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I am submitting herewith a thesis written by A. Andrew Carey entitled "Mobilization of Zinc, Lead, and Chromium from Soil Using Chemical Oxidants: Hydrogen Peroxide and Potassium Permanganate." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

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MOBILIZATION OF ZINC, LEAD, AND CHROMIUM FROM SOIL
USING CHEMICAL OXIDANTS:
HYDROGEN PEROXIDE AND POTASSIUM PERMANGANATE

A Thesis
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Degree
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A. Andrew Carey
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TO

My parents' grandchildren:

Sean

Lisa

Justin

Andrea

Alice

Colleen

and

Patty

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ABSTRACT

Experiments were conducted to determine the mobilization of zinc, lead, and chromium using hydrogen peroxide or potassium permanganate on Hanford (sandy) and Portsmouth (clay) soils. The soils utilized are under consideration for remediation by the DOE for removal of organic contaminants by oxidation with hydrogen peroxide or potassium permanganate. The effect of the two oxidants (hydrogen peroxide and potassium permanganate) on mobilization of three metals (Zn(II), Pb(II), and Cr(III)) from two soils (Hanford and Portsmouth) are the subject of this investigation. The two soils are evaluated in three fashions: untreated, pretreated with hydrogen peroxide, and pretreated with potassium permanganate.

A time of 48 hours was found sufficient to establish equilibrium between soil and solute. The maximum adsorption capacities ($q_{\max}$) and binding value ('b') for zinc and chromium were estimated from single reciprocal plots of the Langmuir isotherm for the two soils. Linear adsorption isotherms were used for lead with the two soils. The maximum adsorption capacity ($q_{\max}$) of Zn(II) soils increased after peroxide or permanganate pretreatment of the two soils. The Zn(II) binding ('b') values to soil were relatively unaffected by oxidation pretreatment of Hanford soil but decreased with the Portsmouth soil. The distribution coefficient, K_d , for Pb(II) and the two soils increased with peroxide and permanganate pretreatment. For Cr(III), adsorption isotherms could not be obtained for peroxide or permanganate pretreated soil because

these soils converted some of the metal ion to Cr(VI) which is poorly sorbed to soil.

The adsorption of metal to soil decreased in the order: Cr(III) > Pb(II) ~ Zn(II).

Batch type (rapid mixing) metal mobilization experiments were performed with peroxide and permanganate with the two soils contaminated with the three metals.

Metal mobilization experiments were also performed with water alone as a reference.

For water alone with the two soils, the mobility decreased in the order: Zn > Pb ~ Cr.

For peroxide solutions with untreated and pretreated soils, the mobility decreased in the order: Cr >> Zn > Pb. For permanganate solutions with untreated and pretreated soils, the mobility decreased in the order: Cr >> Zn > Pb.

Column experiments were performed to determine metal mobilization. In column experiments mass transfer rates were smaller than for batch experiments. The low permeability of the Portsmouth soil did not allow its use in column experiments. Water alone showed no detectable metal mobilization. For peroxide solutions with Hanford soil, the mobility decreased in the order Cr >> Zn > Pb. For permanganate solutions with Hanford soil, the mobility decreased in the order: Cr >> Zn > Pb. For peroxide solutions, increasing the flow rate increased the mobilization of Cr. For permanganate solutions, increasing the flow rate decreased the mobilization of Cr.

The most mobile metal with water was zinc, whereas lead and chromium were not detectable in aqueous solutions. Hydrogen peroxide and potassium permanganate solutions mobilized the most chromium (30% to 95%). Hydrogen peroxide and potassium permanganate solutions mobilized some zinc (0.2% to 4%), while producing no detectable lead mobilization.

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CHAPTER 1

Introduction

Hydrogen peroxide and potassium permanganate are excellent oxidizing agents for a wide variety of both inorganic and organic compounds. These two oxidants may ultimately destroy organic compounds by converting carbon and hydrogen to the environmentally benign compounds carbon dioxide and water. However, oxidation of inorganic metals may change their oxidation state and speciation. The newly formed metal species will exhibit entirely new chemical and physical properties, affecting their mobility and toxicity in the environment.

The Department of Energy (DOE) has recently proposed to use hydrogen peroxide or potassium permanganate to remediate soils contaminated with organic compounds. Many DOE sites under consideration for oxidant treatment are also contaminated with heavy metals. This research is based on the premise that a site needing restoration may contain both organic contaminants as well as inorganic metal contaminants. Experiments were performed to investigate the fate of inorganic metal contaminants upon peroxide and permanganate treatment of soils.

Three potential metal contaminants were chosen: zinc, lead, and chromium. Zinc was chosen because it is relatively mobile in the environment whereas lead was chosen because it is immobile in a soil environment. Chromium was chosen because Cr(III) is immobile, but undergoes facile oxidation to the highly mobile and toxic chromate anion (Cr(VI)). The two soils used were from DOE sites in Hanford, WA,

and Portsmouth, OH. The Hanford soil was obtained outside of the DOE plant in Richland, WA. The Hanford soil is an alkaline sand with a small amount of silt and organic material. The Portsmouth soil was obtained from inside the DOE Portsmouth Gaseous Diffusion Plant in Piketon, OH. The Portsmouth soil is a clay type material with a small amount of organic material (personal communication from S. Cline, ORNL).

The treatments tested correspond to those under consideration for field demonstration at Hanford and Portsmouth DOE sites. Experiments were performed to simulate field activities at these sites. During field testing, oxidants were to be mixed with soil using augers. The oxidant mixing was to occur vertically, from bottom to top. In this scenario, mobilized metal, under the force of gravity, may contaminate a previously treated zone.

The newly contaminated soil may subsequently come in contact with additional oxidants. This is the reason for the three pretreatment regimes: untreated, peroxide pretreated, and permanganate pretreated soils. Note that in this sequence, peroxide pretreated soil does not undergo subsequent permanganate treatment. Therefore experiments using mixed combinations of peroxide and permanganate were not performed.

The goal of this research is to investigate the mobility of zinc, lead, and chromium contaminated soils with hydrogen peroxide or potassium permanganate and compare those results to the mobility of the metals with water alone. Water is the reference for measuring metal mobility because it simulates percolating rain water in natural environmental systems. The goal was achieved through the following steps:

1. Determine the equilibrium time for adsorption/desorption of each metal to the soils.
2. Based on these equilibration times, characterize metal adsorption to soils with an isotherm.
3. Determine metal mobilization as a function of varying oxidant concentrations. Compare the results to the amount of metal mobilized with water alone.

CHAPTER 2

Literature Review

1. Chemistry of Metal Ions

Adsorption of inorganic ions onto soil begins with the nature of the metal ions present in solution. An understanding of physical and chemical properties such as speciation, solubility, affinity for adsorption sites, and redox potential is required for predicting environmental adsorption behavior. Chemical speciation is important, since the types and concentrations of metal ions and ligands present affect the adsorption potential and solubility of the moiety. The solubility determines the maximum aqueous concentration of the metal ion. The solubility of many metal ions varies with pH. The formal charge associated with a metal ion affects its solubility and its adsorption potential by way of electrostatic attraction. Redox properties affect the oxidation state of the metal ion present at the soil surface. Oxidation state changes alter the physical and chemical properties of the metal ion, and therefore, its interaction with the soil. Redox properties are particularly important for chromium and to a lesser extent lead. The soil adsorption potential of the former will decrease (because it changes from an insoluble cation to a soluble anion) and will increase in the latter (because Pb(IV) compounds are more insoluble than Pb(II)). Zinc is unaffected by naturally occurring redox potentials (Merian, 1991).

Reactions between inorganic constituents are best described by their acid or base characteristics. In inorganic chemistry, an acid is defined as an electron deficient species (such as a cation) although it includes any species that is coordinately unsaturated (Cotton & Wilkinson, 1980). In organic chemistry, an acid may be any unsaturated species (such as an alkene and to a lesser extent aromatic molecules) as well as any proton donating species (Morrison & Boyd, 1973). A base is an electron rich species, such as an anion. Bases also include any neutral species that contains unbonded (lone pair) electrons such as those found on the oxygen atom in water or many nitrogen compounds. Organic bases are typically either neutral three coordinate nitrogen complexes, such as amines, or moieties that contain negatively charged oxygen atoms (House, 1972).

Acids and bases, therefore, react to form new complexes. A more sophisticated approach is to break these moieties down to their hard/soft acid or base characteristics. Hard acids prefer hard bases and form ionic complexes whereas soft acids and soft bases form more covalent compounds (Cotton & Wilkinson, 1980). The hardness or softness of an acid or base is a function of the charge to ionic radius ratio. A difficulty arises because metal ions and ligands form a spectrum between the extremes defined by their hard or soft characteristics. Cr(III) is a hard acid (Meriam, 1991), while Pb(II) and Zn(II) are borderline soft acids. Sulfide precipitates and complexes generally do not form in aqueous solutions containing hard acids (for example Na^+), since OH^- ions rapidly displace complexed HS^- or S^{2-} . Soft acids, such as Hg^{+2} or Cu^+ prefer ligands such as sulfide and therefore form sulfide complexes and precipitates in an aqueous environment.

Zinc

Zinc compounds only occur in the +2 oxidation state (Cotton & Wilkinson, 1980); therefore, oxidation and reduction reactions are not environmentally relevant. The majority of aqueous zinc complexes are usually six coordinate, although four coordinate complexes also exist (Cotton & Wilkinson, 1980). In neutral waters the dominant species are $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ and $\text{Zn}(\text{OH})(\text{H}_2\text{O})_5^+$ above pH 7.1, although in carbonate waters species such as $\text{Zn}(\text{CO}_3)(\text{H}_2\text{O})_4^0$ and $\text{Zn}(\text{HCO}_3)(\text{H}_2\text{O})_5^+$ are formed (Lindsay, 1979). Zinc does form a series of complexes with chloride ion and amines such as $\text{Zn}(\text{Cl})(\text{H}_2\text{O})_5^+$ and $\text{Zn}(\text{NH}_3)(\text{H}_2\text{O})_5^+$. The stability constants for amine complex formation $\text{Zn}(\text{NH}_3)_4^{+2}$, are larger by a factor of 10^9 than those for chloride ZnCl_4^{2-} (Cotton & Wilkinson, 1980). Consequently, Zn(II) will partition to N(III) in the environment, regardless whether it is insoluble or soluble.

The solubility of zinc hydroxide is such that a 200 mg/l solution begins to precipitate at a pH of 7.2 (Dean, 1991). Zinc hydroxide is an amphoteric compound, that is it is capable of reacting with both acids (protons) and bases (hydroxides) (Cotton & Wilkinson, 1980). As an acid or proton donor, $\text{Zn}(\text{H}_2\text{O})_6^{+2}$ is converted to $\text{Zn}(\text{OH})(\text{H}_2\text{O})_5^+$ ($\text{pK}_a = 9.0$) (Brummer, 1986), where pK_a is equal to $-\log_{10}K_a$ and K_a is defined as the acid dissociation constant. As a base or hydroxide acceptor, $\text{Zn}(\text{H}_2\text{O})_6^{+2}$ is converted to the soluble tetrazincate anion $\text{Zn}(\text{OH})_4^{2-}$ (Cotton & Wilkinson, 1980). Lindsay (1979) reports the solubility of zinc minerals decreases in the order: $\text{Zn}(\text{OH})_2 > \text{ZnCO}_3$ (smithsonite) $> \text{ZnO}$ (zincite) $> \text{Zn}_2\text{SiO}_4$ (willemite) $> \text{soil-Zn} > \text{ZnFe}_2\text{O}_4$ (franklinite). The author also reports that the solubilities of these zinc minerals decreases 100 fold for each unit increase in pH.

Zinc occurs in almost all minerals in the earth's crust with a medium concentration of about 80 mg/kg (Lindsay, 1979). The principal ores used for commercial production are the sulfides, sphalerite and wurtzite (Merian, 1991). The Zn(II) concentration of non-contaminated soils range from 10 to 300 mg/kg are comparable with those found in rocky subsoils and average 20 mg/kg (Merian, 1991). Table 1 shows typical concentrations of Zn, Pb, and Cr found in minerals and natural waters. Table 1 shows the typical concentrations of common minerals of Zn, Pb, and Cr found in soils. It also shows the values of typical concentrations of the metals found in natural waters. The concentrations of the metals in soils and water represent the natural background levels of the three metals found in the environment. The Zn(II) content can be much higher in the vicinity of ore deposits and smelters. Like other metals, atmospheric deposition has increased zinc concentrations on surface soils from the 19th century to the present, but the exact deposition rate can not be reconstructed, because Zn(II) is rather mobile at the pH levels typically found in the environment (Merian, 1991).

Fresh waters, especially rivers, are frequently contaminated by sewage and wastewater and contain considerably higher zinc levels (Merian, 1991). A great deal of this zinc comes from corrosion of galvanized drinking water pipes. Zinc levels between 0.002 to 1.183 mg/l (mean 0.064 mg/l) were measured at 130 locations in the USA (Merian, 1991). In surface waters zinc occurs mainly bound to suspended matter, such as clay, or is co-precipitated with iron- or manganese oxides (Merian, 1991).

Zinc does react with peroxides to form zinc peroxide $\text{Zn(O}_2\text{)}$ (Vannerberg, 1962), which slowly decomposes to zinc oxide, ZnO , and oxygen gas. Zinc peroxide is

Table 1. Typical concentrations of Zn, Pb, and Cr found in soils and natural waters.

Metal	Typical concentrations found in Earth's crust or soil	Common minerals	Typical concentrations found in natural waters
Zinc	10 - 300 mg/kg	ZnS, Zn(CO ₃), ZnSiO ₃	0.002- 1.183 mg/l
Lead	5-40 mg/kg	PbS, PbSO ₄ , PbCO ₃	5-200 µg/l
Chromium	5- 1500 mg/kg	FeCr ₂ O ₄	1 - 10 µg/l

prepared by the precipitation reaction of a soluble zinc salt, such as nitrate, with hydrogen peroxide. Zinc peroxide is commercially used as an accelerator for rubber curing and as a medicinal antiseptic (Merck, 1976).

Zinc does form a permanganate compound, $\text{Zn}(\text{MnO}_4)_2$. Zinc permanganate is less soluble (33.3 g/l) than the potassium salt (63.4 g/l) (CRC, 1984). As a solution, the zinc permanganate exists as the ions $\text{Zn}(\text{II})$ and MnO_4^- . This compound is a purple solid like the potassium salt, and is used commercially as an antiseptic (Merck, 1976).

Lead

Lead compounds are found in the +2 and +4 oxidation states (Cotton & Wilkinson, 1980). The +4 oxidation state is less common in nature (Merian, 1991) but is found in the mineral mimasite Pb_3O_4 , which is composed of 2Pb^{+2} and PbO_4^{4-} rather than a mixture of 2PbO and PbO_2 (Considine, 1974). Lindsay (1979) states that it is virtually impossible for the higher oxidation state lead oxides to form in soils since soils are nearly always more reduced than $\text{pE} + \text{pH}$ of 20.61, where pE is the negative log of the electron activity. The highest pE found in oxidized soils is 13.5 (Merian, 1991). Therefore, Pb(IV) can be found in highly oxidized soils at $\text{pH} > 7.5$. The Pb(IV) ion is a hard acid and consequently surrounds itself with four oxygen ions. However the low solubility of Pb(IV) complexes, can be ignored in naturally occurring aqueous environmental systems (Lindsay, 1979).

Pb(II) compounds form a series of complexes with water. In neutral waters the dominant species are $\text{Pb}(\text{H}_2\text{O})_6^{2+}$ and $\text{Pb}(\text{OH})(\text{H}_2\text{O})_5^+$, although in carbonate waters species such as $\text{Pb}(\text{CO}_3)(\text{H}_2\text{O})_4^0$ and $\text{Pb}(\text{HCO}_3)(\text{H}_2\text{O})_5^+$ are important, and analogous to

zinc (Cotton & Wilkinson, 1980). The presence of carbonate causes the solubility of lead to decrease, whereas chloride tends to increase it (Dean, 1992). Lead carbonate is more insoluble than zinc carbonate; therefore, alkaline carbonate soils, such as the Hanford soil used in this research, may cause lead to be less mobile than zinc. The presence of chloride ion produces the complex $\text{Pb}(\text{Cl})(\text{H}_2\text{O})_5^+$ since the chloride ion is a softer base than oxygen (Cotton & Wilkinson, 1980). Note that neutral species, or species with a single charge, such as $\text{Pb}(\text{CO}_3)(\text{H}_2\text{O})_4^0$ and $\text{Pb}(\text{HCO}_3)(\text{H}_2\text{O})_5^+$, will have a weaker electrostatic attraction to negatively charged soil sites. Another factor that increases adsorption is ionic radius, which is larger for $\text{Pb}(\text{II})$, $1.8 \text{ \AA}$, than $\text{Zn}(\text{II})$, $0.69 \text{ \AA}$ (Cotton & Wilkinson, 1980). The pK_a of a metal ion decreases with increasing ionic radius. The hydroxy complexes such as $\text{Pb}(\text{OH})(\text{H}_2\text{O})_5^+$, as characterized by their acid dissociation constant $\text{pK}_a = 7.7$, are specifically adsorbed to soil to a greater extent than $\text{Pb}(\text{H}_2\text{O})_6^{2+}$ (Alloway, 1990). This also applies to other metals such as $\text{Cr}(\text{III})$ and $\text{Zn}(\text{II})$. The complexity of natural systems makes the determination of the cause(s) of adsorption difficult, and the identity of the adsorbing species is frequently unknown.

Lead forms many mixed minerals containing carbonate, sulfate, oxide and chloride. In general the solubilities of these minerals at pH 7.5 decrease in the order: $\text{Pb}_2\text{CO}_3\text{Cl}_2 > \text{PbSO}_4 \cdot 3\text{PbO} > \text{PbCO}_3 \cdot \text{PbO} > \text{PbCO}_3 \cdot 2\text{PbO} > \text{PbSO}_4 \cdot \text{PbO} > \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (Lindsay, 1979). Except for the latter mineral, these compounds are too soluble to be important constituents in soils. Lead forms numerous phosphate complexes. Nriagu (1974) examined the solubilities of many lead phosphates and

pointed out how they may be important for controlling the mobility of lead in natural environments.

Only one lead peroxide compound ($\text{Pb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) is known (Vannerberg, 1962). This compound is difficult to prepare because it decomposes rapidly. The possibility exists that Pb(II) can be converted to Pb(IV) in soil upon peroxide treatment; however, Pb(IV) compounds are more insoluble than those of Pb(II).

No information could be found on the reaction of Pb(II) with potassium permanganate. However, based on thermodynamic considerations, permanganate is a sufficiently strong oxidant to oxidize Pb(II) to Pb(IV) (CRC, 1984).

Chromium

Although chromium compounds exist in every oxidation state from -2 to +6 (Cotton & Wilkinson, 1980), the only environmentally significant ones are +3 and +6 (Merian, 1991). Cr(III) is the most stable oxidation state, although Cr(VI) can form stable complexes at pH values above 7 in an oxygen saturated solution (Merian, 1991). Cr(III) is classified as a hard acid (Merian, 1991), and therefore has an affinity for hard base oxygen ligands. There are literally thousands of Cr(III) compounds of which virtually all are hexacoordinate (Cotton & Wilkinson, 1980). The principal reason for the large number of Cr(III) compounds is their kinetic inertness, which allows their isolation. Ligand displacement reactions of Cr(III) may have half-lives of hours (Merian, 1991). Most metal ligand displacement reactions have half-lives in the millisecond to microsecond range.

Cr(III) is also a transition metal and contains three d orbital electrons. In an octahedral field, which is created when six ligands arrange themselves symmetrically around a metal ion, the five d orbitals arrange themselves into two sets. Three orbitals become more stable than the original set and two become less stable (Stumm & Morgan, 1981). The difference in energy of the two sets of orbitals is known as the crystal field stabilization energy. In Cr(III), each of the stable three d orbitals contains one electron, which gives a low energy (stable) configuration. Ligand displacement reaction must overcome this stability, that is, they have a large activation energy. Reactions with large activation energies proceed slowly at room temperature.

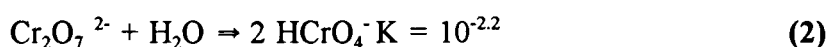
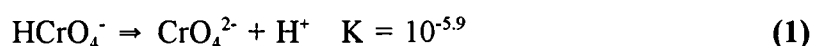
The magnitude of the crystal field stabilization energy is directly determined by the ligands surrounding the transition metal ion and the ligands form a spectrochemical series. For the more common ligands the order is: halide < hydroxide < carbonate < water < nitrogen (amines) < cyanide (Cotton & Wilkinson, 1980). Thus Cr(III) is a hard acid with an affinity for oxygen compounds and a transition metal subject to crystal field stabilization by ligands such as amines or cyanides.

The pKa of Cr(III) is 3.95 and, therefore, should show higher adsorption to soil than Zn(II) (pKa=9.0) or Pb(II) (pKa=7.7) (Brummer, 1986). The higher charge of the Cr(III) ion makes the electrostatic attraction to negative charged soil sites stronger than with Pb(II) and Zn(II).

The average chromium concentration in rocks and sediments is 100 mg/kg with a range of 5- 1500 mg/kg (Merian, 1991). Natural chromium ores are mainly chromite (FeCr_2O_4) and krokoite (PbCrO_4) (Merian, 1991). Fresh water typically contains 1 - 10 $\mu\text{g/l}$ of chromium (Merian, 1991). At a pH 7.2, over 99% of the species present in

gravitational water of a Serpentinic Cambisol soil are the ions $\text{Cr}(\text{CO}_3)_2^-$ and $\text{Cr}(\text{CO}_3)_3^{3-}$ (Juchler & Sticher, 1987).

The chemistry of Cr(VI) or chromate is also complex. In basic solution above pH of 6, the yellow chromate ion CrO_4^{2-} ion forms; between pH 2 and 6, HCrO_4^- and the orange red dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ are in equilibrium. The reactions can be expressed as:



The dominant species between pH 2 to 6 and below 100 mg/l is HCrO_4^- (Edwards, 1972). All three anions (HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$) are collectively referred to as chromate or Cr(VI). Cr(VI) is not a transition metal since it contains no d electrons. The parent compound of chromate anions is the trioxide CrO_3 which solubilizes as anions by adsorption of OH^- or O^{2-} .

The reaction of Pb(II) with chromate solutions to form a yellow precipitate of lead chromate (PbCrO_4) has been used extensively in qualitative inorganic analysis (Vogel, 1979). Also, zinc chromate (ZnCrO_4) may form. It is a slightly soluble yellow powder (CRC, 1984). As an anion, the adsorption of Cr(VI) to soils is poor due to the negative charge usually present on soil surfaces; therefore, it is mobile in the environment.

Chromium peroxides. Reactions between chromium and hydrogen peroxide are complex. Four well characterized chromium compounds can be synthesized when hydrogen peroxide is added to chromium (Connor & Elisworth, 1966). One compound,

$(\text{NH}_3)_3 \text{Cr}(\text{O}_2)_2$, is only formed in the presence of ammonia and is not considered relevant to this research. The other three possible compounds that may form are the red, blue, and violet chromium peroxides. Thus peroxide treatment of chromium contaminated soil may form any or all three chromium compounds.

The red peroxide (M_3CrO_8 , where M= alkali ion) is prepared from hydrogen peroxide and chromium in alkaline solution in the presence of alkali ions. This chromium compound is slightly soluble in water and stable for days in solution. However, the presence of impurities accelerates its decomposition. In alkaline solutions, the red chromium peroxide decomposes to chromate anion Cr(VI) , whereas in acid solutions decomposition is to chromic ion, Cr(III) . In practice, some chromate always forms, but the amount formed decreases with increasing acidity.

The blue chromium peroxide ($\text{Cr(O)(O}_2)_2$) preferentially forms in acidic solutions. This reaction is well known, and the blue color is used as a confirmatory test for the presence of chromate anion in qualitative inorganic analysis (Vogel, 1979). The blue chromium peroxide is unstable in water (it is stable in the presence of ligands such as cyanide and pyridine) and decomposes to Cr(III) at $\text{pH} < 4$. Higher pHs produce some chromate; the amount increases as pH increases.

The violet compound ($\text{MHCr(O)}_2(\text{O}_2)_2$) forms in weakly acidic solution in the presence of alkali metal ions. It decomposes in water to give a mixture of chromic (Cr(III)) and chromate (Cr(VI)) ions. The relative amount depends on the pH.

The relationships of the best known chromium peroxyspecies is shown in Figure 1. The ratio of the three chromium peroxides would depend on the pH of the solution and the decomposition rates of the individual peroxides. Decomposition

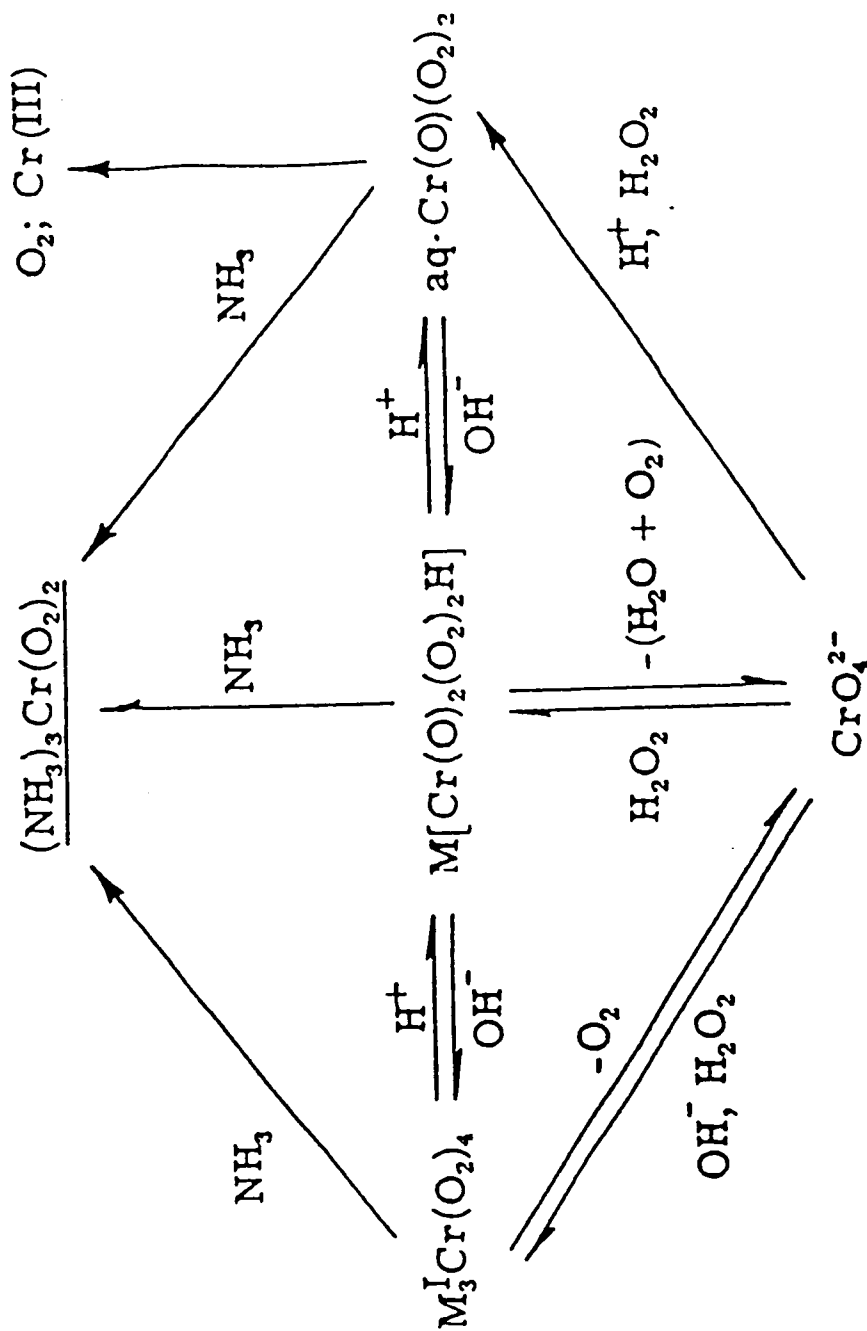


Figure 1: Relationships among the best known peroxochromium species (from Vannerberg, 1962).

chiefly produces chromate (Cr(VI)), but can, under certain conditions, produce Cr(III). Given the complexity of the system, different soils may form different chromium peroxides. These chromium peroxides may ultimately form various amounts of Cr(III) and Cr(VI).

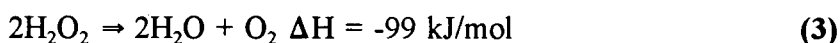
The reaction of chromium (Cr(III)) with potassium permanganate is simple. It produces the chromate anion (Cr(VI)) (Cotton & Wilkinson, 1981). Even a reduced species of permanganate such as manganese dioxide remains a sufficiently powerful oxidant to produce chromate from Cr(III) (Bartlett & James, 1979).

2. Chemistry of Oxidants

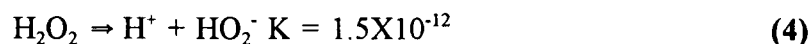
An oxidant possesses a strong affinity for electrons, and cause other substances to be oxidized by abstracting electrons from them. In acting as oxidizing agents, such substances are themselves reduced. Oxidants, such as hydrogen peroxide and potassium permanganate, degrade a wide variety of organic compounds. They may be useful for degrading organic contaminants, for example petroleum hydrocarbons, in the environment. However, oxidants may also affect the mobilization of inorganic metal ions in the environment. They may oxidize soil organic matter and thereby release adsorbed metal ions. Moreover, the partial oxidation of organic material may produce water soluble ligands for complexation with metals. Oxidants may also alter the oxidation state of metal ions in soils, or the redox potential (Eh) of the soils themselves, producing species with new physicochemical properties.

Hydrogen Peroxide

Peroxides are compounds containing oxygen atoms directly bonded to one another, and are thus characterized by a -O-O- bonding (Henning, 1983). The simplest peroxide is hydrogen peroxide, a colorless liquid miscible in water. Hydrogen peroxide resembles water in many of its properties, although it is denser (1.44 g/l at 25° C) and has a higher dielectric constant (CRC, 1984). It readily decomposes in the presence of many heavy metal ions (Cotton & Wilkinson, 1980) according to the equation:



In dilute aqueous systems it is more acidic than water.



Commercial hydrogen peroxide solutions contain stabilizers, for example acetanilide, to prevent its decomposition to oxygen and water (Considine, 1974). Hydrogen peroxide is a strong oxidizing agent in acidic or basic media; only towards very strong oxidizing agents, such as permanganate, will it behave as a reducing agent (Cotton & Wilkinson, 1980). The decomposition of hydrogen peroxide is faster in basic solutions than acidic ones (Cotton & Wilkinson, 1980). The Hanford soil used in this research is more basic than the Portsmouth soil, and therefore more likely to decompose hydrogen peroxide. Ions such as Fe^{+3} or compounds such as manganese dioxide catalyze the decomposition of hydrogen peroxide. Both metals are ubiquitous in soils. The kinetics of the iron decomposition of hydrogen peroxide has been extensively studied and shown to occur by a free radical mechanism (Brown et al., 1969). Generally, the decomposition of hydrogen peroxide is promoted by metals that have more than one stable oxidation state (Connor & Ebsworth, 1964).

