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

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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 nineteenth quarter has concluded studies of the surface functional groups produced on coal by severe thermal and chemical oxidation, and on investigating the partition of metal ions between such strongly oxidized coal samples and aqueous solutions. This partitioning behavior was being followed to obtain further information on the chemistry of the coal surfaces after different oxidation treatments. Adsorption isotherms for the uptake of Cd^{2+} on coal oxidized by different methods were obtained, and these and the Cu^{2+} adsorption isotherms reported in the last report have been scrutinized, and interpreted more exhaustively. The apparent discrepancies noted in the last report for the analysis of surface functional groups have been investigated further. The adsorption behavior has been related to the surface chemistry of Upper Freeport coal oxidized by different methods.

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.

b. Oxidation Treatments

Thermal oxidation: 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.

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

Chemical oxidation: 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 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 overall reaction for decomposition of peroxide would be given by:

$$H_2O_2 = H_2O + 1/2\ O_2 \qquad\qquad (1)$$

However, in acidic solutions of coal containing pyrite, dissolved iron can induce disproportionation of the hydrogen peroxide, and the coal may be oxidized by the Fenton reaction, which produces hydroxyl and hydrogen superoxide radicals, and hydroperoxides[1]. These intermediate decomposition products can oxidize coal before molecular O_2 forms.

The Upper Freeport coal was also oxidized chemically in a pH 3, 8.42×10^{-3} M **potassium permanganate** ($KMnO_4$) solution at 25°C, stirring the suspension magnetically for 4 hours. These treatments 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 $KMnO_4$). Work reported in the 2/28/95 quarterly report had established that Mn(VII) was completely removed from the $KMnO_4$ solution under these conditions, at an equilibrium decomposition potential of 1.22 V (SHE), as measured by platinum and calomel electrodes. The Eh-pH diagram for the Mn-H_2O system at 25°C[2], indicates that MnO_2 is the thermodynamically stable Mn-bearing species at 1.22 V and pH 3. However, X-ray analysis and electron microscopy did not detect crystalline material, which suggests that an amorphous Mn(IV) oxide formed at the coal surface. The coal samples were then dried under vacuum.

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[1]   I. Heard and F.E. Senftle, "Chemical oxidation of anthracite with hydrogen peroxide via the Fenton reaction", *Fuel*, **63**, 1984, 221.

[2]   M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd Ed., National Association of Corrosion Engineers, Houston, TX, 1974.

d. Adsorption Equilibria

Aqueous solutions of approximately 5×10^{-5} M–5×10^{-2} M CuSO$_4$ and CdSO$_4$ were adjusted to pH 4, using 0.01 M H$_2$SO$_4$. 10 g samples of thermally and chemically oxidized coal were contacted with 100 ml of each solution for 48 hours at room temperature. The suspensions were then filtered, and the uptake of metal ions onto the coal was determined by atomic absorption analysis of the metal ions remaining in the filtrate.

Copper: A Freundlich linearization for Cu^{2+} adsorbed on the different oxidized coal samples is shown in Figure 1 (this figure also appeared in our 2/28/95 report, but is included here for comparison with subsequent results). The slopes of the lines may provide some indication of the adsorptive capacity of the coal over the solution concentration range studied, although there could be appreciable error from the large range of concentrations studied. The coal oxidized by H$_2$O$_2$ had the steepest slope (0.73), indicating the highest sensitivity of capacity to solution concentration. The coal oxidized by KMnO$_4$ had the shallowest gradient (0.16), reflecting insensitivity of capacity to solution concentration, and probably a different adsorption mechanism. Thermally oxidized coal had an intermediate gradient of 0.46.

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. The parameters (X$_m$ and b) calculated from a Langmuir linearization (plotting C$_e$/X versus C$_e$) were used to generate Langmuir isotherms over the concentration range studied. These are shown in Figures 2 and 3 for coal oxidized thermally and by KMnO$_4$, along with experimental data. It is clear that although the Langmuir isotherms gave a good fit at high concentrations, they severely underestimate adsorption from very dilute solutions. The adsorption of Cu^{2+} on coal oxidized by H$_2$O$_2$ was not at all well described by the Langmuir isotherm.

The Langmuir isotherms predict 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. However the Langmuir fit is not strong enough to allow us to have much confidence in these figures.

