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**Effect of Oxidation on the Removal of Cu^{2+} , Cd^{2+} and Mn (VII) from
Dilute Aqueous Solutions by Upper Freeport Bituminous Coal**

by

Donna Laura Bodine

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Committee in charge:

**Professor Fiona M. Doyle, Chair
Professor James W. Evans
Professor James R. Hunt**

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The thesis of Donna Laura Bodine is approved:

Francis M. Doyle 6/2/95
Chair Date

James W. Kious May 15, 1995
Date

James R. Hunt 6/2/95
Date

University of California at Berkeley

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1. INTRODUCTION

Toxic metals are present in a wide range of wastes and effluents from mineral and materials processing, finishing and plating industries. If stored or disposed of trivially, these solutions could have a profound impact on the environment and public health. Consequently, new federal, state and local regulations that control their containment and discharge are becoming increasingly more stringent in most developed countries. Some of these laws that affect the mining industry in the United States are briefly discussed below¹.

Federal ordinances such as the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), enacted in 1980 and substantially amended in 1986, imposed new regulations requiring liable parties to remediate both operating and abandoned mine sites. The Resource Conservation and Recovery Act (RCRA), enforced by the Environmental Protection Agency, was enacted in 1976 and amended in 1989. This ordinance imposed more stringent regulations on the disposal and containment of solid wastes (which previously included most mining wastes), and re-characterized some solid mining wastes as hazardous wastes, which were required to meet new discharge and containment specifications.

State regulations that enact federal environmental initiatives, such as those imposed by the California State Water Quality Control Board, also affected the mining industry. Article 7, enacted in 1984, and revised in 1988, which pertains specifically to mining waste management, made significant modifications to waste classification, such as a narrowing of the range of wastes previously characterized as "inert". In addition, the ordinance identified suitable materials for disposal container liners for both inert and hazardous wastes, and issued and enforced new waste discharge requirements.

Federal regulations sanctioned to protect fish, wildlife and plants, such as the Endangered Species Act and The Migratory Bird Treaty Act, also affected the containment and disposal of toxic mining wastes and effluents. For example, heap leach gold operations often store cyanide-metal complexed solutions in uncovered ponds, which could be toxic to migratory birds and other wildlife (primarily because of the cyanide), and under the above regulations, the mine operator could face criminal or civil liability for any resultant death of a protected species.

One of the most significant concerns regards the discharge of acidic leachate from coal mines and high sulfur coal wastes (generated by coal cleaning technologies), resulting from the oxidation of pyrite. Pyrite is oxidized by water and oxygen, and the overall reaction can be represented as:

The reaction produces sulfuric acid and Fe (III) and as the pH decreases, the Fe (III) solubility increases, resulting in the auto-catalytic oxidation of pyrite, which is difficult to arrest once oxidation has commenced. In addition, naturally occurring bacteria such as *Thiobacillus ferrooxidans* can accelerate pyrite oxidation, by reoxidizing Fe (II) to Fe (III). The sulfuric acid produced during the reaction can leach metals (such as aluminum, manganese, zinc, nickel and iron)² from minerals with which it comes into contact. The metal-containing acidic discharge is commonly referred to as acid mine drainage, and can contaminate lakes, surface waters and aquifers. Several abandoned mine sites in California have exhibited evidence of acid mine drainage², and since water and oxygen cannot be completely eliminated at an underground or surface mine site, pyrite oxidation is inevitable. Consequently, methods for treating these acidic metal-bearing effluents must be addressed.

Other potentially heavy-metal containing wastes and effluents typical of the mining and minerals industry include heap leach residues, wet tailings, waste rock runoff, wastewaters from flotation, leaching and solvent extraction facilities, and liquid wastes from the operation of mechanical equipment such as boilers. There are currently many abandoned mines across the country that are on federal or state "Superfund" lists, because there is no identifiable responsible party to rectify environmental damage associated with inapt disposal of the above metal-containing solutions. As a result, public money is required to remediate these sites.

A variety of specialized methods³ has been developed for treating metal-laden industrial effluents and wastes, however, many of these technologies were designed to treat more concentrated streams. Consequently, they may have economic or technical shortcomings when treating the more dilute solutions that can be generated in the mineral and mining industries, as discussed below. These currently employed processes may not be able to reach the metal discharge requirements when treating more dilute solutions. "Dilute" solutions are characterized as containing a total metal concentration of 1–1000 ppm⁴. The large variation in metal ion concentration is due to the wide range of wastes and effluents produced by different processes.

Acidic, metal-containing effluents are usually treated by lime neutralization, which in the presence of sulfate can precipitate the metal as an amorphous hydroxide within a gypsum sludge that must then be disposed of as hazardous waste, which can be costly. Metal recovery is difficult from the large volumes of sludge produced (50 kg of limestone is required to neutralize 1 kg of hydrogen ions), and disposal costs can be significant, because of the difficulty in dewatering the sludge.

Solvent extraction reagents usually have a small but finite solubility in water, which can lead to significant losses when treating large volumes of dilute solutions. Although ion exchange resins are effective in removing heavy metals from dilute spent rinse waters, resins suitable for removing metals from industrial wastewaters are quite expensive (\$4000–\$20,000 per tonne) and can be subject to fouling by fines and trace metals. Electrowinning and hydrogen reduction are not suitable for treating dilute solutions because of increasing cathode polarization. Membrane processes have limitations for treating coal wastes, in particular, because of reduced permeability due to slimes. Membranes can also be degraded by strong oxidizing agents present in plating wastes, such as Cr (VI). Heavy metal removal by biological treatment processes has received much attention lately^{5,6}, however, activated sludges can decompose with time, and unless the material is properly managed, toxic metals can be released back into the environment. Furthermore, the high water content in the biological material can lead to high volume reduction costs.

An alternative to the above unit operations for metal ion recovery is sorption onto activated carbon, which has been used extensively in drinking water treatment to remove organic contaminants, such as phenols and related compounds, and recently has been investigated for its ability to sorb heavy metals. Corapcioglu and Huang⁷ concluded that the removal of copper, lead, nickel and zinc from dilute (1×10^{-5} – 8×10^{-4} M) solutions by adsorption onto various hydrous activated carbons was pH dependent and due to the formation of metal surface complexes. The authors were uncertain of the uptake mechanism at alkaline pH's, but speculated that metal removal from solution was due to adsorption rather than precipitation, even in the absence of complexing agents.

Srivastava and coworkers⁸ investigated the removal of copper (II), chromium (VI), mercury (II), molybdenum (VI), cadmium (II), zinc (II), nickel (II), cobalt (II) and lead (II) from dilute (10^{-5} – 10^{-2} M) solutions at 27°C and 45°C, by a treated fertilizer waste

slurry (which formed an "L"-type activated carbon). Metal affinity for the activated carbon surface varied, but in general, adsorption decreased with increasing temperature. Also, the maximum adsorption occurred at a unique pH for each metal, and in general, this removal appeared to follow the hydrolysis order of the cation. The adsorption of Cr (VI) (present as $\text{Cr}_2\text{O}_7^{2-}$), was at a maximum (about 53%) at low pH, and decreased with increasing initial solution pH. The activated carbon removed almost 100% of chromium, lead and mercury from approximately 10^{-5} – 10^{-4} M solutions, and 75%, 55%, and 48% respectively from approximately 10^{-3} M solutions. Molybdenum and copper were removed to a lesser degree, and the activated carbon showed almost no affinity for the remaining metals.

Tan and Teo⁹ investigated the removal of chromium and lead from dilute solutions (100 ppm) by adsorption onto four powdered activated carbons and determined, when taking into account the combined effect of metal ion concentration and carbon dosage, that Langmuir and Freundlich isotherms could not adequately describe the adsorption process. Modified Langmuir and Freundlich equations accounting for these two variables more accurately modeled the adsorption data.

Koshima and Onishi¹⁰ also investigated the effect of initial solution pH on the adsorption of nineteen metal ions onto activated carbon. However, removal at higher solution pH was regarded as an adsorption process (in the absence of a complexing agent), rather than precipitation. Therefore extremely high metal ion removals were observed at alkaline pH's.

On studying the removal of Cr (VI) by Calgon Filtrasorb-400 activated carbon, Huang and Wu¹¹ determined that Cr (VI) was removed by two mechanisms: adsorption, and reduction to Cr (III) and the participation of each mechanism depended on the solution pH. Reduction of Cr (VI) to Cr (III) occurred only at pH <6. Maximum adsorption of Cr (VI)

onto the activated carbon occurred between pH 5 and 6, and maximum adsorption of the Cr (III) species was at pH 5, but occurred to a lesser extent than Cr (VI) adsorption.

Using coal to treat metal-laden solutions is even more economically attractive than activated carbon, and the ability of low rank coals to remove cations from aqueous solutions, via an ion exchange between the metal and the surface functional groups, has been studied extensively.^{12,13,14} Although higher rank coals have less oxygen in the form of functional groups, it would be advantageous to use them in wastewater and effluent treatment because of their higher calorific value and dewatering ability. These characteristics could be important for coal detoxification and/or disposal in commercial operations, although the methods employed for the above procedures would depend on the manner in which the metals reported to the coal surface. One approach to detoxifying the metal-laden coal would be to incinerate the coal, leach the resulting ash and recover metals by conventional hydrometallurgical processes. However, if the metals become incorporated into mixed aluminosilicates or glasses, there would be no threat of metal toxicity, and the coal could be incinerated and would not require leaching prior to disposal. Alternatively, the coal might be detoxified and possibly regenerated for further use by acid elution. A final advantage of using a higher rank coal for treating coal mining and processing wastes would be its availability at these locations. Accordingly, a bituminous coal was selected for the present work.

There is little information on the use of higher rank coals for removing heavy metals from aqueous solutions. Venkobachar and Bhattacharya¹⁵ investigated the potential of an untreated bituminous Giridih coal to remove cadmium from a rural water supply in India. The bituminous coal was able to remove 97.6% of the cadmium from a 0.5 ppm solution after 24 hours, compared to only 25.4% cadmium removal obtained by Filtrasorb-400 activated carbon. Pandey and Chaudhuri¹⁶ found that nitric acid and other chemical

pretreatments such as sulfonation and sulfurization, improved the sorption capacity of Giridih coal during the uptake of mercury by generating additional surface functional groups.

The aim of the present study was to investigate the behavior of Upper Freeport bituminous coal, oxidized in gaseous and aqueous media, during the uptake of selected model cations from dilute aqueous solutions. Copper and cadmium were chosen as the model cations for this study, since they may be present in a wide range of industrial wastes and effluents, and can be toxic to humans, aquatic life and animals to varying degrees, as discussed below, and might also be recovered for their intrinsic value.

