: DRIFT spectra of HVA bituminous coal DECS-12;
 (A): as-received; (B): oxidized at 230°C for 24 hours.

Figure 10: DRIFT spectra of Anthracite coal PSOC-1461;
(A): as-received; (B): oxidized at 230°C for 24 hours.

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