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OXIDATION OF COAL AND COAL PYRITE
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS
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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 term of the bulk and surface chemistry, the microstructure, and the semiconductor properties of the pyrite.

During the twelfth quarter, wet and dry oxidation tests were done at room temperature on coal samples from the Pennsylvania State Coal Bank. Previous results had indicated that oxidation at high temperatures induced changes in surface properties through loss of volatiles. 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 floatability of as-received and oxidized coals. Surface area measurements were done on as-received coals. In addition, one paper on this work was presented at the Seventh International Conference on Coal Science, Banff, Alberta, Canada in September 1993, and a manuscript has been accepted for presentation at the TMS Annual Meeting in San Francisco in February 1994, and inclusion in the EPD Congress '94 proceedings volume.

EXPERIMENTAL METHODS AND RESULTS

a.- Sample Characteristics

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.- Wet Oxidation Studies

10g samples of coals from the Pennsylvania State Coal Bank were oxidized for 5 hours at room temperature in a well stirred, Pyrex vessel through which argon was passed continuously, using 500 ml of 10% H_2O_2 at pH 1.0, 1.0 M HNO_3 or 0.05 M Fe_2SO_4 at pH 1.0. These concentrations provide solution potentials of about 0.7V. 10 ml samples of slurry were withdrawn periodically and filtered immediately. The coal was washed carefully,

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Table I: Proximate and Sulfur Analysis of Coal Samples 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	Subbitum- inous C	11.27	67.39	21.34	32.60	0.02	0.65	0.11	0.78
PSOC-1494	Kentucky #9 Kentucky	HVB 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

Table II: Weight Percentage of Carboxylic and Phenolic Group Oxygen of As-received Coal, and Coal Oxidized in Different Solutions

Coal Sample	Raw Coal		1.0 M HNO ₃		0.05 M Fe ₂ (SO ₄) ₃		10% H ₂ O ₂	
	Carbox- ylic, %	Phenolic, %	Carbox- ylic, %	Phenolic, %	Carbox- ylic, %	Phenolic, %	Carbox- ylic, %	Phenolic, %
PSOC-1442 Subbit C	0.99	3.23	2.20	10.50	1.80	9.50	1.10	9.10
PSOC-1481 HVA Bitum	0.81	2.84	1.87	3.87	2.81	3.97	1.02	4.12
DECS-12 HVA Bitum	0.15	0.41	0.16	0.50	0.17	0.52	0.19	0.49
PSOC-1527 MV Bitum	0.25	1.22	2.10	10.50	0.80	8.00	2.20	9.10
PSOC-1516 LV Bitum	0.35	0.02	0.44	1.02	0.40	1.20	0.61	1.20
PSOC-1461 Anthracite	0.11	1.47	0.26	1.42	1.40	1.81	0.92	1.61

dried under vacuum, then stored under argon at room temperature. The extent of oxidation was assessed by analyzing the carboxylic and phenolic group concentration. Table II shows the weight percentages of carboxylic and phenolic groups generated by different wet oxidation procedures.

Table II indicates that the amount of carboxylic and phenolic group oxygen generally increased after the oxidation procedures. The phenolic content of the anthracite decreased after oxidation in nitric acid, probably because of conversion to carboxylate. The sub-bituminous and MV bituminous samples underwent much more extensive oxidation than the other samples. However, the susceptibility to oxidation by a given oxidant did vary from sample to sample in no obvious systematic way. Although these differences could be due to the individual structures of each coal sample, or to the presence of different levels of ash and pyrite, they are more likely to reflect experimental error inherent in selecting samples for different treatment, and in analysis.

c.- Film Flotation Tests

The floatability of the samples was determined by film flotation tests, as discussed in our March 31, 1992 report. This technique is extremely powerful as it gives the distribution of particles according to their critical surface tension for wetting, and hence provides useful information on how the material might behave during flotation under a wide range of conditions. Figure 1 shows film flotation curves of as-received and oxidized sub-bituminous C coal (PSOC-1442). Table II showed a strong sensitivity to oxidation, consistent with its low rank. Ferric sulfate markedly reduced the hydrophobicity of the coal, while hydrogen peroxide and nitric acid gave only a minor reduction in hydrophobicity. Comparison with Table II shows that the change in surface properties cannot be due entirely to an increase in carboxylic and phenolic groups, since these were fairly comparable after oxidation with all three aqueous oxidants. The reduction in hydrophobicity was much less dramatic than that observed for the same coal after thermal oxidation, which produced about the same weight percentage of carboxylic and phenolic groups (June 30, 1993 report, Figures 1 and 3). This confirms our previous conclusion that thermal treatment alters the surface properties of coal through loss of volatiles as well as through surface oxidation.