The as-received coal was also used to remove Mn (VII) from a potassium permanganate solution, by reducing the Mn (VII) to Mn (II) and Mn (IV) (in the form of an oxide surface layer). This type of reaction could be used to detoxify effluents containing strong oxidizing contaminants, which are potentially hazardous to the environment and public health. Since the surface oxide itself may participate in ion exchange or adsorption, the behavior of coal oxidized by potassium permanganate in copper and cadmium sulfate solutions was also investigated. Finally, potential industrial applications for treating metal-containing effluents by oxidized Upper Freeport, such as multi-stage counter current operations, are discussed.

In addition to acid mine drainage (present in dilute concentrations) and mining wastes, copper is present in many other industrial wastes, including metal cleaning and plating baths, pulp and paper board mills, chlorosilane (silicone) synthesis, wood preserving and fertilizer manufacturing¹⁷. Although chronic exposure to copper by humans is not extremely hazardous, animals such as sheep are very susceptible to copper toxicity. The maximum contaminant level goal¹⁸ for copper (MCLG) in drinking water is 1.3 ppm (the

U.S. EPA has set a treatment technique requirement rather than a maximum contaminant level (MCL) for copper).

Residual cadmium may be present in acid mine drainage (in dilute concentrations) and other mining wastes and effluents, as well as wastes from metallurgical alloying, ceramics and inorganic pigments manufacturing, electroplating (where it is often complexed with cyanide), nickel-cadmium battery manufacturing and the photographic industry. Cadmium may be extremely toxic to humans (it is a potential carcinogen) as well as other animals, aquatic and plant life and as a result, it has been classified as a priority pollutant by the U.S. EPA.¹⁹ The long half life of cadmium in humans of 20–25 years allows it to accumulate and chronic exposure may eventually affect the kidneys, lungs, heart and bones. The U. S. EPA has recently modified the MCL for cadmium in drinking water from 0.01 ppm to 0.005 ppm.¹⁸

2. BACKGROUND

2.1 Origins and Classification of Coal²⁰

"Coal" is a generic term used to describe a variety of materials, with very different physical and chemical properties. It is a heterogeneous material composed of organic microconstituents (called macerals) and mineral matter, and is considered to have formed from peat deposits produced in swamps through the accumulation of plant substances that were subjected to compression by subsequent deposition of overlying sediments and heating. These conditions account for the coalification of plant matter, which is a continuous evolution from decomposed debris (humic gels, wood, bark, fungi, and algal remains, for example) and degradation of the material toward a pure carbon or graphite structure. Coals are classified by rank, and type. The rank is a measure of the maturity of the coal in the coalification process, and the type identifies the coal macerals of different origins, which will be discussed below. In general, the rank order is arranged as:

Peat → Lignite → Subbituminous → Bituminous → Anthracite

Lignites and subbituminous coals are customarily referred to as low rank, while bituminous coals and anthracites are classified as high rank coals. Increasing rank corresponds to increasing carbon, and decreasing hydrogen and oxygen content. The physical and chemical properties of the coal vary significantly with rank.

2.2 Chemical and Physical Structure of Coal

2.2.1 General Molecular Structure of Coal

The different constituents of coal have very different structures, but in general, coal has a polymeric structure composed of aromatic macromolecules, which are linked by ethers, methylene groups, and some longer alkanes. The aromacity (reported as fraction of aromatic carbon, f_a) is a function of carbon/hydrogen ratio (and therefore coal rank), and ring structure can range from simple benzene rings to large condensed aromatic systems.²¹ The rings form lamellae, which, depending on the rank of the coal, have an average diameter of 20–23 Å. The number of these rings per lamella increases with coal rank, from 1–2 for lower rank coals, 3–5 for bituminous coals and anthracite coals may have more than 40 condensed rings. The corresponding aromacity ranges from 0.66 for lignite, up to 0.99 for anthracite coal.²² The molecular structure of coal is most often studied by ^{13}C nuclear magnetic resonance (NMR), however other techniques include infrared spectrometry, sodium hypochlorite oxidation and fluorination.

2.2.2 Organic Constituents in Coal

The microscopic organic constituents called macerals form the combustible part of the coal. Macerals are divided into three groups, called vitrinite, exinite (or liptinite) and inertinite, which differ in origin and chemical composition. The best characterized macerals are the vitrinites, which are the most abundant maceral component in bituminous coals. The carbon content, hydrogen to carbon ratio, and volatile content differ for the three maceral groups, and vitrinite is intermediate in volatility and hydrogen to carbon ratio. Vitrinite is composed of condensed aromatic rings (or hydroaromatic rings) that are connected by bridging $(\text{CH}_2)_n$ atoms, and occasionally -R-S-R groups. Attached to these rings are various functional groups: carboxyl ($-\text{COOH}$), phenolic ($-\text{OH}$), carbonyl ($-\text{C}=\text{O}$), etheric

(-O-) and alkyl (-C_nH_m). The molecular structure of vitrinite present in bituminous coal (containing 82% C) is shown in Figure 1²³.

Figure 1: Molecular structure vitrinite in bituminous coal (82% C)²³.

For bituminous coals, the functional groups are primarily phenolic and carboxylic, and they have a negative surface charge over a broad pH range, making them attractive sites for cations. A possible (overall) ion exchange reaction between a metal cation in aqueous solution and a surface functional group (carboxylic acid for example) is given by:

As the reaction proceeds and cations are taken up by the carboxylic groups, hydrogen ions are released into solution.

2.2.3 Inorganic Constituents of Coal

The inorganic material in coal is composed of optically identifiable mineral species and phases, and complexed metals and exchangeable cations (Na⁺, K⁺, Ca²⁺, Fe²⁺ and Fe³⁺). The major inorganic constituents are classified into six groups: clays (aluminosilicates), carbonates (primarily siderite, ankerite, calcite and dolomite), oxides, sulfides (pyrite and

marcasite) and occasionally sulfates and chlorides. Oxides include quartz and rutile, and account for up to 20% of all mineral matter. A variety of trace constituents is also present, although some (such as B, Be and Ge) are actually associated with the organic coal substance.

2.2.4 Chemical Composition

The composition of coal is defined in terms of ultimate (elemental) and proximate analysis, and ASTM standards for determining these parameters have been developed^{24,25}. Ultimate analysis quantitatively determines the amount of carbon, hydrogen, nitrogen, organic sulfur and oxygen present in the coal. Proximate analysis uses destructive distillation to determine the amount of moisture, volatile matter, ash and fixed carbon present in the coal.

The range of proximate and ultimate analyses for bituminous coals is given in Table 1, and specific properties of the Upper Freeport bituminous coal used in this study are shown in Table 2.

2.2.5 Porosity and Surface Area

Coal has a complex internal pore structure, similar to a series of molecular sieves. The pores are classified as macropores ($d > 500 \text{ \AA}$), mesopores (or transitional pores) ($d = 20\text{--}500 \text{ \AA}$), micropores ($d < 20 \text{ \AA}$), and submicropores ($d < 8 \text{ \AA}$). There are three different intrinsic structures in the coal matrices, which vary according to rank. These structural models are shown in Figure 2.²⁶

Table 1: Range of ultimate and proximate analyses of bituminous coal¹⁹

Carbon Weight %	79–85
Oxygen Weight %	2.9–8.8
Hydrogen Weight %	4.6–5.8
Organic Sulfur Weight %	.7–1.7
Volatile Content (Low Volatile–High Volatile Bituminous) Weight % Moisture Mineral Matter Free	14–50
Ash* Weight %	~17–39
Fixed Carbon* Weight %	~40.9–70.5
Moisture Weight %	1–15
Calorific Value BTU/lb Moisture Mineral Matter Free	10,500–>14,000

Table 2: Specific properties of as-received Upper Freeport²⁷

(all values reported in weight %)

Fixed Carbon	55.35
Organic Sulfur	1.12
Ash	17.59
Volatile Matter	27.05
Moisture	1.5

* Values based on specific bituminous coal samples studied by Herrera²⁷

Figure 2: Representation of the three different structures in coals²⁶.

Low rank coals have an "open" structure, containing non oriented lamellae connected by cross links; the porosity is due primarily to macropores. Bituminous coals have a "liquid structure" (because the structure is similar to that of a liquid), with somewhat oriented lamellae that form a layered structure. There are fewer crosslinks than the "open" structure, and few pores. Approximately 80% of the existing porosity is from micro and mesopores. The structure of higher rank coals, referred to as an "anthracite structure", consists of a large number of directionally oriented lamellae, with virtually no cross linking. As a result, these coals are highly porous, with the porosity contained in the micropores.

Surface areas of coals can be measured by BET gas adsorption, using nitrogen or carbon dioxide as the adsorbent, which provides the monolayer capacity of the solid (moles/unit area). This monolayer capacity multiplied by the cross-sectional area per molecule of the adsorbent yields the total surface area.

However, BET gas adsorption requires that all of the adsorbate be distributed in a monolayer, which is unrealistic for a microporous solid such as coal. The Polanyi-Dubinin

relationship, shown in equation (3), accounts for the micropore surface area, and in general, it is agreed that it calculates more accurate coal surface areas than the BET equation.

$$\log V = \log V_o - \left(\frac{BT^2}{\beta} \right) \log \left(\frac{P_o}{P} \right)^2 \quad (3)$$

- V = amount of gas adsorbed (cm³/g)
- V_o = the micropore capacity (cm³/g)
- T = temperature (K)
- P = the vapor pressure (atm)
- P_o = the saturation vapor pressure of the adsorbate at T (K) (atm)
- β = the affinity coefficient of the adsorbate relative to nitrogen or benzene
- B = a constant which measures the micropore size

The intercept of a plot of log V versus log(P_o/P)² yields the micropore capacity, which when multiplied by the cross-sectional area of the adsorbed molecules, calculates the micropore surface area.

CO₂ is generally considered a much better adsorbent for measuring coal surface areas than N₂ because of its lower activation energy for gas diffusion into the coal pores. Also, surface areas determined by N₂ adsorption are measured at lower temperatures than areas measured by CO₂ adsorption (-160°C up to -80°C, compared to -78°C or 25°C), and the thermal energy required to overcome the high activation energy required for N₂ diffusion into the very fine pores may be unavailable at these lower temperatures. Furthermore, the smaller molecular size of CO₂ as compared to N₂ (3.3Å versus 3.65Å) makes CO₂ accessible to smaller pores than those accessible to N₂²⁸. Walker and Geller²⁹ measured the surface area of an anthracite coal by CO₂ and N₂ adsorption, and calculated an area of 175 m²/g for the former at -78°C, and only 11 m²/g using the latter at -196°C. Other researchers have shown that surface areas of subbituminous to bituminous coals measured

by CO₂ adsorption at -78°C ranged from 125–200 m²/g, while those measured by N₂ at -196°C ranged from 3–10 m²/g.³⁰

It has been suggested that surface areas measured by CO₂ adsorption may also be erroneous because of the polar interaction of the CO₂ molecules with surface oxygen functional groups. Dietz and coworkers³¹ postulated that CO₂ produced “bicarbonate structure” surface complexes upon interaction with surface hydroxyl groups on carbons. The amount of CO₂ adsorbed increased with the increase in the fraction of the surface covered by hydroxyl groups. Also, CO₂ adsorption may induce swelling within the coal pores, which results in uncharacteristically high surface areas.³² It has been suggested that this swelling accounts for up to 50% of the surface area in lignites and sub-bituminous coals, and up to 20% in bituminous coals. Consequently, there is some uncertainty regarding the accuracy and significance of coal surface areas. Marsh³³ suggests that a “true” or “absolute” surface area is non-existent for a microporous solid, because the parameter depends on the employed measurement technique, as well as data interpretation. It may be more rigorous to report *relative* surface areas, which should be related in conjunction with the measurement technique, gas adsorbate and coal particle size.