Most reactions involving hydrogen peroxide in solution occur by a free radical mechanism. A free radical is a species containing one or more unpaired electrons. If the species bears a charge, it is known as a radical ion (Orchin et al., 1980). Metal ions catalyze the decomposition of hydrogen peroxide to free radicals, of which $\text{HO}_2\cdot$ and $\text{OH}\cdot$ are the most important moieties (Cotton & Wilkinson, 1980), and are known as Fenton-type reactions. These radicals are extremely reactive to organic compounds (Morrison & Boyd, 1973).

Peroxide compounds exist for all alkali and alkaline earth metals (Vanneberg, 1962) and most transition metals (Connor & Ebsworth, 1964). In most cases metal peroxides can be prepared by the addition of hydrogen peroxide to an appropriate metal compound, for example an oxide (Connor & Ebsworth, 1964). Metal peroxides are not thermodynamically stable and decompose because of the weakness of the oxygen-oxygen ($-\text{O}-\text{O}-$) bond. However, some peroxide compounds are kinetically stable. Kinetically stable compounds under ambient conditions have a rate of decomposition that is very slow or unmeasurable (Eyring et al., 1980). Metal peroxides disproportionate to metal oxides and oxygen gas (Vanneberg, 1962). Usually, the decomposition leaves the metal in its highest common oxidation state. Peroxide compounds also exist for many non-metallic elements (Cotton & Wilkinson, 1980).

Hydrogen peroxide is also highly reactive to a wide variety of organic compounds. A standard advanced organic chemistry book devotes more than 50 pages to organic peroxide reactions (House, 1972). Since it reacts by a free radical mechanism, peroxide reactions with organic compounds occur with a small activation energy (Morrison & Boyd, 1973). Activation energy is the energy that must be

provided for a reaction to occur. Reactions with small activation energy proceed relatively rapidly and to thermodynamic completion at room temperature. The influence of hydrogen peroxide on soil has been extensively studied. The studies are complex and ambiguous because of the wide variety of soils and conditions used. A total of 46 naturally occurring elements with peroxide compounds were discussed by Vanneberg (1962), and Connor and Ebsworth (1964). Some of these elements, like chromium, have more than one peroxide compound. Therefore, the interaction of hydrogen peroxide with inorganic constituents of soil may produce numerous peroxide compounds, most of which are rapidly decomposed. Hydrogen peroxide can also react with the organic constituents present in soil, generally converting them to simpler constituents.

Bartlett et al. (1937) studied the effect of hydrogen peroxide on the exchange capacity of soils. They found considerable variation in the amount of organic matter following peroxide treatment. Generally, the exchange capacity of the soil decreased after peroxidation, which was attributed to loss of organic matter.

McLean (1930) found that 86% of the carbon and 89% of the nitrogen was removed from the organic component of soil, using a 6% hydrogen peroxide solution. Larger volumes of peroxide oxidized more of the organic carbon, but not the nitrogen. Moreover, he concluded that the oxidation of organic compounds using 3% hydrogen peroxide was sufficient for most non-carbonate soils with a $\text{pH} < 7$ (similar to Portsmouth soil), whereas 5% hydrogen peroxide was required for soils containing calcium carbonate (similar to Hanford soil).

Griffith and Schnitzer (1977) investigated the organic compounds formed from hydrogen peroxide oxidation of soil. They found 65% to 82% of the carbon and 23% to 36% of the nitrogen was volatilized or solubilized from the soil organic matter. At high pH and high clay content, the oxidation of organic matter was low. As noted, the decomposition of hydrogen peroxide is faster at higher pHs, allowing less time for reaction with organic matter. Peroxide resistant organic matter was found as humic acids strongly bonded to inorganics, such as hydrous metal oxides and clays (Griffith & Schnitzer, 1977).

Hosking (1932) verified that high pH resulted in incomplete destruction of organic matter. The study also found that the presence of manganese dioxide reduces the destruction of organic matter. As noted earlier, manganese dioxide catalyzes the decomposition of hydrogen peroxide, allowing less time for reaction with organic matter. Presumably, the catalytic decomposition of hydrogen peroxide results in the incomplete oxidation of organics.

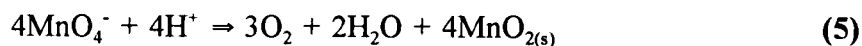
Martin (1954) found that peroxide treatment of soil forms calcium oxalate $\text{Ca}(\text{C}_2\text{O}_4)$. The oxalate ligand may form from the partial oxidation of organic matter. A different study found that the presence of oxalate after peroxidation increases the solubility of aluminum in soils by complexing as aluminum oxalate (Farmer & Mitchell, 1963). Douglas and Fiessinger (1971) investigated the effect of hydrogen peroxide on 2:1 vericulite and bentonite clays. X-ray diffraction studies showed peroxide treatment had a minimal affect on the clays. However, the addition of sucrose to clay and treatment with peroxide significantly altered the X-ray diffraction pattern of the clay. Peroxides in the presence of pyrophosphates in soils causes mica

exfoliation and manganese dioxide dissolution as well as calcium oxalate formation (Sequin & Aringheri, 1977).

Potassium Permanganate

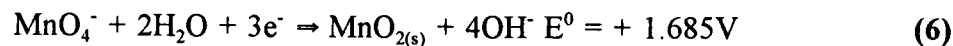
Potassium permanganate, KMnO_4 , is a deep purple solid with a water solubility of 63 g/l (CRC, 1984). In solution it forms K^+ and MnO_4^- ions and is a more powerful oxidizing agent than hydrogen peroxide. Manganese forms compounds with oxidation states from -3 to +7 (Cotton & Wilkinson, 1980). The oxidation states found in the environment are +2, +3, and +4 (Lindsay, 1979). The +2 state oxidizes in the presence of air to +4, and the reaction is catalyzed by the presence of a base (Cotton & Wilkinson, 1980).

Manganese exists in the +7 oxidation state (Mn(VII)) in permanganates and is a powerful oxidant. Permanganates are thermodynamically unstable, decomposing slowly but observably in acidic solutions:

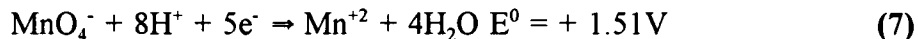


An acidic soil such as the Portsmouth soil used in this investigation is more likely to catalyze the decomposition of potassium permanganate. In neutral or slightly alkaline solutions in the dark, decomposition is immeasurably slow (Cotton & Wilkinson, 1980). However, decomposition occurs in the presence of light.

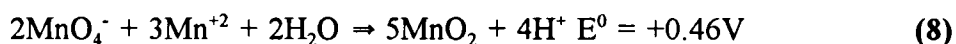
In basic solutions, permanganate acts as a powerful oxidizing agent:



In acidic solutions, permanganate is reduced to Mn(II) by an excess of reducing agent (Cotton & Wilkinson, 1980):



But because permanganate oxidizes Mn(II):



the product in the presence of excess permanganate is manganese dioxide, which is also an oxidizing agent (Cotton & Wilkinson, 1980). When used in soil treatment, permanganate initially decomposes to manganese dioxide and maintains an in-situ oxidizing capacity (Bartlett and James, 1979). Manganese dioxide is a sufficiently powerful oxidizing agent to convert chloride ions to chlorine gas (Meites, 1963).

Permanganate affects many inorganic metals by directly increasing their oxidation state. For example, the following elements undergo oxidation state changes by permanganate (Meites, 1963): $\text{Fe(II)} \rightarrow \text{Fe(III)}$, $\text{Cr(III)} \rightarrow \text{Cr(VI)}$, $\text{Mn(II)} \rightarrow \text{Mn(IV)}$, $\text{Cl}^- \rightarrow \text{Cl}_2$, $\text{U(IV)} \rightarrow \text{U(VI)}$, $\text{V(IV)} \rightarrow \text{V(V)}$, $\text{As(III)} \rightarrow \text{As(V)}$, $\text{Sb(III)} \rightarrow \text{Sb(V)}$, $\text{S}^{-2} \rightarrow \text{SO}_4^{2-}$. This process is simpler than with peroxides, as discussed earlier. Hydrogen peroxide reacts to form intermediate peroxide compounds, which subsequently decompose. Usually (for elements with multiple oxidation states) the decomposition results in a higher oxidation state.

Permanganates can oxidize numerous organic compounds such as alcohols, alkenes, aldehydes, and ketones. As an analytical reagent, it is capable of oxidizing oxalate ligands (Skoog & West, 1969). House (1972) devotes a chapter to manganese (and chromium) oxidation of organic compounds.

A literature search revealed no information on the reaction of permanganates with soils or soil organic matter. However, potassium permanganate has been extensively used in municipal water treatment as a disinfectant, for control of

biological growth, and as an oxidant for iron (Fe^{+2}) and manganese (Mn^{+2}) in groundwater (Pontius, 1990). It is also used for color removal, reduction of specific organic compounds, and as a flocculation aid.

Based on the chemistry of potassium permanganate and the reactions of other oxidizing agents on soil, solutions of potassium permanganate may be expected to have the following effects:

1. Potassium permanganate oxidizes organic matter present in soil,
2. Potassium permanganate oxidizes inorganic metal species for example Fe^{+2} or Mn^{+2} ,
3. The potassium ion (K^{+}) in solution may cause the displacement of other cations on the soil surface (Pontius, 1990),
4. The presence of manganese dioxide in soils, which is a decomposition product of permanganate, is known to oxidize chromic cations (Cr(III)) to chromate anions (Cr(VI)) (Bartlett & James, 1979). Moreover, the manganese dioxide precipitate presents new metal adsorption sites (Pontius, 1990).
5. The ions present in a potassium permanganate solution affect the ionic strength of the medium. The result is that ions in soil have a lower solubility in solution (Atkins, 1978).
6. Anions are poorly sorbed to soil (Alloway, 1990). Therefore, the permanganate anion is also expected to be poorly sorbed to soil.

3. Adsorption of Metal Ions to Soil

Adsorption Forces

Adsorption is a complex, imperfectly understood phenomenon. A variety of forces may be involved in adsorption at the solid-liquid interface, including hydrogen bonding, ligand exchange, electrostatic attraction, and van der Waals forces. The total adsorption force is the sum of each force multiplied by the number of moles of atoms under its influence. Knowledge of the total adsorption force allows the estimation of metal partitioning between soil and solution by way of the Gibbs free energy relationship (Alloway, 1990). Depending on the nature of the metal species and the type of soil, each of the forces discussed may be the dominant mechanism for adsorption.

Hydrogen bonding is an important adsorption force. Hydrogen bonding is caused by the asymmetric interaction of a proton between two electronegative atoms such as fluorine, oxygen, or chlorine (Cotton & Wilkinson, 1980). The proton, while covalently bonded to one atom, is also attracted by the negative charge of the other atom. Hydrogen bonds dominate the structure of water, the chemistry of aqueous solutions, and the reactions of OH-containing species. In soils, OH-containing species are ubiquitous and may be found on organic matter, silicates, metal oxides, and as ligands bound to metal cations. Hydrogen bonds produce an attractive force of 8 to 42 kJ/mol. Hydrogen bonding, when it occurs, is frequently the dominant mode of adsorption.

Ligand exchange/coordination may occur at the soil-solution interface. Many cations form coordinate complexes with ligands that range in complexity from simple linear molecules to highly complex chelate complexes found with organic molecules (Cotton & Wilkinson, 1980). The coordinate complex may contain a net charge associated with the central metal atom, or it may be found on the ligand. The bonded complex may be displaced by other complexes to satisfy electroneutrality, provided it also satisfies steric requirements. The attractive force for ligand exchange is 8 to 60 kJ/mol, about the same or a little greater than hydrogen bonding.

Electrostatic forces result from the coulombic attraction of the metal cation to the soil surface which usually carries a negative charge. The charged surface can be a pH dependent quantity caused by protonation or deprotonation at oxygen sites. It also arises from isomorphous substitution in crystalline lattices; for example, the substitution of aluminum for silicon produces a net negative charge (Alloway, 1990). The excess charge on the surface may be surrounded by a layer of cations of exponentially decreasing thickness. This positive shell in turn is surrounded by negatively charged ions to maintain electroneutrality. The magnitude of electrostatic attraction is difficult to predict for an individual molecule. The attractive force is from 1 to 50 kJ/mol.

Van der Waals forces arise from instantaneous dipole induced forces. The fluctuating electric field surrounding an atom produces resonance contributions with asymmetric distributions of electrons. The asymmetric electron distributions produce an instantaneous dipole. This dipole may then interact with a neighboring atom producing a weak attractive force of 4 to 8 kJ/mol.

Other forces may make minor contributions. Chemisorption occurs whereby new chemical bonds are formed at surface sites with unsaturated valencies.

Chemisorption is more common with organic molecules, although ligand exchange with inorganic species is a type of chemisorption (Adamson, 1976). Metal ion complexation with the organic component of soil can be considered as a type of chemisorption. Adsorption also occurs from dipole interaction energy which results from the attractive forces of permanent dipoles between the cation and soil surface (Alloway, 1990). In addition, entropy forces may overcome thermodynamic considerations allowing metal ions to distribute between the solution and solid, producing a more disordered system.

pH Effects

The adsorption behavior of ionizable inorganic species (as well as ionizable organics) between soil and solution is influenced by pH. Generally, the adsorption of inorganic cations decreases with decreasing pH (Kinniburgh & Jackson, 1981). In a study of lead adsorption of landfill leachate by kaolinite (Griffith & Shimp, 1976), it was found that the adsorption of lead was pH dependent and increased with increasing pH. In batch adsorption experiments, where the pH was adjusted by the addition of acid or base to values between 4 and 6, a sharp change in the slope of the adsorption isotherm was attributed to the precipitation of lead carbonate (Griffith & Shimp, 1976).

Based on solubility products of metal hydroxides at pH 7, the solubilities of the three metals are: $\text{Pb}(\text{OH})_2$ (25,000 mg/l), $\text{Zn}(\text{OH})_2$ (77 mg/l), and $\text{Cr}(\text{OH})_3$ (0.000039

mg/l) (Dean, 1992). The solubility of zinc carbonate ($pK_{sp} = 10.84$) is greater than lead carbonate ($pK_{sp} = 13.13$) (Dean, 1992), whereas at pH 7.2 over 99% of the Cr(III) is complexed as anionic carbonate (Juchler & Sticher, 1987). This research investigation used deionized water exposed to atmospheric carbon dioxide and therefore contained hydroxide and carbonate ions. Thus, as pure compounds, lead hydroxide is more soluble than zinc hydroxide in pure water at pH 7, whereas zinc carbonate is more soluble than lead carbonate.

At pH 4.2 to 6.6 zinc is mobile and lead is slowly mobile, whereas at pH 6.7 to 8.8 zinc is moderately mobile and lead is still slowly mobile (Merian, 1991). The higher mobility of zinc in the environment may be due to the presence of naturally occurring soluble organic and inorganic ligands (such as carbonate, sulfate, etc.). The reduction in adsorption under acidic pH conditions was attributed to increased competition for adsorption sites by protons and Al(III) dissolved from clays (Merian, 1991). The pH of the soil also has an effect on anionic adsorption. The adsorption of Cr(VI) by kaolinite passed through a maximum at a pH of 4 to 5 at low chromium concentrations. As explained, this effect would be consistent with the adsorption of the HCrO_4^- ion (rather than the more negative anions CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$), which is the dominant species within this pH range.

Adsorption is not only influenced by the bulk solution pH, but also by local effects at the soil solution interface. Soil pH is measured by mixing 2 to 2.5 times the weight of water with soil and allowing 30 minutes before measuring. However, pH of a soil solution also includes the proton concentration present in soil pores at equilibrium with the predominantly negative charged surface of the soil particles. The

diffusive layer close to the negatively charged surface has a higher proton concentration than the bulk solution. When the soil solution is diluted, the diffuse layer expands causing the pH of the bulk solution to increase (Alloway, 1991). The pH value of the bulk solution is about 1 to 1.5 units higher than those occurring in the soil pores. The speciation of the metal ion may change when crossing from the bulk solution to the soil-solution interface, depending on the kinetics of ligand exchange.

Hydrogen peroxide is a weak acid ($K_a = 1.5 \times 10^{-12}$). Based on this dissociation constant, a 3% peroxide solution has a calculated pH of 6.0, although the actual pH of solutions may be influenced by the presence of stabilizers. Potassium permanganate is the salt of a strong base, potassium hydroxide (KOH) and a strong acid, permanganic acid (HMnO_4) (Cotton & Wilkinson, 1980). Such salts are inherently neutral and have no direct affect on pH (Skoog & West, 1969). However, solutions of potassium permanganate have an indirectly affect because of the change in ionic strength of the medium influences the activity coefficients of protons in solution (Atkins, 1978).

The pH of a soil suspension is controlled by three factors. First is the natural pH of the adsorbent and its buffering capacity to maintain that pH. Soils have several mechanisms to buffer pH, including hydroxyaluminium compounds at low pH and carbonates at high pH (Alloway, 1991). Second is the pH and composition of the liquid phase. Third is adsorption reactions that directly or indirectly change the proton or hydroxide concentration in solution.

Redox Effects

Redox effects are important in the presence of oxidants like hydrogen peroxide and potassium permanganate. Redox equilibria are controlled by the aqueous free electron activity, which can be expressed as either the pE value (the negative log of the electron activity) or Eh (the millivolt difference in potential between a Pt electrode and the standard H electrode). The conversion factor for the units is $Eh\text{ (mV)} = 59.2\text{ pE}$ (Alloway, 1990). The oxygen content of the soil solution influences its redox status since the oxygen molecule can act as an electron acceptor (Merian, 1991). The redox potential may reach +700mV in oxidized and -400 mV in strongly reduced soils and is pH sensitive (about -59 mV per pH unit) (Merian, 1991). At pH 7, oxidized soils have $+7 < pE < +13.5$, moderately reduced soils have $+2 < pE < +7$, and reduced soils can have values down to a pE of -6.8. The status of some ions is affected by the redox potential, particularly iron and manganese which are commonly present in soils. Lead and chromium may also be affected.

Indirectly, the speciation of metals can change through oxidation of the ligand. This change may commonly occur with carbon, nitrogen, oxygen and sulfur ligands. The effect of redox on adsorption may be caused by the presence of oxidant (or reductant) in solution, for example, dissolved oxygen (or Fe(II)). It may also be affected by the presence of oxidant or reductant in soil, for example, manganese dioxide or sulfide ion. Cr(III) was found to be oxidized to Cr(VI) in soils that contain manganese dioxide (Bartlett and James, 1979). In this study, it was found that the addition of Cr(III) to air dried soil did not cause any oxidation of chromium, but direct use of field moist samples produced Cr(VI). The amount of Cr(III) oxidized was

directly proportional to the amount of manganese that was reducible by hydroquinone (which is consistent with the presence of manganese dioxide), and the amount of Cr(VI) produced correlated with an increase in the amount of Mn(II). Furthermore, the redox potential of the soil is also affected by the pH of the soil solution.

Soil-Solution Ratio Effects

In this investigation, a soil solution ratio of 1:15 was chosen by the sponsor. However, it is proposed to use in the field a 1:1 soil solution ratio. The soil solution ratio is an important variable that can affect the outcome of experiments. For example, the soil solution ratio may affect the pH and consequently the ion speciation present for adsorption. At high soil solution ratio the pH of the solution may dominate that of the soil suspension whereas at low soil solution ratios the pH of the soil suspension may be dominant (EPA-530, 1991). Furthermore, the soil-solution ratio will impact the ionic strength of the solution, as will be discussed.

Ionic Strength Effects

The ionic strength of a solution has several effects on the adsorption of a contaminant on soil. These effects may be direct or indirect depending on the magnitude of the ionic strength, the ionic charge, composition and concentration of the constituents. In this investigation a maximum potassium permanganate concentration of 2.33 g/l was used. The sponsor proposes to use a concentration of 35 g/l in the field (molality = 0.40 moles/kg).

Ionic strength may affect adsorption in two ways: (1) by changing the thickness of the diffuse double layer associated with colloidal particles and (2) by changing the

solute activity coefficients. The shielding effect caused by neighboring ions results in a decrease in activity coefficients as the ionic strength increases. Therefore, adsorption data based on concentrations rather than ionic activity may produce calculated results that do not agree with observed results because of departure from ideality.

A basic tenet of the diffuse double layer theory states that the physical thickness of the electrical double layer composed of adsorbed cations around a colloidal particle is inversely proportional to the ionic strength (Adamson, 1976). This phenomenon can not only affect exchange and adsorption reactions at the soil-liquid interface, but may control the physicochemical properties of the material, such as coagulation (Pontius, 1990).

Some investigators, attempting to minimize ionic strength in the construction of adsorption isotherms, have added water soluble compounds to serve as a background electrolytes to solutions containing solutes. The use of background electrolytes may, however, cause competitive interactions between the solute and background electrolyte for adsorption sites. As already discussed (Griffith & Au, 1977), the adsorption of Pb(II) by montmorillonite was reduced when 0.1M $\text{Ca}(\text{ClO}_4)_2$ was used as the background electrolyte. The excess Ca(II) in the solution was also adsorbed onto the clay, reducing the number of adsorption sites available to the Pb(II) ion.

4. Evaluation of Metal Adsorption

Equilibration Time

Adsorption at the solid-liquid interface is a thermodynamic process, and adsorption isotherms are constructed after the system has equilibrated. The

equilibration time in batch type experiments occurs when the concentration of the solution does not change with time, that is $dC/dt = 0$. ASTM D4646 recommends an equilibration time of 24 hrs, but this may not be appropriate in all situations.

Adsorption is typically regarded as a fast reaction (seconds to minutes), and frequently subsequent removal of solute may be attributed to other processes. Further reduction in solute concentration occurs at an exponentially decreasing rate and approaches a constant concentration. Sometimes equilibrium can not be entirely obtained; this occurs more frequently with the adsorption of anions than cations. For most systems involving complicated adsorbents such as soils, it is difficult to determine when adsorption processes predominate and when other processes, such as precipitation or ion penetration, become significant. The EPA (EPA-530) recommends a rate of change of solute concentration in solution be less than 5% per 24 hour interval. This procedure recommends that equilibration time should be determined before construction of an isotherms and that this should be typically 24 hours.

Adsorption Isotherms

An adsorption isotherm curve is a graphic representation showing the amount of solute adsorbed as a function of the equilibrium concentration of the solute. This relationship is quantitatively defined by some type of partition function or adsorption isotherm that is statistically applied to the data to generalize the adsorption process. The two most common adsorption isotherms, the Freundlich and Langmuir, will be discussed.

Freundlich Isotherms

The Freundlich equation is an empirical equation that is widely used for the adsorption of materials onto solids. This equation has the form

$$q_e = KC_e^{1/n} \quad (9)$$

where q_e is the amount of solute adsorbed per unit mass of the adsorbent, C_e is the equilibrium solute concentration, and K and $1/n$ are constants (Pontius, 1990). The Freundlich equation was originally proposed as an empirical equation without theoretical foundation. However, some investigators have interpreted K as being related to the capacity or affinity of the adsorbent (Pontius, 1990). The exponential term may be an indicator of the intensity of adsorption or how the capacity of the adsorbent varies with the equilibrium solute concentration (Pontius, 1990). The Freundlich equation is used because of its simplicity, especially when it is linearized in its logarithmic form:

$$\log q_e = \log K + 1/n \log C_e \quad (10)$$

This equation is simple to solve by linear regression. However, the Freundlich equation predicts infinite adsorption at infinite solute concentration. Not only would an infinite adsorption capacity be thermodynamically inconsistent, but experience has shown that the extent of adsorption is limited in some fashion by the surface area of the adsorbent. Thus there are two drawbacks to use of the Freundlich equation: (1) it cannot be extrapolated beyond the experimental range used in its construction, and (2) it does not yield a maximum capacity term, which is usually a simple single value parameter that estimates the maximum adsorption that may occur in soils.

Langmuir Isotherms

The Langmuir equation is also commonly used to express adsorption and can be generalized as:

$$q_e = (q_{\max} b C_e) / (1 + b C_e) \quad (11)$$

where q_e and C are the same as the Freundlich equation and $q_{\max}$ and b are constants. Some investigators have tried to relate b to the bonding energy between the adsorbed ion and adsorbent (Kinniburgh, 1986), but this relationship remains uncertain. The constant $q_{\max}$ is generally accepted as the adsorption maximum of the adsorbent with respect to the specific solute and is interpreted as the maximum amount or concentration that an adsorbent can retain.

Kinniburgh (1986) gives an extensive discussion of four methods for linearizing the Langmuir equation. The two most common forms are the reciprocal

$$C_e/q_e = 1/q_{\max} b + C_e/q_{\max} \quad (12)$$

and the double reciprocal

$$1/q_e = 1/q_{\max} b C_e + 1/q_{\max} \quad (13)$$

Veith and Sposito (1977) state that the double reciprocal method should be avoided and that the Eadie-Hofstee transformation is a better indicator of adsorption.

$$q_e = q_{\max} - (1/b)(q_e / C_e) \quad (14)$$

The fourth method for linearizing sorption data is the distribution coefficient or Scatchard plot which has the form

$$q_e/C_e = b q_{\max} - b q_e \quad (15)$$

Transformations of the Langmuir isotherm tend to weigh low q_e observations more heavily than high b values. In addition, the Eadie-Hofstee equation (14) and Scatchard plots equation (15) suffer the disadvantage that they have q_e , which is usually assumed to contain all the measurement error, in the independent variable which in conventional regression analysis is assumed to be error free (Kinniburgh, 1986).

Other adsorption isotherm equations such as the multisite Langmuir, modified Dubinin-Radushkevich and Toth isotherms are able to describe a wide variety of adsorption data of interest in environmental science (Kinniburgh, 1986). They offer more flexibility than the Langmuir and Freundlich isotherms, although they are not as simple or as well known.

All isotherms might reasonably be called "empirical" because they are not derived from molecular or thermodynamic principles. They are purely descriptive, and description is not the same as an explanation (Kinniburgh, 1986).

5. Metal Mobilization

Metal mobilization in the environment represents a vast variety of complex processes. It may occur by atmospheric deposition, biological transformation, and mobilization in natural waters. Metal cations may be classified into Type A or Type B. Type A metal have an inert gas electron configuration. These ions may be visualized as being of spherical symmetry; their electrons are not easily deformed under the influence of electronic fields, such as those produced by adjacent charged ions. Type B metals cations have a more deformable electrons than type A metals (Merian, 1991). Type B metals are typically atmophiles because they are more volatile and are

transported through the atmosphere (Merian, 1991). Type B metals are also important biologically because they complex to sulfur groups in enzymes (Merian, 1991). Type A elements are lithophiles and are more easily transported in water (Merian, 1991).

Only mobilization of metals from soil to water will be discussed here. In this context, metal mobilization can be considered the complement to adsorption. In adsorption, the solution contains an excess of metal ions that migrate to the soil. In metal mobilization (desorption), the solution is depleted in metal ions. Consequently, migration occurs from soil to solution.

The solution pH will have a very large affect on the mobility of metals, including Zn(II), Pb(II), and Cr(III). The solubility of metal hydroxides increases with decreasing pH (Dean, 1992). Furthermore, the presence of protons in solutions results in the displacement of surface adsorbed cations (Pontius, 1991).

Ligands in solution control the solubility of many metals (Skoog & West, 1969). The solubility of metal compounds with inorganic ligands such as carbonate, oxide, and phosphate typically increase 10 to 100 fold for each unit decrease in pH (Lindsay, 1979). Organic ligands, especially chelates can control the solubility of metal ions in solution (Skoog & West, 1969). Some organic ligands have much greater affinity for metals than others (Cotton & Wilkinson, 1980). For example, amines have a higher affinity for Zn(II) than Pb(II) or Cr(III) (Cotton & Wilkinson, 1980).

The ionic strength of the solution may affect the partitioning of metal ion from soil to solution. It is proposed to use in the field a 35 g/l potassium permanganate solution (ionic strength = 0.44 moles/l). As the ionic strength of a solution increases, the solubility and activity coefficients of ions decreases (Stumm & Morgan, 1981).

Redox capacities may change the partitioning of metals between soil and solution. The solubility of metal ions may be directly affected by changes in their oxidation state. For example the oxidation of Pb(II) to Pb(IV) reduces the solubility of lead (Lindsay, 1979). However the oxidation of Cr(III) to Cr(VI) increases the solubility of chromium (Dean, 1992). Metal solubilities may be indirectly affected by oxidizing a ligand such as sulfide to sulfate (Merian, 1991). Oxidation of organic ligands may affect the solubilities of metal ions. Generally, the more oxidized organic ligands have more places for complexation with metals (Cotton & Wilkinson, 1980). Also, more oxidized organic ligands are more water soluble (Morrison & Boyd, 1973).

The mobilization of Zn(II), Pb(II), and Cr(III) contaminated soils is affected by solution pH. As the pH increases, the solubility of the three metal hydroxides decreases. For soils containing carbonate, such as Hanford soil, the solubility of the three metals decreases, because carbonates are less soluble than hydroxides.

The effect of oxidants (peroxide and permanganate) on Zn(II), Pb(II), and Cr(III) may affect metal mobility directly (by changing metal oxidation states), or indirectly (by changing soil structure or properties). Zinc(II) is not directly affected by oxidants, whereas Pb(II) may produce more insoluble Pb(IV) compounds. Chromium(III) easily oxidizes to the highly soluble chromate anion Cr(VI). Therefore (to a first approximation), the mobility of Zn(II) is unchanged while lead may become less mobile and chromium more mobile.

Indirectly, oxidation of soil organic matter, such as humic acids, may release metal already sorbed to it, and increase metal mobilization. Furthermore, oxidants may oxidize soil particulate surface matter, exposing new sites for metal adsorption, and

decreasing metal mobilization. These two opposing affects, especially for Zn(II), may increase or decrease metal mobilization.

CHAPTER 3

Overview of Research

Batch experiments were conducted to determine the equilibration time for the adsorption of three metals (zinc, lead and chromium) on two soils (Hanford and Portsmouth). The time required to achieve equilibrium formed the time basis for other experiments, such as adsorption isotherms and metal mobilization. The two soils underwent three pretreatment regimes: untreated, pretreatment with peroxide, and pretreatment with permanganate for a total of six combinations of soil experiments.

The treatments tested correspond to those under consideration for field demonstration at Hanford and Portsmouth DOE sites. Experiments were performed to simulate field activities at these sites. During field testing, oxidants were to be mixed with soil using augers. The oxidant mixing was to occur vertically, from bottom to top. In this scenario mobilized metal, under the force of gravity, may contaminate a previously treated zone. The newly contaminated soil may subsequently come in contact with additional oxidants. This is the reason for the three pretreatment regimes: untreated, pretreatment with peroxide, and pretreatment with permanganate.