Figures 2 and 3 shows film flotation curves for HVA bituminous coal samples (PSOC-1481 and DECS-12, respectively). None of the oxidizing procedures significantly affected the wetting behavior of these samples, which is consistent with the very slight increase in carboxylic and phenolic concentrations experienced by these samples on oxidation.

Figure 4 shows the film flotation curves for raw and oxidized MV bituminous (PSOC-1527) coal. The hydrophobicity is markedly reduced at surface tensions higher than 40 mN/m, with oxidation by 10% H₂O₂ having the most severe effect, followed by ferric sulfate. As with figure 1, comparison with Table II shows that although reduction in hydrophobicity is qualitatively consistent with an increase in carboxylic and phenolic groups, the agreement is not quantitative. Figure 5 shows the film flotation curves of LV bituminous coal (PSOC-1516). The critical surface tension was not modified by the different oxidizing treatments, although the hydrophobicity was somewhat reduced at surface tensions exceeding 45 mN/m. This coal underwent moderate increases in phenolic group concentration on oxidation, and very minor increases in carboxylate groups.

Figure 6 shows film flotation curves of as-received and oxidized anthracite (PSOC-1461) using different oxidizing agents. Although this sample experienced only minor increases in carboxylic and phenolic group concentrations after treatment with the oxidants, the hydrophobicity was reduced markedly, particularly by 10% H_2O_2 and 0.05M $\text{Fe}_2(\text{SO}_4)_3$. This could not be due to loss of volatile material, because the wet oxidation tests were done at room temperature.

Figure 7 compares the effect of 1M HNO_3 on the hydrophobicity of sub-bituminous C (PSOC-1442), HVA-bituminous (DECS-12) and anthracite (PSOC-1461). The sub-bituminous coal and anthracite experienced the most significant reduction in hydrophobicity, especially at the lower surface tensions. Figures 8 and 9, which compare the behavior with 0.05M $\text{Fe}_2(\text{SO}_4)_3$ and 10% H_2O_2 , show similar trends.

d.- Dry Oxidation Studies

5g samples of coals from the Pennsylvania State Coal Bank, spread to about 1 mm, were oxidized at ambient humidity at room temperature (mean 20°C) for extensive time periods. Room temperature tests were also done at approximately 100% humidity in a desiccator with water at the bottom. The desiccator valve was left slightly open, to ensure an adequate supply of oxygen. The extent of the oxidation was assessed from the concentration of carboxylic and phenolic functional groups.

Figure 10 shows the carboxylate and phenolic contents of sub-bituminous (PSOC-1442), HVA bituminous (DECS-12) and anthracite (PSOC-1461) coals oxidized at room temperature for 90 days at ambient humidity. The HVA bituminous coal experienced the highest increase in total acidity (carboxylic plus phenolic) in 90 days, whereas the anthracite coal experienced the lowest. The rate of carboxylic group generation appeared to be steady for all coals, with anthracite showing the slowest rate. The HVA bituminous coal had the highest rate of phenolic group generation. Figure 11 shows the carboxylate and phenolic contents for the same coals after oxidation at room temperature and 100% humidity. With the exception of anthracite, the rate of oxidation was initially low but increased markedly after 30 days. Comparing with Figure 10, it is clear that there was more extensive oxidation under humid conditions. Water could accelerate the oxidation of coal by a physical effect, or the oxidation mechanism could involve surface hydroxyl groups.

e.- Surface Area Measurements

Surface area measurements were done on as-received samples from the Penn State Coal Bank (the surface area measurement procedure was reported in our March 31, 1993 report). The results of the surface area measurements are shown in Table III. There is a general decrease in surface area with increasing coal rank (with the exception of the PSOC-1481 HVA bituminous sample). The anthracite might show a more marked reduction in hydrophobicity upon modest oxidation because the resulting functional groups are concentrated at the surface.

Table III: Surface Areas of Coal Samples Measured by CO₂ Adsorption at Room Temperature.