Cadmium: A Freundlich linearization for Cd^{2+} adsorbed on the different oxidized coal samples is shown in Figure 4. The coal oxidized by KMnO$_4$ gave the best linear fit, with a gradient of 0.47. The thermally oxidized coal did not fit the linearization as well, although a least squares fit yielded a gradient of 0.39. The behavior of coal oxidized by H$_2$O$_2$ was surprising, with almost no adsorption from the most concentrated solution. We have found no satisfactory explanation for this observation.

Langmuir adsorption parameters were also derived for the uptake of cadmium on coal oxidized thermally and by KMnO$_4$. The Langmuir isotherms generated by these parameters are shown in Figures 5 and 6 for coal oxidized thermally and by KMnO$_4$, along with experimental data. It is clear that the adsorption of Cd on coal oxidized thermally and by KMnO$_4$ follows Langmuir isotherms much better than did the adsorption of Cu^{2+}. The adsorption of Cd^{2+} on coal oxidized by H$_2$O$_2$ also gave a very poor fit to the Langmuir isotherm.

The Langmuir isotherms predict the maximum Cd^{2+} sorbed on the thermally oxidized coal to be 1.6×10^{-5} moles/gram, and for coal oxidized by KMnO$_4$, 1.64×10^{-5} moles Cd^{2+}/gram. The latter is rather lower than the uptake of cadmium reported previously onto coal oxidized by KMnO$_4$. The discrepancy probably reflects the error in curve-fitting over a large composition range with limited data.
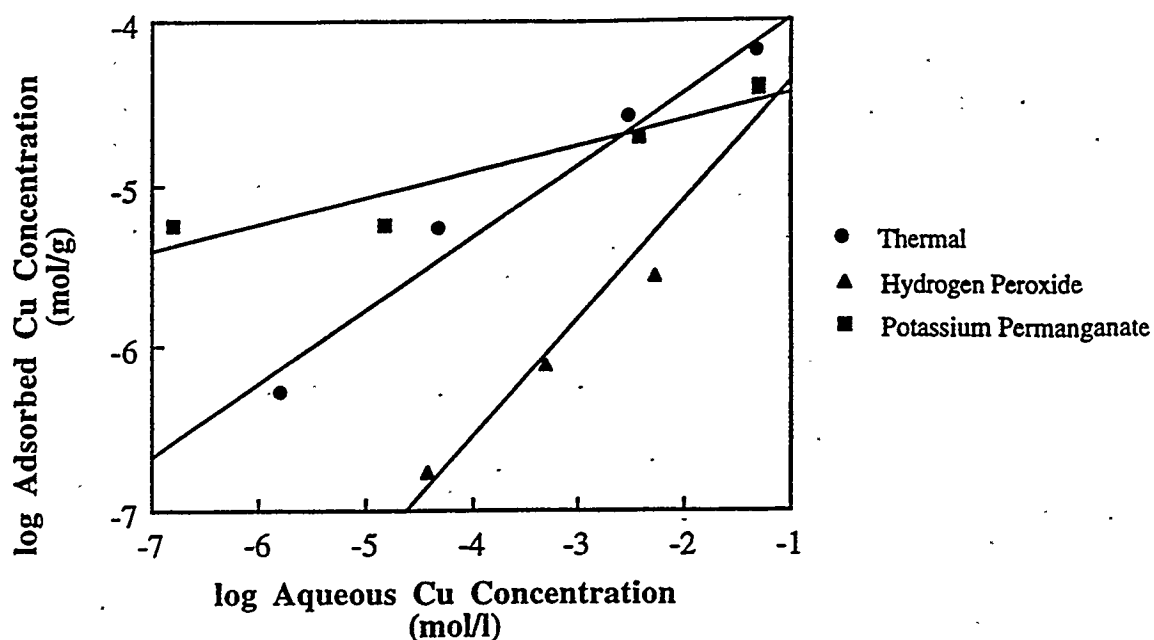
Figure 1: Freundlich linearization for copper uptake on the different oxidized coal samples. $CuSO_4$ solutions initially contained 3463, 359, 37 and 3.5 ppm Cu^{2+}, respectively and were initially at pH 4.
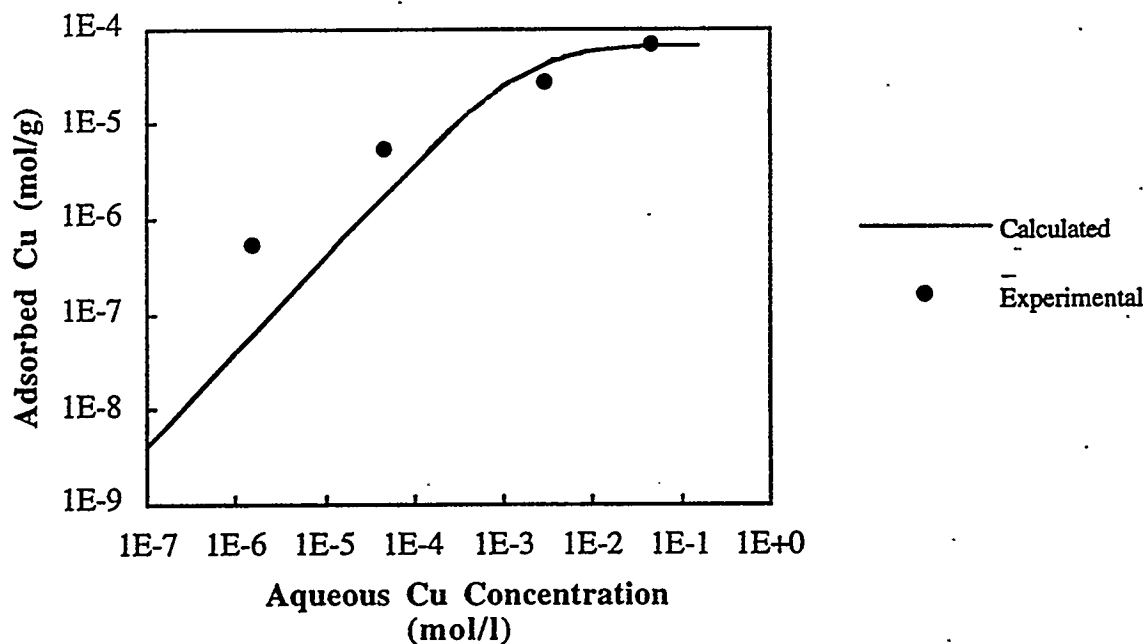

