**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.

Work during the eighteenth quarter has focused on severe oxidation of coal by thermal and chemical treatment, and on investigating the partition of metal ions between such strongly oxidized coal samples and aqueous solutions. This partitioning behavior is being followed to obtain further information on the chemistry of the coal surfaces after different oxidation treatments, for example, whether partition occurs by an ion-exchange mechanism, or whether the surface is capable of changing the oxidation state of metallic species, with concurrent surface or bulk precipitation.

EXPERIMENTAL METHODS AND RESULTS

a. Coal Sample

Upper Freeport coal from the Troutville #2 Mine, Clearfield County, Pennsylvania was used in this study. Table I shows the composition of this sample. The coal was stored under argon after mining to prevent oxidation, and was ground in a ball mill and sieved. The +250-200 mesh (63-75 μm) size fraction was stored under argon for use in this work.

Table I: Proximate, Sulfur, and Oxygen Group Analysis of Upper Freeport Coal Sample

Origin	Rank	Proximate (As-rec'd, %)				Sulfur Forms (dry, %)		Wt% Phenolic oxygen, As-rec'd	Wt% Carboxyl oxygen, As-rec'd
		Ash	Volatile Matter	Fixed Carbon	Moisture	Pyritic	Total		
Upper Freeport Penn.	MV Bituminous	17.59	27.05	55.35	1.50	0.66	1.12	0.68	1.01

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b. Oxidation Treatments

Upper Freeport bituminous coal from the Troutville #2 Mine, Clearfield County, Pennsylvania was oxidized thermally in air by heating the coal in a Precision mechanical convection oven at 230°C for 28 hours.

Coal was oxidized chemically by hydrogen peroxide by adding 20 g of coal to 500 ml of 30% hydrogen peroxide (pH = 4.9) solution. The temperature was controlled by immersing the beaker in an ice bath, and the suspension was stirred magnetically throughout the reaction. The overall decomposition reaction is given by:

However, intermediate decomposition products can oxidize coal before molecular O_2 forms. The reaction was allowed to proceed to completion. The average coal oxidation time was 2.5 hours, with the actual required time depending on the solution temperature, which ranged from 15°C to as high as 95°C during the course of the reaction. The decomposition potential of the solution was determined using platinum and calomel electrodes. The solution reached a steady potential of about 0.76V(SHE) after 1 hour. The oxidized coal samples were then dried under vacuum before performing metal partition experiments.

The Upper Freeport coal was also oxidized chemically in a pH 3, 8.42×10^{-3} M KMnO_4 solution at 25°C, stirring the suspension magnetically for 4 hours. Preliminary tests investigated the uptake of manganese as a function of the coal-to-solution ratio. Table II shows the effect of the coal-to-solution ratio on the final Mn concentration. It is clear that there is a minimum in the final concentration of Mn as a function of weight of coal added, at 5 and 10 g coal in 100 ml solutions. The equilibrium decomposition potential, as measured by platinum and calomel electrodes, was 1.22 V (SHE) in the test with 10 g coal. This suggests that at low coal-to-solution ratios, the Mn(VII) is reduced to Mn(IV), which forms MnO_2 at 1.22 V and pH 3. However, X-ray analysis and electron microscopy did not detect crystalline material, which suggests that the MnO_2 is amorphous. With increasing coal-to-solution ratios the redox potential was lower; Mn would then have been at least partially reduced further to Mn^{2+} , with an increase in aqueous solubility.

Subsequent oxidation treatments prior to Cu and Cd uptake experiments used a ratio of 1 gram of coal to 10 ml of KMnO_4 solution (typical oxidations used 30 g of coal and 300 ml KMnO_4), under which conditions Mn(VII) was completely removed from the KMnO_4 solution. The coal samples were then dried under vacuum.