Penn. State Coal Bank No.	Rank	Surface Area, m ² /g
PSOC-1442	Sub-bituminous C	321.7
PSOC-1494	HVB Bituminous	289.3
PSOC-1481	HVA Bituminous	114.5
DECS-12	HVA Bituminous	245.3
PSOC-1527	MV Bituminous	234.2
PSOC-1516	LV Bituminous	215.9
PSOC-1461	Anthracite	181.2

f. Future Work

Oxidized samples will be studied by DRIFT, to identify functional groups other than phenolic and carboxylic that might be responsible for reducing the hydrophobicity of coal samples that did not appear to experience extensive oxidation. Flotation tests at controlled potentials and pH are planned, to correlate coal cleaning with the electrochemical work done earlier in the project. The influence of electrode potential on the surface properties of pyrite will be tested using contact angle measurements on polarized coal pyrite electrodes.

g. Publications (Copies attached)

M.N. Herrera and F.M. Doyle, "Modification of coal and coal pyrite surface properties by oxidation", *Proceedings, 7th International Conference on Coal Science*, Ed. K.H. Michaelian, Banff, Alberta, Canada, September 1993, Vol. I, pp. 160-163.

M.N. Herrera and F.M. Doyle, "Electrochemistry of coal pyrite samples at different pH", accepted for publication in *EPD Congress '94*, Ed. G.W. Warren, TMS, Warrendale, PA (1994)

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Figure 1: Film flotation curves of sub-bituminous C (PSOC-1442) coal after wet oxidation by different oxidizing agents for 5 hours: ○: raw, ■: 1.0 M HNO_3 , ●: 0.05M $\text{Fe}_2(\text{SO}_4)_3$, ▲: 10% H_2O_2

Figure 2: Film flotation curves of HVA bituminous (PSOC-1481) coal after wet oxidation by different oxidizing agents for 5 hours: ○: raw, ■: 1.0 M HNO_3 , ●: 0.05M $\text{Fe}_2(\text{SO}_4)_3$, ▲: 10% H_2O_2

Figure 3: Film flotation curves of HVA bituminous (DECS-12) coal after wet oxidation by different oxidizing agents for 5 hours: ○: raw, ■: 1.0 M HNO_3 , ●: 0.05M $\text{Fe}_2(\text{SO}_4)_3$, ▲: 10% H_2O_2

Figure 4: Film flotation curves of MV bituminous (PSOC-1527) coal after wet oxidation by different oxidizing agents for 5 hours: ○: raw, ■: 1.0 M HNO_3 , ●: 0.05M $\text{Fe}_2(\text{SO}_4)_3$, ▲: 10% H_2O_2

Figure 5: Film flotation curves of LV bituminous (PSOC-1516) coal after wet oxidation by different oxidizing agents for 5 hours: ○: raw, ■: 1.0 M HNO₃, ●: 0.05M Fe₂(SO₄)₃, ▲: 10% H₂O₂

Figure 6: Film flotation curves of anthracite (PSOC-1461) coal after wet oxidation by different oxidizing agents for 5 hours: ○: raw, ■: 1.0 M HNO₃, ●: 0.05M Fe₂(SO₄)₃, ▲: 10% H₂O₂

Figure 7: Film flotation curves of raw and after oxidation with 1.0 M HNO₃ for 5 hours. Sub-bituminous C (PSOC-1442): □: raw, ■: oxidized; HVA-Bituminous (DECS-12): Δ: raw, ▲: oxidized; Anthracite (PSOC-1461): ○: raw, ●: oxidized.

Figure 8: Film flotation curves of raw coal samples, and after oxidation with 0.05 M Fe₂(SO₄)₃ for 5 hours. Sub-bituminous C (PSOC-1442): □: raw, ■: oxidized; HVA-Bituminous (DECS-12): Δ: raw, ▲: oxidized; Anthracite (PSOC-1461): ○: raw, ●: oxidized.

Figure 9: Film flotation curves of raw coal samples, and after oxidation with 10% H_2O_2 for 5 hours. Sub-bituminous C (PSOC-1442): $\square$: raw, $\blacksquare$: oxidized; HVA-Bituminous (DECS-12): Δ : raw, $\blacktriangle$: oxidized; Anthracite (PSOC-1461): $\circ$: raw, $\bullet$: oxidized.

Figure 10: Wt% phenolic and carboxylic oxygen of coals oxidized at room temperature. Sub-bituminous C (PSOC-1442): $\square$: phenolic, $\blacksquare$: carboxylic; HVA-Bituminous (DECS-12): Δ : phenolic, $\blacktriangle$: carboxylic; Anthracite (PSOC-1461): $\circ$: phenolic, $\bullet$: carboxylic.

Figure 11: Wt% carboxylate and phenolic oxygen of coals oxidized at room temperature and 100% humidity. Sub-bituminous C (PSOC-1442): $\square$: phenolic, $\blacksquare$: carboxylic; HVA-Bituminous (DECS-12): Δ : phenolic, $\blacktriangle$: carboxylic; Anthracite (PSOC-1461): $\circ$: phenolic, $\bullet$: carboxylic.

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