Figure 2: Fitted Langmuir isotherm (calculated) and experimental data for copper uptake by thermally oxidized coal. $CuSO_4$ solutions initially contained 3463, 359, 37 and 3.5 ppm Cu^{2+}, respectively and were initially at pH 4.
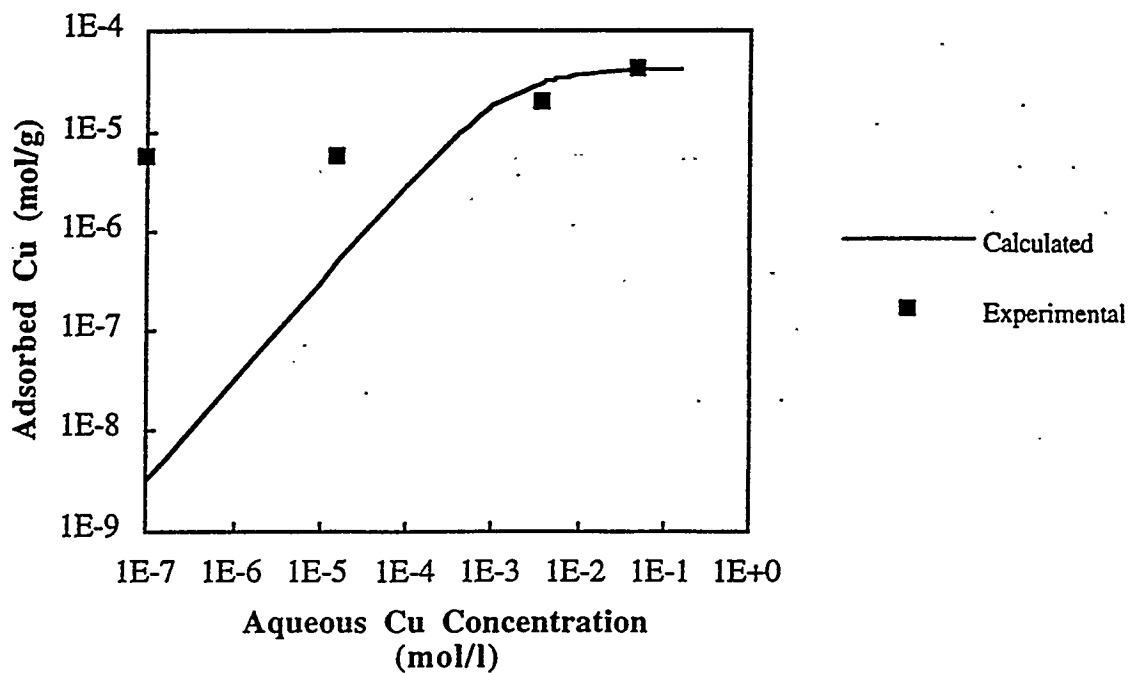
Figure 3: Fitted Langmuir isotherm (calculated) and experimental data for copper uptake by coal oxidized by $KMnO_4$. $CuSO_4$ solutions initially contained 3463, 359, 37 and 3.5 ppm Cu^{2+}, respectively and were initially at pH 4.
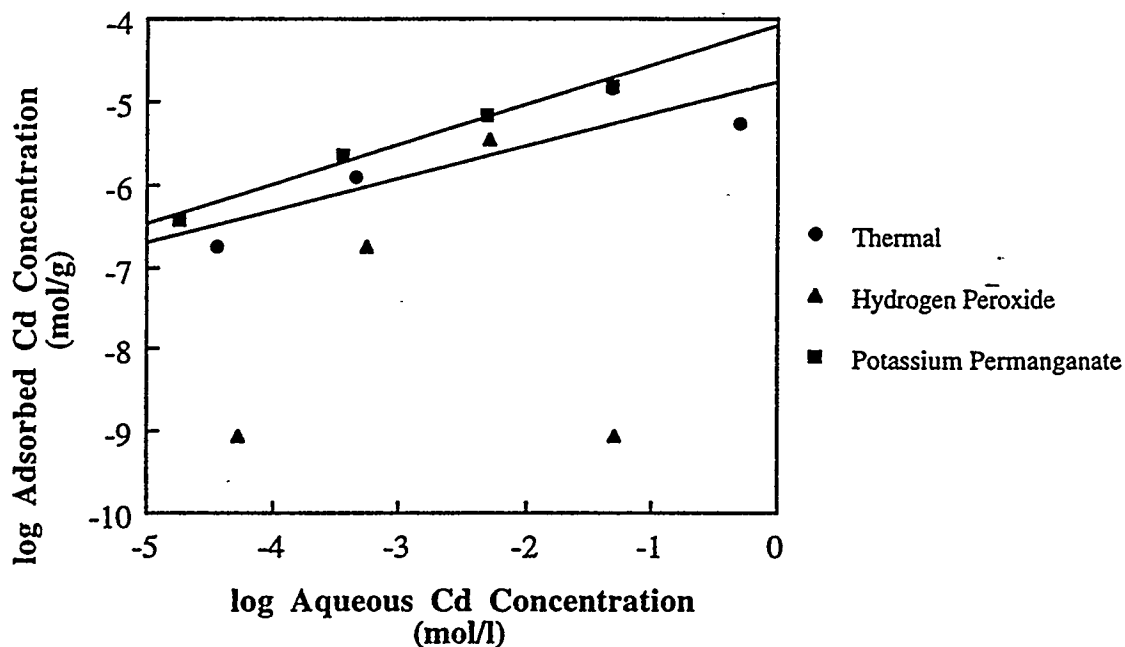