c. Metal Uptake Kinetics on Coal Oxidized by KMnO_4

Since preliminary kinetic experiments suggested that both copper and cadmium uptake on coal oxidized by KMnO_4 had reached steady state within two hours (see November 30, 1994 quarterly report), further experiments were performed, sampling the suspension more frequently. A 0.05M copper stock solution was prepared and diluted with no further pH adjustment. A ratio of 1 gram of Upper Freeport coal to 10 ml of metal solution (a total of 15 g of coal with 150 ml of copper solution) was placed in a 250 ml polyethylene bottle, and shaken in a suspension adsorption agitator at 25°C. 10 ml samples of the suspension were withdrawn periodically, and filtered under vacuum. The filtrate was analyzed using a Perkin Elmer 3110 Atomic Absorption Spectrometer. Figure 1 shows that steady state was reached within ten minutes. Sample filtration took about ten minutes with the filtration equipment available for these tests, hence it was not possible to obtain meaningful results for shorter contact times. The adsorption kinetics were much more rapid than those observed for coal samples oxidized by other methods, suggesting that both the metal uptake

Table II: Effect of coal-to-solution ratio on the removal of Mn(VII) by Upper Freeport coal. Initial Mn(VII) concentration = 462 ppm (8.4×10^{-3} M), initial pH = 3, after 4 hours of contact

Grams of Coal in 100 ml KMnO ₄ Solution	Final Mn Concentration (ppm)
1	347
3	168
5	not detected
10	not detected
12.5	12
15	5
20	18

Figure 1: Removal of copper from a 4.9×10^{-3} M (312 ppm) copper solution by Upper Freeport coal (pre-oxidized by pH 3, 8.42×10^{-3} M KMnO₄ solution at 25°C) with a coal-to-solution ratio of 1:10 during both oxidation and copper uptake.

mechanism and transport of sorbing species were completely different and distinctive. The distinctive metal uptake kinetics suggest that the amorphous MnO_2 layer participates in the uptake of copper, either in addition to coal surface functional groups or in their place.

d. Adsorption Equilibria

Aqueous solutions of approximately $5 \times 10^{-5} \text{ M}$ – $5 \times 10^{-2} \text{ M}$ CuSO_4 , at pH 4, were contacted with thermally and chemically oxidized coal samples for 48 hours. pH adjustments were made with $0.01 \text{ M H}_2\text{SO}_4$.

Figure 2 shows a Freundlich linearization for Cu^{2+} on the different oxidized coal samples. It appears that metal uptake data for the coal oxidized by all three treatments fit the Freundlich equation, although the significant differences in both slopes and intercepts of these lines indicate appreciable differences in both the sorptive capacities and intensities of adsorption for the coal samples.

The adsorption behavior was also studied to establish whether it followed the Langmuir isotherm. Coal oxidized thermally and by KMnO_4 appeared to follow this behavior, and the adsorption behavior was used to estimate the total surface site saturation for Cu^{2+} at pH 4, on the coal. These data covered a large range, and hence are presented on a logarithmic scale in Figure 3. However, the true linearization was used to estimate the capacity of the coal surface for Cu^{2+} . The slope of the aqueous copper concentration/surface copper concentration as a function of the aqueous copper concentration yields the reciprocal of the capacity of the coal surface for Cu^{2+} at the pH studied. The Langmuir adsorption isotherm predicts the maximum Cu^{2+} sorbed on the thermally oxidized coal to be 6.9×10^{-5} moles/gram, and for coal oxidized by KMnO_4 , 4.13×10^{-5} moles Cu^{2+} /gram.

e. Functional Group Analysis

The amount of carboxylic and phenolic functional groups was determined for untreated and oxidized Upper Freeport coal, following the method described by Brooks and Sternhell. The total carboxylic acid content is determined by measuring the amount of acetic acid liberated while contacting coal with a concentrated (3M) sodium acetate solution. The reaction is represented by:

Similarly, the total acidic functional groups are determined by measuring the H^+ ions liberated during coal contact with a 0.15M Ba(OH)_2 solution. The reactions are represented by:

and

The contacts were performed for at least 16 hours to establish equilibrium. For carboxyl group analysis, 25 ml of the filtrate was titrated with $0.22\text{--}0.21\text{M NaOH}$, using phenolphthalein as indicator. For the total acid group analysis, 10 ml of the filtrate was titrated with 0.31M HCl , using phenolphthalein as indicator. Phenolic concentrations were obtained from the difference between total acidic groups and carboxylic groups. A 0.02M benzoic acid solution in 200 proof ethanol was used to standardize the NaOH . The base was then used to standardize the HCl .