The six combinations of soils were contaminated with each metal (zinc, lead, and chromium) and metal mobilization evaluated. Metal mobilization was performed with various combinations of the three metals and six combinations of soils using two oxidants (hydrogen peroxide and potassium permanganate) and varying concentrations. Therefore, a total of 36 possible metal mobilization experiments exists from the

combination of two soils (Hanford and Portsmouth), three pretreatments (untreated, peroxide and permanganate), three metals (zinc, lead and chromium), and two oxidants (hydrogen peroxide and potassium permanganate). Only 24 metal mobilization experiments were performed (Table 2). Mixed oxidant combinations of peroxide and permanganate pretreated soils followed by metal mobilization with peroxide and permanganate were not performed. Why? The answer is, in the field only one oxidant is used. This eliminated 12 combinations: two soils, two mixed oxidant combinations, and three metals. In each case, a comparison was made of the relative amount of metal mobilized with each oxidant compared to water alone.

Additionally, column experiments were performed with Hanford soil only, using varying concentrations of the two oxidants (hydrogen peroxide and potassium permanganate) and varying flows to determine the mobilities of the three metals. The Portsmouth soil's hydraulic conductivity was too low for column experiments.

Table 2. Summary of batch experiments performed.

Metal	Soil	Soil pretreatment	Equilibration time	Adsorption isotherm	Metal mobilization oxidants
Zn(II)	Hanford	untreated	yes	yes	peroxide
					permanganate
		peroxide	yes	yes	peroxide
		permanganate	yes	yes	permanganate
	Portsmouth	untreated	yes	yes	peroxide
					permanganate
		peroxide	yes	yes	peroxide
		permanganate	yes	yes	permanganate
Pb(II)	Hanford	untreated	yes	yes	peroxide
					permanganate
		peroxide	yes	yes	peroxide
		permanganate	yes	yes	permanganate
	Portsmouth	untreated	yes	yes	peroxide
					permanganate
		peroxide	yes	yes	peroxide
		permanganate	yes	yes	permanganate
Cr(III)*	Hanford	untreated	yes	yes	peroxide
					permanganate
		peroxide	yes	yes	peroxide
		permanganate	yes	yes	permanganate
	Portsmouth	untreated	yes	yes	peroxide
					permanganate
		peroxide	yes	yes	peroxide
		permanganate	yes	yes	permanganate

*Equilibration and adsorption of Cr(VI) were unsuccessful.

CHAPTER 4

Materials and Methods

1. Standards Preparation and Analysis

Reasonable efforts were made to conform to EPA SW-846 for standards preparation, preservation, and analysis. Every attempt was made to adhere to the good lab practices outlined in textbooks by Skoog and West (1969), and Vogel (1978 and 1979).

Standards Preparation

All glassware used in the preparation of standards and samples was acid washed to prevent possible metal contamination. The glassware was first soaked in a 3% Baxter SP Micro Laboratory Cleaning solution for at least one day. It was flushed with water and rinsed with deionized (DI) water. The glassware was immersed in a 6M HNO_3 AR (analytical reagent grade) solution for at least one day. It was rinsed in DI water and dried prior to use.

Zinc Atomic Adsorption standards were prepared from a stock solution (Baker Chemical) containing 1000 mg/l of zinc as $\text{Zn}(\text{NO}_3)_2$ preserved in nitric acid. Standards were prepared by serial dilution of this stock material using 10 ml (or greater) volumetric pipettes with 100 ml (or greater) calibrated volumetric flasks and adjusted to a $\text{pH} < 1$. Since zinc atomic adsorption is linear to 1.0 mg/l, calibration standards were prepared at 0, 0.250, 0.500, 0.750, and 1.00 mg/l and stored at 4° C.

Zinc concentrations were determined by EPA SW-846, method 7950. The method lists the practical quantification limit for zinc as 0.050 mg/l. The same 1000 mg/l zinc standard (Baker Chemical) as that used for Atomic Adsorption measurements was used in all experiments. The solution was diluted to 200 mg/l with DI water and the pH adjusted to ~5.5. At this pH, zinc hydroxide will not precipitate.

Lead AA standards were prepared from a stock solution (Baker Chemical) containing 1000 mg/l of lead as $\text{Pb}(\text{NO}_3)_2$ preserved in nitric acid. Since lead atomic adsorption is linear to 10.0 mg/l, calibration standards were prepared at 0, 2.5, 5.0, 7.5, and 10.0 mg/l and stored at 4° C. Lead was determined by EPA SW-846, method 7420. The method lists the practical quantification limit for lead as 1.0 mg/l. The 1000 mg/l lead standard was diluted to 200 mg/l and the pH adjusted to ~4.5 for use in all experiments. At this pH, lead hydroxide will not precipitate.

Chromium AA standards were prepared from crystalline potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ (Malinckrodt Chemical). The potassium dichromate was first dried for 24 hours at 105° C. A 1.3621 gram sample was then placed in a one liter flask and diluted with DI water. This pale yellow solution (1000 mg/l of chromium) is stable indefinitely (Skoog & West, 1969). Since chromium atomic adsorption is linear to 5.0 mg/l, calibration standards were prepared at 0, 1, 2.5, 3.5 and 5.0 mg/l and stored at 4° C. Chromium was determined by EPA SW-846, method 7190. The method lists the practical quantification limit for chromium as 0.50 mg/l.

Two chromium solutions were utilized, chromate (Cr(VI)) and chromic (Cr(III)). The chromic (Cr(III)) solution was prepared from crystalline (99.6% pure) chromic nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker Chemical, MW = 400.15). A 7.695 gram sample

(equivalent to 1000 mg/l of Cr(III)) was placed in a one liter volumetric flask and diluted with DI water. This violet solution (after pH adjustment to 5) was used for the following: contaminating soils, equilibration time experiments, adsorption isotherms, and column experiments. At a pH of ~5.0, a 200 mg/l solution will not precipitate chromium hydroxide.

Reagent grade 3% or 30% hydrogen peroxide (Baker Chemical) solutions, containing stabilizers were used as received. The solutions were utilized to pretreat soils and in metal mobilization experiments. The solutions were stored at 4° C until needed.

Potassium permanganate solutions were prepared from crystalline KMnO_4 (99.4% pure). The stock potassium permanganate solution used was 2.33 g/l. The solution was utilized to pretreat soils and in metal mobilization experiments. This concentration was chosen to correspond to a maximum soil loading of 35 g KMnO_4 /Kg of soil using a 1:1 soil solution ratio, as suggested by the sponsor.

Sample Preservation

All metal solution samples were placed in 25 ml glass scintillation vials (Kimble) with Teflon lined caps. The samples were preserved by addition of a few drops of concentrated HNO_3 (AR grade), and stored at 4° C prior to analysis.

Sample Analysis

Atomic Adsorption (AA) analysis was performed using an Allied Analytical Instrument laboratory apparatus. Instrument parameters such as wavelength, photocurrent, and spectral width were set according to the recommendations of the

manufacturer. Analysis of zinc and lead were performed with an air/acetylene flame whereas, chromium required a nitrous oxide/acetylene flame. The instrument was calibrated using DI water and four standards within the linear adsorption range of each metal. The instrument produces a calibration curve from which sample concentrations are determined. Sample concentrations were determined as the average of three separate measurements.

All pH measurements were taken using an Orion 250A pH meter, calibrated at pH 4.01 (potassium hydrogen phthalate) and 10.0 (sodium carbonate and bicarbonate buffer).

2. Soil Collection and Treatment

The two soils utilized in this work (Hanford and Portsmouth) were obtained from DOE sites under consideration for soil oxidative treatment. The Hanford soil was collected from the Richland sanitary landfill in the State of Washington. The Portsmouth soil was collected from a borrow pit area used for construction fills from the Portsmouth Gaseous Diffusion Plant in Piketon, Ohio. The soils were initially passed through a # 40 mesh screen (0.417 mm) to remove larger particles, then washed with DI water, centrifuged in polycarbonate tubes (10,000 rpm for 10 minutes in a Dupont RC5C centrifuge), and air dried prior to use. Air drying as opposed to oven drying, is the preferred method according to EPA 530 method. The air dried soils are later referred to as 'untreated', since no oxidative pretreatment was performed. A portion of each soil was then subjected to peroxide or permanganate pretreatment before use.

Peroxide Pretreatment

Approximately 100 grams of each soil (Hanford and Portsmouth) was placed in separate polypropylene containers. A 150 ml solution of 30% hydrogen peroxide was added to the soil. The mixture was stirred occasionally with a glass stirring rod for several hours, then allowed to air dry prior to use. Peroxide pretreated soil was used in metal adsorption experiments and in metal mobilization experiments using hydrogen peroxide.

Permanganate Pretreatment

Approximately 100 grams of each soil (Hanford and Portsmouth) was placed in separate polypropylene containers. A 150 ml solution of 2.33 g/l potassium permanganate was added to each soil. The characteristic deep purple color did not change after two days of contact with the Hanford soil. The Portsmouth soil solution was decolorized, indicating reaction/decomposition of permanganate. This implies that permanganate was consumed in soil oxidation reaction and precipitated as manganese dioxide (MnO_2). The Hanford soil did not noticeably catalyze permanganate decomposition. After two days, the permanganate pretreated soils were centrifuged at 10,000 rpm for 10 minutes and the aqueous contents decanted. The soils were washed twice with DI water and centrifuged, then allowed to air dry prior to use. Permanganate pretreated soil was used in metal adsorption experiments and in metal mobilization using permanganate.

Soil Contamination

The Hanford and Portsmouth soils (untreated, peroxide, and permanganate pretreated), were individually contaminated with each of the three target metals (Zn(II), Pb(II) and Cr(III)).

In a typical batch experiment, 50 grams of soil were placed in a polypropylene container. A 200 mg/l solution containing only one of the test metals (pH 4.5 to 5.5) was added to the container, then mixed for 2 days in an NBS type rotary extractor (Wheaton) as recommended by EPA method 530. The suspension was centrifuged, the supernatant collected and the volume measured. The soil was washed three times with DI water, centrifuged, the supernatant collected and the volume measured. Aliquots of each supernatant solution were analyzed by AA for the amount of soluble metal. Metal loading of the soil (in terms of mg/kg of soil) was calculated by difference.

Soil used in column experiments was contaminated with all three metals simultaneously. Approximately 100 grams of soil was placed in a polypropylene container. A 200 ml solution containing 200 mg/l of each metal was added to the container, then mixed for two days in an NBS type rotary extractor. The suspension was centrifuged, the supernatant collected and the volume measured. The soil was washed three times with DI water, centrifuged, the supernatant collected, and the volume measured. Aliquots of each supernatant solution were analyzed by AA for the concentration of each metal in solution. The information was used to calculate the metal loading of the soil in terms of mg/kg of soil.

3. Metal Adsorption Experiments

Metal adsorption experiments were performed to determine the time required to establish an equilibrium and to construct adsorption isotherms.

Equilibration Time

In a typical equilibrium experiment, 1.00 gram of soil was placed in each of ten polycarbonate centrifuge tubes. A 15.0 ml solution containing 200 mg/l of the target metal (pH 4.5 to 5.5) was added to each tube. The soil slurries were mixed in an NBS rotary extractor and samples were removed at approximately 1, 2, 3, 4, 8, 24, 48, 72, 96, and 120 hour intervals. The samples were immediately centrifuged (10,000 rpm for 10 minutes), the supernatant decanted, pH measured, and preserved with concentrated nitric acid, then stored at 4° C. The amount of metal sorbed over time was determined by subtracting the mass of metal in solution at a given time from the mass of metal in the initial solution.

Equilibration time experiments were also performed using a chromate anion (Cr(VI)) solution (pH of 5.0) and the two untreated soils. A 1.00 gram sample of each soil was placed in ten separate centrifuge tubes. A 15.0 ml solution containing 10.0 mg/l of chromium as $K_2Cr_2O_7$ was added and the slurries mixed for a total of one month. Samples taken over the time course of the experiment were immediately centrifuged, decanted, and stored at 4° C. Analysis by AA showed a +3 to -5% chromium variation from the initial solution after one month. It was concluded that measurably significant adsorption of the anion did not occur under these experimental

conditions. Therefore, experiments were performed using chromic ion (Cr(III)) which did adsorb to the test soils.

Adsorption Isotherms

In a typical experiment, 1.00 gram of soil was placed in ten different polycarbonate centrifuge tubes. A 15.0 ml solution containing a different concentration of metal (200, 160, 133.3, 120, 106.7, 93.3, 80, 66.7, 40, and 0 mg/l) was added to each of the tubes. The samples were mixed for two days, centrifuged at 10,000 rpm for 10 minutes, and the supernatant decanted then preserved with nitric acid. Aqueous metal concentrations were analyzed by EPA SW 846 using the appropriate method.

The amount of metal adsorbed was determined by subtracting the mass of the metal left in solution from the mass of metal in the original 15.0 ml solution. A blank solution containing water only was used to determine background metal levels.

Adsorption isotherm parameters were determined as single reciprocal Langmuir plots (zinc and chromium) or as linear adsorption isotherms (lead).

4. Metal Mobilization

Metal mobilization was measured as a function of varying peroxide or permanganate concentrations over a time interval (48 hours) based on equilibration time experiments. Each experiment measured the metal mobilization with water alone as a reference.

Hydrogen Peroxide

In a typical experiment, 1.00 gram of metal contaminated soil (untreated or peroxide pretreated) was placed into 14 centrifuge tubes. Duplicate samples of a 15.0 ml hydrogen peroxide solution (30, 15, 8, 4, 2, 1, and 0% hydrogen peroxide) were added to the tubes. The initial rapid evolution of oxygen gas caused pressure to buildup in sealed tubes. Consequently, the tubes were not sealed nor were they mechanically mixed for the first several hours. However, mixing of the suspension did occur due to oxygen evolution in the samples which resulted in agitation of the slurry. Caps were placed on the tubes after several hours and the tubes mixed on the NBS type rotary extractor. Mixing was occasionally stopped and the pressure inside the tubes relieved by twisting the caps. The samples, after 48 hours, were centrifuged at 10,000 rpm for 10 minutes, the contents decanted and preserved with AR grade concentrated nitric acid. The mass of metal mobilized was determined by subtracting the mass of metal in solution from the mass of metal contaminants initially on the soil. The amount is expressed as a percent of the metal mobilized.

Potassium Permanganate

In a typical experiment, 1.00 gram of metal contaminated soil was placed in 10 centrifuge tubes. Duplicate samples of a 15.0 ml potassium permanganate solution at different metal concentrations (2.33, 1.17, 0.58, 0.29, and 0 g/l) were added to each of five tubes. Unlike hydrogen peroxide experiments, no noticeable oxygen gas evolved. The caps were placed on the tubes and the tubes mixed for 48 hours. Samples were

collected then centrifuged at 10,000 rpm for 10 minutes, the contents decanted and preserved with concentrated nitric acid.

The mass of metal mobilized was determined by subtracting the mass of metal in solution from the mass of metal contaminants initially on the soil. The amount is expressed as a percent metal mobilized.

5. Column Experiments

Column experiments were performed to further investigate metal mobilization with test oxidants. Column tests may more accurately simulate field conditions than batch experiments.

Only Hanford soil was used for column experiments. The hydraulic conductivity of the Portsmouth soil was too low for column experiments. Experiments were also performed using a mixture of 40% Portsmouth soil: 60% Ottawa sand to improve permeability. However, the high clay content of the Portsmouth soil resulted in column plugging in all cases. Therefore, the use of Portsmouth soil in the column apparatus was discontinued.

The column utilized in this work was made of borosilicate glass (Spectrum) containing a mounting insert kit to adjust for variable sample sizes. Teflon tubing was used to connect the column to a fraction collector (Gilson FC 203B), and the B. Braun Miebruger precision syringe pump using Chemfluor fittings (Figure 2). Approximately 10 grams of metal contaminated soil, compacted into five equal layers as recommend ASTM standard method D 4874, was placed in the column. The amount of material (10 grams) was chosen such that half the column (0.90 cm ID x 15.0 cm) would be

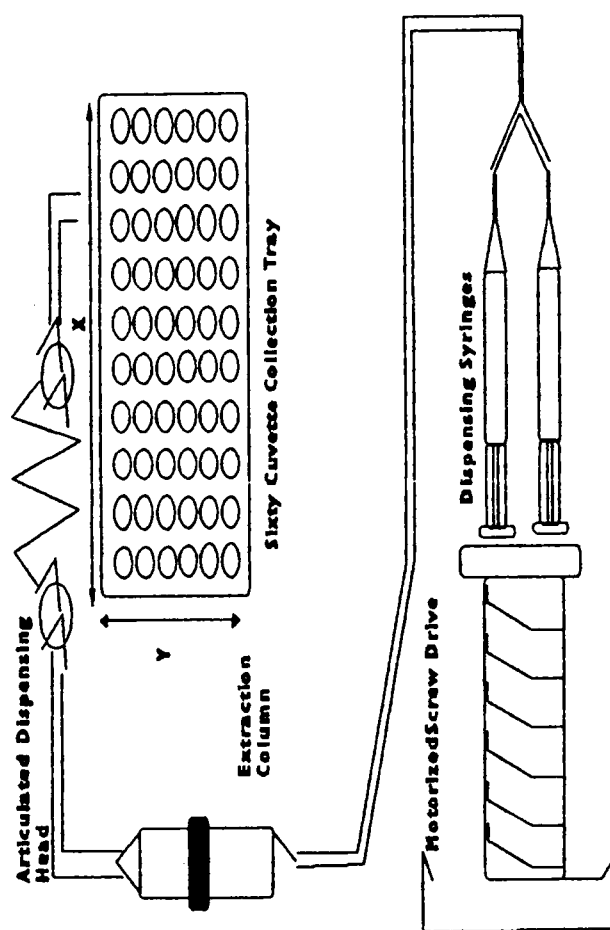


Figure 2: Schematic of column apparatus.

filled. Since all batch experiments were performed with 1.00 gram of soil and 15.0 ml of solution, the elution volume through the column was 150 ml. Thus column experiments were scaled by a factor of ten with respect to the batch experiments, while maintaining a soil to solution ratio of 1:15. This size was a compromise between the size of the batch experiments (1 gram) and the recommendations of ASTM standard method D 4874 for leaching solid waste (about 1 kg). Since soil is more homogenous than solid waste, a factor of ten larger than batch experiments was chosen. The column was operated in the solution upflow mode as recommended (ASTM 34.02 preliminary, 1994). After the soil was placed in the column, it was topped with a small amount of glass wool to prevent soil movement.

Six column experiments were performed with the Hanford soil: one was with water alone, three were with varying hydrogen peroxide concentrations (1.5, 3, and 10%), and two with varying potassium permanganate concentrations (2.33 and 1.17 g/l). The hydrogen peroxide and potassium permanganate concentrations were chosen to correspond to those utilized in batch experiments. These six experiments were performed over an approximately 48 hours period, the same time period as that used in batch experiments. Two additional column experiments, one with each oxidant (1.5 % hydrogen peroxide and 2.33 g/l potassium permanganate), were performed at five times the flow rate (5X), for about 10 hours, using 10 grams of soil and a soil to solution ratio of 1:15.

The syringe pump flow rate was calibrated by collecting water in a graduate cylinder over a specified period of time. At the lower flow rate, the pump produced (at 0 head) 3.0 ml/ hour. The faster rate (at 0 head) produced a flow of 15.1 ml/ hour.

Water and oxidant solutions were placed in two (50 ml each) Hamilton borosilicate glass, gas tight syringes. The syringes were refilled half way through the experiment. Fractions were collected in borosilicate glass tubes (Kimble) containing two drops of concentrated nitric acid. Since ~ 1 to 2 ml of sample solution is required for each metal analysis by, sample fraction collection was timed to produce about 4.5 ml of solution. Therefore, samples collected at the lower flow rate (3.0 ml/hr) were collected every 90 minutes. Samples at the higher flow rate (15.1 ml/hr) were collected at 15 minutes intervals.

Since fractions were collected over a two day period, an experiment was performed to determine the amount of water evaporation from the tubes over time. If significant evaporation were to occur, it would affect the measured concentration of metal in solution. It would not affect the amount of metal mobilized- since it is determined by the product of concentration and volume. The evaporation rate was determined as follows: a test tube was half filled with DI water and weighed. It was allowed to evaporate over a one week period. During this time interval the tube was periodically weighed and the time recorded. The results show the average weight loss was 0.077 g/ day. Solution volumes were measured prior to analysis by AA.

The solution elution volume (approximately 150 ml) is reported as bed volumes. A bed volume is calculated from the mass of soil in the column divided by the bulk volume of the soil. A bulk volume of 1.5 gram/ cm³, which is typical for loosely packed sandy soils (Freeze & Cherry, 1978), was assumed. For example, a 10.00 grams of soil would have a bed volume of 6.667 ml. Bed volumes were determined by dividing the volume (in ml) eluted through the column by 6.667 (ml).

Water

Metal mobilization was performed with water only. Like batch experiments, metal mobilization was measured by elution of water through the column for comparison with mobilization with oxidants.

Hydrogen Peroxide

The following solutions were used: 1.5%, 3%, and 10% hydrogen peroxide. Additionally, the 1.5% hydrogen peroxide solution was used for the high flow rate experiment. All hydrogen peroxide experiments occurred with evolution of oxygen gas. The decomposition of 1 ml of 1.5% hydrogen peroxide produces 5.3 ml of oxygen gas. Oxygen evolution was apparent in the Teflon tubing (1/16" ID) connecting the effluent port of the column to the fraction collector. In a 3 foot section one could typically observe more than 20 gas/liquid interfaces. The majority of material inside the Teflon tubing coming from the column was composed of gas, and the volume increased at higher peroxide concentrations. Although the fractions were collected over the same time interval (90 minutes), the fractions had differing volumes. The total sample volumes varied from 3 to 5.5 ml.

The round bottom fraction collection tubes were 10.0 cm in length. The volume of the fraction collection tube was determined by placing a known volume of water in the tube and measuring its height. The solution volume was estimated to the nearest 0.1 ml by measuring the tube height to the nearest 0.1 cm.

In order to estimate the rate of decomposition of hydrogen peroxide, the following experiment was performed: 10 grams of Hanford soil was placed in a

polycarbonate tube and a 30% hydrogen peroxide solution (10 ml) was placed with the soil. The tube was lightly capped, to allow oxygen to escape, and placed on an analytical balance. The weight loss was monitored over one day. The results show that 76% of the weight loss, caused by the evolution of oxygen gas, occurred over the first 90 minutes. In other words, the half-life for decomposition of hydrogen peroxide in the Hanford soil is about 45 minutes.

Potassium Permanganate

The potassium permanganate solutions used were 2.33 and 1.17 g/l. Additionally the 2.33 g/l potassium permanganate solution was used for the high flow rate experiment. Potassium permanganate caused no noticeable evolution of oxygen. The fractions collected had the same height and therefore the same apparent volume. The first fraction collected was colorless, indicating complete consumption of the permanganate solution. The second fraction was of lighter color than all subsequent fractions, indicating partial consumption of permanganate. Other fractions were as intensely colored as the original permanganate solution.

CHAPTER 5

Results and Discussion

1. Soil Collection and Treatment

The Hanford soil was collected from the Richland sanitary landfill in Richland, Washington. The landfill is located outside of the boundaries of the Hanford DOE site, and it closely resembles the soil at the DOE site. The soil was 'likely' collected from depths of 20 feet or less (personal communication from S. Cline, ORNL). The Portsmouth soil came from the DOE Portsmouth Gaseous Diffusion plant at Piketon, Ohio. The clean soil was obtained from one of the plants borrow pits for construction fills from depths of 0 to 200 feet.

The physical and chemical properties of the two soils are shown in Table 3. Untreated and peroxide pretreated Hanford and Portsmouth soils were evaluated. However, permanganate pretreated Hanford and Portsmouth soil was not. Therefore, the impact of permanganate oxidation on soil CEC (cation exchange capacity) and TOC (total organic carbon) cannot be evaluated. The data were obtained from the Environmental Science Division of Oak Ridge National Laboratory (Table 3) (personal communication from S. Cline, ORNL). Hanford is an arid region east of the Cascade mountains in the State of Washington and receives less than 10 inches of rain per year (Viessman et al., 1989). The soil has the general appearance of a sand containing a

Table 3. Physical and chemical properties of test soil materials.

Soil	Soil composition	pH	% CaCO ₃	CEC (meq/100g)**	CEC (meq/100g)***	% TOC**	% TOC***
Hanford	n/a*	8.7	5.28	3.2	7.92	1.61	0.2
Portsmouth	63% sand 37% silt and clay	5.5	~ 0	2.8	6.18	1.98	0.2

*n/a = Not available. However, the composition of similar soil on the Hanford reservation is reported as 91% sand and 9% silt and clay.

**Before = before peroxidation.

***After = after peroxidation (peroxide pretreated).

small amount of silt. The soil is alkaline with a pH of 8.7 and contains 5.28% CaCO_3 . Besides the Ca^{+2} ion, calcium carbonate dissolves in water to produce carbonate anion (CO_3^{2-}) and by reaction with water both bicarbonate (HCO_3^-) and hydroxide (OH^-). Therefore, aqueous systems in the presence of Hanford soil generate substantial quantities of OH^- , HCO_3^- , and CO_3^{2-} ions. Metal cation chemistry is influenced in by the presence of these anions, and their mobility is influenced, in part, by the solubility products of their hydroxide and carbonate precipitates.

Portsmouth is located in southeast Ohio and receives about 40 inches of rain per year. The Portsmouth soil is finely divided and composed of sand with a substantial amount of silt and clay. It contains no detectable calcium carbonate; consequently, aqueous systems of the soil are not buffered by the carbonate ion. The pH of the soil is 5.5, so metals should be more mobile than in the Hanford soil (pH = 8.7), since the solubility of metals increases with decreasing pH (Skoog & West, 1969).

Table 3 shows an increase in the cation exchange capacity (CEC) of both soils following peroxide treatment. This increase was believed due to stripping of bound metal cations from the inorganic fraction of the soil resulting in an increase in the CEC (Griffith & Schnitzer, 1977). Other researchers (Burford et al., 1964) have shown that peroxide treatment results in an increase in CEC due to an increase in soil surface area. This increase was attributed to removal of organic coatings from clay. The increase in CEC observed in the Hanford and Portsmouth soil following peroxide pretreatment may be attributed to one or both of these processes.

The total organic carbon (TOC) content decreased upon peroxide pretreatment. Previous studies have shown 65% to 90% destruction of organic matter from peroxide

treatment (McLean, 1930; Griffith & Schnitzer, 1977). Organic matter such as humic acid, consists of a mixture of complex macromolecules having polymeric phenolic structures with the ability to chelate with metals (Merck, 1976). Since chelates bind metal strongly (Cotton & Wilkinson, (1980), destruction of organic matter may decrease the number of adsorption sites and their binding strengths. Furthermore, Griffith and Schnitzer (1977) found that 75% of the organic residue after peroxide treatment (described in this study as pretreatment-peroxide) was composed of alkanes and carboxylic acids. Alkanes do not complex to metals, whereas carboxylic acids do complex to metals but are not chelates (Cotton & Wilkinson, 1980). The remainder was composed of phenolic and humic acids.

2. Adsorption of Metals from Solution to Soil

Adsorption of test metals from solution to soil was initially investigated. For simplicity, all experiments are considered in the following sequence. Metals are considered in the order of: zinc, lead, and chromium. Hanford soil was considered first, then Portsmouth soil. The untreated soil was discussed followed by the peroxide and permanganate pretreated soils. The purpose of equilibration time experiments was to determine the time required for performing adsorption isotherms. Adsorption isotherms indicate the binding energy and the adsorption capacity of the metal to the soil. This information is useful for estimating the mobilization of metals under various conditions.

Binding Rate Experiments

Since metal speciation is affected by pH, binding rate experiments may be influenced by rate of change of pH. In Table A.1, Portsmouth soil shows little pH change over time. However, Hanford soil shows a rapid pH change (2 to 3 pH units after 2 hours). The Hanford soil contains about 5% calcium carbonate, so binding rate may be influenced by precipitation of metal carbonates and hydroxides. The equilibration time for Hanford soil adsorption of lead, zinc, and chromium may be controlled by the rate of dissolution of calcium carbonate. The solubility of Ca^{+2} in calcite (calcium carbonate) in an open system is about 5×10^{-4} moles/l at 25°C (Freeze & Cherry, 1978). The hydrogen ion concentration, H^+ , can be estimated from the equation (Freeze & Cherry, 1978),

$$[\text{H}^+] = 10^{-4.9} \{[\text{Ca}^{+2}]\text{P}_{\text{co}_2}\}^{1/2} \quad (16)$$

where P_{co_2} is the partial pressure of carbon dioxide in bars (3.3×10^{-4}). The calculated pH of the calcite solution is 8.3, in close agreement with the measured pH, 8.5. As the calcium ion concentration increases, it competes for adsorption sites with Zn(II) or Pb(II) and thereby decreases the extent of adsorption. Griffith and Au (1977) found the adsorption of Pb(II) by montmorillonite was reduced by the presence of a 0.1M $\text{Ca(ClO}_4)_2$. Zinc carbonate is more soluble and the hydroxide is less soluble than the corresponding lead compounds.