Figure 4: Freundlich linearization for cadmium uptake on the different oxidized coal samples. $CdSO_4$ solutions initially contained 6109, 625, 64 and 6 ppm Cd^{2+}, respectively and were initially at pH 4.
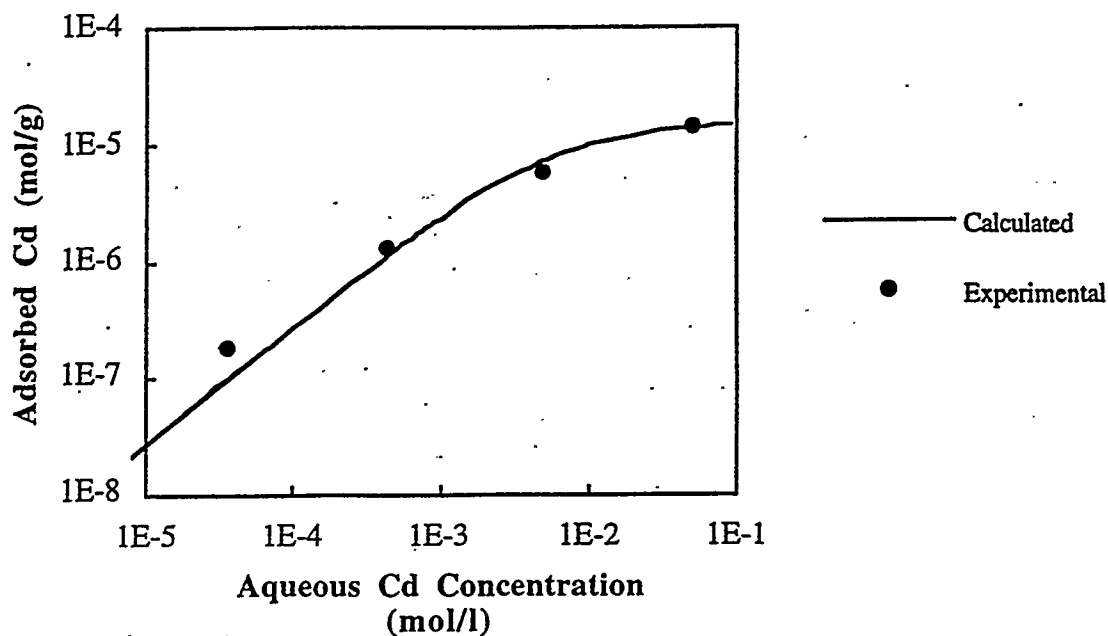
Figure 5: Fitted Langmuir isotherm (calculated) and experimental data for cadmium uptake by thermally oxidized coal. CdSO$_4$ solutions initially contained 6109, 625, 64 and 6 ppm Cd^{2+}, respectively and were initially at pH 4.
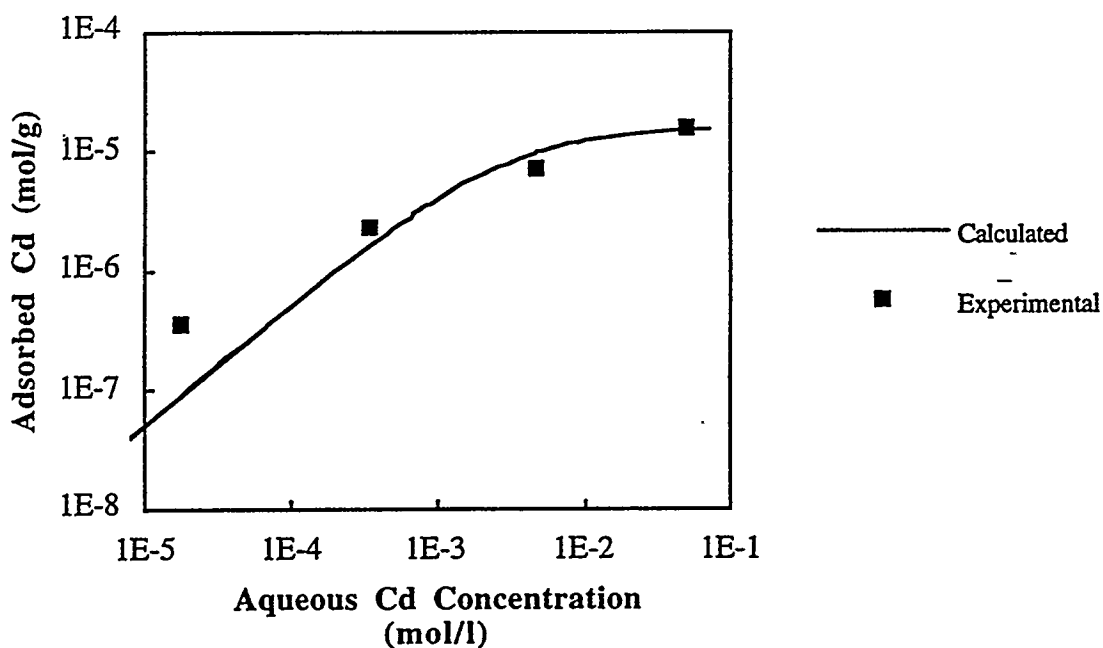