The surface area of as-received Upper Freeport Bituminous, calculated by Herrera²⁷, using the Polanyi-Dubinin equation, with CO₂ as the gas adsorbate, was 120.5 m²/g. The surface area increased by about 54% after thermal oxidation in air at 230°C for 24 hours.

2.3 Mechanisms of Coal Oxidation

Coal oxidizes extremely easily in air or oxygen and this process, depending on coal rank, can significantly affect properties such as coking ability, reactivity, hydrophobicity, heat of combustion and surface area.

In general, it is agreed that oxidation of coal occurs by a series of steps, which can proceed to different degrees, depending on whether the oxidation occurs in gaseous or aqueous media^{9,10}. Extensive research has investigated the oxidation mechanisms of coals, especially those oxidized in air at relatively low temperatures (60–200°C)^{34,35,36}. In general, it has been established that coal oxidation proceeds in three stages. The initial stage of oxidation affects the surface only and involves the chemisorption of oxygen at readily accessible surface sites. The presence of moisture catalyzes the reaction, causing the chemisorbed oxygen to form peroxide or hydroperoxide complexes, which decompose into ketones, alcohols, acids, aldehydes, esters and ethers.³⁷ Aldehydes are easily oxidized to carboxylic acids.

During the second stage of oxidation, a large portion of the organic material in the coal is converted into alkali-soluble humic acids, which retain similar condensed cyclic structures to the parent coal, but have lower molecular weights due to the slight depolymerization.¹⁹ The humic acids contain sufficient amounts of hydrophilic groups, such as hydroxyl and carboxyl, to confer alkali solubility. Upon further, or more severe oxidation, the humic acids degrade to carbon monoxide, carbon dioxide, water and aromatic and aliphatic compounds, including simple benzenoids, formic, acetic, and oxalic acids, which are soluble in water, alkali, or acidic solutions.

Air oxidation generally stops at the first stage¹⁹, however oxidation in aqueous media, such as hydrogen peroxide, sulfuric acid, nitric acid, dichromate, hypochlorite and permanganate, may proceed to the final stage. Oxidation in aqueous media has also been studied to gain insight into structural changes induced by oxidation, because the formation of soluble products can often be correlated to specific chemical structures. Nevertheless, the nature of the chemical changes within the coal structure are not fully understood. It is thought that oxidation first attacks the aliphatic structure of the coal, although more severe

oxidation, or oxidation that proceeds past the initial surface oxidation phase, can degrade aromatic structures. Oxidation may also result in an increase in crosslinking by ether structures³⁰. Loss of swelling properties in coking coals have often been attributed to this particular behavior.

Hydrogen peroxide oxidation of coal proceeds via the peroxide decomposing on the coal surface producing molecular oxygen, which oxidizes the coal. This reaction is given by:

But in acidic solution, the presence of dissolved iron induces disproportionation of the hydrogen peroxide and the coal may be oxidized via the Fenton reaction, which produces hydroxyl and hydrogen superoxide radicals, and hydroperoxides³⁸. The hydroperoxides can then decompose to form various functional groups. The Fenton reaction is shown below:

Coal oxidation in alkaline potassium permanganate produces carbon dioxide and oxalic acid, the latter being attributed to the formation of benzoid structures¹⁹. Smith and Mapstone³⁹ concluded that oxalic acid and other simple products were produced during the initial stages of oxidation of an Australian brown coal and with further oxidation, little more oxalic acid was formed. Due to the complexity of the mechanism, the series of reactions

were not quantified, however, the authors suggested that since significant quantities of oxalic acid were formed only during the initial stage of the reaction, that oxidation was confined to the coal surface, and the reaction did not necessarily reach the stage where alkali soluble substances were produced. As a result, the main chemical structure of the coal was little affected.

2.4 Adsorption Equilibria

When a solute is being adsorbed from solution onto an adsorbent, adsorption equilibrium is reached when the rates of adsorption and desorption become equal. Under these conditions, no change can be observed in the concentration of the solute on the surface of the adsorbent, or in the bulk solution. Adsorption isotherms, which plot the amount of solute adsorbed per unit of adsorbent as a function of the bulk solution equilibrium concentration at constant temperature, provide qualitative information regarding the adsorption process as well as the extent of surface coverage by the adsorbate. Brunauer classified adsorption isotherms into five basic shapes, and Type I, or Langmuir isotherms are often used to model the adsorption of solutes from aqueous solutions onto activated carbon. The principal assumptions of the Langmuir isotherm are:

1. The maximum adsorption corresponds to a complete monomolecular layer.
2. Adsorption occurs on localized sites, and adsorbed molecules cannot migrate across the surface or interact with neighboring molecules.
3. The energy of adsorption is constant, and all sites have the same energy.

For adsorption from solution onto solid adsorbents, the Langmuir equation is given by:

$$X = \frac{X_m b C_e}{1 + b C_e}, \text{ where} \quad (9)$$

X = the amount of solute (moles) adsorbed per unit weight (grams) of adsorbent

C_e = equilibrium concentration of the solute in solution (moles/l)
 X_m = amount of solute adsorbed (moles) per unit weight (grams) of adsorbent required for monolayer coverage of the surface, also called the monolayer capacity
 b = a constant (l/mole) equal to the ratio of adsorption rate constant to the desorption rate constant and is equal to:

$$b = b_0 e^{\frac{Q}{RT}}, \text{ where } Q = \text{heat of adsorption.} \quad (10)$$

The Langmuir isotherm may be linearized by writing equation (9) in the form:

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad (11)$$

If the data fit the Langmuir equation, a plot of C_e/X versus C_e , yields a straight line, with a slope of $1/X_m$ and an intercept of $1/bX_m$. Another linear form can be obtained by dividing equation (11) by C_e , and plotting $1/X$ against $1/C_e$, which gives a slope of $1/bX_m$ and an intercept of $1/X_m$. The surface area may be obtained by multiplying the monolayer capacity by the cross-sectional area of the adsorbent, however, these values may be in error in the case of a microporous solid, such as coal, since much of the surface area is within the pore space.

The Freundlich isotherm is used extensively to model adsorption from aqueous solutions, and the isotherm is an empirical expression that accounts for surface heterogeneity, and an exponential distribution of surface sites and their energies. The Freundlich equation is expressed as:

$$X = K C_e^{1/n}, \text{ where} \quad (12)$$

X = the amount of solute (moles) adsorbed per unit weight (grams) of adsorbent
 C_e = equilibrium concentration of the solute in solution (moles/l),

and K and n are constants characteristic of the system.

The isotherm can be linearized by writing equation (12) as:

$$\log X = \log K + \frac{1}{n} \log C_e. \quad (13)$$

Plotting $\log X$ against $\log C_e$ results in a straight line, with a slope of $1/n$ and $\log K$ is the intercept at $\log C_e = 0$. Since the expression is empirical, the slopes and intercepts of the linearization have less physical meaning than the Langmuir isotherm, however, the slopes may provide an indication of the change in adsorptive capacity of the oxidized coal in the concentration ranges covered by the isotherm.

3. EXPERIMENTAL PROCEDURES AND METHODS

3.1 Coal Sample

Upper Freeport bituminous coal from the Troutville #2 Mine, Clearfield County, Pennsylvania was stored after mining under 99.995% argon to prevent oxidation. The samples were ground in a ball mill and sieved, and a +250–200 mesh size fraction (+75–63 μm) was used for all experimental work. This size fraction was stored under argon for use.

3.2 Materials

Reagent grade (Fisher Scientific) chemicals were used to prepare all solutions, except the potassium permanganate solution, which was a waste by-product from the preparation of MnO_2 . Reagent grade potassium permanganate was acidified with concentrated hydrochloric acid, to precipitate manganese oxide. The manganese oxide was filtered, and the resulting waste solution contained 8.42×10^{-3} M potassium permanganate and small amounts of KCl.

3.3 Analysis

All copper, cadmium and manganese solution concentrations (during metal uptake experiments) were analyzed using a Perkin Elmer Atomic Absorption Spectrometer 3110. The lowest metal ion concentration that could be measured confidently was 0.1 ppm, since this was the concentration of the lowest prepared standard for each metal. The measurement error was $\pm 5\%$.

The solution pH's were measured using a Corning Model 240, or a Beckman Model 21 pH meter.

3.4 Coal Oxidation

3.4.1 Potassium Permanganate Oxidation to Reduce Mn (VII)

Preliminary oxidation tests were done to determine whether Upper Freeport could remove Mn (VII) from a pH 3, 8.42×10^{-3} M KMnO_4 waste solution. The effect of coal-to-solution ratio was determined by magnetically stirring 1, 3, 5, 10, 12.5 and 20 grams of coal in 100 ml KMnO_4 solution in a Pyrex beaker, at 25°C (measured with a thermometer), for 4 hours. The suspensions were filtered and the filtrates were analyzed for total residual manganese by atomic absorption spectroscopy.

3.4.2 Potassium Permanganate Oxidation for Metal Uptake Experiments

A ratio of 1 gram of coal in 10 ml of 8.42×10^{-3} M KMnO_4 solution was magnetically stirred for 4 hours in a Pyrex beaker at 25°C , after which no residual manganese was detected in solution. The decomposition potential of the suspension, measured by platinum and calomel electrodes, was 1.22V SHE. The coal samples were dried under vacuum in a dessicator containing CaSO_4 , at room temperature, before performing metal uptake experiments.

3.4.3 Thermal Oxidation for Metal Uptake Experiments

The coal was oxidized in air, in a Precision mechanical convection oven, Model 26, at $230^\circ\text{C} \pm 5^\circ$ for 28 hours. Preliminary exploratory experiments had shown that the amount of copper removed from an approximately 5×10^{-3} M CuSO_4 solution by thermally oxidized coal increased with oxidation time (samples were oxidized for 4 to 28 hours). Hence 28 hours was selected as the standard oxidation time.