Zinc. Figure 3 shows the adsorption over time of zinc on untreated and pretreated Hanford soil. Adsorption of Zn(II) on untreated and peroxide pretreated Hanford soil was rapid and complete within 12 hours (Figure 3). The permanganate

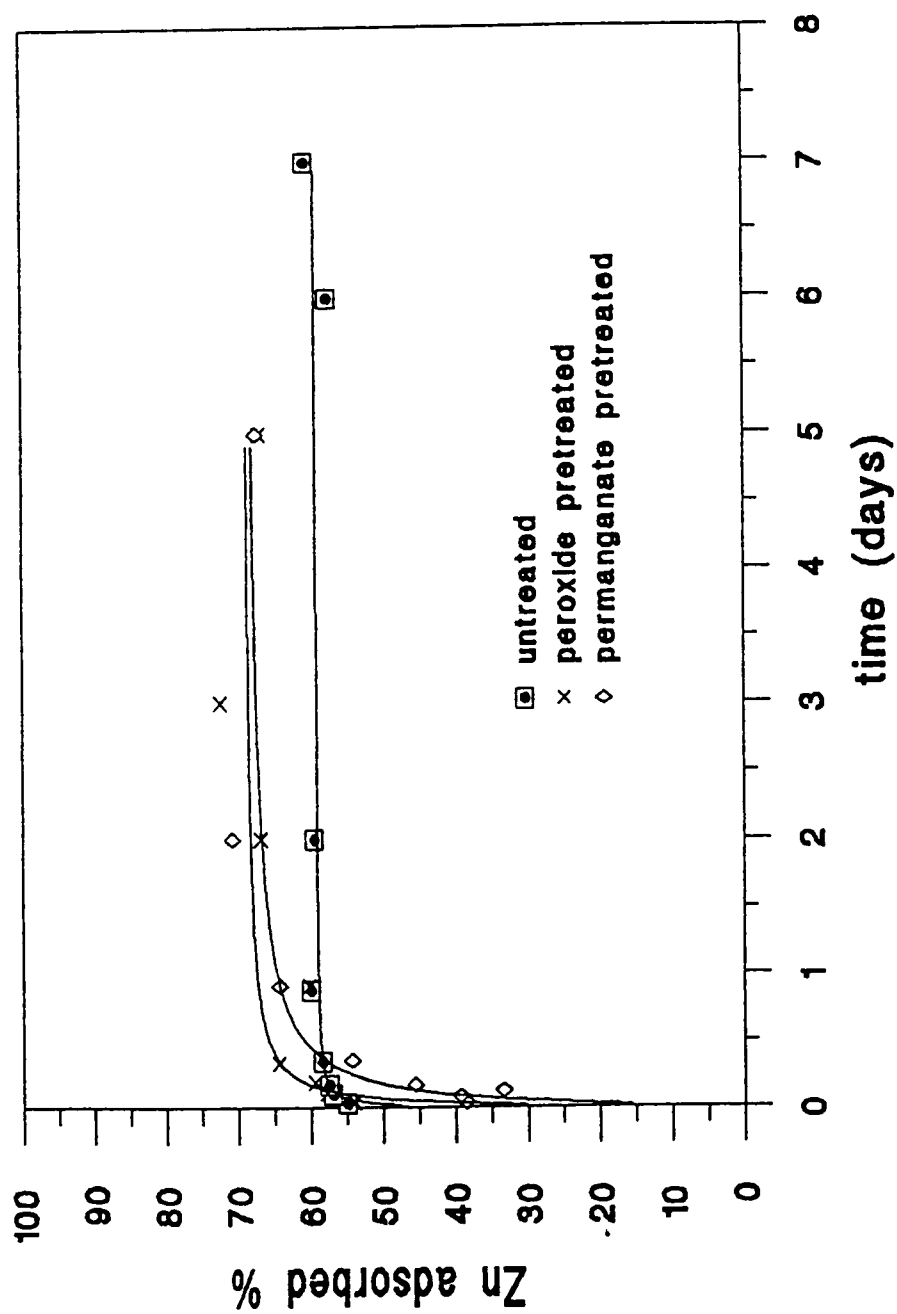


Figure 3: Adsorption of Zn on untreated and pretreated Hanford soil.

pretreated Hanford soil showed a somewhat slower uptake of zinc compared to the untreated and peroxide pretreated soils achieving equilibrium between 1- 2 days.

Figure 4 shows the adsorption profile of Zn(II) on untreated and pretreated Portsmouth soil. The adsorption of Zn(II) on the untreated soil was rapid within the first few hours (> 50%) but required about one day to reach equilibrium. The peroxide pretreated Portsmouth soil showed a rapid > 60% of increase in Zn(II) within the first few hours, and reached equilibrium in one day. The permanganate pretreated Portsmouth soil also reached equilibrium with Zn(II) in one day. Ogwanda and Sparks (1986) investigated the binding rate of K^+ to a series of soils. They found first order rate constants of reciprocating batch reactors (similar to this experiment) to vary from 0.099 to 3.764 min^{-1} compared to 0.021 to 0.037 min^{-1} for static reactors. These rate constants show that 95 % of the potassium is adsorbed from about 1 minute (reciprocating batch reactors) to 140 minutes (static reactors). Since adsorption is a diffusion controlled process (Pontius, 1990), the adsorption of Zn(II) should occur at a comparable rate to that of potassium in soils.

The untreated Hanford soil adsorbed zinc faster than the untreated Portsmouth soil (Figures 3 and 4). The peroxide pretreated Hanford soil also adsorbed zinc faster than the peroxide pretreated Portsmouth soil. In both these cases, faster adsorption of Hanford soil may be controlled by the larger pH increase compared to Portsmouth soil (Table A.1). Table A.1 indicates whether the solution is expected to be over saturated (that is precipitate) or under saturated with respect to metal hydroxide or carbonate precipitation. The calculations assume a saturated calcium carbonate concentration of 5×10^{-4} moles/l for Hanford soil (Freeze & Cherry, 1979). The acid dissociation

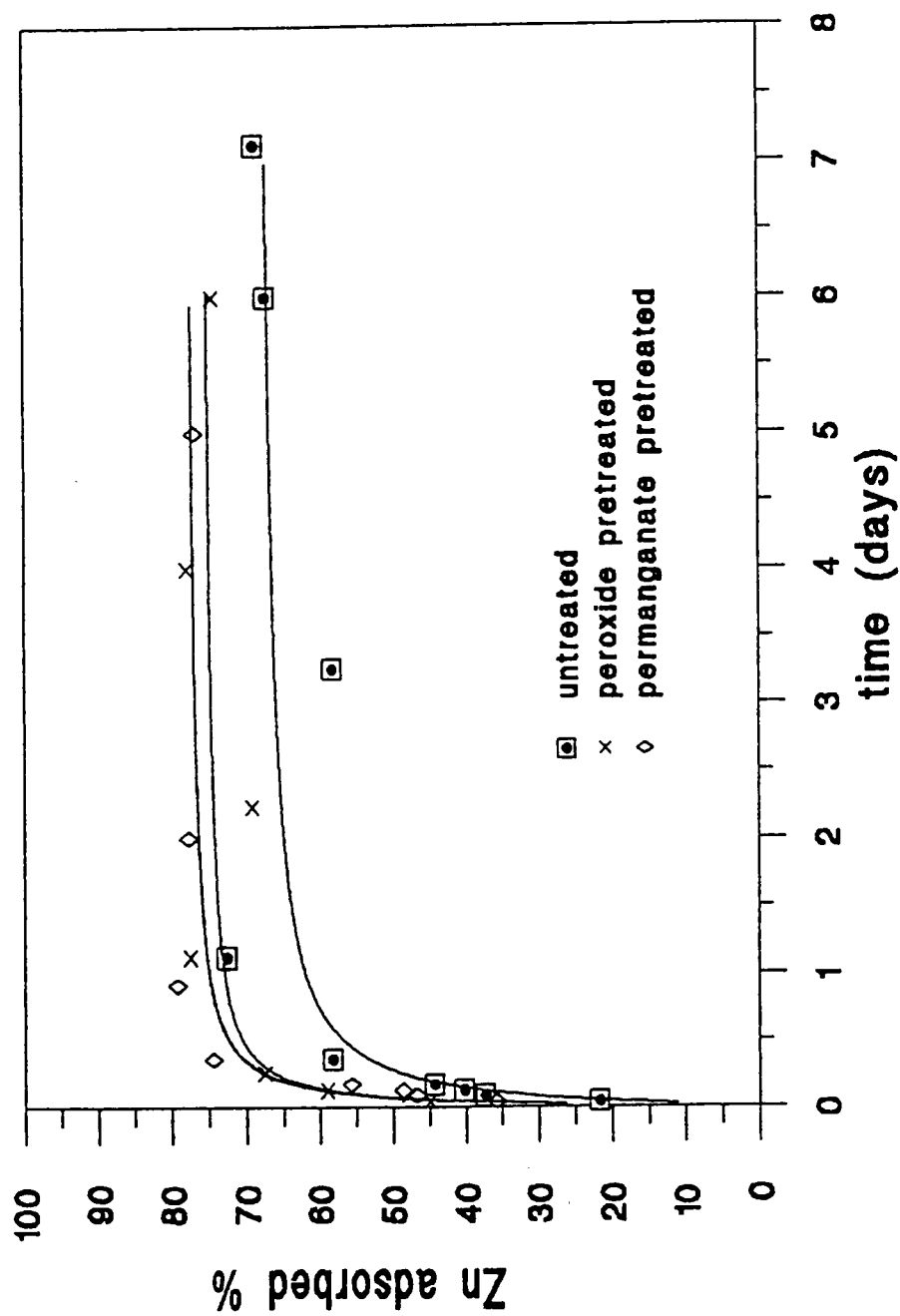


Figure 4: Adsorption of Zn on untreated and pretreated Portsmouth soil.

constants for carbonic acid ($K_{a1} = 4.2 \times 10^{-7}$, $K_{a2} = 4.8 \times 10^{-11}$), the solubility products of zinc ($[Zn^{+2}][OH^{-}]^2 = 1.2 \times 10^{-17}$, $[Zn^{+2}][CO_3^{2-}] = 1.4 \times 10^{-11}$), lead ($[Pb^{+2}][OH^{-}]^2 = 1.2 \times 10^{-15}$, $[Pb^{+2}][CO_3^{2-}] = 7.4 \times 10^{-14}$), and chromium ($[Cr^{+3}][OH^{-}]^3 = 6.3 \times 10^{-30}$) were used as the basis for metal solubility calculations (Dean, 1992). Chromium carbonate is not included in solubility calculations because it is a non stoichiometric compound $Cr_2O_3 \cdot xCO_2 \cdot yH_2O$ (Merck, 1976). The chromium in Table A.1 shown saturation at the end of the experiment. It is likely that the saturation is due to some complexing with carbonate to form soluble compounds, or caused by the formation of Cr(VI) with peroxide and permanganate pretreated soils.

Lead. Figure 5 shows the adsorption of Pb(II) on untreated and pretreated Hanford soil over time. The adsorption of Pb(II) to untreated soil was initially rapid, with about 50% completed within the first hour. The adsorption was then slower and equilibrium was achieved within 1 to 2 days. Similarly, the peroxide and permanganate pretreated soils also showed a rapid initial adsorption followed by a slower adsorption; this process was also complete within 1 to 2 days.

Figure 6 shows the adsorption of lead on Portsmouth soil. The untreated and pretreated soils showed very rapid adsorption. Adsorptions were essentially complete within the first hour or two of contact with the soil. Longer times showed little change in lead concentrations. The adsorption of Pb(II) (Figure 6) is faster than Zn(II) (Figure 4) for Portsmouth soil. The specific adsorption of metals increases with decreasing pKa (acid dissociation constant) (Brummer, 1986). Therefore, the adsorption of zinc (pKa = 9.0) is less than lead (pKa = 7.7), which may account for

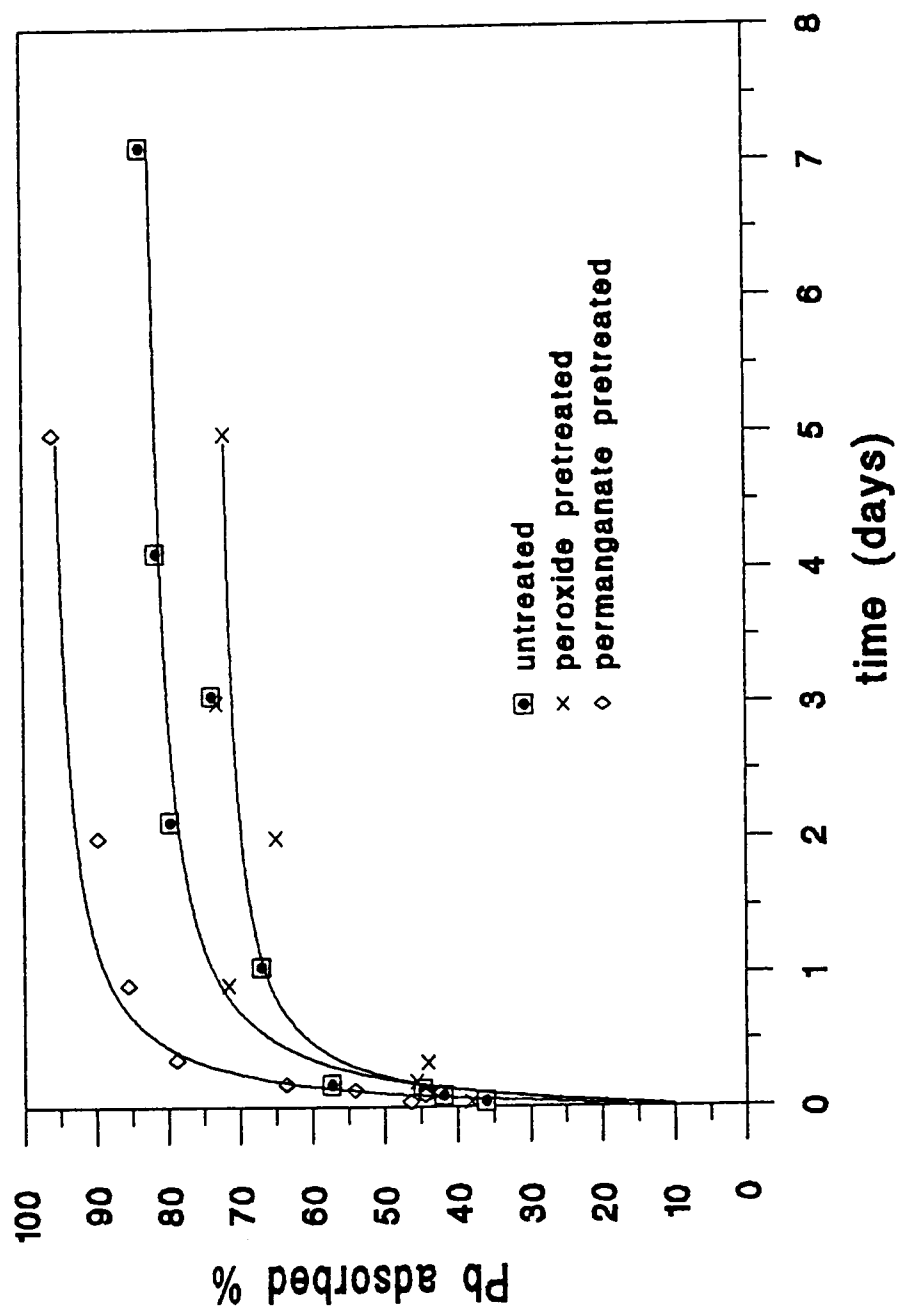


Figure 5: Adsorption of Pb on untreated and pretreated Hanford soil.

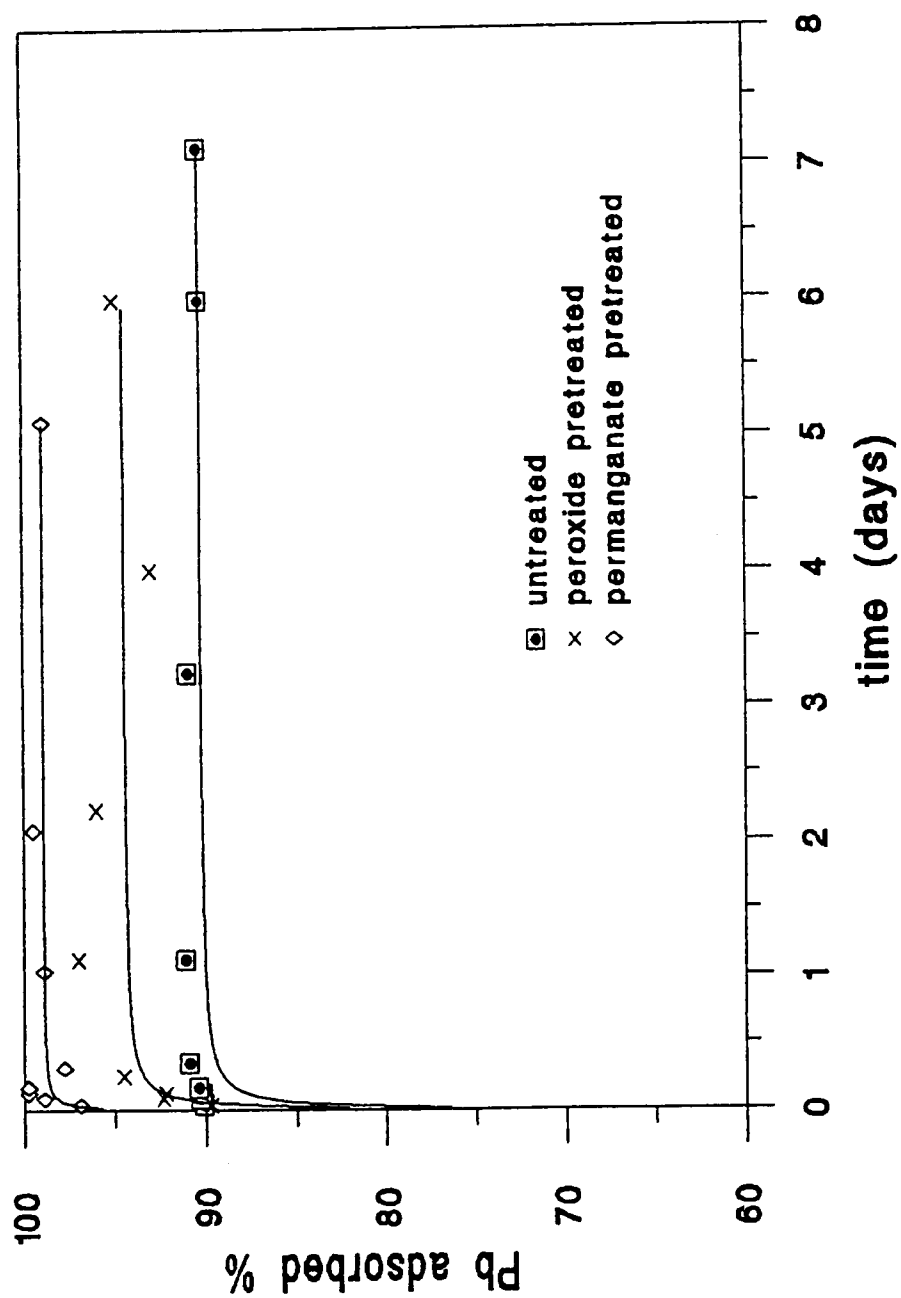


Figure 6: Adsorption of Pb on untreated and pretreated Portsmouth soil.

the faster adsorption of Pb(II). The adsorption of Zn(II) compared to Pb(II) on the Portsmouth soil was slower; this result is consistent with zinc's greater mobility in the environment.

Chromium. Figure 7 shows the adsorption of Cr(III) on untreated and pretreated Hanford soils over time. The adsorption of Cr(III) on untreated Hanford soil is rapid and essentially complete within a half day. Chromium was expected to have the highest adsorption of the three metals, since it is classified as a hard acid and would have the highest affinity for oxygen sites in the soil.

The adsorption of Cr(III) on Portsmouth soil is shown in Figure 8. Adsorption on the untreated, peroxide, and permanganate pretreated soils was rapid and essentially complete within the first hour.

3. Adsorption Isotherms

An adsorption isotherm is a graphic representation showing the amount of solute adsorbed by an adsorbent as a function of the equilibrium concentration. This relationship is quantitatively defined by some type of adsorption isotherm that is statistically applied to the adsorption data. Generally, the choice of an isotherm equation is based on the coefficient of determination, (r^2), obtained in a given case, and the simplicity of the equation (EPA, 1991).

The Langmuir isotherm was used in this analysis. The Langmuir adsorption equation can be expressed as:

$$q_e = (q_{\max} b C_e) / (1 + b C_e) \quad (11)$$

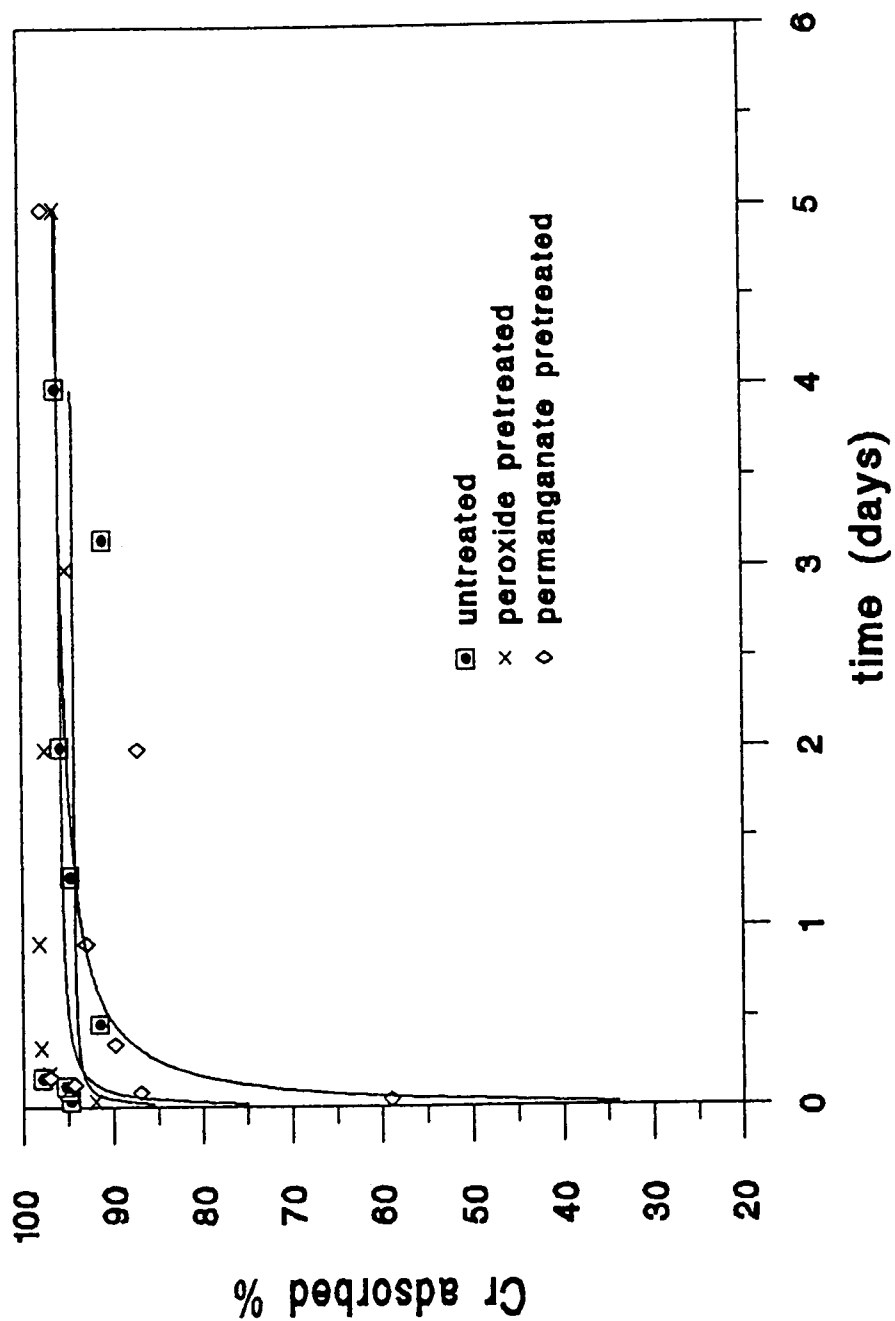


Figure 7: Adsorption of Cr on untreated and pretreated Hanford soil.

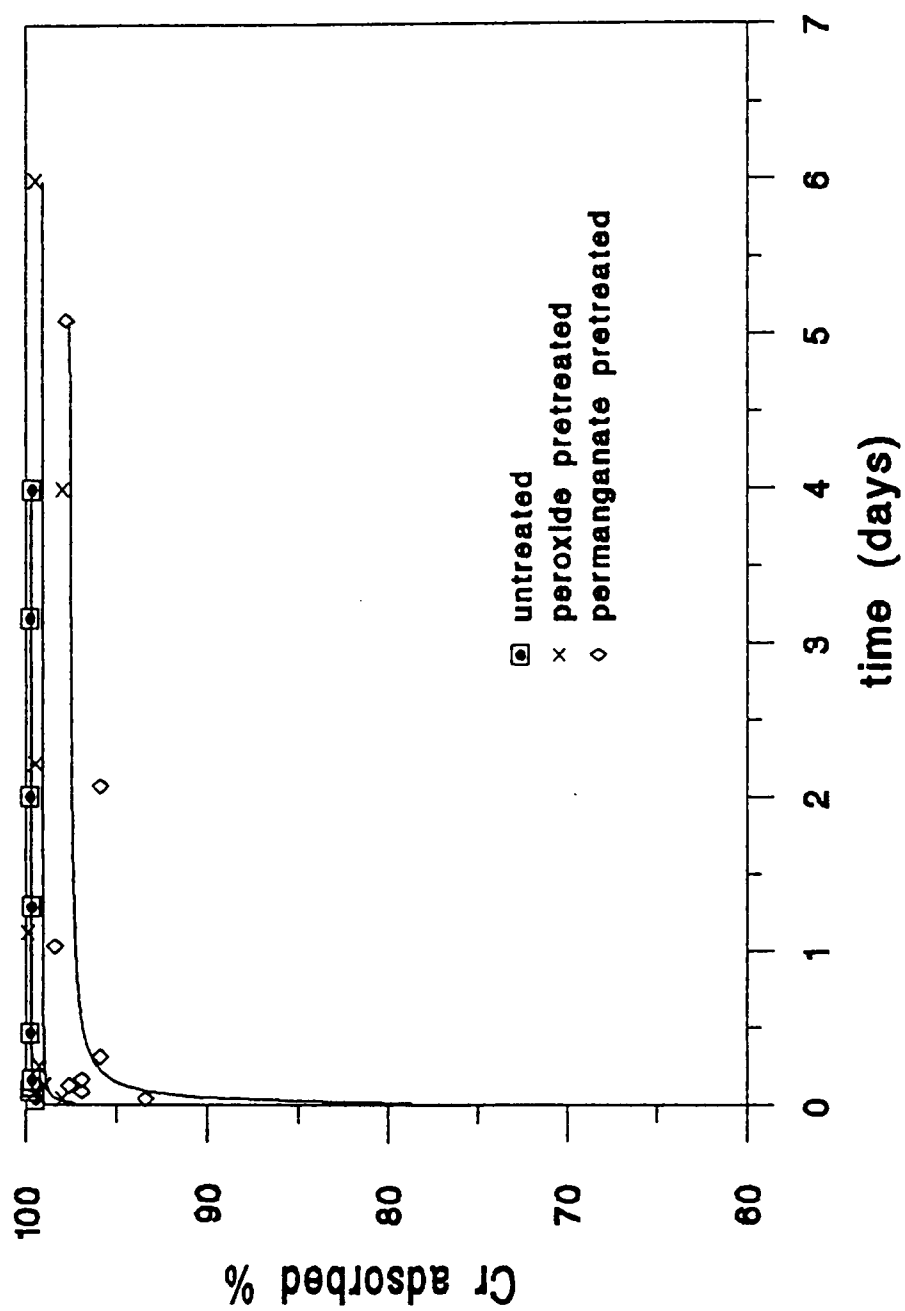


Figure 8: Adsorption of Cr on untreated and pretreated Portsmouth soil.

Where q_e represents the amount of metal sorbed per mass of soil (mg/kg), $q_{\max}$ is the maximum amount of metal adsorbed per mass of soil (mg/kg), C_e is the equilibrium concentration of metal (mg/l), and b represents a constant related to the energy of adsorption and increases as the strength of adsorption increases (1/mg) (Kinniburgh, 1986).

When bC_e is < 0.1 , then equation (11) can be approximated as a linear equation, as used for Pb(II):

$$q_e = q_{\max} b C_e \quad (17)$$

The slope of the line $q_{\max} b$ is sometimes represented as the distribution coefficient K_d (l/kg) and is a useful parameter for comparing sorptive capacities of different soils for any particular metal ion.

A technique for linearizing the Langmuir isotherm is the reciprocal method. The equation for the reciprocal method is:

$$C_e/q_e = 1/q_{\max} b + C_e/q_{\max} \quad (12)$$

Equation (12) was used as the basis for linearizing Zn(II) and Cr(III) adsorption and determining the constants $q_{\max}$ and b . The slope of the equation gives $1/q_{\max}$, and the intercept $1/q_{\max} b$. Therefore, for plots using equation (12), lines closer to the 'x' axis have larger values of $q_{\max}$, while plots with smaller intercepts have greater values of $q_{\max} b$. Equation (17) was used for lead adsorption isotherms (slope = $q_{\max} b$).

Zinc

Figure 9 shows the adsorption isotherms of Zn(II) on untreated and pretreated Hanford soil. Sorption of Zn(II) increased with increasing zinc equilibrium

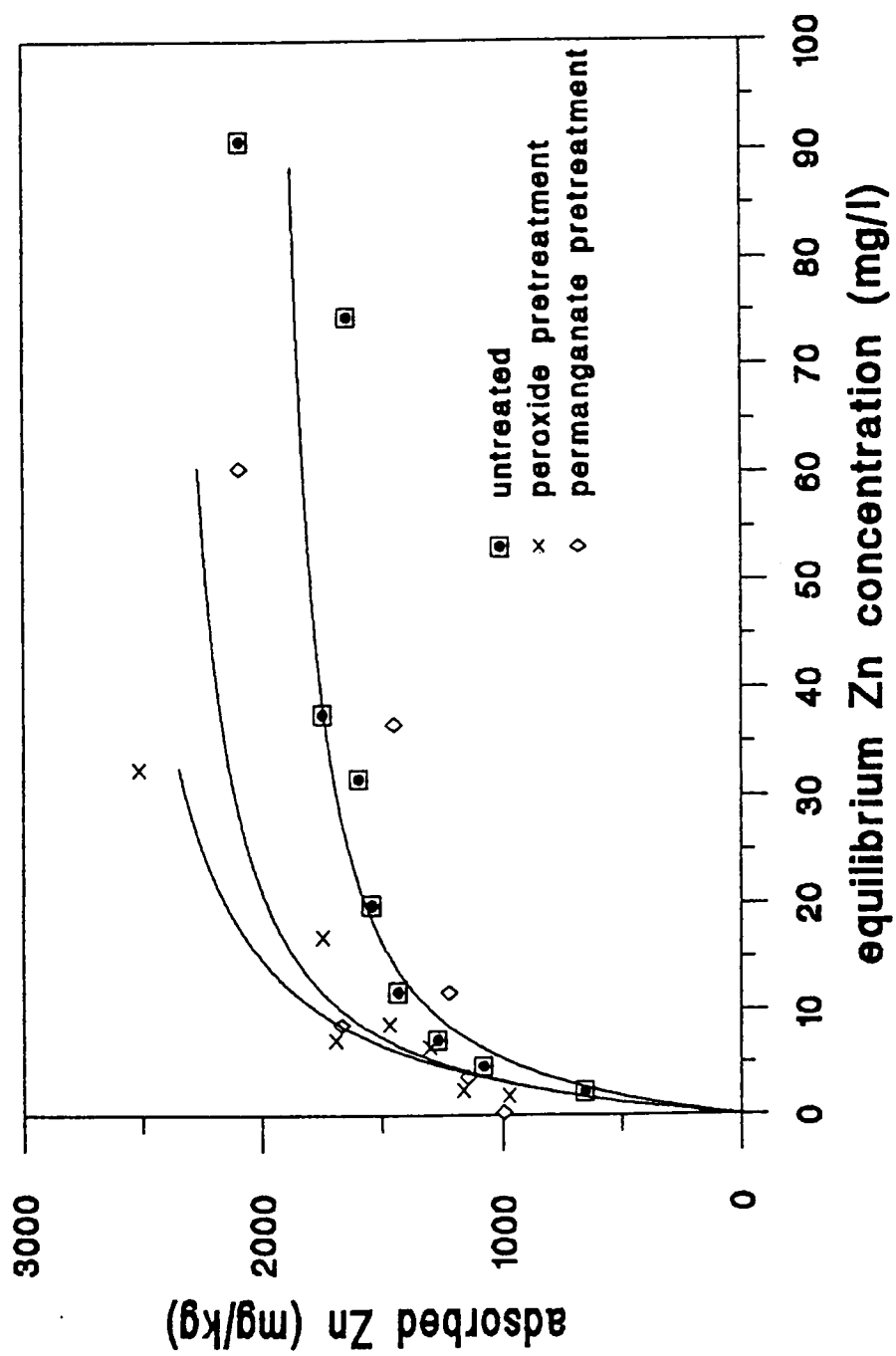


Figure 9: Adsorption isotherms of Zn on untreated and pretreated Hanford soil.

concentration, for all three soils, however, binding appeared to follow saturation at higher metal concentrations. For a given equilibrium zinc concentration untreated soil bound less zinc than peroxide pretreated soil. Permanganate pretreated soil exhibited the greatest binding of the three soil pretreatments evaluated. Saturation binding of Zn(II) ranged from 2000 to 2500 mg/kg for the three soils based on this data.