Figure 6: Fitted Langmuir isotherm (calculated) and experimental data for cadmium uptake by coal oxidized by KMnO$_4$. CdSO$_4$ solutions initially contained 6109, 625, 64 and 6 ppm Cd^{2+}, respectively and were initially at pH 4.
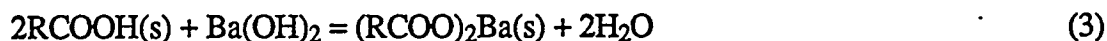
e. Functional Group Analysis

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[3]. The **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:

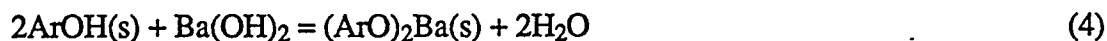$$2RCOOH + CH_3COONa = RCOONa(s) + CH_3COOH \qquad (2)$$
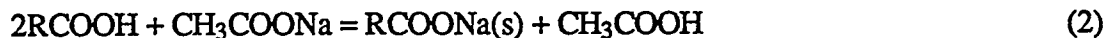
With a high concentration of sodium acetate, the equilibrium is displaced sufficiently far to the right to give near quantitative release of acetic acid.

The **total acidic functional groups** are determined by measuring the H^+ ions liberated after contacting the coal with a 0.15M $Ba(OH)_2$ solution. The overall reactions are represented by:

$$2RCOOH(s) + Ba(OH)_2 = (RCOO)_2Ba(s) + 2H_2O \qquad (3)$$

and

$$2ArOH(s) + Ba(OH)_2 = (ArO)_2Ba(s) + 2H_2O \qquad (4)$$

where (s) denotes a surface species, and Ar is an aryl group.

The contacts were performed for at least 16 hours to establish equilibrium. For carboxyl group analysis, 25 ml of the filtrate was titrated with 0.22–0.21M 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. The titer was compared with that obtained using a blank of 10 ml of the original 0.15M $Ba(OH)_2$ solution. **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.

Table II shows the surface acidic functional group content (moles/gram of coal) of untreated coal, and thermally oxidized coal samples before and after contact with the 3463 ppm Cu^{2+} and 6109 ppm Cd^{2+}, pH 4 solutions used in the adsorption equilibria experiments reported above. Replicates are shown to demonstrate the reproducibility in the analyses. It is clear that the analysis of carboxylate content had a 5-6% scatter, which is probably the best that could be expected given the difficulties in sampling inherently heterogeneous material. In contrast, the replicates of total acid group determination by Ba^{2+} exchange varied by a factor of up to 1.7. OH groups were determined by the difference between total acid groups and carboxylate groups, and consequently also show significant scatter, up to a factor of 2.5. These errors stem from two sources; the first is that the $Ba(OH)_2$ solution absorbed atmospheric CO_2 exceedingly easily, despite being stored and used under nitrogen. This causes $BaCO_3$ to be precipitated, with concurrent neutralization of OH^-:

$$Ba^{2+} + 2OH^- + CO_2 = BaCO_3{}_{(ppt)} + H_2O$$
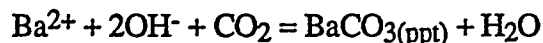
The OH^- lost by carbonate precipitation would be interpreted as having neutralized surface acid groups, and hence would lead to an overestimation. Although this difficulty should, in principle,

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[3]   J.D. Brooks and S. Sternhell, "Chemistry of brown coals. 1. Oxygen containing functional groups in Victorian brown coals", *Austr. J. Appl. Sci.*, **8**, 1957, 206.

<u>Table II</u>: Surface acidic functional groups (moles/gram of coal) on untreated coal, and thermally oxidized coal samples before and after contact with the 3463 ppm Cu^{2+} and 6109 ppm Cd^{2+}, pH 4 solutions used in adsorption equilibria experiments. Replicates are shown to demonstrate the poor reproducibility in the analysis of total acid groups by Ba^{2+} exchange, and hence in the analysis of OH groups, determined by difference

Coal Sample	COOH Groups (mol/g coal)	Phenolic OH Groups (mol/g coal)	Total Acid Groups (mol/g coal)	% of sites occupied by M^{2+}
Untreated	7.5×10^{-4}	2.7×10^{-4}	7.8×10^{-4}	-
Thermal oxidation: 1	2.2×10^{-3}	4.2×10^{-3}	6.4×10^{-3}	-
Thermal oxidation: 2	2.1×10^{-3}	1.7×10^{-3}	3.8×10^{-3}	-
Thermal/Cu^{2+}: 1	1.8×10^{-3}	3.8×10^{-3}	5.6×10^{-3}	12.5
Thermal/Cu^{2+}: 2	1.9×10^{-3}	1.7×10^{-3}	3.6×10^{-3}	5.3
Thermal/Cd^{2+}: 1	1.7×10^{-3}	2.3×10^{-3}	4.0×10^{-3}	37.5
Thermal/Cd^{2+}: 2	1.6×10^{-3}	1.3×10^{-3}	2.9×10^{-3}	23.7