3.4.4 Hydrogen Peroxide Oxidation for Metal Uptake Experiments

Upper Freeport coal was oxidized by a 30% hydrogen peroxide solution, initially at pH 4.9. 20 grams of coal was placed in a Pyrex beaker with 500 ml H₂O₂, and the suspension was magnetically stirred. The steady state decomposition potential of the solution, as measured after one hour using platinum and calomel electrodes, was 0.76V SHE. The exothermic nature of the reaction made it necessary to immerse the beaker in an ice bath to control the temperature. The reaction was allowed to proceed to completion and although each suspension exhibited slightly different thermal behavior, the average reaction time was about two hours. The oxidized coal samples were dried under vacuum at room temperature, in a dessicator containing CaSO₄, before metal uptake experiments were performed.

3.5 Oxygen Functional Group Analysis

The concentration of surface carboxylic and phenolic functional groups on untreated and oxidized Upper Freeport was determined by the method of Brooks and Sternhell⁴⁰. The carboxylic group concentration was determined from the acetic acid liberated while contacting coal with a concentrated (3M) sodium acetate solution. The reaction is represented by:

where (s) denotes a surface species. The equilibrium is sufficiently displaced to the right by the large excess of sodium acetate.

Similarly, the total acidic functional groups were determined by measuring the H⁺ ions liberated during coal contact with a 0.15M Ba(OH)₂ solution. The overall reactions are represented by:

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

The 3M sodium acetate solution was prepared gravimetrically. The 0.15M Ba(OH)₂ solution was prepared using CO₂-free triply distilled water, which was boiled for two hours, and purged with 99.7% N₂ for one hour. The Ba(OH)₂ solution was shaken for 16 hours under N₂ to prevent as much BaCO₃ precipitation as possible and then allowed to settle for two days. While purging a titrator beaker with N₂, the supernatant was standardized using 0.31 M HCl, with phenolphthalein as indicator.

One gram of each coal sample was contacted with 100 ml of sodium acetate or barium hydroxide for at least 16 hours to ensure equilibrium. It was necessary to perform barium hydroxide adsorption under N₂ to prevent the formation of BaCO₃. For carboxylic 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 .31M HCl, with phenolphthalein as indicator, and the difference between the volume of HCl required to titrate a blank Ba(OH)₂ solution and the volume required to titrate the filtrate after Ba²⁺ exchange with coal functional groups, gave the total acid groups on the coal surface. Surface phenolic concentrations were obtained from the difference between total acidic groups and carboxylic groups.

The NaOH solution was standardized with 0.02M C₆H₅COOH (benzoic acid), in 200 proof ethanol. The benzoic acid was predried in a mechanical convection oven for 5 hours

at 55°C, and cooled under vacuum, then the benzoic acid was prepared gravimetrically. The NaOH solution was then used to standardize the HCl solution.

The amount of carboxylic and phenolic groups present on the oxidized coal after contact with the most concentrated copper and cadmium solutions used in the adsorption equilibria experiments (Sections 3.7 and 4.5) was also determined. Since the coal surfaces were probably saturated after contact with these metal ion solutions, functional group analyses indicated the maximum percentage of these functional groups participating in the uptake of copper or cadmium from solution.

3.6 Metal Uptake Kinetics

Acidified (pH 2) 0.05M CuSO_4 and CdSO_4 stock solutions (analyzed by atomic absorption) were prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ salts, and diluted to the appropriate concentrations for each experiment. No further pH adjustments were made to the diluted metal ion solutions. A ratio of 1 gram of Upper Freeport coal in 10 ml of metal ion solution (for most experiments 15 grams of coal was added to 150 ml of metal ion solution) was placed in a 250 ml polyethylene bottle, and shaken in a suspension adsorption agitator at room temperature. 10 ml portions of the suspension were withdrawn periodically, filtered using a vacuum, and the filtrate was analyzed for residual copper or cadmium. Preliminary metal uptake experiments were conducted for up to 45 hours, by running two consecutive experiments for each oxidation treatment [labeled (1) and (2) on plots]. Because there was little change in the metal ion removed from solution between 12 and 48 hours, subsequent experiments were conducted for 12 hours.

3.7 Metal Uptake at Different pH by Coal Oxidized by KMnO_4

Since cations must be removed from acidic effluents, the pH dependence of metal uptake should be known. Also, the pH at which metal removal is due to precipitation rather than adsorption from solution was of interest. Upper Freeport coal oxidized by $8.42 \times 10^{-3} \text{ M}$ KMnO_4 was contacted with $4.9 \times 10^{-3} \text{ M}$ CuSO_4 (312 ppm Cu^{2+}) and $4.3 \times 10^{-3} \text{ M}$ CdSO_4 (486 ppm Cd^{2+}) solutions, with pH 1-13 (adjusted with concentrated HCl and NaOH). For each experiment, 1 gram of coal was added to 10 ml of solution, placed in a 250 ml polyethylene bottle, and shaken at room temperature for 2 hours, since the kinetic data confirmed that a 2 hour contact time with the coal oxidized by KMnO_4 was sufficient to establish steady state conditions. The suspensions were filtered using a vacuum and the filtrates were analyzed for residual copper or cadmium.

3.8 Adsorption Equilibria

Langmuir and Freundlich adsorption isotherms (and linearizations of the data) were generated to estimate the total surface capacity of oxidized Upper Freeport for copper and cadmium, and to determine the adsorptive capacity of the different oxidized coal samples over the range of the four solution concentrations covered by the isotherms. 10 grams of oxidized coal was contacted with 100 ml of CuSO_4 or CdSO_4 solution, at pH 4, at room temperature. The four CuSO_4 solutions initially contained 3463, 359, 37 and 3.5 ppm Cu^{2+} . The four CdSO_4 solutions initially contained 6109, 625, 64 and 6 ppm Cd^{2+} , respectively. Although the suspensions containing coal oxidized by H_2O_2 and KMnO_4 reached steady state within two hours, the experiments were run for 48 hours to ensure steady state conditions for the suspensions containing thermally oxidized coal. pH adjustments were made with 0.01M H_2SO_4 .

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 KMnO₄ Oxidation of Coal to Reduce Mn (VII)

After 100 ml of the 8.42×10^{-3} M KMnO₄ (463 ppm Mn (VII)) solutions were contacted with coal for four hours, the extent of Mn (VII) reduction could be gauged from the intensity of their color. The solutions containing one gram and three grams of coal were still purple, while the other solutions were colorless. Table 3 shows the total residual manganese in solution after the different amounts of coal were contacted with 100 ml of KMnO₄ (atomic absorption spectroscopy cannot distinguish oxidation states). The solutions containing the smaller amounts of coal contained the most residual manganese, and the intense purple color suggested that most of the Mn (VII) was not reduced. At moderate coal concentrations, no manganese was detected in solution. Some residual manganese was present at higher coal concentrations, although these solutions were also colorless, suggesting that Mn (VII) was not present in solution.

The observed behavior might be explained by considering the Eh-pH diagram for the Mn-H₂O system at 25°C, which is shown in Figure 3⁴¹. The slurry containing 10 grams of coal in 100 ml KMnO₄ had a decomposition potential of 1.22V SHE, with a final pH of 6.5. These conditions of potential and pH border the region where the predominant Mn species is solid MnO₂. The reduction of permanganate in the presence of coal (which provides the electrons) to produce MnO₂ might be expressed as:

The redox potentials of the other coal-KMnO₄ slurries were not measured, but the solutions containing more coal would have had a lower redox potential than 1.22V SHE, and solutions with less coal would have had a higher redox potential. Although the final solution pH's were not reproducible, they tended to decrease with increasing coal concentration, from about 7.8 to 5.3 (although all of the final solution pH's increased from the initial solution pH of 3). Therefore, at lower levels of coal in solution, the permanganate ion persisted and in the presence of excess coal (providing additional electrons), MnO₂ was further reduced to Mn²⁺. Permanganate reduction to Mn²⁺ might be expressed as:

These tests demonstrated the potential of Upper Freeport to treat effluents containing Mn (VII). At moderate coal concentrations (5 or 10 grams of coal in 100 ml), all of the Mn (VII) was reduced to a less hazardous valence state of Mn (IV), in the form of an insoluble MnO₂ layer on the coal.

Table 3: Total residual manganese after treating coal samples for 4 hours, at room temperature, with 8.42×10^{-3} M KMnO₄ (463 ppm Mn (VII)) solutions.

Grams of Coal in 100 ml KMnO ₄	Total Residual Mn After Oxidation (ppm)
1	347
3	168
5	none detected
10	none detected
12.5	12
20	18

Figure 3: Eh-pH Diagram for the Mn-H₂O system at 25°C.⁴¹

Even though the Eh-pH diagram predicted that solid MnO₂ should have been formed when 10 grams of coal was contacted with 100 ml of KMnO₄ solution, X-ray diffraction of the coal for six hours using a Siemens D5000 Diffractometer did not detect a crystalline phase, suggesting that any manganese oxide is amorphous, microcrystalline, or too thin to be detected. Similarly, energy dispersive X-ray analysis attached to a 35CF JEOL scanning electron microscope detected only the bulk constituents of the coal sample. A beam energy of 15 kV correlated to a penetration depth of approximately 2–3 μm, therefore any surface layer would have been thinner than 2 μm. However, Smith and Mapstone³⁶ observed a MnO₂ precipitate in solution during the oxidation of an Australian brown coal by alkaline potassium permanganate. Drandão and Galembeck⁴² formed a non-crystalline MnO₂ layer on the surface of cellulose acetate fibers, by oxidizing the fibers in an acidic KMnO₄ solution at 60°C (X-ray diffraction of the fibers did not detect a crystalline phase). The amount of Mn (IV) oxide deposited was determined colorimetrically by oxidation to permanganic acid, using potassium periodate as the oxidizing agent. Residual manganese

was detected when the fibers were contacted with copper, zinc, and lead sulfate and chloride solutions.

4.2 Functional Group Analysis

Table 4 shows the amount of surface oxygen functional groups on the untreated coal and on the thermally oxidized coal samples before and after contact with the 3463 ppm Cu^{2+} and 6109 ppm Cd^{2+} pH 4 solutions from the adsorption equilibria experiments (written as Thermal/ Cu^{2+} for example). The two different experiments (surface functional group analyses on the three samples were performed twice) indicated that the $\text{Ba}(\text{OH})_2$ titrations used to determine the total amount of surface acid groups had poor reproducibility. There was also appreciable uncertainty in the amount of surface phenolic groups, since they were determined from the difference between the total surface acid groups and carboxylic groups. The same CH_3COONa solution was used for experiments 1 and 2 to determine carboxylic groups, however a new, slightly more concentrated $\text{Ba}(\text{OH})_2$ solution was used in the second experiment (0.17 M compared to 0.15 M) to determine total acid groups. Much less Ba^{2+} exchange with the coal surface functional groups was observed in the 0.17 M solution, therefore the total surface acid groups on the thermally oxidized coal determined by the two experiments varied by about 40%. Since BaCO_3 precipitated rather quickly and easily, the titrator beaker was purged with N_2 , which caused some of the filtrate to splash on the sides of the beaker. This may have affected the reproducibility of the titrations. Also, the 25 ml burette used for all of the titrations was only accurate to 0.1 ml and smaller volumes were estimated. Two titrations were done for each sample and the average of the two as used to calculate carboxylic and total acid groups, however, this average was of two numbers with significant error. The raw data for the titrations are shown in Appendix I.