Figure 10 shows the same isotherm plotted as a single reciprocal. The values of the parameters $q_{\max}$ and b are shown in Table 4. The value of $q_{\max}$ is 1990 mg/kg (untreated), 2740 mg/kg (peroxide pretreated), and 2440 mg/kg (permanganate pretreated). The effect of peroxide on soils is complex. Bartlett et al. (1937) found a decrease in exchange capacity after peroxide treatment, that was attributed to the destruction of organic matter binding sites. Other researchers (Bufford et al., 1964) have shown peroxide pretreatment results in an increase in CEC due to an increase in soil surface area. This was attributed to removal of organic coatings from clay. Sequin and Aringheri (1977) discovered that the oxidative destruction of organic matter coatings on the soil creates new adsorption binding sites. As noted (Table 3) the CEC of both the Hanford and Portsmouth soils increased after peroxide pretreatment. Shuman (1976) found values for $q_{\max}$ to vary from 1.86 to 4.33 mg/g (1860 to 4330 mg/kg) for Zn(II) adsorption to a series of (untreated) Georgia clays. Another investigation of zinc adsorption to soils (Harter & Baker, 1976) found values of $q_{\max}$ to vary from 0.021 to 0.081 meq/q (680 to 2590 mg/kg of Zn(II)) using the Langmuir equation. These investigators experimentally measured the maximum adsorption and found it between 0.020 to 0.129 meq/g (660 to 4190 mg/kg of Zn(II)). The authors attributed this discrepancy to a curvature in the single reciprocal plot of the adsorption

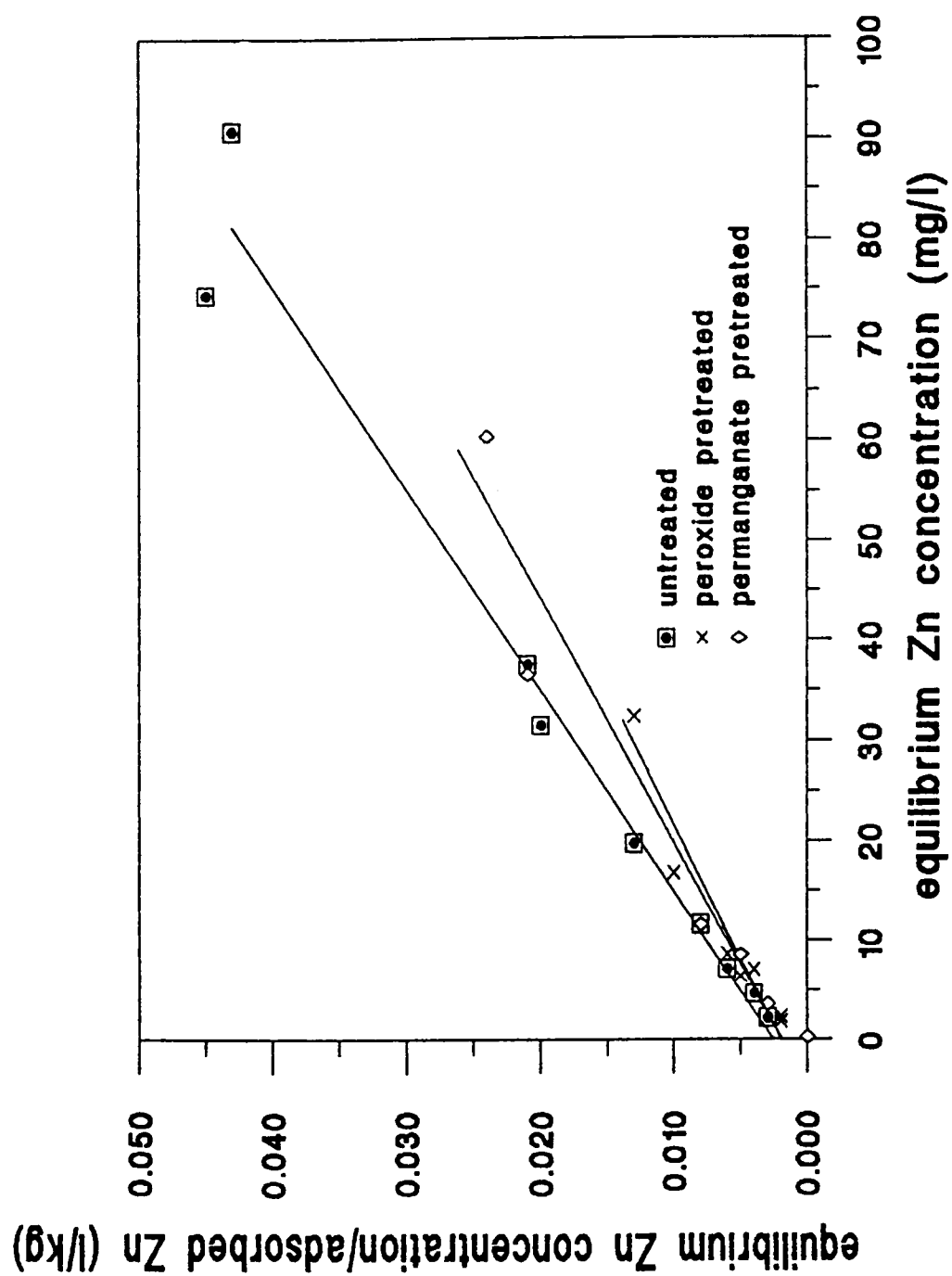


Figure 10: Linearized Langmuir adsorption isotherms of Zn on untreated and pretreated Hanford soil.

Table 4. Summary of adsorption isotherm parameters.

Metal	Soil	Pretreatment	$q_{\max}$ (mg/kg)	b (l/mg)	$q_{\max}b =$ K_d (l/kg)	r^2
Zn(II)	Hanford	untreated	1990	.188	376	.974
		peroxide	2740	.184	502	.944
		permanganate	2440	.217	529	.942
	Portsmouth	untreated	820	.595	488	.922
		peroxide	2080	.0868	180	.932
		permanganate	2010	.251	505	.940
Pb(II)	Hanford	untreated	Not determined from simple linear plot.		128	.993
		peroxide			3906	.801
		permanganate			8220	.784
	Portsmouth	untreated	Not determined from simple linear plot		330	.990
		peroxide			2385	.744
		permanganate			3000	.888
Cr(III)	Hanford	untreated	2180	7.22	15750	.922
		peroxide	2800	2.55	7150	.962
		permanganate	*			
	Portsmouth	untreated	3000	5.83	17300	.967
		peroxide	**			
		permanganate	*			

*Qualitative testing showed the oxidation of Cr(III) to Cr(VI) during isotherm adsorption.

**Qualitative testing not performed, but data consistent with oxidation of Cr(III) to Cr(VI).

data. The b values (Table 4) were relatively unaffected by oxidative pretreatment of Hanford soils. The b values obtained by Shuman (1976) varied from 0.348 to 0.781, compared to 0.184 to 0.217 found in these experiments. The parameter $q_{\max}b$, also known as the distribution coefficient K_d (Thibodeaux, 1979), represents the low concentration linear portion of Figure 9. This parameter increases when the soil undergoes oxidative pretreatment.

Appendix Table A.2 gives the final pH values for the Zn(II) adsorption isotherm experiments using Hanford soil. The initial solution pH for the untreated Hanford soil was 6.49. The final pH varied from 7.00 (highest zinc concentration) to 9.02 (blank, water only). A likely explanation for this is the presence of protons, H^+ in the layer surrounding soil particles, which are displaced by Zn^{+2} cations (Alloway, 1990). The protons then neutralized alkalinity produced by the carbonate ions and lower the pH, compared to solutions with lesser amounts of Zn(II) cations. For peroxide pretreated Hanford soil, the pH changed from 6.96 to 7.57 as the concentration of the zinc decreased. Similarly, the permanganate pretreated soil solution changed from 7.04 to 7.96. Table A.2 shows that the untreated Hanford soil solution was saturated with respect to zinc precipitation, whereas the peroxide and permanganate pretreated soil solutions were undersaturated. The Portsmouth soil solution (untreated, peroxide, and permanganate) was also under saturated with respect to zinc precipitation (not shown). Consequently, the isotherms for untreated Hanford soil represent removal by both precipitation and adsorption. The remaining five zinc adsorption isotherms (two Hanford and three Portsmouth) show no precipitation. Ideally, an adsorption isotherm should be carried out at constant pH, in order to

minimize chemical speciation changes influencing adsorption potential. Constant pH adsorption isotherms are therefore easier to interpret, but may not always represent natural processes in the environment. In this work no attempt was made to control pH (in equilibration and adsorption isotherm experiments), as suggested by the sponsor and EPA-530. Table 3 shows no discernible difference in adsorption isotherm parameters for zinc in saturated solutions (untreated Hanford) and the other five under saturated solutions.

Figure 11 shows the isotherm of adsorbed Zn(II) vs. equilibrium metal concentration for Portsmouth soil. Sorption of Zn(II) increased with increasing zinc equilibrium concentration, for all three soils. However, binding appeared to follow a saturation profile at higher Zn(II) concentrations. For a given zinc concentration, untreated soil bound less zinc than peroxide or permanganate pretreated soil.

Figure 12 is a Langmuir single reciprocal plot of the isotherm data. Table 4 shows that the maximum adsorption capacity for the untreated Portsmouth soil (820 mg/kg) was less than that for peroxide and permanganate pretreated soil (2080 and 2010 mg/kg, respectively), indicating oxidant treatment increases the number of adsorption sites. However, the 'b' values decreased upon oxidation, especially with peroxide. The implication is that more, but weaker, binding sites formed with oxidative pretreatment. The parameter $q_{\max}b$ (the slopes of the lines in Figure 12 are $1/q_{\max}b$) decreased when values were compared for no treatment and peroxide treatment. This parameter was the only decrease following oxidation (peroxide or permanganate) shown in the column in Table 4 and is caused by the large apparent reduction in the 'b' value.

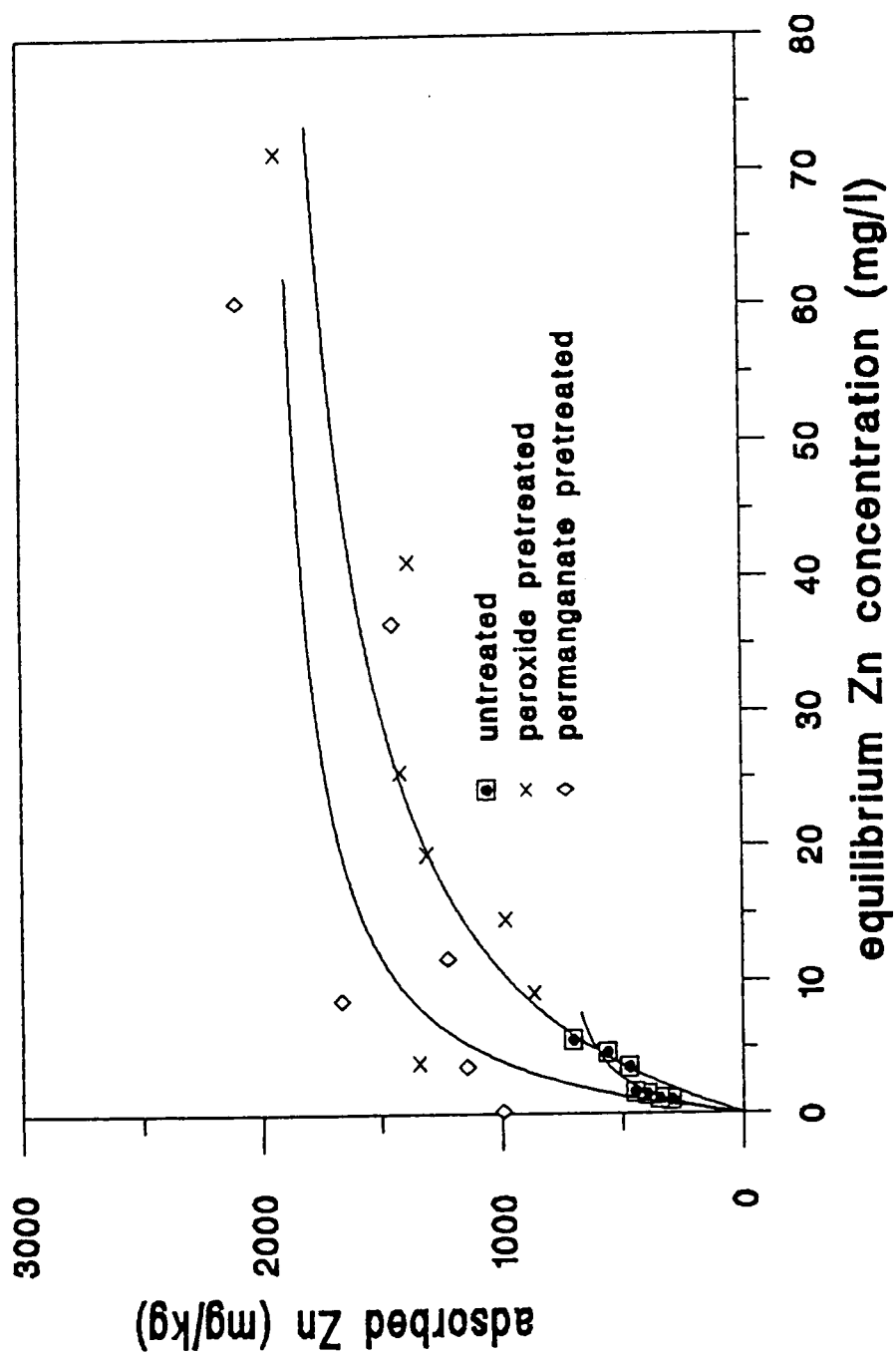


Figure 11: Adsorption isotherms of Zn on untreated and pretreated Portsmouth soil.

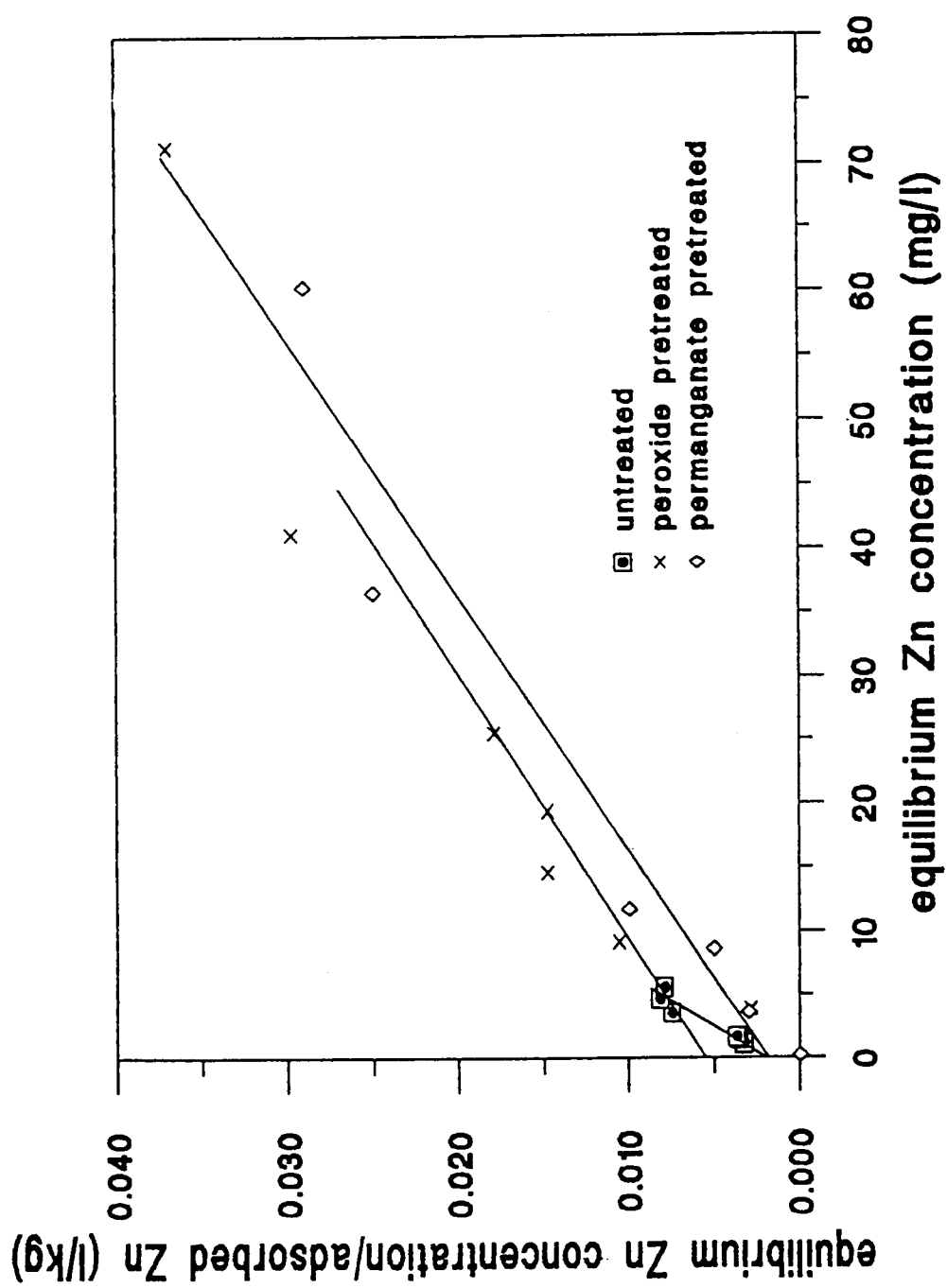


Figure 12: Linearized Langmuir adsorption isotherms of Zn on untreated and pretreated Portsmouth soil.

The untreated Hanford soil had a higher $q_{\max}$ and a lower 'b' or binding value compared to the untreated Portsmouth soil. This was consistent with more, but weaker binding sites present in the Hanford soil. Permanganate had a larger effect on the 'b' value on Hanford soil than peroxide pretreatment. A reasonable explanation is that permanganate reacted with soil material and precipitated manganese dioxide. The manganese dioxide precipitate then presented stronger binding surfaces for adsorption of metal ions.

Lead

Figure 13 shows a linear adsorption isotherm for lead on untreated and pretreated Hanford soil. Sorption of lead increased with increasing lead equilibrium concentration for all three soils. For a given equilibrium lead concentration, untreated soil bound less lead than peroxide pretreated soil. Permanganate pretreated soil exhibited the greatest binding of the three soils evaluated. Appendix Table A.3 shows the final pH values for Pb(II) adsorption isotherms with Hanford soil. Again, the simplest explanation for this pH effect is the displacement of protons by cations, and the subsequent lowering of pH in the bulk solution.

Unlike Zn(II), lead adsorption isotherms are linear beyond a metal loading of 2000 mg/kg of soil. A more accurate comparison of adsorption capacity of soil is based on cation equivalents per kg of soil. Equivalents can be calculated as the mass of absorbed cation/equivalent weight of cation. The equivalent weights of Zn(II) and Pb(II) are 32.7 and 103.6 g/eq, respectively. The adsorption of 19.3 meq/kg of soil corresponds to the adsorption of 2000 and 630 mg/kg of soil for Pb(II) and Zn(II)

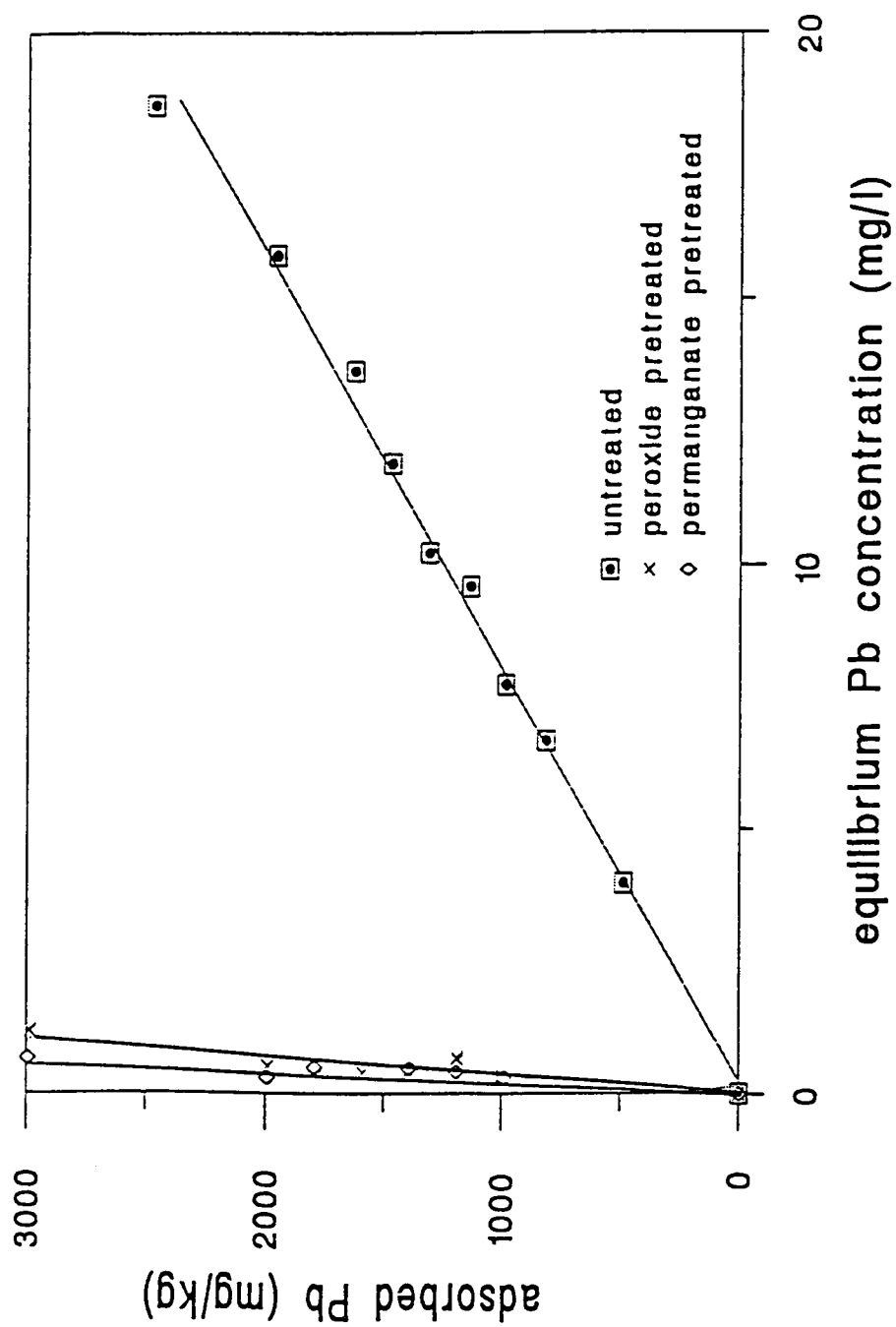


Figure 13: Linear adsorption isotherms of Pb on untreated and pretreated Hanford soil.

respectively. Both Figure 11 and Figure 13 are approximately linear within their respective ranges.

Again, the untreated Hanford soil had the lowest distribution coefficient $q_{\max}b$ of the three treatments tested (untreated, peroxide pretreatment, and permanganate pretreatment). Oxidation of the soil increased the value of this parameter (Table 4). The maximum value of K_d (largest slope) for lead adsorption with Hanford soil was obtained with permanganate pretreatment (Figure 13). It is likely that the adsorption potential of the soil was enhanced by the presumed presence of precipitated manganese dioxide. The reaction of permanganate with Hanford soil would produce manganese dioxide because of the presence of oxidizable organic compounds and the inherent decomposition potential of permanganate (Cotton & Wilkinson, 1980). The maximum K_d value with zinc also occurred with Hanford permanganate pretreated soil. This result could be explained by: (1) oxidation of organic coatings on soil particles creating new adsorption sites (Sequin & Aringheri, 1977) and (2) precipitation of manganese dioxide creating new adsorption sites (Pontius, 1990).

Figure 14 shows a linear adsorption isotherm of Pb(II) on untreated and pretreated Portsmouth soil. Figure 13 shows the beginning of saturation binding for the peroxide pretreated soil. However, since the other five curves in Figures 13 and 14 are better expressed as linear adsorption isotherms, the peroxide pretreated soil is also expressed as a linear adsorption isotherm. The pH of the three Portsmouth soils with lead only showed comparative slight changes compared to Hanford soil.

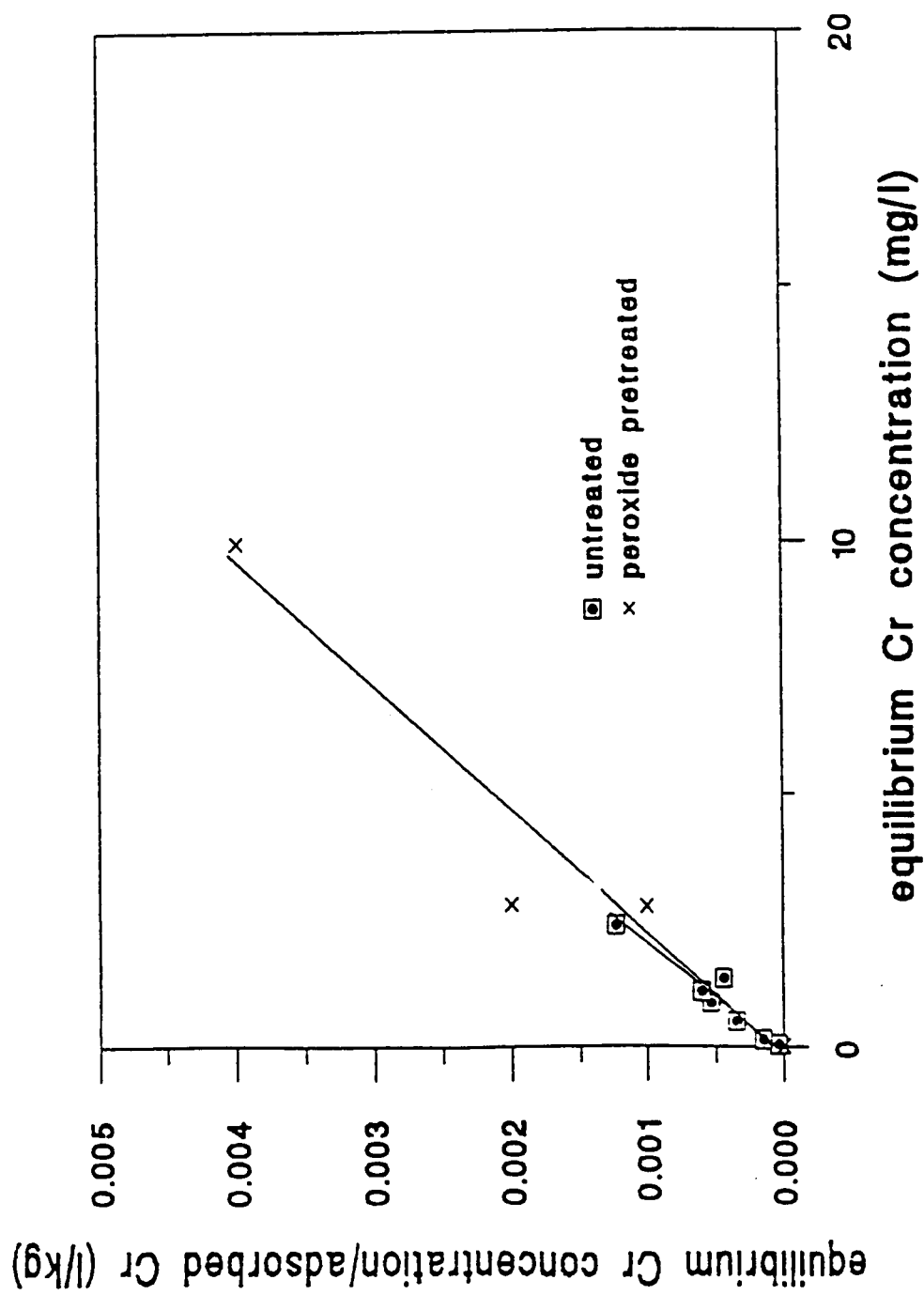


Figure 14: Linearized Langmuir adsorption isotherms of Cr on untreated and pretreated Hanford soil.

Again, the isotherms are best described by a linear model for the reasons stated in the previous paragraphs. Also, the values of $q_{\max}b$ (K_d) were greatest for the permanganate soil and least for the untreated.

Comparisons of $q_{\max}b$, the distribution coefficient (Figures 9, 11, 12, and 13), between Pb(II) and Zn(II) with Hanford and Portsmouth soils show the following: (1) Portsmouth (both Pb(II) and Zn(II)) > Hanford and (2) permanganate pretreatment (both Pb(II) and Zn(II)) > untreated.

Chromium

Figure 15 shows the adsorption of chromium on untreated and peroxide treated Hanford soil. Sorption of chromium increased with increasing metal ion concentration, however binding appeared to follow a saturation profile at higher chromium concentrations. The peroxide pretreated Hanford soil had a higher saturation level than the untreated soil (Table 4). The untreated Hanford soil showed a pH increase from 6.91 to 7.90 as the metal ion concentration decreased. The peroxide pretreated Hanford soil showed pH variations from 7.25 to 7.88. Permanganate pretreated Hanford soil showed pH variations from 6.83 to 7.71.