Note: All analyses denoted as 1 were performed with the same reagent solutions, and all analyses denoted as 2 were performed with a different set of reagent solutions at a later date. According, tests 1 are compared to obtain the percentages of sites occupied by M^{2+}, as are tests 2.

be corrected for by ensuring that the standard $Ba(OH)_2$ solution used as a blank has had identical exposure to CO_2 as the test solutions, this is difficult to achieve in practice, as the coal samples contacted with the solutions are likely to contain some CO_2. The second source of error stems from the fact that an excess of $Ba(OH)_2$ is used, to ensure complete adsorption on the coal. Consequently the actual amount of acid released into the $Ba(OH)_2$ solution is determined from the difference between two rather similar titrations with HCl. It appears that when analyzing high rank coals, which are less oxidized than the brown coals for which Brooks and Sternhell developed their techniques, it would be appropriate to use a larger coal:$Ba(OH)_2$ solution volume, in order to enhance the difference between the titers for the blank and the samples. However this recommendation requires further study, since it is essential to ensure that there is enough $Ba(OH)_2$ to give quantitative release of H^+ from acid groups.

Table III shows the surface acidic functional groups (moles/gram of coal) on untreated coal, and chemically oxidized coal samples before and after contact with the 3463 ppm Cu^{2+} and 6109 ppm Cd^{2+}, pH 4 solutions used in the adsorption equilibria experiments reported above. There was insufficient time to perform replicate tests on these analyses, but it must be understood that the concentrations of phenolic OH groups and total acid groups are associated with the same uncertainties as those demonstrated in Table II.

Examination of Tables II and III indicates that thermally oxidized coal has a higher concentration of carboxylate and phenolic groups than untreated coal. Further, the coal oxidized by either $KMnO_4$ or H_2O_2 has fewer carboxylate groups than the untreated coal, although the phenolic content increased dramatically. A decrease in carboxylates is not unexpected after oxidation by $KMnO_4$, since Mn(IV) might be occupying carboxylate sites, but is surprising after treatment with H_2O_2. This is probably due to soluble carboxylic acids present in the untreated coal dissolving in the aqueous permanganate and peroxide solutions. Hence it is clear that analysis of surface carboxylate groups, and total surface acid groups, at best gives only a gross description of the

Table III: Surface acidic functional groups (moles/gram of coal) on untreated coal, and chemically oxidized coal samples before and after contact with the 3463 ppm Cu^{2+} and 6109 ppm Cd^{2+}, pH 4 solutions used in adsorption equilibria experiments

Coal Sample	COOH Groups (mol/g coal)	Phenolic OH Groups (mol/g coal)	Total Acid Groups (mol/g coal)	% of sites occupied by M^{2+}
Untreated	7.5×10^{-4}	2.7×10^{-4}	7.8×10^{-4}	-
$KMnO_4$ oxidation	3.3×10^{-4}	3.3×10^{-3}	3.6×10^{-3}	-
$KMnO_4/Cu^{2+}$	2.9×10^{-4}	7.0×10^{-4}	9.9×10^{-4}	72.5
$KMnO_4/Cd^{2+}$	3.4×10^{-4}	9.4×10^{-5}	4.3×10^{-4}	88.1
H_2O_2 oxidation	3.8×10^{-4}	4.6×10^{-4}	8.4×10^{-4}	-
H_2O_2/Cu^{2+}	$3.3x 10^{-4}$	4.8×10^{-4}	8.1×10^{-4}	3.6
H_2O_2/Cd^{2+}	3.8×10^{-4}	2.3×10^{-4}	6.1×10^{-4}	27.4

surface chemistry of coals. Much better techniques that can assess the solubility and reactivity are clearly needed.

Comparing the surface acidic functional groups of oxidized coal samples with the acid content of the samples after equilibration with Cu^{2+} or Cd^{2+}, it is clear that only a relatively small proportion of the surface acid groups have interacted with Cu^{2+} or Cd^{2+}. There are still an appreciable number of exchangeable hydrogens on the surface. The proportions of sites occupied, as determined from analysis of the acidic functional groups, are also given in Tables II and III. In section f below, these figures are compared with uptake information derived from adsorption isotherms.