Table 5 shows the amount of surface carboxylic and phenolic functional groups on the other oxidized coal samples and the untreated coal, as well as the oxygen functional groups remaining after the oxidized coal samples were contacted with the 3463 ppm Cu^{2+} and 6109 ppm Cd^{2+} solutions. These analyses were only performed once, and it is probable that total acid group (and therefore phenolic groups) data have significant error. Consequently, the functional group analyses can provide only an approximate assessment of the increase in surface oxygen functional groups resulting from the three oxidative pretreatments.

The functional groups analyses indicated that the most carboxylic groups were present on the thermally oxidized coal. The coal oxidized by KMnO_4 had fewer carboxylic groups than the untreated coal; KMnO_4 oxidation may have produced carboxyl-manganous salts on the coal surface and the exchange with CH_3COONa only calculated the carboxylic acids. H_2O_2 oxidation generated the least amount of carboxylic and phenolic groups, and this coal also had fewer carboxylic functional groups than the untreated coal. The H_2O_2 might have oxidized some of the carboxylic groups, however this behavior would have probably required a stronger oxidant ($E^\circ \text{H}_2\text{O}_2 = 0.76 \text{ SHE}$).

The oxygen functional group analyses for the oxidized coal samples contacted with the copper and cadmium solutions from the adsorption equilibria experiments are discussed in Section 4.5 and related to the adsorption isotherms.

4.3 Metal Uptake Kinetics

4.3.1 Copper Removal

The residual copper in a solution initially containing $4.8 \times 10^{-3} \text{ M CuSO}_4$ (305 ppm Cu^{2+}) at pH 3.1, after contact with the different oxidized coal samples is shown in Figure 4. Untreated coal removed little copper from solution, which suggests that oxygen functional

groups, or some other active sites introduced during oxidation, are responsible for metal uptake, and not ash minerals in the coal (which can exhibit ion exchange behavior in some coals).

Table 4: Surface oxygen functional groups (moles/ gram of coal) on thermally oxidized coal before and after contact with the 3463 ppm Cu²⁺ and 6109 ppm Cd²⁺ pH 4 solutions used in adsorption equilibria experiments. The data indicate the irreproducibility of total acid groups analysis, as determined by Ba²⁺ exchange.

Sample	Experiment	COOH Groups (moles/ g coal)	OH Groups (moles/ g coal)	Total Groups COOH + OH (moles/ g coal)
Untreated	1	7.5×10^{-4}	2.7×10^{-4}	7.8×10^{-4}
Thermal	1	2.2×10^{-3}	4.2×10^{-3}	6.4×10^{-3}
	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}
	2	1.9×10^{-3}	1.7×10^{-3}	3.6×10^{-3}
Thermal/ Cd ²⁺	1	1.7×10^{-3}	2.3×10^{-3}	4.0×10^{-3}
	2	1.6×10^{-3}	1.3×10^{-3}	2.9×10^{-3}

Table 5: Surface oxygen functional groups (moles/ gram of coal) on untreated and oxidized coal samples before and after contact with the 3463 ppm Cu²⁺ and 6109 ppm Cd²⁺ pH 4 solutions used in adsorption equilibria experiments.

Sample	COOH Groups (moles/ g coal)	OH Groups (moles/ g coal)	Total Groups (COOH + OH) (moles/ g coal)
Untreated	7.5×10^{-4}	2.7×10^{-4}	7.8×10^{-4}
KMnO ₄	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}
KMnO ₄ / Cd ²⁺	3.4×10^{-4}	9.4×10^{-5}	4.3×10^{-4}
H ₂ O ₂	3.8×10^{-4}	4.6×10^{-4}	8.4×10^{-4}
H ₂ O ₂ / Cu ²⁺	3.3×10^{-4}	4.8×10^{-4}	8.1×10^{-4}
H ₂ O ₂ / Cd ²⁺	3.8×10^{-4}	2.3×10^{-4}	6.1×10^{-4}

The thermally oxidized coal removed copper slowly, but steadily with time. Copper uptake on coal oxidized by H_2O_2 appeared to reach steady state within two hours. The coal oxidized by KMnO_4 removed as much copper as the thermally oxidized coal, however, most of the copper was removed within two hours, after which very little removal was observed. Metal uptake on coal oxidized by H_2O_2 and KMnO_4 exhibited appreciable scatter, which may possibly be due to the presence of microscopic coal fines. Copper adsorbed onto the fines, which might be small enough to pass through the filter paper, would increase the metal ion concentration reported to be in solution. The disparity in the kinetics of metal uptake on the oxidized coal samples may be a function of the different pore structures (produced from the oxidation pretreatments) onto which the ions were being adsorbed.

Figure 5 shows copper removal from a more dilute solution, initially containing 4.6×10^{-4} M CuSO_4 (29 ppm Cu^{2+}), at pH 5.3. Once more, the thermally oxidized coal removed copper steadily with time, in this case resulting in 2.6 ppm residual copper after 45 hours of contact. Conversely, the coal oxidized by H_2O_2 was virtually ineffective in removing copper from solution. This behavior may have been a function of the surface area of the coal oxidized by H_2O_2 , which may have been smaller than the surface area of the thermally oxidized coal. The coal oxidized by H_2O_2 may have also had a very fine pore structure and since the solution pH was high enough for hydrolysis to occur, $\text{Cu}(\text{OH})_2$ may have precipitated and blocked the pores, preventing further metal uptake on the surface of the coal, as well as metal diffusion into the internal coal pore structure.

As with the more concentrated solution, the coal oxidized by KMnO_4 removed copper rapidly, and residual copper concentrations were comparable to those obtained by thermally oxidized coal contacted with the solution for about 20 hours.

Figure 4: Effect of Upper Freeport oxidation treatment on copper removal. Initial solution concentration = 4.8×10^{-3} M CuSO_4 (305 ppm Cu^{2+}), initial solution pH = 3.1.

Figure 5: Effect of coal oxidation treatment on copper removal. Initial solution concentration = 4.6×10^{-4} M CuSO_4 (29 ppm Cu^{2+}), initial solution pH = 5.3.

Because copper uptake on the coal oxidized by KMnO_4 was so rapid, the kinetics were studied in further detail. Figure 6 shows copper removal from a solution initially containing 320 ppm Cu^{2+} . The data indicate that the maximum metal removal occurred within ten minutes. Shorter time periods could not be studied reliably with the existing experimental equipment because of the time required to filter the suspensions. The rapid metal ion removal suggests that metal uptake was chemically limited rather than under diffusion control, which would have resulted in slower metal uptake kinetics due to the diffusion of copper into the internal pores. The amorphous MnO_2 surface layer could have certainly influenced the rapid copper uptake kinetics.

Figure 6: Copper removal from 4.8×10^{-3} M CuSO_4 solution (305 ppm Cu^{2+}), initial solution = pH 3.1, by KMnO_4 oxidized coal.

Figures 7–9 replot the data from Figures 4 and 5 (for the first 24 hours only, since most of the data lie between 2 and 24 hours) as the percentage of copper remaining in solution after

contact with the different oxidized coal samples. The efficiency of copper removal from solution increased with decreasing copper concentration for the coal oxidized thermally and by KMnO_4 . If equation (2) is rewritten specifically for copper removal by carboxylic groups (although phenolic groups may participate in sorption), an equilibrium constant may be expressed by equation (16):

$$K = \frac{\{(\text{RCOO})_2\text{Cu}_{\text{surf}}\} \{\text{H}^{+}_{\text{aq}}\}^2}{\{\text{Cu}^{2+}_{\text{aq}}\} \{\text{RCOOH}_{\text{surf}}\}^2} \quad (16)$$

Noting that sorption of copper would decrease the concentration of surface functional groups from their initial value, and that the two CuSO_4 solutions had different initial pH's, which affects the position of equilibrium, it is clear that the data for the coal oxidized thermally and by KMnO_4 are not inconsistent with equation (16), however, the behavior of the coal oxidized by H_2O_2 is not fully understood. However, since both carboxylic and phenolic functional groups are participating in ion exchange or adsorption, there is likely to be a range of equilibrium constants, rather than a unique value as appears in equation (16).

Although the coal oxidized by KMnO_4 was effective in removing copper from solution, manganese ions were released from the coal surface during copper uptake, suggesting that sorption alone was not responsible for copper uptake. Figure 10 shows the magnitude of the change in copper and manganese concentrations with time in the solution that initially contained $4.8 \times 10^{-3} \text{ M CuSO}_4$. The exchange between manganese and copper does not appear to be related by an exact stoichiometric relationship, which suggests that there is also some ion exchange between hydrogen ions and copper. This particular behavior is discussed in further detail in Section 4.4.

Figure 7: Effect of copper solution concentration (4.8×10^{-3} M CuSO_4 (305 ppm Cu^{2+}) pH= 3.1, 4.6×10^{-4} M CuSO_4 (29 ppm Cu^{2+}) pH= 5.3) on copper removal by thermally oxidized coal.

Figure 8: Effect of copper solution concentration (4.8×10^{-3} M CuSO_4 (305 ppm Cu^{2+}) pH= 3.1, 4.6×10^{-4} M CuSO_4 (29 ppm Cu^{2+}) pH= 5.3, 4.4×10^{-5} M CuSO_4 (2.8 ppm Cu^{2+}) pH= 5.4, 4.6×10^{-2} M CuSO_4 (2919 ppm Cu^{2+}) pH= 2.0, on copper removal by coal oxidized by hydrogen peroxide.

Figure 9: Effect of copper solution concentration (4.8×10^{-3} M CuSO_4 (305 ppm Cu^{2+}) pH= 3.1, 4.6×10^{-4} M CuSO_4 (29 ppm Cu^{2+}) pH= 5.3) on copper removal by coal oxidized by potassium permanganate.

Figure 10: Magnitude of change in concentration of copper and manganese ions during contact of KMnO_4 oxidized coal with 4.8×10^{-3} M CuSO_4 (305 ppm Cu^{2+}) (Copper concentrations decreased, manganese concentrations increased.)

4.3.2 Cadmium Removal

Cadmium removal by the untreated and oxidized coal from a 4.43×10^{-3} M CdSO_4 (498 ppm Cd^{2+}), pH 6 solution is shown in Figure 11. In contrast to the behavior in copper solutions, the thermally oxidized coal was only marginally more effective in removing cadmium than the untreated coal, suggesting that the surface functional groups had a lesser affinity for cadmium than for copper. This behavior is consistent with both the hydrolysis order of the two cations and their affinity for carboxylic groups, as observed in solvent extraction.⁴³ The kinetics of cadmium removal by coal oxidized by H_2O_2 and KMnO_4 were similar to those for copper removal, with rapid initial metal uptake, followed by little additional change in cadmium solution concentration. The difference between the cadmium removed by the thermally oxidized coal and the coal oxidized by KMnO_4 was significant, suggesting that the amorphous MnO_2 surface layer on the KMnO_4 oxidized coal had a greater influence on metal ion removal than the surface oxygen functional groups.