An isotherm for permanganate pretreatment of Hanford soil was not included because the isotherm generated produced a negative slope with an $r^2 = .017$. A test of the supernatant showed the presence of Cr(VI) in the solution. Therefore, the interaction between permanganate pretreated soil showed adsorption of Cr(III) as well as reaction to Cr(VI). A reasonable explanation is that permanganate pretreatment produced manganese dioxide. Manganese dioxide is known to react with Cr(III) to

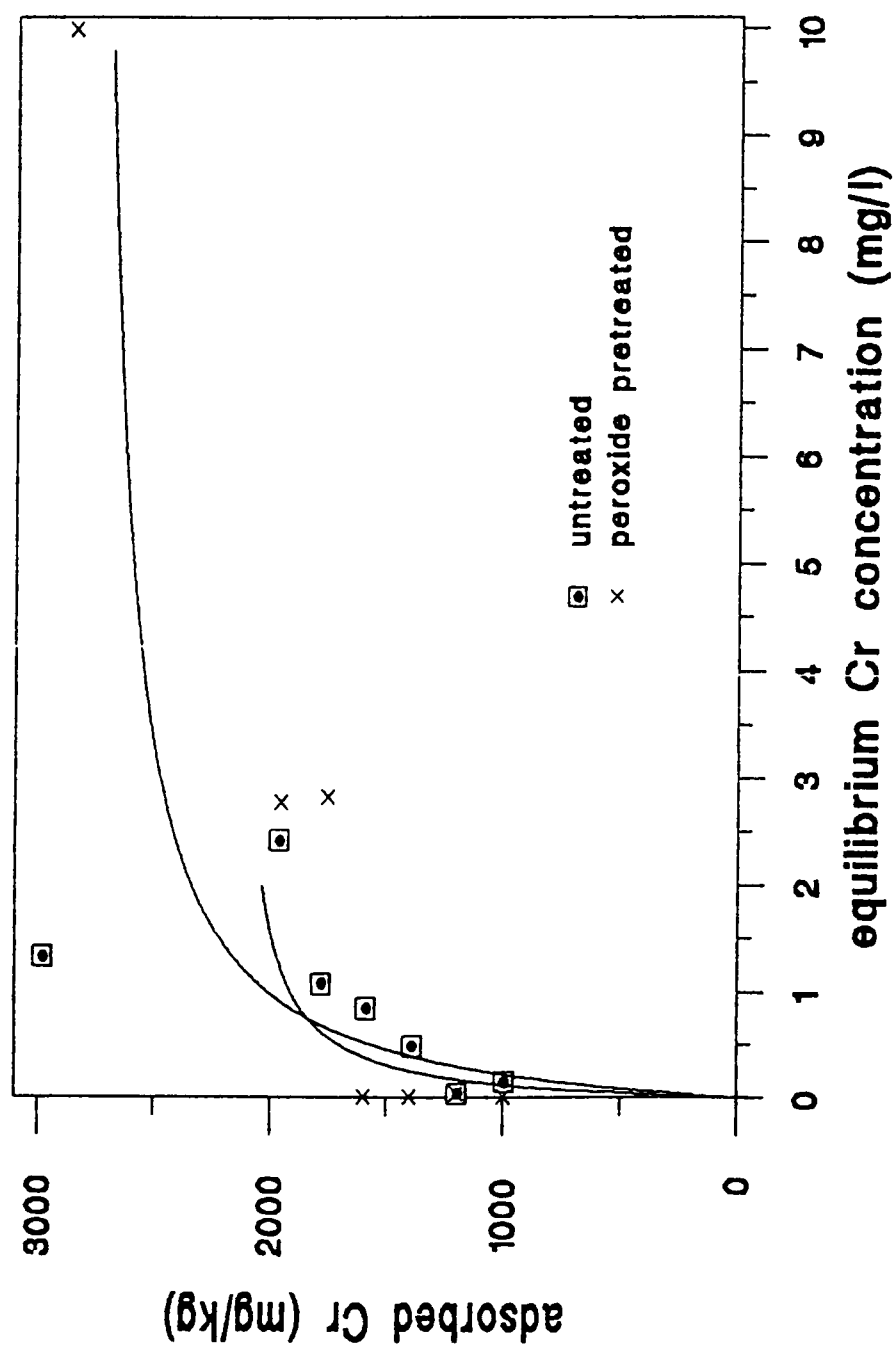


Figure 15: Adsorption isotherms of Cr on untreated and pretreated Hanford soil.

produce Cr(VI) (Bartlett & James, 1979). Consequently, the isotherm generated included both Cr(III) adsorption and Cr(VI) formation. Testing for the presence of Cr(VI) was not performed with peroxide pretreated Hanford soil, so it is possible that a 'small' amount of Cr(III) oxidation occurred (Figures 15). In binding rate experiments shown in Figure 7, testing for the presence of Cr(VI) (e.g. permanganate pretreated Hanford soil) was not performed. It appears likely that some Cr(VI) anion was present.

The Cr(III) and Hanford soil isotherm in Figure 15 shows the onset of adsorption site saturation at high adsorption levels. The data was plotted as a single reciprocal Langmuir isotherm in Figure 16. The values of q_{max} for the untreated and peroxide soils, 2180 and 2800 mg/kg, respectively, were approximately the same as for Zn(II) and Hanford soil. However, the 'b' values, 7.22 and 2.55 are more than an order of magnitude higher, implying that the Cr(III) binding is much stronger than that of zinc. Binding sites in silicates (which typically comprise sand) are the hard base oxygen type. Since Cr(III) is a hard acid, the adsorption of chromium is expected to be stronger to the hard base sites than the 'softer' acids Zn(II) and Pb(II) (Merian, 1991).

Figure 17 shows the adsorption of Cr(III) on untreated Portsmouth soil. The peroxide pretreated soil isotherm was not included because, it was suspected (although not tested) that Cr(VI) was produced during the experiment. The data generated for peroxide pretreated Portsmouth soil gave an $r^2 = 0.33$. A likely explanation is that the presence of peroxide oxidizable constituents in the soil, such as manganese compounds found in clay type soils (Alloway, 1990), caused the reaction of Cr(III) to Cr(VI).

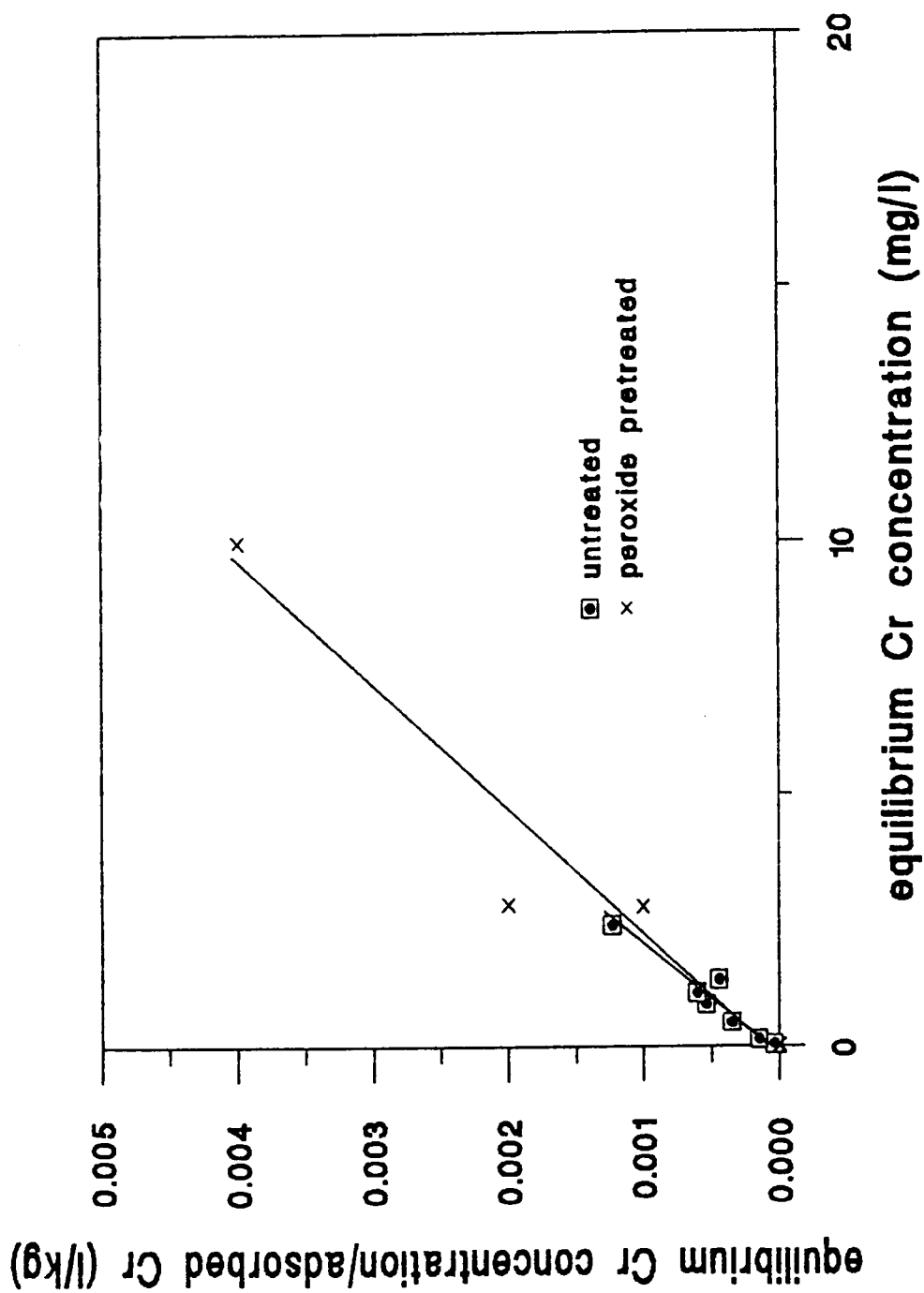


Figure 16: Linearized Langmuir adsorption isotherms of Cr on untreated and pretreated Hanford soil.

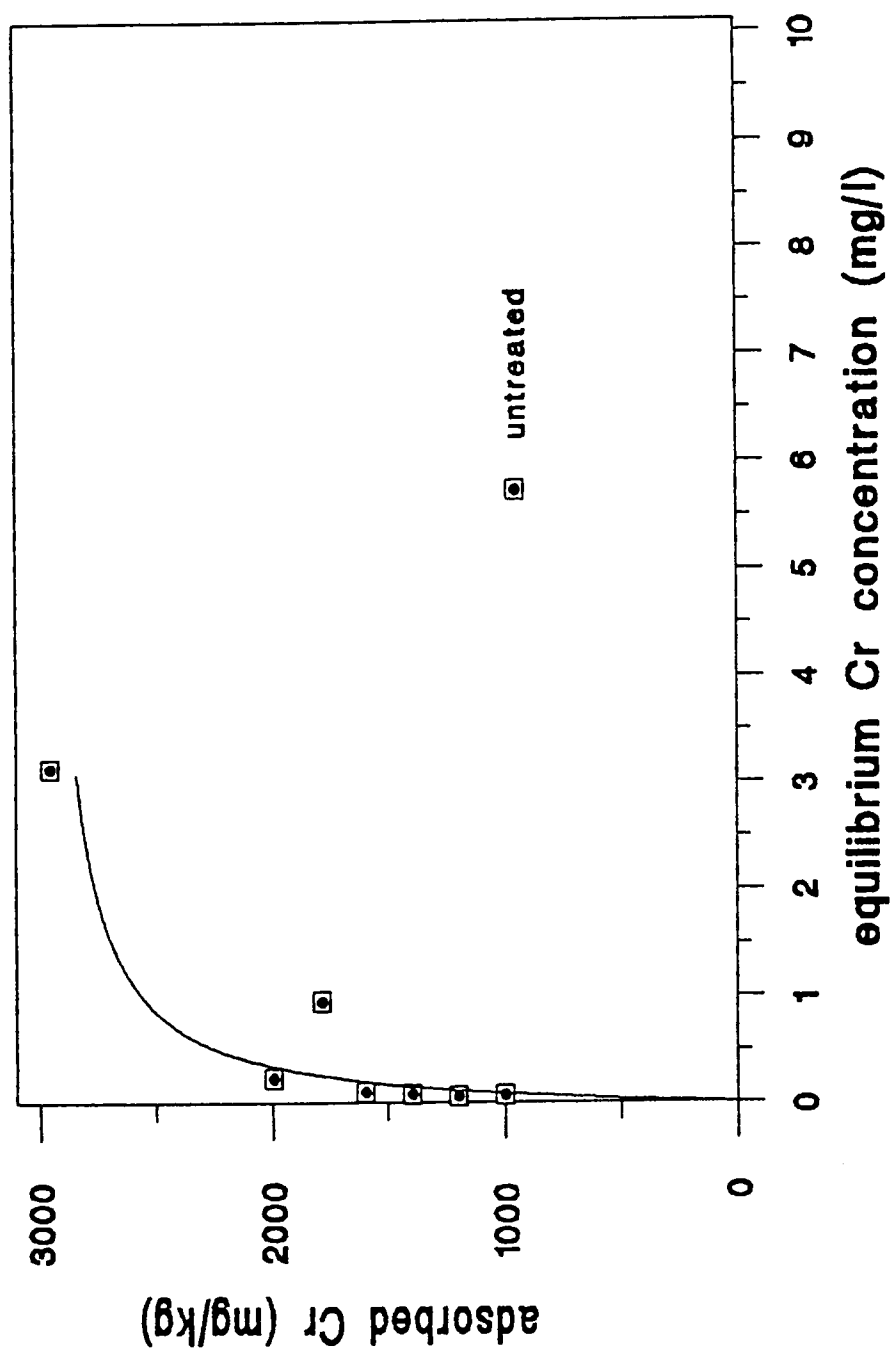


Figure 17: Adsorption isotherm of Cr on untreated Portsmouth soil.

Therefore, the data generated for the isotherm includes the effects of adsorption and reaction. Again, permanganate pretreated soil showed a positive test for Cr(VI) at the conclusion of the adsorption isotherm experiment. The untreated soil showed a pH change from 5.51 to 6.14 during the experiment. The unsuccessful experiments on peroxide (5.82 to 5.89) and permanganate (6.19 to 6.44) pretreated soils showed small pH variations.

The Cr(III) adsorption isotherm on untreated Portsmouth soil (Figure 17) shows the onset of saturation at high adsorption values. Figure 18 shows a single reciprocal plot of the adsorption isotherm. The saturated adsorption value, $q_{\max}$, was 3000 mg/kg, the highest value in Table 4. The 'b' values are also an order of magnitude higher than for Zn(II) and Portsmouth soil, indicating stronger binding.

Chromium adsorption was different from Zn(II) and Pb(II) for several reasons. (1) Chromium is a tripositive cation (Cr(III)). The larger positive charge of the cation charge gives it a higher binding affinity for negatively charged sites present at soil surfaces. In other words, it is a "hard acid" with an equivalent weight of 17.3 g/eq which would give it a larger 'b' value with the Langmuir isotherm. (2) Cr(III) oxidizes to Cr(VI) easily, even under mild oxidizing conditions (Cotton & Wilkinson, 1980), and yields a very soluble dichromate anion. Experiments on this work have shown that chromate anions poorly sorb to soil.

4. Peroxide and Permanganate Oxidation of Metal Contaminated Soils

Peroxides and permanganate are excellent oxidants for organic compounds that may contaminate a site and require remediation (Morrison & Boyd, 1973). The effects

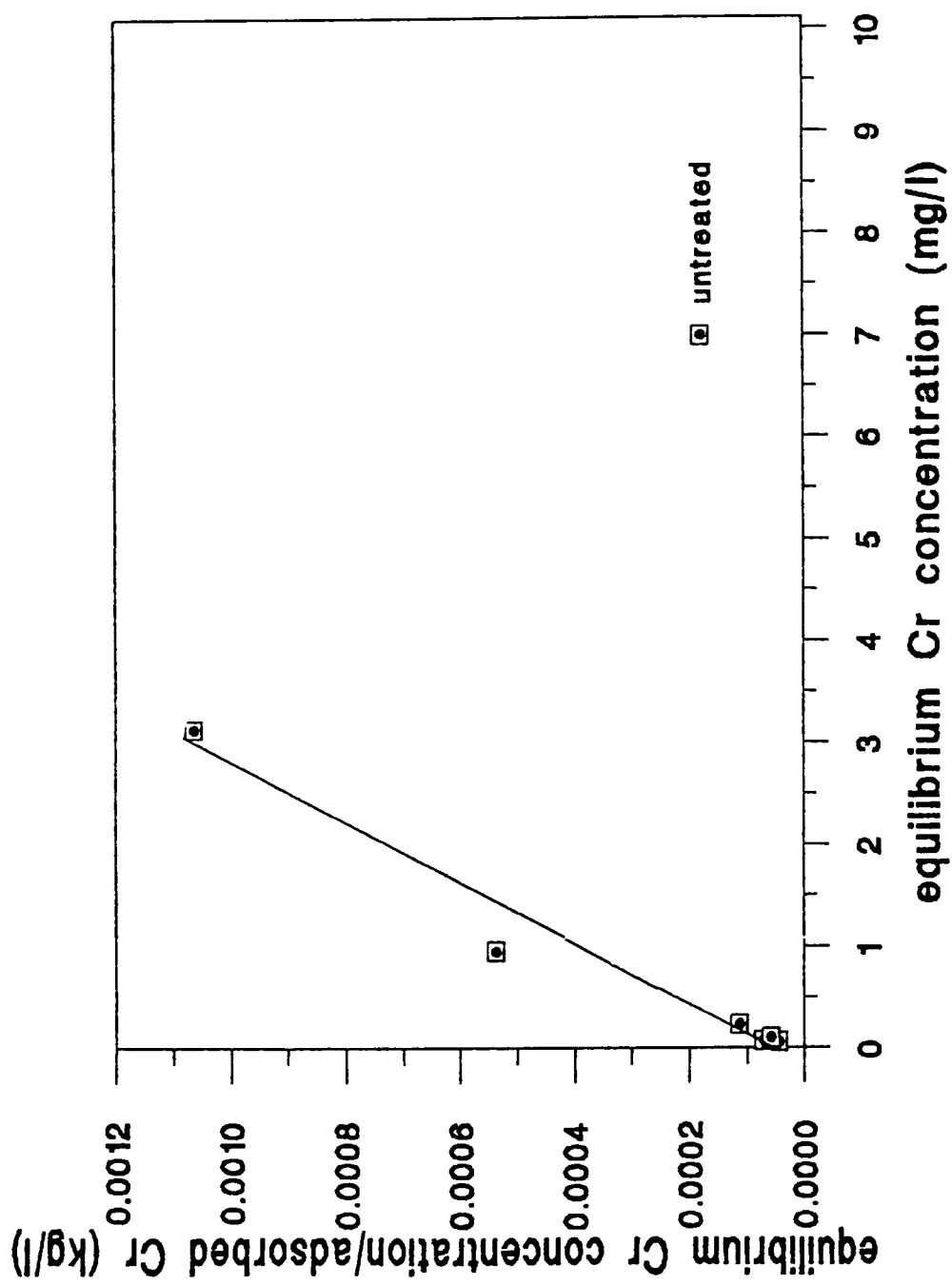


Figure 18: Linearized Langmuir adsorption isotherm of Cr on untreated Portsmouth soil.

of these oxidants, particularly permanganate, on inorganic contaminants that may also be present in soils is not well known. Three metals were chosen to assess their mobility under oxidizing conditions: (1) zinc because it is relatively mobile in the environment, (2) lead because it is relatively immobile, and (3) chromium, because it is immobile (Cr(III)) but undergoes facile oxidation to the very mobile Cr(VI) anion. Adsorption and desorption processes often occur on different time scales; nevertheless, 48 hours was chosen for both adsorption and demobilization experiments.

During treatment, oxidized soil could become contaminated with metals and subsequently come in contact with oxidants. Therefore, the mobility of metals with each oxidant was evaluated on pre-oxidized soils, as well as untreated soils. The mobility of metals was determined at various oxidant concentrations. Table 1 outlines the reactions of various metals, soils, and soil pretreatments with peroxide and permanganate oxidants.

The measurement of pH in the presence of hydrogen peroxides is imprecise for two reasons. First, the dielectric constant of hydrogen peroxide (84.2) is different from that of water (78.6) (CRC, 1984). Second, the acid dissociation constant is different from water as shown in equation (4). For experiments discussed in this section, pH measurements were made after 48 hours when the hydrogen peroxide concentrations were small, so the pH measured may be approximately accurate.

Zinc Mobilization from Soils Using Peroxide and Permanganate

Table 5 summarize zinc mobilization in the two soils under various oxidant treatment schemes. When zinc was detected in both water and oxidant, figures are shown.

Hanford soil with peroxide treatment. Figure 19 shows zinc mobilization from untreated Hanford soil using varying peroxide concentrations. The soil was initially loaded with 115.6 mg Zn/kg of soil. The detection limit of zinc by Atomic Adsorption (AA) spectroscopy (0.05 mg/l) was converted to a percent of zinc removed as a reference.

Figure 19 shows that water alone (0% peroxide) mobilized the most zinc (6.5%) from this soil. Small concentrations (0 to ~4%) of peroxide appeared to suppress zinc mobilization. Concentrations from 4% to 15% peroxide increased mobilization, whereas 30% peroxide suppressed mobilization. The final solution pH varied from 7.79 to 8.29 as the concentration of peroxide decreased.

An explanation for the complex shape of Figure 19 is the following: Low peroxide concentrations (< 4%) create new binding sites on the soil for zinc and suppress zinc mobilization compared to water. For example, low peroxide concentrations partially oxidize organic matter, creating new adsorption sites. However, the organic matter remains largely insoluble. Higher peroxide (4% to 15%) concentrations may mobilize zinc by forming zinc complexes with soluble organic ligands, such as oxalate (Martin, 1954). The organic ligands (and chelates) result from the partial destruction of organic matter by peroxide solutions producing water soluble

Table 5. Summary of zinc mobilization from soils under various oxidation treatments.

Contami- nant	Soil	Pretreatment	Oxidant	Detectable Zn(II)?*	
				In water	In oxidant
Zn(II)	Hanford	untreated	peroxide	yes*	yes*
			permanganate	yes*	yes*
		peroxide	peroxide	yes	no
		permanganate	permanganate	yes*	yes*
	Portsmouth	untreated	peroxide	yes	no
			permanganate	yes	no
		peroxide	peroxide	no	no
		permanganate	permanganate	yes	no

*Zn(II) detectable (> 0.05 mg/l) in both water and oxidant are shown as figures.

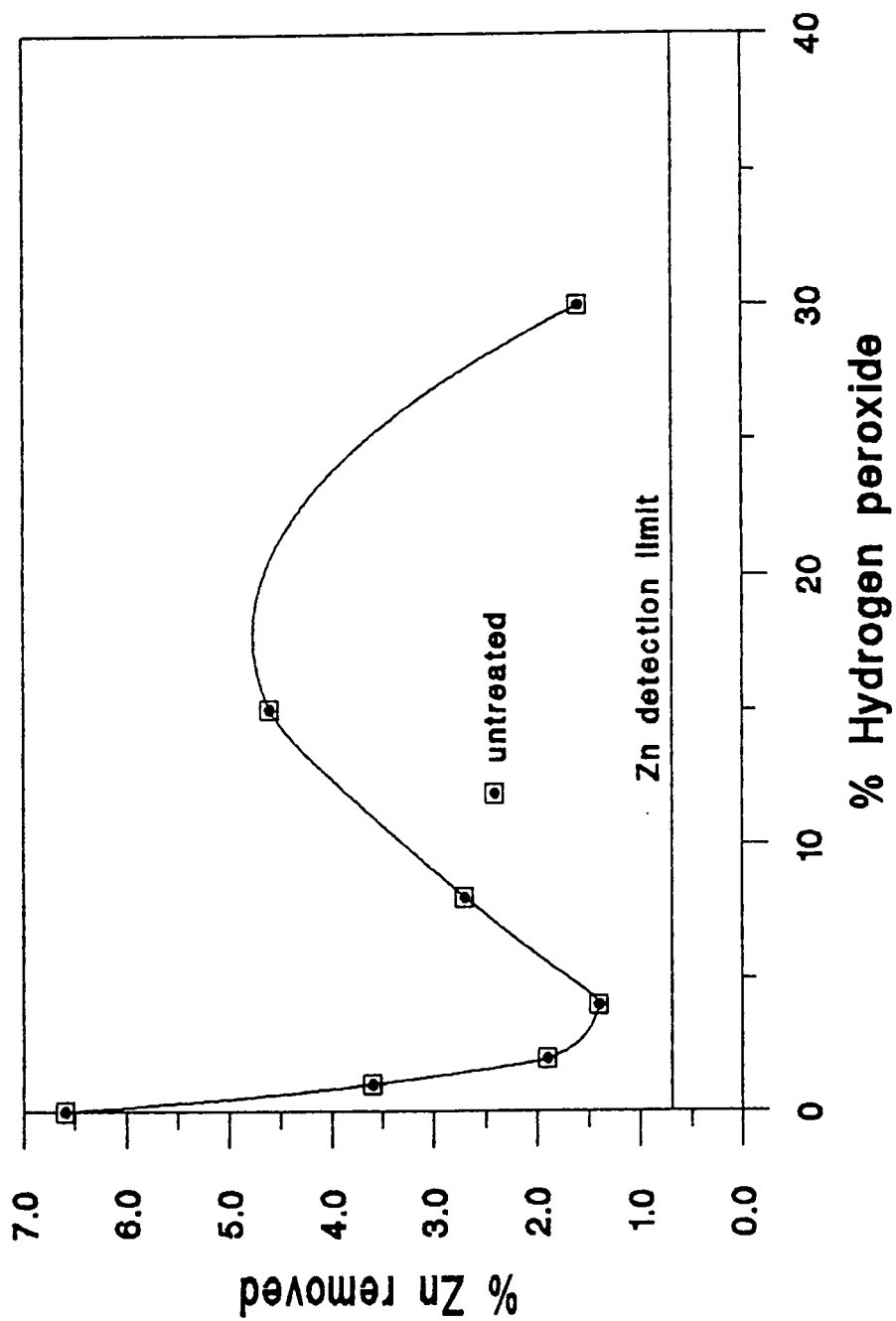


Figure 19: Mobilization of Zn from untreated Hanford soil using peroxide.

ligands. The first stability constant ($\log K_1$) for zinc oxalate (4.89) is higher than that of the calcium compound (3.0) (Dean, 1992), indicating that oxalate binds to zinc rather than calcium. Thus, zinc mobilization at intermediate peroxide concentrations may be controlled by the formation of soluble chelates. Very high peroxide concentrations ($> 15\%$) apparently suppress zinc mobilization, due to the complete destruction of organic material. Adsorption isotherm experiments with Zn(II) on Hanford soil showed an increase in $q_{\max}$ when the soil was pretreated with 30% hydrogen peroxide solution (Table 4). Verification of this hypothesis was beyond the scope of this work.

Peroxide pretreated Hanford soil (30% hydrogen peroxide) was contaminated with zinc (146.2 mg/kg of soil) and reacted with hydrogen peroxide. Water (0% peroxide) mobilized 0.55% zinc, and all peroxide concentrations produced zinc below the detection limit (0.45% zinc removed). Therefore, these data are not shown as a figure. In this experiment the soils was pretreated with 30% hydrogen peroxide and then contaminated with zinc. As stated this increases the maximum adsorption capacity for the soil with Zn(II) (Table 4). Moreover this soil was then treated with varying peroxide concentrations. Thus this double peroxide treatment appears to suppress Zn(II) mobilization.

A comparison of the untreated and peroxide pretreated Hanford soils suggests that zinc mobilization occurs in the presence of organic matter. The reaction of soil organic matter with peroxide produces a variety of volatile and water soluble products (Griffith & Schnitzer, 1977), that may complex zinc. Peroxide also causes the destruction of organic matter on mineral surface films and occlusions (Sequin &

Aringheri, 1977), which opens new sites for binding to zinc. Because of these new binding sites, peroxide pretreated soil shows less zinc mobilization than untreated soil. Moreover, as Table 4 shows, the distribution coefficient $q_{\max}b$ is higher for the peroxide pretreated soil, which implies stronger binding than the untreated soil.

Hanford soil with permanganate treatment. Figure 20 shows mobilization of zinc from untreated and permanganate pretreated Hanford soil. The untreated soil showed neither zinc mobilization nor suppression as a function of varying permanganate concentrations. The amount mobilized was only slightly above the detection limit (0.5% Zn removed) for all permanganate levels tested, indicating zinc mobilization was independent of permanganate concentration. The zinc contamination level was 115.6 mg/kg of soil. The pH of the solution varied from 6.95 to 7.8 with decreasing permanganate concentration.

In contrast, permanganate pretreated Hanford soil (Figure 20) showed increasing zinc mobilization with increasing permanganate concentrations. Figure 20 shows zinc mobilization is linear, with up to 5% zinc mobilization at the highest permanganate concentration. The simplest explanation is the direct displacement of potassium ion, K^+ , for adsorbed Zn^{+2} ions on the soil. For example, at the highest potassium permanganate concentration (2.33 g/l), the potassium ion concentration was 576 mg/l, whereas the zinc ion solution concentration after equilibrium was achieved is 0.95 mg/l. In other words, zinc has about a 600 times greater affinity to soil binding sites than potassium. In this instance the presence of the permanganate ion may be unimportant; it is the presence of the large amount of potassium ion that causes zinc

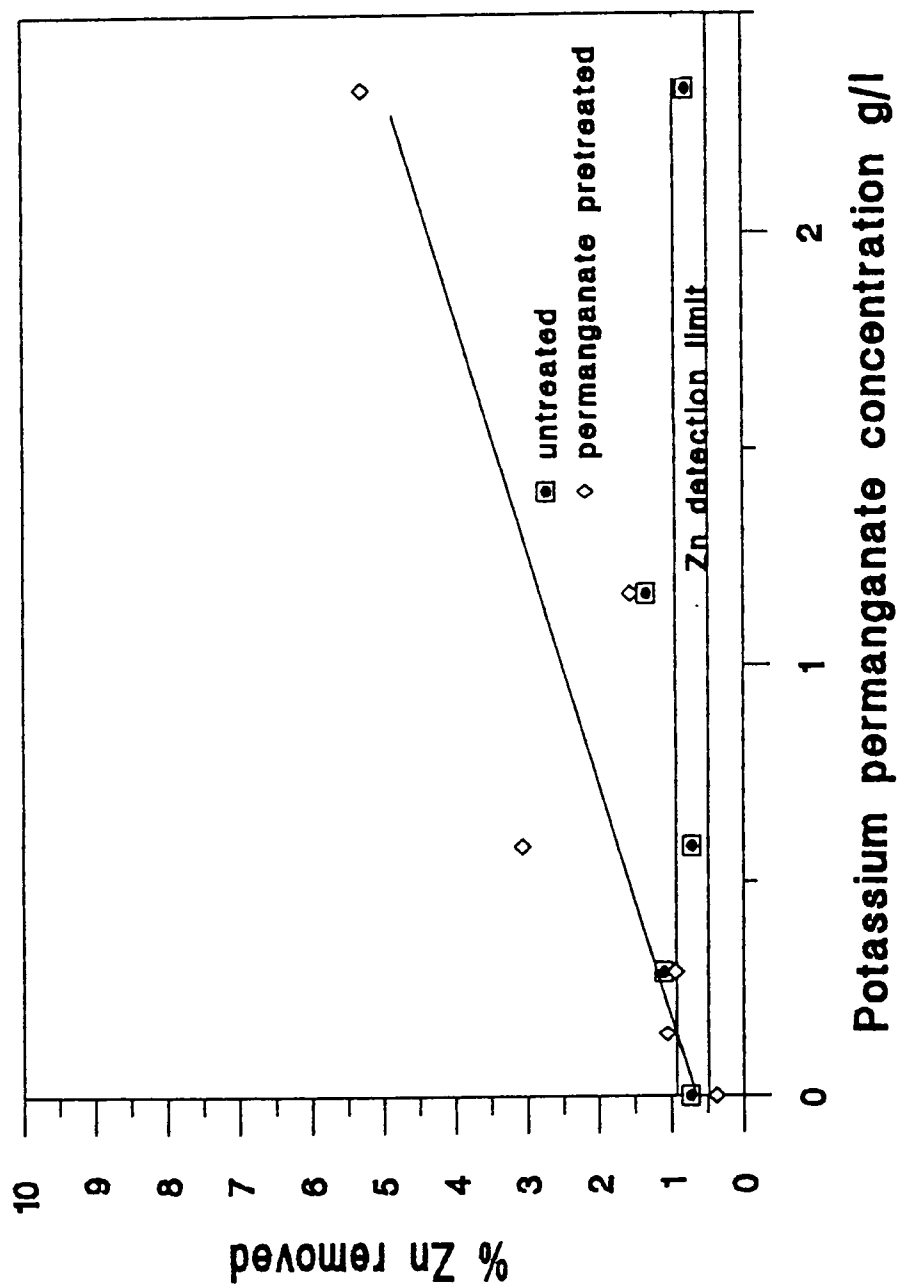


Figure 20: Mobilization of Zn from untreated and permanganate pretreated Hanford soil using permanganate.

mobilization. The Merck Index (1976) lists zinc permanganate, $\text{Zn}(\text{MnO}_4)_2$ as a compound similar in appearance to potassium permanganate.