Figure 2: Freundlich adsorption linearization for copper uptake on Upper Freeport coal samples oxidized by different treatments

Figure 3: Langmuir adsorption linearization for copper uptake on Upper Freeport coal samples oxidized by different treatments (these data covered a large range, and hence are presented on a logarithmic scale)

Table III: Preliminary concentrations of carboxylic acid and phenolic groups, expressed as weight percentage of total coal

Coal Sample	COOH Groups (wt %)	OH Groups (wt %)	Total Acid Groups (wt %)
Untreated	3.37	0.046	3.42
Thermal Oxidation	9.74	7.12	16.83
KMnO ₄ Oxidation	1.49	5.55	7.04
H ₂ O ₂	1.70	0.81	2.51
Thermal/Cu ²⁺	8.02	6.46	14.48
KMnO ₄ /Cu ²⁺	1.30	1.19	2.49
H ₂ O ₂ /Cu ²⁺	1.49	0.81	2.30

Table III shows preliminary results for untreated and oxidized Upper Freeport (these measurements are being repeated to resolve apparent inconsistencies in the number of acid groups). Oxidized coal contacted with the 3463 ppm copper solution used in the adsorption equilibrium experiments was also analyzed to determine the amount of free carboxylic acid and phenolic sites, and hence the number occupied by copper. The concentration of total acid groups on the thermally oxidized coal was similar to the percentage of functional groups determined using potentiometric titration with a Fisher automatic titrimeter (16.84 wt%, M.N. Herrera Ph.D. thesis, University of California at Berkeley, December 1994).

The data suggest that thermally oxidized coal has the largest amount of acidic functional groups, however, only 14% of these participate in adsorption/ion exchange with copper in a pH 4, 3463 ppm solution. Since the saturation capacity obtained assuming a Langmuir model indicates that only 2.17 wt% of the functional groups can be occupied by copper, these measurements are being repeated.

The coal oxidized by KMnO₄ has less than half as many carboxyl and phenolic groups than the thermally oxidized coal, and 64% of these participate in copper uptake. (Data obtained from the Langmuir isotherm suggest that 2.3 wt% of total functional groups can participate.) The decrease in carboxylic acid groups after oxidation may be due to the formation of manganese carboxylate salts on the surface. The rapid uptake kinetics shown in Figure 1, as well as the extent of metal uptake, suggest that active sites on a hydrous manganese oxide surface layer generated during oxidation may be participating in adsorption/ion exchange, as well as undergoing acid dissolution.

PLANS FOR THE NEXT QUARTER

During the nineteenth quarter, the functional group analyses reported here will be repeated to resolve apparent discrepancies. Surface functional group analysis will also be performed on coal oxidized by H₂O₂, and oxidized coal contacted with approximately 0.05 M CdSO₄ solutions at pH 4. The Master's thesis of Donna L. Bodine will be completed. In the final quarter of the project, analytical methods for determining functional groups on coal will be analyzed theoretically, considering aqueous phase chemistry during titration, electrophoretic data and transport properties.

PUBLICATIONS

Donna L. Bodine and Fiona M. Doyle, "Removal of Cu^{2+} , Cd^{2+} and Mn(VII) from Dilute, Aqueous Solutions by Oxidized Bituminous Coal", *Treatment and Minimization of Heavy Metal-Containing Wastes*, Ed. J.P. Hagar et al., TMS, Warrendale, PA, 1995, pp. 81-93. (Copy attached)

Fiona M. Doyle and Donna L. Bodine, "Treatment of aqueous streams containing strong inorganic oxidants using bituminous coal", *Engineering Foundation Conference on Technological Solutions for Pollution Prevention in the Mining and Mineral Processing Industries*, Palm Coast, Florida, January 22-27, 1995.

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