Figure 11: Effect of Upper Freeport coal oxidation treatment on cadmium removal. Initial solution concentration = 4.43×10^{-3} M CdSO_4 (498 ppm Cd^{2+}), initial solution pH = 6.0.

The change in concentration of cadmium and manganese ions in solution during sorption by KMnO_4 oxidized coal is displayed in Figure 12. The cadmium in solution decreased slightly after the first two hours of contact with the oxidized coal, after which very little sorption occurred. Less manganese was released into solution during cadmium uptake than was released during copper removal, and it is even more clear that there is no simple stoichiometric relationship between the changes in the cadmium and manganese concentrations. The implications of this behavior are discussed in Section 4.4.

Figure 12: Magnitude of change in concentration of cadmium and manganese ions during contact of KMnO_4 oxidized Upper Freeport coal with $4.43 \times 10^{-3} \text{ M CdSO}_4$ (498 ppm Cd^{2+}) pH 6 solution. (Cadmium concentrations decreased, manganese concentrations increased.)

4.4 Metal Uptake at Different Solution pH on Coal Oxidized by KMnO_4

The pH at which the removal of cations from solution is enhanced by precipitation is of interest. It is also important to understand whether metal uptake depends primarily on the affinity for coal surface functional groups generated by oxidation, or is predominantly influenced by bulk hydrolysis of the cations.

Given that the preliminary tests reported above indicated that most of the uptake of copper or cadmium on coal oxidized by KMnO_4 occurred within the first two hours of contact, the effect of solution pH was screened using two-hour experiments. Figure 13 shows the change in concentration of copper and manganese ions in solution, as a function of initial solution pH. Very little copper or cadmium was removed at very low pH, which is consistent with equation (23). The amount of copper and cadmium removed increased with increasing pH, steadily for copper, and up to a plateau for cadmium. Each system then reached a threshold where the metal was almost completely removed from solution, between pH 5 and 6 for copper, and between pH 8 and 9 for cadmium. These thresholds coincided with the pH's where visible precipitation of metal ion from solution was observed during solution preparation. This behavior also correlated well to precipitation diagrams constructed by Monhemius⁴⁴, which indicate the pH at which a cation of a given activity should precipitate from solution as a hydroxide. The activity coefficient (γ) of Cu^{2+} ions in the 4.9×10^{-3} M CuSO_4 solution was taken to be 0.53, as estimated using the mean salt method of Garrels and Christ⁴⁵:

$$\gamma_{\text{Cu}^{2+}} = \frac{\gamma_{\pm}^2 \text{CuSO}_4 \gamma_{\pm}^2 \text{KCl}}{\gamma_{\pm}^3 \text{K}_2\text{SO}_4} \quad (17)$$

The mean ionic activities were determined by Latimer⁴⁶ and the values used in the calculation were the mean ionic activities of 0.005 molal solutions.

The activity of Cu^{2+} ions in the 4.9×10^{-3} M CuSO_4 solution was taken to be 2.6×10^{-3} . The precipitation diagram predicts that copper hydroxide should precipitate from this solution at pH 5.5, as indicated by the arrow on Figure 12 (at pH 5.5). At this pH, metal removal was significantly enhanced. The activity coefficient for Cd^{2+} in the 4.3×10^{-3} M CdSO_4 solution, was also taken to be 0.53, since mean ionic activity coefficients were not available for CdSO_4 , and the corresponding activity of Cd^{2+} in solution was 2.3×10^{-3} . The arrow on Figure 14 (at about pH 8.3) indicates the pH at which $\text{Cd}(\text{OH})_2$ should be formed according to the hydroxide precipitation diagram.

It is apparent from Figures 13 and 14 that the amount of manganese released into solution decreased with increasing initial pH, and was not related to the uptake of copper or cadmium. It is likely that the manganese oxide present on the coal surface underwent reductive dissolution, with the coal providing the necessary electrons, a reaction shown in equation (18):

The increase in CuSO_4 and CdSO_4 solution pH after contact with these oxidized coal samples indicated that H^+ ions were being consumed, which is consistent with equation (18). The above data indicate that there is little ion exchange between manganese and copper or cadmium. Furthermore, the MnO_2 layer appeared to undergo similar reductive dissolution in dilute H_2SO_4 (pH 3) in the absence of copper or cadmium. Copper and cadmium may be adsorbed onto the MnO_2 surface layer, and they may also participate in ion exchange with, or be sorbed by, surface oxygen functional groups, and form surface precipitates at higher pH. The predominant mechanism is clearly pH dependent.

Figure 13: Magnitude of change in concentration of copper and manganese ions during contact of KMnO_4 oxidized Upper Freeport coal with $4.9 \times 10^{-3} \text{ M}$ (312 ppm Cu^{2+}) CuSO_4 , as a function of initial solution pH. The arrow indicates the pH corresponding to the formation of Cu(OH)_2 , according to hydroxide precipitation diagrams⁴⁴.

Figure 14: Magnitude of change in concentration of copper and manganese ions during contact of KMnO_4 oxidized Upper Freeport coal with $4.3 \times 10^{-3} \text{ M}$ (486 ppm Cd^{2+}) CdSO_4 , as a function of initial solution pH. The arrow indicates the pH corresponding to the formation of Cd(OH)_2 , according to hydroxide precipitation diagrams⁴⁴.

4.5 Adsorption Equilibria

4.5.1 Copper

Figure 15 shows the Freundlich linearization for Cu^{2+} on the different oxidized coal samples. The slopes of the lines may provide an indication of the adsorption capacity of the coal over the given solution concentration range. A steep slope (close to 1) implies that the adsorptive capacity of the adsorbate decreases significantly at lower equilibrium solution concentrations. Relatively flat slopes ($\ll 1$) imply that the adsorptive capacity is only slightly reduced at lower equilibrium concentrations. The coal oxidized by H_2O_2 had the steepest slope (0.73), followed by thermally oxidized coal (0.46), while coal oxidized by KMnO_4 had the flattest slope (0.16). At the lower concentrations, the coal oxidized by KMnO_4 removed the most copper from solution and at higher concentrations, the three oxidized coal samples removed comparable amounts of copper from solution. These slopes can only provide a rough qualitative assessment of the change in the adsorption capacity of the oxidized coal samples over the given range of metal ion solution concentrations and probably have appreciable error due to the fact that the metal ion solution concentrations ranged over several orders of magnitude. All of the calculated parameters for the Freundlich and Langmuir linearizations for copper (and cadmium) uptake on the oxidized coal samples are located in Appendix II.

Figures 16 and 17 plot the fitted Langmuir isotherms generated by using the parameters (X_m and b) calculated from a Langmuir linearization (plotting C_e/X versus C_e) along with the experimental data, for the coal oxidized thermally and by KMnO_4 . The data for the coal oxidized by H_2O_2 were not adequately described by Langmuir behavior and are therefore not shown (there was almost no removal from the most concentrated copper solution). The actual linearizations are not shown because the data could not be displayed effectively on a linear scale due to the wide concentration range of the copper (and cadmium) solutions used in the experiments.

The coal oxidized by H_2O_2 removed more copper from the more dilute solutions than was observed in the kinetic experiments. The solution pH's used in the adsorption equilibria experiments were lower than the pH's of the solutions used for the kinetic experiments (4.0 compared to 5.3 and 5.4), and were low enough that cation hydrolysis did not occur. It is proposed that fine pores in the coal were not blocked by $\text{Cu}(\text{OH})_2$ precipitates at the lower solution pH.

The inverse of the slopes calculated by the Langmuir linearizations (not shown) for copper uptake on thermally oxidized coal, and coal oxidized by KMnO_4 yielded the surface saturation by Cu^{2+} at the given pH. The Langmuir adsorption isotherm predicted that the maximum Cu^{2+} sorbed on the thermally oxidized coal from the pH 4 solution was 6.92×10^{-5} moles/gram, and for coal oxidized by KMnO_4 , 4.13×10^{-5} moles Cu^{2+} /gram. However, this estimate of the saturation capacity of the coal samples may be significantly in error, since the slope of the lines generated by the linearizations was taken from only four data points over an extremely broad concentration range and the experimental data deviates from the fitted isotherm at the lower concentrations (especially in the case of the copper uptake by coal oxidized by KMnO_4).

4.5.2 Cadmium

Figure 18 shows the Freundlich linearization of Cd^{2+} on the oxidized coal samples. The coal oxidized by KMnO_4 best fit the linearization. The behavior of the coal oxidized by H_2O_2 in the most concentrated solution (6109 ppm Cd^{2+}) was unusual, since the coal appeared to remove almost no cadmium. The slopes of the linearizations for the thermally oxidized coal and the coal oxidized by KMnO_4 were 0.39 and 0.47.

Figures 19 and 20 plot the fitted Langmuir isotherms for Cd^{2+} uptake on the coal oxidized thermally and by KMnO_4 as well as the adsorption isotherms generated from the experimental data. The coal oxidized by H_2O_2 did not follow Langmuir behavior because it appeared to remove the most cadmium from a solution of intermediate concentration. This behavior was also observed during kinetic copper uptake experiments on the coal oxidized by H_2O_2 , even though those solutions had different initial solution pH.

The maximum amount of cadmium sorbed from the pH 4 solutions onto the thermally oxidized coal, as calculated by the Langmuir linearization (not shown) was 1.56×10^{-5} moles/gram and for the coal oxidized by KMnO_4 , the capacity was 1.64×10^{-5} moles Cd^{2+} /gram of coal. Comparing the adsorption capacity of the coal oxidized by KMnO_4 with the amount of cadmium removed from the 4.3×10^{-3} M solution at pH 4, from Figure 14, it is clear that the cadmium concentration on the coal surface (in Figure 14) was about 2.0×10^{-5} moles/gram, which is greater than the saturation capacity calculated by the Langmuir adsorption data. However, the Langmuir adsorption capacities for cadmium on the oxidized coal samples can only be taken as rough estimates, for reasons previously discussed.