If potassium ions replace zinc ions on soil particles, then why does the untreated Hanford soil contaminated with zinc not show increasing zinc mobilization with increasing potassium concentration? The answer is that it should. However, in the untreated soil, reaction of permanganate with organic matter or other reducing species should produce manganese dioxide (Cotton & Wilkinson, 1980). The insoluble manganese dioxide then presents new adsorption sites for zinc (Pontius, 1990). The apparent overall result is that these two effects cancel each other.

Portsmouth soil with peroxide treatment. The reaction of peroxide with untreated Portsmouth soil contaminated with zinc (147 mg/kg of soil) showed 2.2% mobilization with water only (0% peroxide). No figure is shown for this experiment. Varying peroxide concentrations showed zinc below the detection limit (0.45% zinc removed). The value of q_{max} increases from 820 mg/kg to 2080 mg/kg of Zn(II) for peroxide treatment of Portsmouth soil (Table 4). This can be accounted for by the creation of new binding sites for zinc during peroxidation, for example by binding to precipitates of iron and aluminum hydroxide (Sequin & Aringheri, 1977). The solution pH varied from 7.57 to 7.53 and was insensitive to varying peroxide concentrations.

Peroxide pretreated Portsmouth soil showed no detectable zinc in water and no detectable zinc, with varying peroxide concentrations. Again, this can be accounted for by peroxide pretreatment creating new adsorption sites for zinc. In this experiment, peroxide pretreatment increased the number of adsorption sites for Zn(II) on the

Portsmouth soil (Table 4). The soil was subsequently treated with peroxide on Zn(II) contaminated soil, which may have produced new adsorption sites.

So why are Hanford and Portsmouth soils (untreated and peroxide pretreated) so different at mobilizing zinc, when treated with hydrogen peroxide? Shuman (1977) reports that Zn(II) is strongly adsorbed by hydrous metal oxides in clays and the adsorption is highly pH dependent. In this case, the Portsmouth soil is a clay type soil, and therefore the Zn(II) may be tightly bound to the soil during peroxide mobilization. That is, the Zn(II) may be chemically bound to iron by way of hydroxide bridges. The value of the binding value b (Table 4) with Zn(II), is larger for Portsmouth soil than Hanford soil, suggesting less mobilization. The Hanford soil is almost entirely sand, and the zinc is much less strongly bound to it. In this case, the zinc (Zn^{+2}) is electrostatically attracted to the oxide surface of silicates.

Portsmouth soil with permanganate treatment. The reaction of untreated Portsmouth soil contaminated with zinc (147 mg/kg of soil) showed 1.8% mobilization with water only (0% peroxide). Varying permanganate concentrations showed zinc below the detection limit (0.45% zinc removed). No figure is shown for this experiment. As already noted, Portsmouth soil reacted with potassium permanganate, precipitating manganese oxide compounds and producing new adsorption sites. The pH of the solution varied from 6.72 to 7.58 as the permanganate concentration decreased.

Permanganate pretreated Portsmouth soil contaminated with zinc (243 mg/kg of soil) showed 6.3% mobilization with water only (0% permanganate). Varying permanganate concentrations showed zinc concentrations below the detection limit

(0.30% zinc removed). During permanganate pretreatment, the purple permanganate solution was decolorized, indicating a chemical reaction and precipitation of manganese oxides. Any continuation of this reaction should create new adsorption sites for zinc, suppressing its mobilization. The permanganate ion is more stable in alkaline conditions; therefore, it is more likely to decompose in the more acidic Portsmouth soil compared to the Hanford. The permanganate ion is decomposed by metals that have mixed valencies such as iron, a frequent component in clay type soils, which is found in Portsmouth soil. Therefore, the decomposition of permanganate and subsequent precipitation of manganese dioxide decreases the mobilization of Zn(II).

Lead Mobilization from Soils Using Peroxide and Permanganate

Table 6 summarizes lead mobilizations with the two soils and various oxidant treatment schemes. The solution detection limit was 1 mg/l and lead measurements were below the detection limit throughout the course of the experiment. The lead contamination in the soil was in the range of 140-320 mg/kg of soil for these experiments. Zinc was expected to be more mobile than lead, and some zinc mobilization was quantified during mobilization experiments (Table 5). However, the detection level of zinc was more than twenty times that of lead, 0.05 mg/l vs. 1 mg/l respectively. Therefore, the combination of lower mobility and larger detection level of lead compared to zinc yielded no information (i.e., not detected) in lead mobilization experiments. It should be noted that the possibility exists that peroxide and permanganate may convert Pb(II) to more insoluble Pb(IV). If this occurred, then lead may become less mobile following oxidative treatment.

Table 6. Summary of lead mobilization from soils under various oxidant treatments.

Contami- nant	Soil	Pretreatment	Oxidant	Detectable Pb(II)?*	
				In water	In oxidant
Pb(II)	Hanford	untreated	peroxide	no	no
			permanganate	no	no
		peroxide	peroxide	no	no
		permanganate	permanganate	no	no
	Portsmouth	untreated	peroxide	no	no
			permanganate	no	no
		peroxide	peroxide	no	no
		permanganate	permanganate	no	no

*Detectable Pb > 1.0 mg/l.

Hanford soil with peroxide treatment. Lead was not detectable in water or in varying peroxide concentrations in Hanford soil. In peroxide pretreated Hanford soil, lead was not detected in water or varying peroxide concentrations. The pH of the final solution varied from 8.22 to 8.27 for these experiments.

Hanford soil with permanganate treatment. Lead was not detected in water or in varying permanganate concentrations in Hanford soil. In permanganate pretreated Hanford soil, lead was not detected in water or in varying permanganate concentrations. The pH of the final solution varied from 7.76 to 7.90 for these experiments.

Portsmouth soil with peroxide treatment. Lead was not detectable in water or in varying peroxide concentrations in Hanford soil. In peroxide pretreated Hanford soil, lead was not detected in water or varying peroxide concentrations. The pH of the final solution varied from 7.54 to 7.72 for these experiments.

Portsmouth soil with permanganate treatment. Lead was not detected in water or in varying permanganate concentrations in Hanford soil. In permanganate pretreated Hanford soil, lead was not detected in water or in varying permanganate concentrations. The pH of the final solution varied from 6.61 to 7.00 for these experiments.

Chromium Mobilization from Soils Using Peroxide and Permanganate

Table 7 summarizes the results of chromium mobilization from the two soils using various oxidant treatment schemes. Chromium was detected in water only with

Table 7. Summary of chromium mobilization from soils under various oxidation treatments.

Contami- nant	Soil	Pretreatment	Oxidant	Detectable Chromium?*	
				In water	In oxidant
Cr(III)	Hanford	untreated	peroxide	no	yes
			permanganate	no	yes
		peroxide	peroxide	no	no
		permanganate	permanganate	no	yes
	Portsmouth	untreated	peroxide	no	yes
			permanganate	no	yes
		peroxide	peroxide	no	yes
		permanganate	permanganate	yes	yes

*Detectable is > 0.50 mg/l.

permanganate pretreated Portsmouth soil. It was readily detected in both soils using peroxide or permanganate

Hanford soil with peroxide treatment. Figure 21 shows the percent chromium mobilized using varying peroxide concentrations. Initial chromium contamination in the soil was 375 mg/kg. The detection limit for chromium using AA was 0.5 mg/l which corresponded to a measurable detection limit of 2% chromium removed. Water alone produced no detectable chromium; however, all peroxide concentrations produced detectable chromium. Small amounts of peroxides (0.2% to 2%) remove more than 20% of the chromium initially bound. Increasing peroxide concentrations removed up to 75% of the chromium.

The simplest explanation for the chromium removal is the ultimate oxidation of Cr(III) to Cr(VI). A 15 ml solution containing 0.2% hydrogen peroxide (30 mg of H_2O_2) is more than sufficient to oxidize the 375 micrograms of Cr(III) present on 1.00 gram of soil. The reaction of Cr(III) with hydrogen peroxide produces three distinct chromium peroxide compounds (Connor & Elisworth, 1966). These chromium peroxides are unstable and decompose to the Cr(VI) anions or Cr(III) cations. The Cr(VI) exists as an anion, such as CrO_4^{2-} or Cr_2O_7^- and is not adsorbed by the Hanford (or Portsmouth) soil. Therefore, the chromium removed is dependent on the oxidation of Cr(III) to the peroxide(s), which decompose to Cr(VI) (usually) or Cr(III). The Cr(VI) anions are poorly sorbed and, therefore, partition to the solution. The Cr(III) cations strongly adhere to soil and are not removed unless subsequently oxidized. The pH of the final solution varied from 8.31 to 8.24 for these experiments.

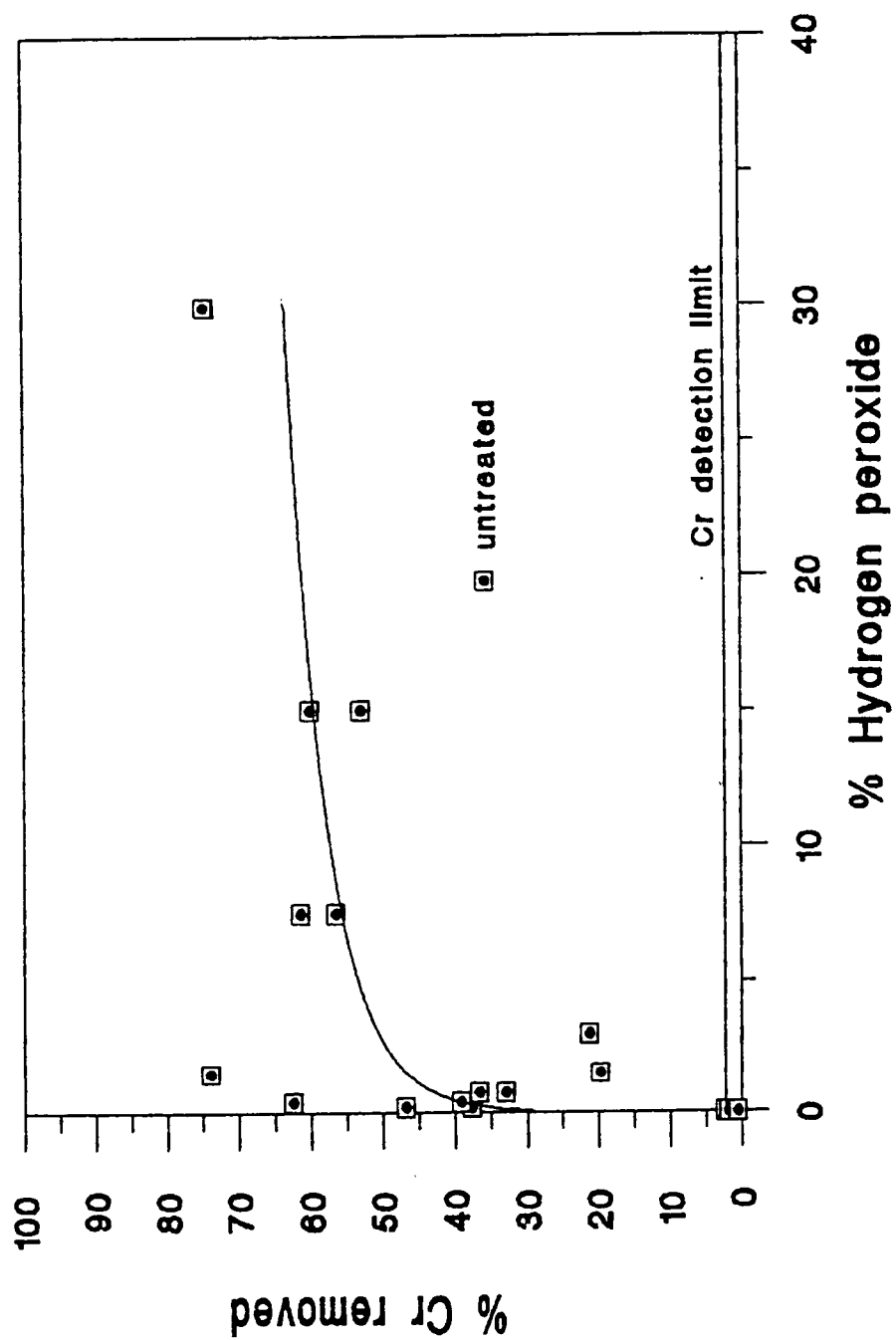


Figure 21: Mobilization of Cr from untreated Hanford soil using peroxide.

Peroxide pretreated Hanford soil, contaminated with chromium (148 mg/kg of soil), was reacted with varying peroxides concentrations. Water alone (0% peroxide) showed no detectable chromium removed. Varying peroxide concentrations also showed no chromium mobilization. Actually, some samples contained detectable chromium, but were detected below the practical quantification limit. This result was unexpected. A repeated experiment yielded the same result. A possible explanation is that peroxide pretreatment of Hanford soil produced new sites on the soil. These sites were then contaminated with chromium and treated with peroxides. The result was that the soil enhanced the decomposition of chromium peroxide(s) to Cr(III) (Connor & Elisworth, 1966) instead of the Cr(VI) anion. Another possibility is peroxide pretreatment produces adsorption sites for chromium which are inaccessible to reaction with hydrogen peroxide.

Hanford soil with permanganate treatment. Figure 22 shows the mobilization of chromium from Hanford soil with varying permanganate concentrations. The initial chromium contamination in the soil was 375 mg/kg of soil. Water alone (0% permanganate) showed no detectable chromium mobilization. Low permanganate concentrations (0.15 g/l) showed more than 30% chromium mobilization. A potassium permanganate concentration of 1.0 g/l can mobilize about 60% of the chromium. The pH of the final solution varied from 7.91 to 8.75 as the concentration of permanganate decreased.

The permanganate pretreated Hanford soil was similar to the untreated Hanford soil when reacted with permanganate (Figure 22). The chromium content of the soil

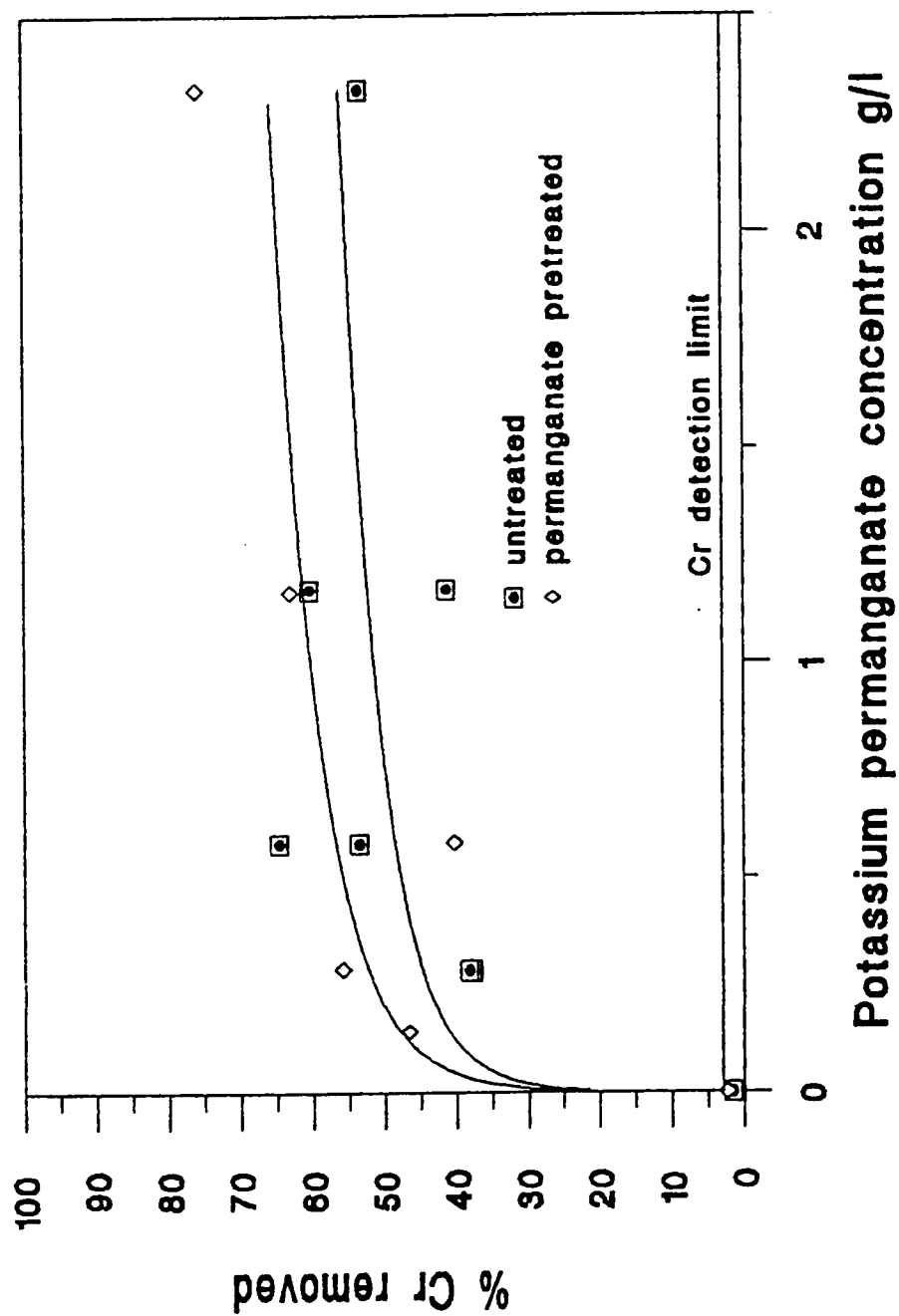


Figure 22: Mobilization of Cr from untreated and permanganate pretreated Hanford soil using permanganate.

was 389 mg/kg. Water alone (0% permanganate) showed no chromium mobilization. Varying permanganate concentrations showed 45% to 70% chromium mobilized. The pretreated Portsmouth soil showed about 10% greater overall removal of chromium as opposed to the untreated soil, although the curves are substantially similar.

A comparison of chromium mobilization from untreated Hanford soil using peroxide and permanganate show a maximum removal of about 60% from each soil although mobilization occurs via different mechanisms. The hydrogen peroxide produces a chromium peroxide which usually decomposes to chromate anions such as $M_3Cr(O_2)_4$ or $Mcr(O)(O_2)_2H$ as shown in Figure 1. The permanganate acts by way of direct oxidation of Cr(III) to Cr(VI) anions. A possible explanation for both mobilizing the same amount of chromium is that about 60% of bound chromium is available for free exchange into the bulk solution, where chemical reaction occurs; that is, the chromium is labile. The remainder of the chromium is inaccessible for reaction and is not labile.

However, the chromium mobilization was not detectable with the peroxide pretreated Hanford soil. This can be accounted for by the formation of chromium peroxide that decomposes almost exclusively to Cr(III) such as $Cr(O)(O_2)_2$ as shown in Figure 1. Reaction of permanganate with the permanganate pretreated Hanford soil (Figure 22) allows for the direct oxidation of Cr(III) to chromate anion and is, therefore, detectable.

Portsmouth soil with peroxide treatment. Figure 23 shows the percent chromium mobilized from Portsmouth soil with varying peroxide concentration. The initial

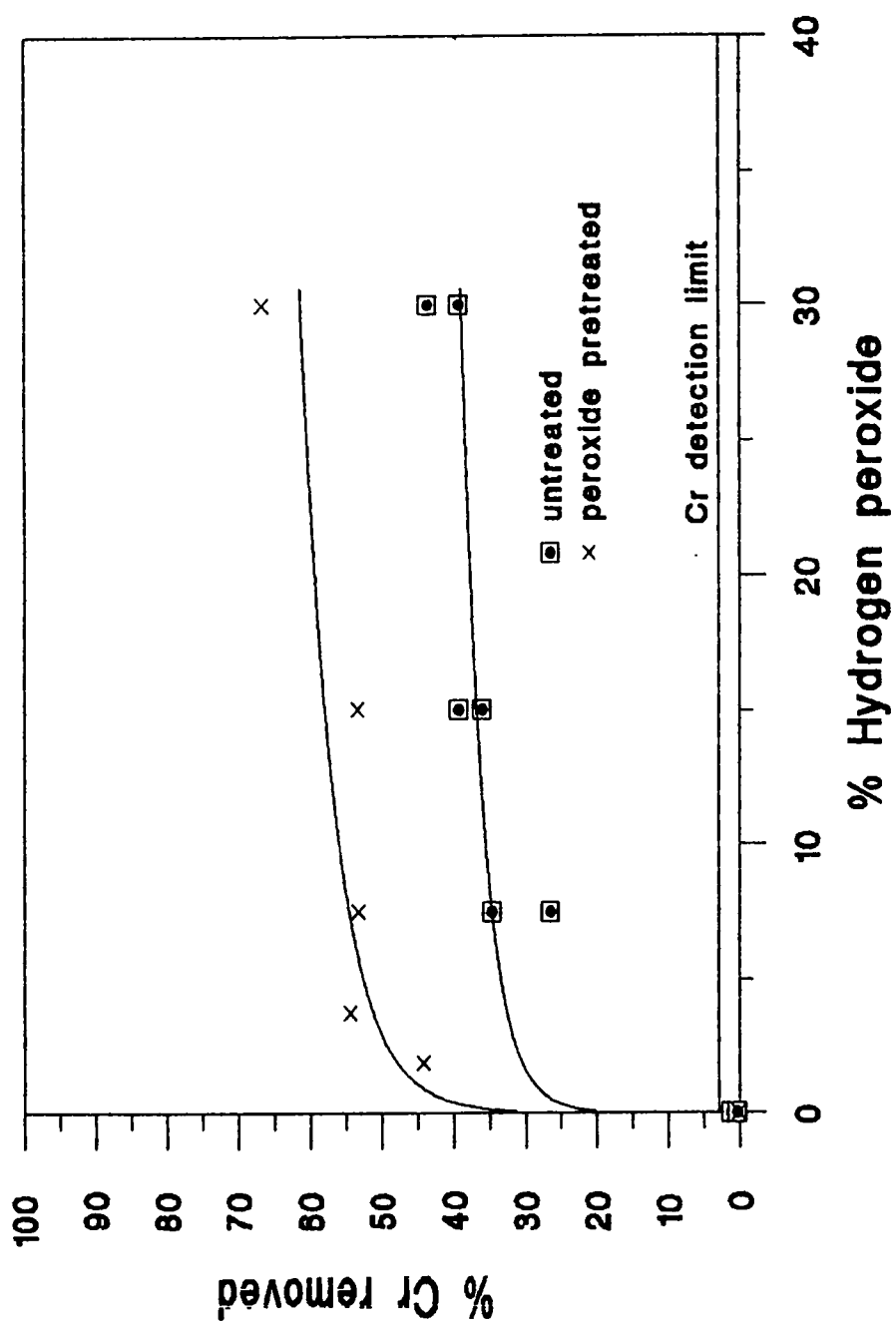


Figure 23: Mobilization of Cr from untreated and pretreated Portsmouth soil using peroxide.

chromium contamination in the Portsmouth soil was 370 mg/kg. Water alone (0% peroxide) showed no detectable chromium, whereas peroxide concentrations between 7% and 30% mobilized about 30%-40% of the chromium initially bound. Once again the production of chromium peroxide(s) which slowly decomposed chiefly to chromate anions was the primary mechanism of chromium mobilization. The pH of the final solution varied from 7.34 to 7.54.

Peroxide pretreated Portsmouth soil was contaminated with chromium (147 mg/kg of soil). Water alone (0% peroxide) showed no detectable chromium mobilization. Reaction with varying peroxide concentrations showed 50%-60% chromium mobilization, even at low (2%) hydrogen peroxide levels. Enhanced mobilization of chromium from peroxide pretreated Portsmouth soils can be explained as follows: (1) Peroxide pretreatment yields additional chromium binding sites that later may allow reaction with the oxidant. (2) In peroxide pretreated soil, the chromium peroxide that forms preferentially decomposes to chromate anions.

Unlike the peroxide pretreated Hanford soil (Figure 21), the Portsmouth soil showed substantial chromium mobilization. The pH of the final solution varied between 7.27 and 7.53. These differences can be accounted for by the type of chromium peroxide formed and the ratio of its decomposition to Cr(III) or chromate anions.

Portsmouth soil with permanganate treatment. Figure 24 shows the percent chromium mobilized from Portsmouth soil using varying permanganate concentrations.

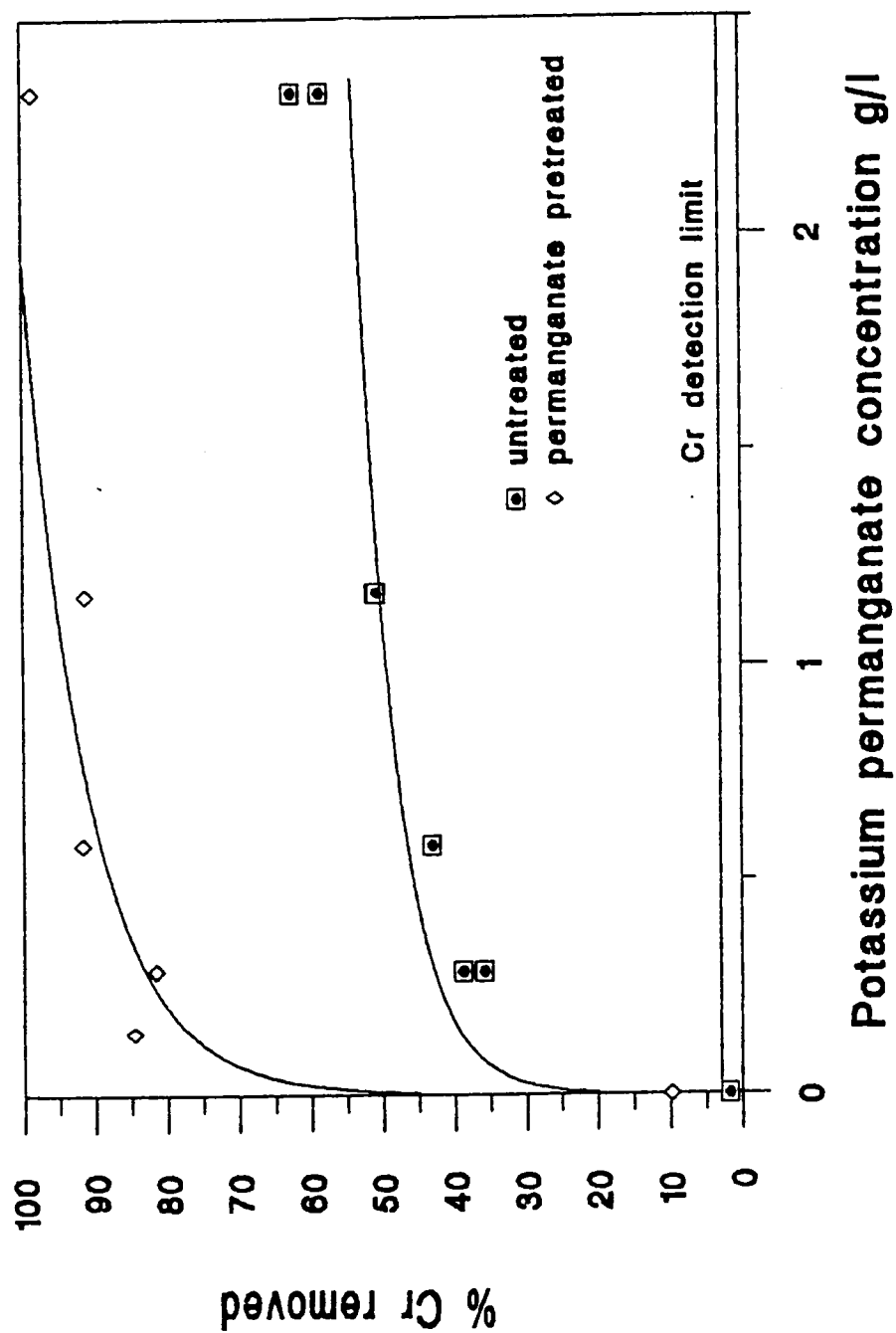


Figure 24: Mobilization of Cr from untreated and pretreated Portsmouth soil using permanganate.

The chromium contamination was 375 mg/kg of soil. Water alone (0% permanganate) mobilized no detectable chromium. From 30% to 60% of the chromium was mobilized with varying permanganate concentrations. The pH of the final solution varied from 7.16 to 6.97.

A comparison of chromium mobilization on untreated Hanford soil using peroxide and permanganate show a maximum removal of about 60% from each soil, although mobilization occurs via different mechanisms (Figures 22 and 24). A possible explanation for both mobilizing the same amount of chromium in Hanford soil is that about 60% of bound chromium is available for free exchange in the bulk solution, where chemical reaction occurs. This was the amount of chromium in the soil readily accessible to the oxidant solution.