## f. Comparison of Adsorption Equilibria and Surface Functional Group Studies

Table IV compares the maximum adsorption capacity of oxidized coal samples for Cu^{2+} and Cd^{2+}, as predicted by the Langmuir isotherm in section d, with total acid groups available on the oxidized coal samples, as reported in section e. Assuming that two acid groups are needed to adsorb one M^{2+} ion, the Langmuir maximum is then presented as a percentage of the measured available sites. Comparing these percentages with the percentages presumed occupied from the measurement of

Table IV: Comparison of maximum adsorption capacity of oxidized coals for Cu^{2+} and Cd^{2+}, as predicted by Langmuir isotherm, with total acid groups available on the oxidized coal samples.

Oxidation method/metal	Total Acid Groups on Oxidized Coal (mol/g coal)	Langmuir Max Ads Capacity (mol/g coal)	Langmuir Max as % of 0.5(Total Acid)
Thermal/Cu^{2+}	5.1×10^{-3} (mean)	6.9×10^{-5}	12.7
Thermal/Cd^{2+}	5.1×10^{-3} (mean)	1.6×10^{-5}	0.6
$KMnO_4/Cu^{2+}$	3.6×10^{-3}	4.13×10^{-5}	2.3
$KMnO_4/Cd^{2+}$	3.6×10^{-3}	1.64×10^{-5}	0.9

surface functional groups, there are clearly large discrepancies for all but adsorption of Cu^{2+} on thermally oxidized coal. First, this probably reflects the limited accuracy of the Langmuir fit. Second, it could reflect extraneous hydrolysis reactions that sorbed metals might have undergone during analysis of the surface functional groups. However it is clear that regardless of the method of estimating capacity, only a small percentage of the acidic functional groups on coal are capable of adsorbing Cu^{2+} and Cd^{2+}. Ba^{2+}, the larger cation used to determine the total acid groups, is clearly much more strongly sorbed. This could reflect the relative stabilities of the Cu-, Cd-, and Ba-carboxylate and phenolate interactions. However it could also reflect the spatial distribution of groups capable of adsorbing metal ions. At the pH values used for the adsorption tests, the cations are largely unhydrolyzed. Charge neutrality requires that two acid groups are needed to coordinate an M^{2+} ion. Because we are considering acid groups that are part of the coal matrix, and hence are immobile, metal ions can only be adsorbed if there are two acid groups close enough to interact with a single cation. If the resulting bond has a substantially covalent character, rather than being primarily ionic, then there is a further constraint introduced by the geometry of the bond, and the acid groups must have a fairly narrowly defined separation. If one considers, for simplicity, a random array of acid groups on the coal surface, as denoted by dots in the sketch below, it is clear that the larger this separation is, and hence the larger is the diameter of a circle representing the locus of all points at this required separation from a central ion, the greater will be the probability of a functional group lying on or near the locus. Examination of Tables II and III demonstrates that indeed, a higher percentage of the measured, available acid functional groups are occupied by cadmium than by copper. Such steric considerations are thought to be exceedingly important in accounting for the difference in behavior that we have observed several times in the ability of coals oxidized in different ways to interact with metal ions.

It is also likely that there are significant differences in the ability of different acid groups to interact with metal ions, and further that differences in the structure and porosity of the coal are as important as differences in the nature of the oxidized functional groups. Accordingly, it seems that much more sensitive, direct characterization of the surface chemistry of the coal is needed to better understand the effects of different oxidation treatments.
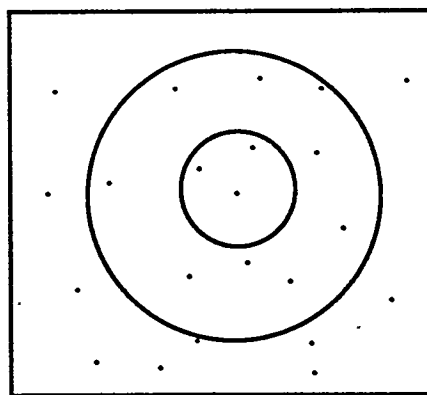
PLANS FOR THE NEXT QUARTER

Outstanding areas of work will be completed in the final quarter. The Master's thesis of Donna L. Bodine, which includes the work reported in the last three quarterly reports, will be completed and filed. A paper "Treatment of aqueous streams containing strong oxidants using bituminous coal" will be prepared for inclusion in the proceedings of the Engineering Foundation Conference on Technological Solutions for Pollution Prevention in the Mining and Mineral Processing Industries. The meeting was held in Palm Coast, Florida in January 1995, but when the PI gave the talk it became apparent that there were a few additional studies that should be done to strengthen the work. Finally the possibility of using coal for treating commercial effluents containing toxic metals will be considered.

DISCLAIMER