4.5.3 Comparison with Functional Group Analyses

The oxygen functional group analyses for the thermally oxidized coal calculated the total surface groups to be 5.1×10^{-3} moles/gram of coal (an average of the two experiments was used). Assuming that 2 moles of surface functional groups are required to remove 1 mole of Cu^{2+} from solution, a surface capacity of 6.92×10^{-5} moles Cu^{2+} /gram on the thermally oxidized coal corresponds to about 2.7% of the functional groups used during sorption. The functional group analyses (an average of the two experiments) of the thermally oxidized coal after contact with the 3463 ppm Cu^{2+} solution indicated that 9.8% of the available functional groups participated in sorption. Although there are discrepancies

Figure 15: 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 16: 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 17: 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 18: 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 19: 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 20: 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.

between the results calculated by the two different methods, both methods indicated that a very low percentage of functional groups participated in the uptake of copper. Similarly, assuming 2 moles of functional groups were required to remove 1 mole of Cd^{2+} , a surface capacity of $1.56 \times 10^{-5} \text{ M Cd}^{2+}/\text{gram}$, on the thermally oxidized coal indicated that only about 0.6% of the available functional groups were participating in Cd^{2+} sorption. In contrast, surface functional group analyses (using an average of the two experiments) of the thermally oxidized coal contacted with the 6109 ppm Cd^{2+} solution indicated that about 31% of the available functional groups participated in Cd^{2+} uptake, which was more than the functional groups participating in Cu^{2+} uptake. Since the kinetic data also indicated that the thermally oxidized coal has a lesser affinity for cadmium than copper, a greater fraction of the original number of surface functional groups would be expected after contact with the cadmium solution, than after contact with the copper solution.

The functional group analysis calculated that coal oxidized by KMnO_4 had 3.6×10^{-3} moles $\text{COOH} + \text{OH}/\text{gram}$ of coal, and the Langmuir surface saturation of 4.13×10^{-5} moles $\text{Cu}^{2+}/\text{gram}$ implied that about 2.3% of the available functional groups were participating in copper sorption. The Langmuir surface saturation of 1.64×10^{-5} moles $\text{Cd}^{2+}/\text{gram}$ implied that about 0.9% of the available functional groups participated in cadmium sorption. Direct functional group analyses produced large discrepancies with the above data, calculating that about 73% of the available functional groups participated in copper sorption, and 88% participated in the uptake of cadmium.

Although saturation capacities of the coal oxidized by H_2O_2 could not be obtained confidently (since the data did not fit the Langmuir isotherm very well), surface functional group analyses indicated that about 3.4% of the available functional groups participated in copper sorption, and about 27% for cadmium sorption. There were some obvious discrepancies here, since the adsorption equilibria data indicated that almost no cadmium

was removed from the 6109 ppm Cd^{2+} solution. However, the functional group analysis indicated that cadmium removal by H_2O_2 -oxidized coal was only due to phenolic groups, and none of the carboxylic groups participated in sorption. Carboxylic groups are known to have a lesser affinity for cadmium than for copper.

Comparing the amount of functional groups on the different oxidized coals with the kinetic and adsorption equilibria data, it is clear that metal uptake was not a function of the amount of surface oxygen functional groups alone. It is proposed that sorption was also influenced by the pore structures resulting from the different oxidative pretreatments.

The thermally oxidized coal removed copper steadily (although cadmium was not removed to an appreciable extent in the kinetic experiments) with time, which suggests that this coal had a more tortuous pore structure, and metal uptake was limited by diffusion into these pores.

Since the coal oxidized by KMnO_4 removed comparable amounts of copper and cadmium to the thermally oxidized coal (although it had fewer oxygen functional groups than the thermally oxidized coal), metal uptake was influenced predominantly by the amorphous MnO_2 surface layer and not oxygen functional groups. The rapid metal uptake kinetics on the coal oxidized by KMnO_4 were also probably due to interaction with the amorphous MnO_2 surface layer. The kinetics also suggest that metal adsorption was chemically limited, rather than under diffusion control.

The coal oxidized by H_2O_2 generally removed the least amount of metal ion from solution, which was consistent with the small amount of surface functional groups on this oxidized coal. However, since most of the metal ions were removed very rapidly, this suggests that sorption occurred primarily on the coal surface and was chemically and not diffusion

limited. This coal may have had a very fine pore structure, and at higher solution pH's, $\text{Cu}(\text{OH})_2$ precipitation may have blocked these pores, and a decrease in metal ion removal was observed.

5. POTENTIAL APPLICATION FOR TREATING EFFLUENTS

Since the adsorption equilibria and functional group analysis indicated that the total capacity of oxidized coal surfaces for copper and cadmium was quite low, and generally, a very small percentage of surface functional groups participated in metal uptake, the commercialization of such a process is questionable. An industrial process might use a multi-stage counter-current operation to enhance mass transfer, and the oxidized coal would be subsequently loaded with increasingly more concentrated metal ion solutions, until the surface sites were saturated.

In order to simulate such conditions, 5 grams of the thermally oxidized coal that had been contacted with the 3.5 ppm, pH 4, Cu^{2+} solution in the adsorption equilibria experiments (10 grams of coal in 100 ml), and after which had 0.034 mg Cu^{2+} /gram (5.35×10^{-6} moles Cu^{2+} /gram coal), was then contacted with 50 ml of more concentrated, pH 4 feed solutions containing either 3617 ppm (5.7×10^{-2} M CuSO_4) or 374 ppm Cu^{2+} (5.9×10^{-3} M CuSO_4). Table 6 shows the copper loading on the coal surface after two and four hour contacts with these solutions, and the residual copper concentration in the effluents. The progression of coal surface saturation by copper, as predicted by the Langmuir isotherms (in Section 4.5) at pH 4 is given as the % of maximum loading obtained.

The oxidized coal, which was already loaded with some copper, was clearly able to remove the metal from more concentrated solutions, however, the coal used in this experiment had an extremely small amount of copper on its surface and was not close to saturation.

Additionally, considering that a relatively large amount of coal was added to the metal-containing solutions (a ratio of one gram of coal in 10 ml solution), the residual copper was quite high.

Table 6: Copper loading (moles/gram) on thermally oxidized coal already containing 5.35×10^{-6} moles Cu^{2+} /gram, after 2 and 4 hour contact with 5.7×10^{-2} M (3617 ppm Cu^{2+}) or 5.9×10^{-3} M CuSO_4 (374 ppm Cu^{2+}), pH 4 feed solutions and residual effluent concentrations (ppm).

CuSO_4 Feed	Contact Time (hours)	Cu Loading (moles/gram)	% of Maximum Loading	Residual Effluent Cu^{2+} (ppm)
5.9×10^{-3} M (374 ppm Cu^{2+})	2	9.8×10^{-6}	12	312
	4	1.5×10^{-5}	22	277
5.7×10^{-2} M (3617 ppm Cu^{2+})	2	2.7×10^{-5}	39	3444
	4	3.6×10^{-5}	52	3391

Using this coal-to-solution ratio in a commercial operation, and assigning an arbitrary flow rate to an effluent treatment plant of $100 \text{ m}^3/\text{day}$, would require 10^4 kg/day of oxidized coal, which is an exorbitant amount of coal that would require disposal. The coal containing toxic metals might be detoxified by incinerating the coal, and leaching the ash, but considering the calorific value of bituminous coal, incineration would have to be done in conjunction with power generation (and some generated heat might be used to oxidize fresh coal). Moreover, it does not appear that the thermally oxidized coal, which probably had the greatest potential for scale-up, can achieve the low residual solution concentrations required for disposal. Upper Freeport does not appear to have a high affinity for cations, but may be better utilized for adsorption of organic pollutants (it would be cheaper than activated carbon), or as a reducing agent for wastes containing oxidizing contaminants, such as Mn (VII) and possibly Cr (VI), which is present in plating industry wastes.

6. SUMMARY AND CONCLUSIONS

Upper Freeport bituminous coal was able to remove Mn (VII) from dilute aqueous solution by concurrent adsorption and reduction of the manganese to lower valence, less toxic states. This type of reaction indicated the potential of using coal to remove oxidizing contaminants from effluents. Since oxidizing anions can degrade ion exchange resins and membranes, coal may be a viable alternative for detoxification.

On analysis of the kinetics of copper and cadmium uptake from dilute aqueous solution, adsorption equilibria and functional groups analyses, it was apparent that the different oxidative pre-treatments affected both the surfaces and pore structure of Upper Freeport coal. The large amount of carboxyl and phenolic functional groups remaining after contact with copper and cadmium solutions, as determined by functional groups analyses, indicated the low affinity of the surface acid groups for these cations. Furthermore, there was almost no metal ion removal at low solution pH's, which precludes the use of Upper Freeport for treating acidic wastes and effluents such as acid mine drainage.

The coal surface functional groups are indeed able to exchange with cations, since the amount of these groups are measured by ion exchange with Na^+ and Ba^{2+} , however, it may be more difficult to displace the waters of hydration around Cu^{2+} and Cd^{2+} , to allow their uptake on the coal surface functional groups.

Improved metal ion removal might be obtained using a lower rank coal, such as a subbituminous coal, which would be more susceptible to oxidation.

APPENDIX I: DATA FOR SURFACE FUNCTIONAL GROUP CALCULATIONS

Carboxylic Groups

Sample	Sample Weight (grams)	NaOH Concentration (M)	Volume NaOH Consumed (ml) (2 titrations)
Untreated	1.0101	0.22	1. 1.0 2. 0.7 Average: 0.85
Thermal Exp #1	1.0047	0.22	1. 2.46 2. 2.59 Average: 2.525
Thermal Exp#2	0.9975	0.21	1. 2.50 2. 2.45 Average: 2.475
Thermal/Cu ²⁺ Exp #1	1.0134	0.22	1. 2.00 2. 2.05 Average: 2.025
Thermal/Cu ²⁺ Exp #2	1.0074	0.21	1. 2.22 2. 2.30 Average: 2.26
Thermal/Cd ²⁺ Exp #1	0.9984	0.21	1. 2.09 2. 2.00 Average: 2.045
Thermal/Cd ²⁺ Exp #2	1.0010	0.21	1. 1.90 2. 1.88 Average: 1.89
KMnO ₄	1.0012	0.22	1. 0.35 2. 0.40 Average: 0.375
KMnO ₄ /Cu ²⁺	1.0065	0.22	1. 0.26 2. 0.40 Average: 0.33
KMnO ₄ /Cd ²⁺	1.0157	0.21	1. 0.40 2. 0.41 Average: 0.405
H ₂ O ₂	1.0039	0.21	1. 0.48 2. 0.42 Average: 0.45
H ₂ O ₂ /Cu ²⁺	1.0139	0.22	1. 0.40 2. 0.35 Average: 0.375
H ₂ O ₂ /Cd ²⁺	1.0084	0.21	1. 0.45 2. 0.45 Average: 0.45

APPENDIX I (CONTINUED)

Total Acid Groups

Volume of 0.31M HCl required to titrate 10 ml blank 0.15M Ba(OH)₂ = 9.925 ml
(average of 2 titrations)

Sample	Sample Weight (grams)	Volume 0.31M HCl Consumed (ml)
Untreated	1.0036	1. 9.63
		2. 9.72
		Average: 9.675
Thermal Exp #1	0.9996	1. 7.85
		2. 7.90
		Average: 7.875
Thermal/Cu ²⁺ Exp #1	1.0046	1. 8.15
		2. 8.10
		Average: 8.125
KMnO ₄	1.0029	1. 8.65
		2. 8.88
		Average: 8.765
KMnO ₄ /Cu ²⁺	1.0103	1. 9.65
		2. 9.56
		Average: 9.605
H ₂ O ₂ /Cu ²⁺	1.0077	1. 9.59
		2. 9.74
		Average: 9.665

Volume of 0.31M HCl required to titrate 10 ml blank 0.15M Ba(OH)₂ = 9.94 ml
(average of 2 titrations)

Sample	Sample Weight (grams)	Volume 0.31M HCl Consumed (ml)
H ₂ O ₂	1.0107	1. 9.69
		2. 9.65
		Average: 9.67
H ₂ O ₂ /Cd ²⁺	0.9994	1. 9.78
		2. 9.71
		Average: 9.745
KMnO ₄ /Cd ²⁺	1.0038	1. 10.0
		2. 9.80
		Average: 9.90
Thermal/Cd ²⁺ Exp #1	1.0059	1. 8.60
		2. 8.69
		Average: 8.649

APPENDIX I (CONTINUED)

Total Acid Groups

Volume of 0.31M HCl required to titrate 10 ml of 0.17M Ba(OH)₂ = 11.045 ml

Sample	Sample Weight (grams)	Volume 0.31M HCl Consumed (ml)
Thermal Exp #2	1.0033	1. 9.80
		2. 9.88
		Average: 9.84
Thermal/Cu ²⁺ Exp #2	1.0045	1. 9.88
		2. 9.89
		Average: 9.89
Thermal/Cd ²⁺ Exp #2	0.9996	1. 10.10
		2. 10.14
		Average: 10.12

APPENDIX II

Freundlich parameters obtained from linearization: $\log X = \log K + \frac{1}{n} \log C_e$

Sample	Slope = 1/n	Intercept = log K	K
Thermal/Cu ²⁺	0.46	-3.47	3.39 x 10 ⁻⁴
H ₂ O ₂ /Cu ²⁺	0.73	-3.66	2.19 x 10 ⁻⁴
KMnO ₄ /Cu ²⁺	0.16	-4.28	5.25 x 10 ⁻⁵
Thermal/Cd ²⁺	0.61	-3.96	1.10 x 10 ⁻⁴
KMnO ₄ /Cd ²⁺	0.47	-4.11	7.76 x 10 ⁻⁵

Langmuir parameters obtained from linearization: $\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m}$

Sample	Slope = 1/X _m	X _m (mol/l)	Intercept = 1/bX _m	b (l/mol)
Thermal/Cu ²⁺	14000	6.92 x 10 ⁻⁵	25.25	570
KMnO ₄ /Cu ²⁺	24000	4.13 x 10 ⁻⁵	32.54	740
Thermal/Cd ²⁺	64000	1.56 x 10 ⁻⁵	363.27	180
KMnO ₄ /Cd ²⁺	61000	1.64 x 10 ⁻⁵	189.14	- 320

REFERENCES

1. Eddy, R. M., A. J. Gilbert and T. P. Erwin, in *Mining and Mineral Processing Wastes. Proceedings of the Western Regional Symposium on Mining & Mineral Processing Waste*, F. M. Doyle, Ed., (Littleton, CO: Society for Mining, Metallurgy, and Exploration, Inc., 1990.)
2. Hutchison, I.P.G. and R. D. Ellison, Ed., *Mine Waste Management* (Lewis Publishers, 1992).
3. Peters, R. W., Young Ku, and Dibakar Bhattacharyya, "Evaluation of Recent Treatment Techniques For Removal of Heavy Metals From Industrial Wastewaters," *AIChE Symposium Series: Separation of Heavy Metals and Other Trace Contaminants*, 81 (243) (1985), 165-203.
4. Pletcher, D. and F. C. Walsh, *Industrial Electrochemistry* (London: Chapman and Hall, 1989.)
5. Cheng, M. H., J. W. Patterson and R. A. Minear, "Heavy Metals Uptake by Activated Sludge," *Journal of Water Pollution Control Federation*, 47 (2) (1975), 362-376.
6. Nelson, P. O., A. L. Chung and M. C. Hudson, "Factors Affecting the Fate of Heavy Metals in the Activated Sludge," *Journal of Water Pollution Control Federation*, 53 (8) (1981), 1323-1333.
7. Corapcioglu, M. O. and C. P. Huang, "The Adsorption of Heavy Metals onto Hydrous Activated Carbon," *Water Research*, 21 (9) (1987), 1031-1044.
8. Srivastava, S. K., R. Tyagi and N. Pant, "Adsorption of Heavy Metal Ions On Carbonaceous Material Developed from the Waste Slurry Generated in Local Fertilizer Plants," *Water Research*, 23 (9) (1989), 1161-1165.
9. Tan, T. C. and W. K. Teo, "Combined Effect of Carbon Dosage And Initial Adsorbate Concentration on The Adsorption Isotherm of Heavy Metals on Activated Carbon," *Water Research*, 21 (10) (1987), 1183-1188.
10. Koshima, H. and H. Onishi, "Adsorption of Metal Ions on Activated Carbon from Aqueous Solutions At pH 1-13," *Talanta*, 33 (5) (1986), 391-395.
11. Huang, C. P. and M. H. Wu, "The Removal of Chromium from Dilute Aqueous Solution by Activated Carbon," *Water Research*, 11 (1977), 673-679.
12. Lafferty, C. and M. Hobday, "The Use of Low Rank Brown Coal as an Ion Exchange Material," *Fuel*, 69 (1990), 79-83.
13. Buravtsova, O. A., L. F. Butuzova, G. N. Butusov and S. G. Kremeneva, "Cation-Exchange Properties of Coals and Products of Their Thermal Oxidation Degradation," in *Solid Fuel Chemistry*, 23 (New York: Allerton Press, 1989.)
14. Bel'kevich, P. I. et al., "An Investigation of the Process of Ion Exchange in Granulated Peat," in *Solid Fuel Chemistry*, 22 (New York: Allerton Press, 1985.)

15. C. Venkobachar and A. K. Bhattacharya, "Cadmium Removal from Domestic Waters by A Low Cost Sorbent," *Water Supply*, 3 (1985), 157-163.
16. Pandey, Mahesh P. and Malay Chaudhuri, "Removal of Inorganic Mercury from Water by Bituminous Coal," *Water Research*, 16 (1982), 1113-1118.
17. Patterson, J. W., *Industrial Wastewater Treatment Technology*, 2nd Edition (Boston: Butterworth Publishers, 1985.)
18. Pontius, F. W., "An Update of the Federal Drinking Water Regs," *American Water Works Association Journal*, 87 (2) (1995), 48-58.
19. Carson, B. L., H. V. Ellis III and J. L. McCann, *Toxicology and Biological Monitoring of Metals in Humans. Including Feasibility and Need* (Chelsea, Michigan: Lewis Publishers, Inc., 1986.)
20. Berkowitz, N., *An Introduction to Coal Technology* (New York: Academic Press, 1979.)
21. Davidson, R. M., in *Coal Science*, Volume 1, M. L. Gorbaty, J. W. Larson and I. Wender, Ed. (New York: Academic Press, 1982.)
22. Tsai, S. C., *Coal Science and Technology 2. Fundamentals of Coal Beneficiation and Utilization* (Amsterdam: Elsevier Scientific Publishing Company, 1982).
23. Given, P. H., *Fuel*, 39 (147) (1960).
24. ASTM Standard Test Number D3176M, "Ultimate Analysis of Coal and Coke."
25. ASTM Standard Test Number D3172M, "Proximate Analysis of Coal and Coke."
26. Karr, C., in *Analytical Methods for Coal and Coal Products, Volume 1*, O. P. Mahajan and P. L. Walker, Jr., Ed. (New York: Academic Press, 1978.)
27. Herrera, M. N., "Further Studies of the Effects of Oxidation on the Surface Properties of Coal and Coal Pyrite", (Ph.D. Thesis, University of California, Berkeley, 1994.)
28. Thomas, J. and H. H. Damberger, *Circ III. State Geol. Surv.* (1976), 493.
29. Walker, P. L., Jr. and I. Geller, *Nature* (London), 164 (1956), 1001.
30. Fuller, E. L., et al., "Annual Report of ORNL Chemistry Division for 1978," ORNL-5485, Oak Ridge National Laboratory, Oak Ridge, TN, (1979), 13.
31. Dietz, V. R., F. G. Carpenter and R. B. Arnold, *Carbon*, 1 (1964), 245.
32. Mahajan, O. P., "CO₂ Surface Areas of Coals: the 25-Tear Paradox," *Carbon*, 29 (6) (1991), 735.
33. Marsh, H., "Adsorption Methods to Study Microporosity in Coals and Carbons—a Critique," *Carbon*, 25 (1) (1987), 53.

34. Rhoads, C.A. et al., "Further Studies of Coal Oxidation," *Fuel*, 62 (1983), 1387–1392.
35. Pisupati, S. V. and A. W. Scaroni, "Natural Weathering and Laboratory Oxidation of Bituminous Coals: Organic and Inorganic Structural Changes," *Fuel*, 74 (4) (1993), 531–542.
36. Kister, J. et al., "Changes in the Chemical Structure of Low Rank Coal After Low Temperature Oxidation or Demineralization by Acid Treatment. Analysis by FT-i.r. and u.v Fluorescence," *Fuel*, 67 (1988), 1076–1082.
37. Painter, P.C. et al., "Fourier Transform Infrared Study of the Variation in the Oxidation of a Coking Coal," *Fuel*, 59 (1980), 282.
38. Heard, I. and F. E. Senftle, "Chemical Oxidation of Anthracite with Hydrogen Peroxide via the Fenton Reaction," *Fuel*, 63 (1984), 221.
39. Smith, J. W. and G. E. Mapstone, "The Alkaline Permanganate Oxidation of Coal," *Fuel*, 35 (2) (1957), 191–204.
40. Brooks, J. D. and S. Sternhell, "Chemistry of Brown Coals. 1. Oxygen Containing Functional Groups in Victorian Brown Coals," *Aust. J. Appl. Sci.*, (8) (1957), 206.
41. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd. Edition (Houston, TX: National Association of Corrosion Engineers, 1974).
42. Brandão, M S. and F. Galembeck, "Copper, Lead and Zinc Adsorption on MnO₂-Impregnated Cellulose Acetate," *Colloids and Surfaces*, 48 (1990), 351–362.
43. Flett, D. S., "A Selectivity Reversal in Solvent Extraction," *Nature*, 200 (1963) 465.
44. Monhemius, A. J., *Trans. IMM*, 86 (1977), C202-206.
45. Garrels, R. M. and C. L. Christ, *Solutions, Minerals and Equilibria* (New York: Harper & Row, 1965.)
46. Latimer, W .M., *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd Ed. (Englewood Cliffs, N. J.: Prentice-Hall, 1952).