Permanganate pretreated Portsmouth soil contaminated with chromium (389 mg/kg of soil) showed detectable chromium mobilization (about 10%) with water only (0% permanganate, Figure 24). Varying permanganate concentrations showed nearly quantitative (> 95%) recovery of chromium. Permanganate pretreatment of the soil results in precipitation of manganese dioxide. Manganese dioxide (Bartlett & James, 1979) oxidizes Cr(III) to chromate anions. The presence of both Cr(III) and manganese dioxide results in chromate anion formation. The detectable chromium in water is presumably caused by the dissolution of Cr(III) and its subsequent oxidation by manganese dioxide. The combination of manganese dioxide present in the soil and permanganate solution may account for the very large chromium recovery.

Permanganate pretreated Hanford soil (Figure 22) showed only about 70% chromium mobilization. The higher mobilization with the Portsmouth soil may be

accounted for by the presence of larger quantities of manganese dioxide during pretreatment. The manganese dioxide then caused additional Cr(III) oxidation.

5. Column Experiments Hanford Soil

Only Hanford soil is discussed in this section. Repeated experiments with the Portsmouth soil, even diluted with Ottawa sand, were unsuccessful because its low permeability did not allow passage of oxidant solution. Table 8 summarizes the results from eight column experiments. All batch experiments (equilibration times, adsorption isotherms, and oxidant reactions) were performed with 1.0 g of soil and 15.0 ml of solution for ~ 48 hours reaction time. For qualitative comparisons, column experiments were scaled by a factor of ten, that is 10 gm of soil and 150 ml of solution were utilized for a ~ 48 hour period. A total of eight column experiments were performed on the Hanford soil: one with water, three with differing hydrogen peroxide concentrations, and two with differing potassium permanganate concentrations. Two column experiments, one with each oxidant, were performed at five times the flow rate for one fifth the time.

Column experiments with hydrogen peroxide were complicated by the evolution of oxygen during the experiment. The reaction occurs as follows:



The decomposition of 1 ml of 1.5% hydrogen peroxide produces 5.29 ml of oxygen. One ml of 3% and 10% hydrogen peroxide concentrations produce 10.59 and 35.3 ml of oxygen, respectively. The oxygen, being more buoyant than water, travels through the column faster than the solution. The flow of a 1.5% hydrogen peroxide

Table 8. Summary of detectable metals from column experiments.

				Detectable Metal?		
Soil	Oxidant	Concent ration	Time*	Zn	Pb	Cr
Hanford	none	0% (water only)	1x	no	no	no
	peroxide	1.5%	1x	no	no	no
		3.0%	1x	trace***	no	yes
		10%	1x	some**	no	yes
		1.5%	5x	some**	no	yes
	permanganate	1.67 g/l	1x	no	no	yes
		2.33 g/l	1x	no	no	yes
		2.33 g/l	5x	trace***	no	yes

*Time = 1x ~ 10 g of soil @ 3 ml/hr for 50 hours.

Time = 5x ~ 10 g of soil @ 15 ml/hr for 10 hours.

**Some-detectable zinc present in at least 20% of the fractions.

***Trace-detectable zinc present in at least two adjacent fractions.

solution at 3 ml/hr produces 16 ml/hr of oxygen (assuming a complete reaction).

Higher peroxide concentrations, or faster flow rates, proportionally produce more oxygen per unit time. The evolution of oxygen may affect solution flow patterns in the column. The half life for decomposition of hydrogen peroxide with Hanford soil was approximately 45 minutes, based on experiments. The empty bed contact time for the column was about 2 hours. Therefore, during column reactions with hydrogen peroxide, the peroxide concentrations will be substantially different at each end of the column.

Zinc Mobilization from Hanford Soil

Water. Zinc was not detectable in Hanford soil when water only was used as a mobilizing agent. In batch experiments (Figure 19), water alone mobilized about 6.5% of the zinc. This would correspond to a zinc concentration of 1.5 mg/l (detection limit 0.05 mg/l) in all fractions.

Peroxide. Figure 25 shows the zinc concentration vs. bed volumes with 1.5%, 3%, and 10% hydrogen peroxide. All three peroxide concentrations show the elution of zinc at small bed volumes. The 1.5% peroxide showed the highest initial zinc concentration (3.6 mg/l which declined quickly. The zinc concentration was just above the detection limit up to 12 bed volumes. The 3% peroxide solution showed a lower initial zinc concentration (0.6 mg/l) which also declined rapidly. The zinc concentration was above the detection limit for the first seven bed volumes. The 10% peroxide also showed an initial zinc concentration of 0.6 mg/l. However, the shape of

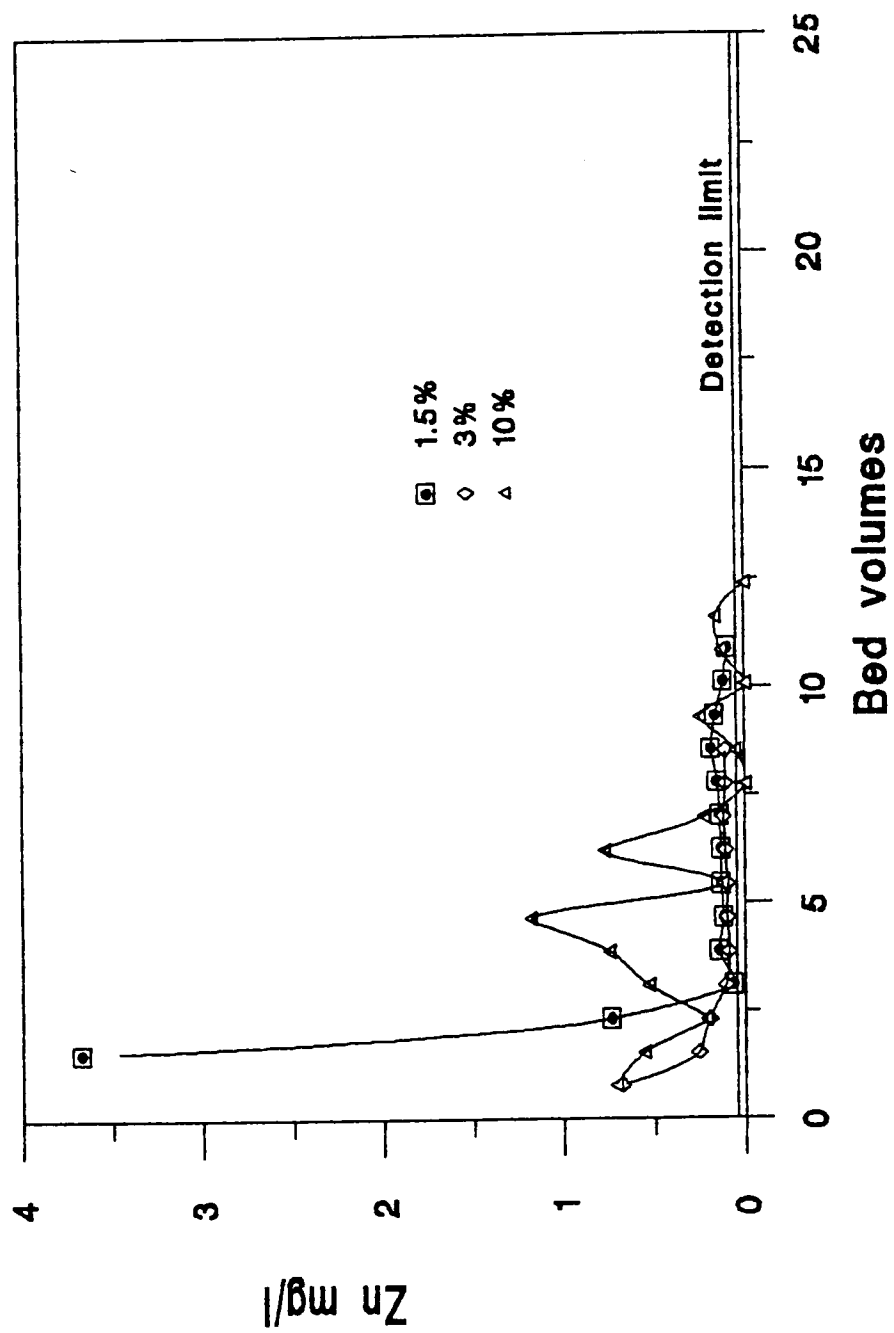


Figure 25: Zn concentration vs. bed volumes with 1.5%, 3%, and 10% hydrogen peroxide.

the curve is characteristic of chromatographic breakthrough occurring. Breakthrough occurs when the effluent concentration of a component is larger than the influent concentration (Pontius, 199). The large evolution of oxygen is likely to produce channeling during the experiment, causing zinc breakthrough.

Figure 26 shows the zinc concentration vs. bed volumes with a 1.5% hydrogen peroxide at regular and high flow rates. Both curves are approximately parallel for the first six bed volumes. The faster flow rate shows breakthrough, possibly caused by the larger evolution of oxygen producing channeling in the column. This curve is similar to the breakthrough curve for 10% hydrogen peroxide (Figure 25). The oxygen evolution rate for the former (1.5% hydrogen peroxide at high flow rate) was 79 mg/hr while the latter (10% hydrogen peroxide at regular flow rate) was 106 ml/hr. In both cases, the large evolution of oxygen may result in channeling (and mixing), causing breakthrough of zinc.

Figure 27 shows the percent zinc removal vs. bed volumes at varying peroxide concentrations and flow rates. Zinc concentrations below the detection limit are assumed as 0 mg/l. Figure 26 shows that maximum zinc mobilization (1.7%) occurred with 1.5% hydrogen peroxide at the high flow rate. Under regular flow conditions, 1.5% and 10% hydrogen peroxide both mobilized about 0.7% of the zinc initially bound, while 3% peroxide mobilized about 0.2% of the zinc. Figure 19 shows a similar phenomenon for untreated Hanford soil using hydrogen peroxide in batch tests. Minimum zinc mobilization occurs at about 4% hydrogen peroxide concentration, whereas higher and lower concentrations showed more zinc mobilization.

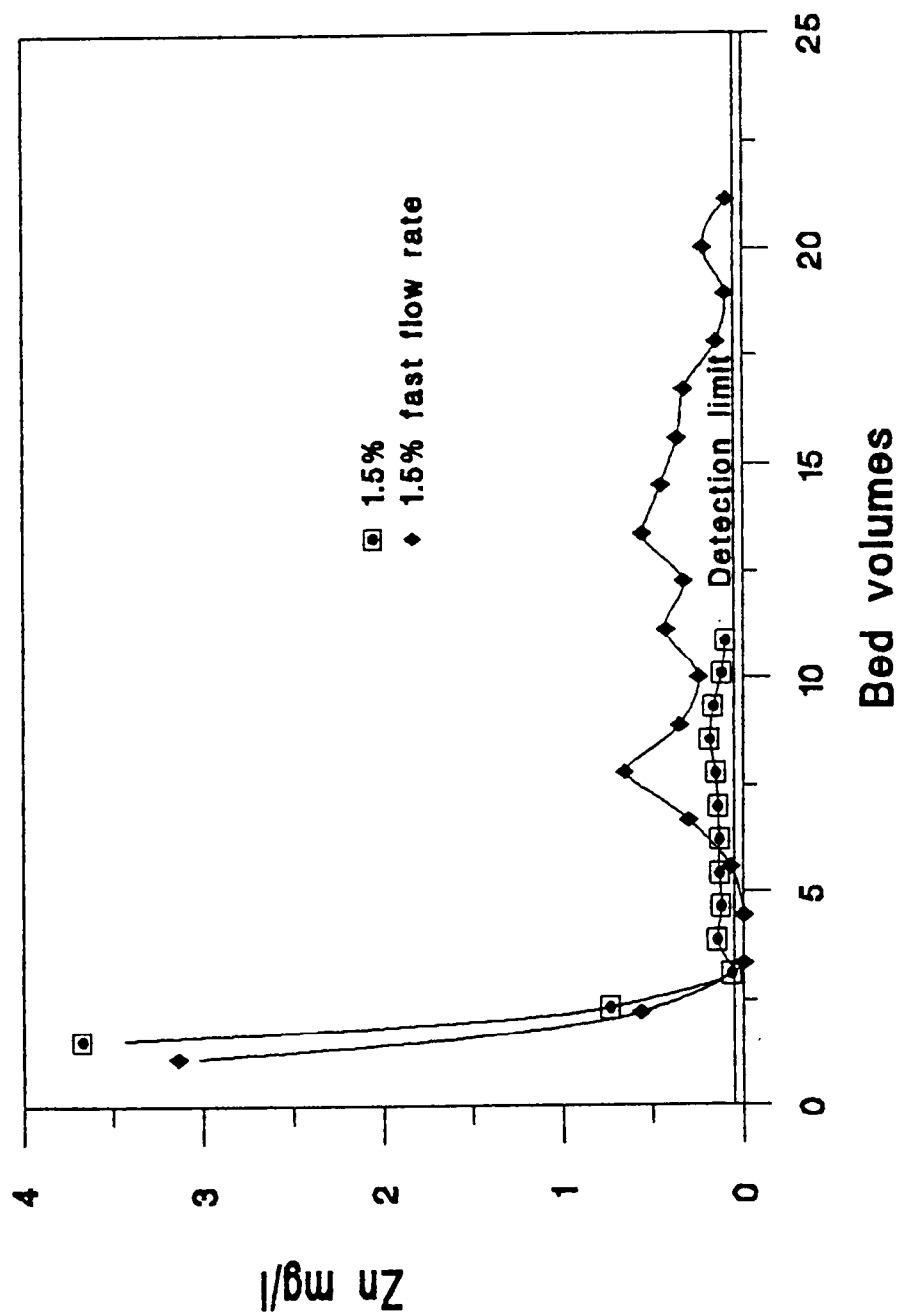


Figure 26: Zn concentration vs. bed volumes with 1.5% hydrogen peroxide at 3 ml/hr and 15 ml/hr flow rates.

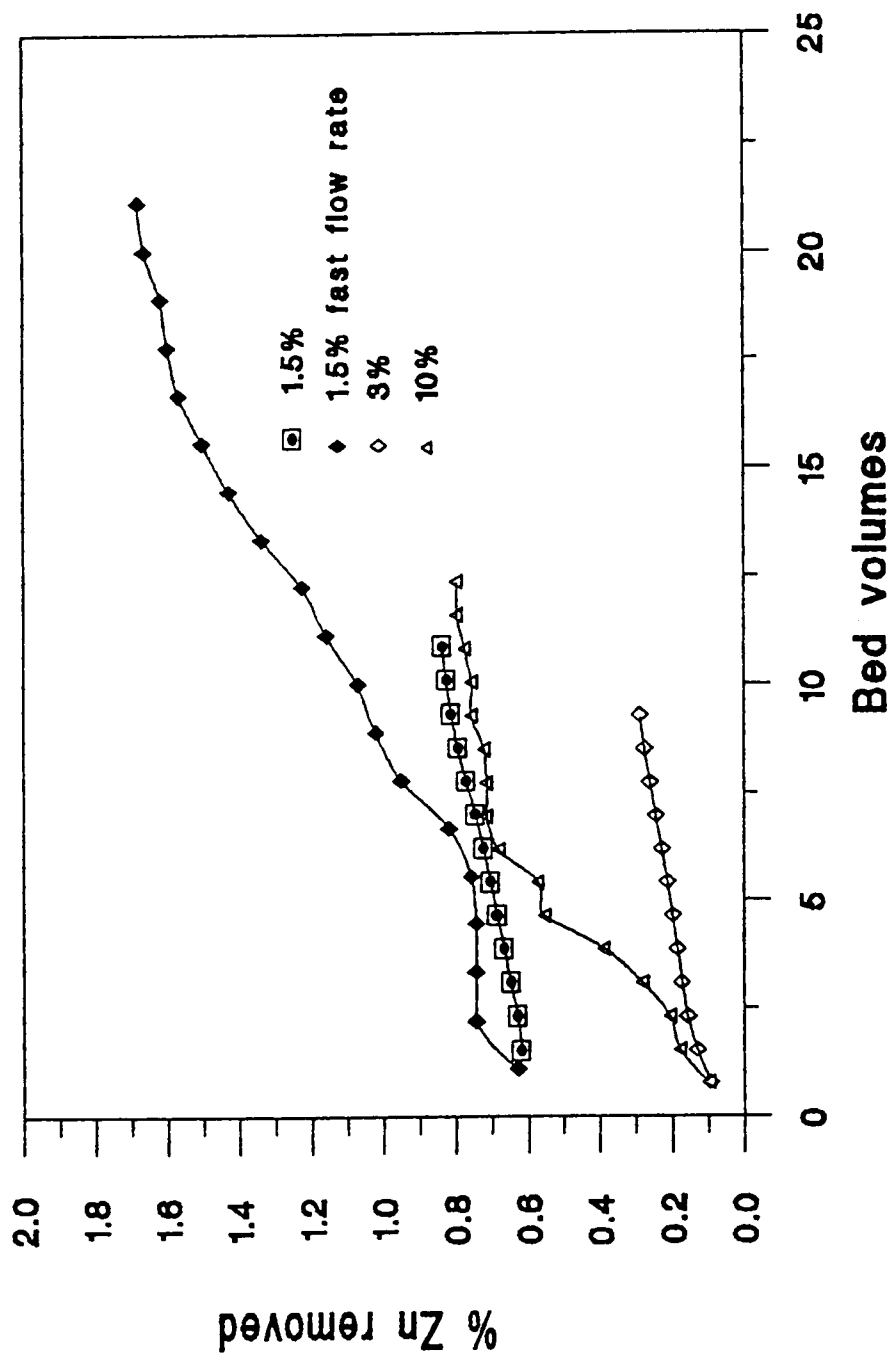


Figure 27: Percent Zn removed vs. bed volumes at varying hydrogen peroxide concentrations and flow rates.

Permanganate. Zinc was not detectable in the effluent using permanganate concentrations of 1.67 or 2.33 g/l at regular flow rates. At a concentration of 1.67 g/l and the fast flow rate, a small amount of zinc was detectable in the first three (0.086 to 0.053 mg/l) of 36 fractions. The total amount of zinc mobilized represented <0.1% of the zinc initially bound to the soil. Batch experiments on untreated Hanford soil using permanganate showed about 0.9% zinc initially bound was mobilized (Figure 20).

Comparison of zinc mobilization in batch experiments with column experiments using water, peroxide, and permanganate showed less zinc mobilization in column experiments than batch experiments. Zinc may be more mobile in batch experiments than column experiments for several reasons. (1) The soil used in column experiments was contaminated with three contaminants rather than one. (2) The soil was thoroughly mixed by tumbling during the course of the reaction for batch experiments. This is expected to cause more particle abrasion, causing the erosion of surface adsorbed zinc. The flow of the water was laminar in column experiments ($v = 3.39$ cm/hr for $n = 0.5$ and mesh = 0.417 mm, gives a Reynolds number of 14) and turbulent in batch experiments (because the tubes contained soil, water, and air mixed at 50 rpm). In an aqueous environment, molecular diffusion coefficients are of the order 10^{-4} to 10^{-5} cm²/sec. They may be 10^2 to 10^3 cm²/sec in a turbulent environment, like those found in batch experiments (Thibodeaux, 1979). (3) The contact time for solution/soil was about 2.5 hours (assuming a porosity of 0.5) in column experiments and 48 hours in batch experiments. (4) In the lower portion of the column, the soil pore space is

predominantly liquid when using hydrogen peroxide, while in the upper portion of the column, the pore space is predominantly gaseous because of the evolution of oxygen.

Column experiments were performed under conditions where mass transfer was dominated by low diffusion coefficients. Therefore, equilibrium may not have been achieved during the course of the experiment. The result was that only small amounts of zinc (compared to batch experiments) eluted through the column. Batch experiments were well mixed where diffusion coefficients were on the order of 100 to 1,000 cm^2/sec (Thibodeaux, 1979) and achieved equilibrium in 48 hours, based on equilibration experiments. In column experiments, channeling and wall effects may dominate the contact of solution and soil, thereby suppressing the transfer of zinc to water. ASTM D 4874 recommends a flow rate of one void volume every 24 $\pm$ 3 hours for effective mass transfer in column experiments. Column experiments were performed at about 10 void volumes per 24-hour period.

Lead Mobilization from Hanford Soil

Water. Lead was not detectable in any column fraction when water was used as the eluent.

Peroxide. Lead was not detectable in any fraction using different peroxide solutions (1.5%, 3%, and 10%) and flow rates (regular and fast).

Permanganate. Lead was not detectable in any fraction using different permanganate concentrations (1.17 and 2.33 g/l) and flow rates (regular and fast).

Column experiments mirrored batch experiments. In all cases (water, peroxide and permanganate) lead was not detectable. This is caused by the lack of mobility of lead, and its large detection limit (1 mg/l).

Chromium Mobilization from Hanford Soil

Water. Chromium was not detectable in any fraction using water alone. Chromium was present at a level of 390 mg/kg of soil. Batch experiments (Table 7) with Hanford soil also showed no detectable chromium using water only. The chromium detection limit in solution is 0.5 mg/l.

Peroxide. Figure 28 shows the amount of chromium mobilized vs. bed volumes with 1.5%, 3% and 10% hydrogen peroxide for the lower flow rate (3 ml/hr). The 10% hydrogen peroxide solution (Figure 28) produced the highest initial chromium concentration (about 110 mg/l). This curve shows the fastest decline in chromium concentration and declined to below the detection limit in less than 15 bed volumes. The 3% peroxide solution showed an initial chromium concentration of about 65 mg/l and remained above the detection limit throughout the experiment. The curve shows some evidence of chromium breakthrough at five and ten bed volumes. The 1.5% peroxide solution began at 15 and peaked at 40 mg/l in the first two fractions. A reasonable explanation is that the initial peroxide in solution was depleted in the lower half of the column, for example by reaction with organic matter, and two bed volumes were required for peroxide to achieve steady state in the column. This peroxide

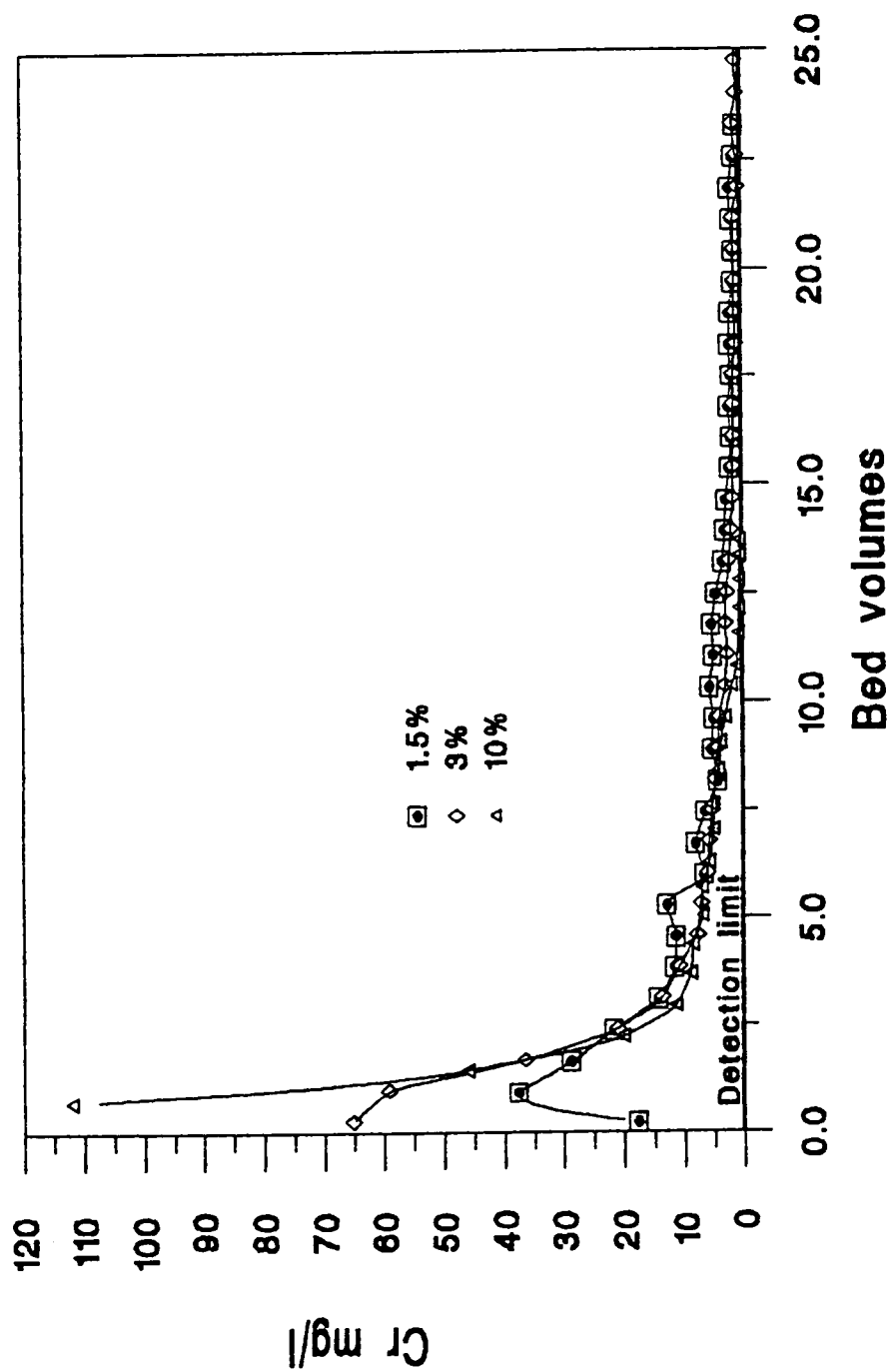


Figure 28: Cr concentration vs. bed volumes with 1.5%, 3%, and 10% hydrogen peroxide.

concentration also showed a slow decline in chromium concentration with each fraction collected.

Figure 29 shows the chromium concentration vs. bed volumes for a 1.5% peroxide solution under two flow conditions. The 1.5% peroxide data points are the same as Figure 28. Except the chromium concentration scale in this figure is smaller for comparison with data from the high flow rate experiment. The curves overlap each other at small bed volumes, but the faster flow rate plateaus at a higher chromium concentration. Both plots have a saw-toothed pattern characteristic of chromatographic breakthrough of chromium. In this experiment, based upon the 45 minute half life of peroxide in the soil and the three hour EBCT, the peroxide is most likely consumed in the lower half of the column.

Figure 30 shows the percent chromium removed as a function of bed volume. The 1.5%, 3%, and 10% hydrogen peroxide solutions all converged to about 30% chromium removal. At this flow rate, chromium mobilization may be dictated by the decomposition of hydrogen peroxide in the column. In this experiment, the peroxide was essentially depleted in the lower half of the column. Chromium mobilization was not as extensive as that found in the batch experiments, where about 60% was recovered from the soil (Figure 21). The faster flow rate resulted in higher chromium removal; unfortunately, maximum mobilization cannot be determined from the experiment. There are two possible explanations for the greater mobilization of chromium in batch experiments compared to column experiments: (1) The peroxide solution may decompose in the lower half of the column so the top of the column sees little oxidant. Thus, 30% of the chromium was recovered in column experiments

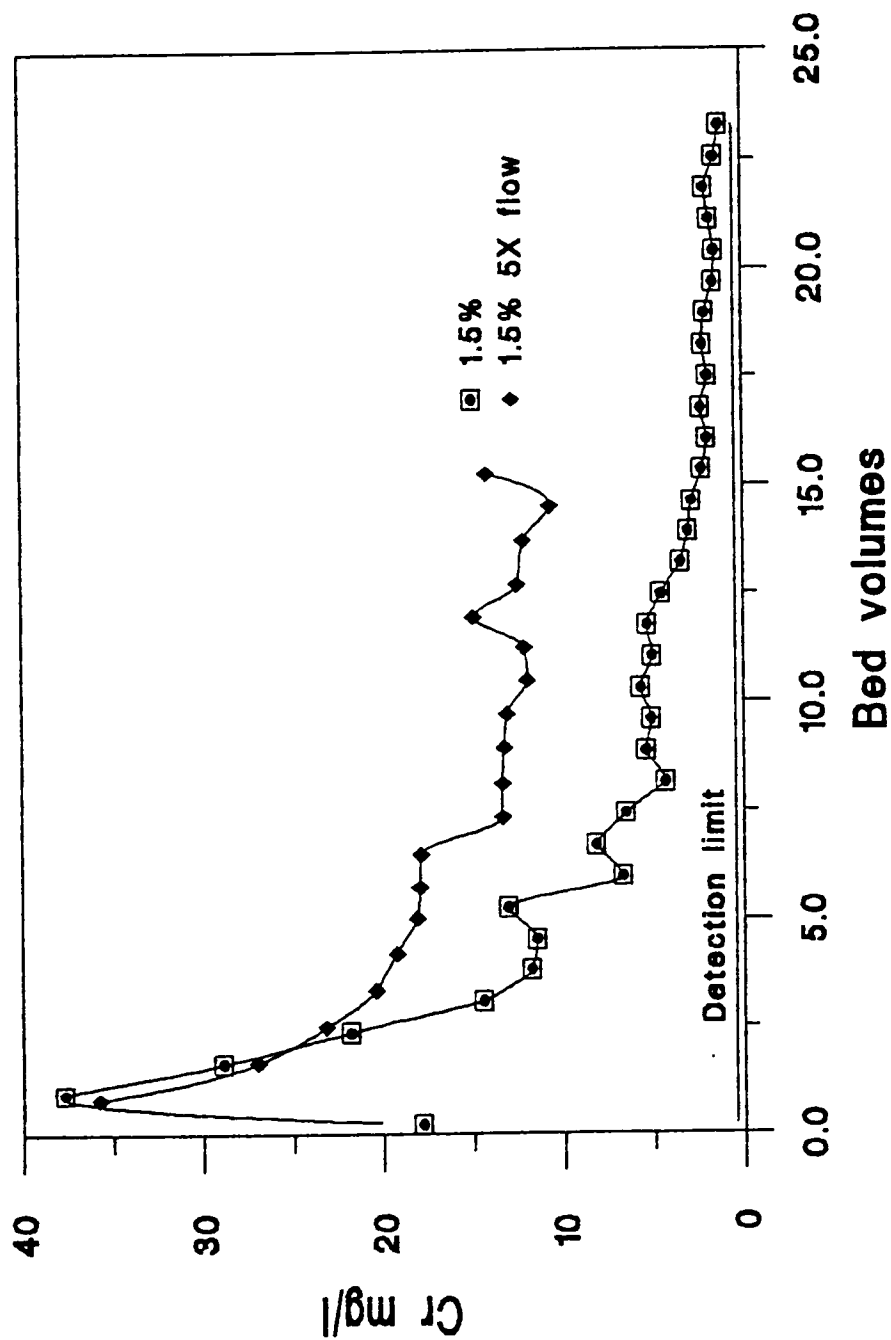


Figure 29: Cr concentration vs. bed volumes with 1.5% hydrogen peroxide at 3 ml/hr and 15 ml/hr flow rates.

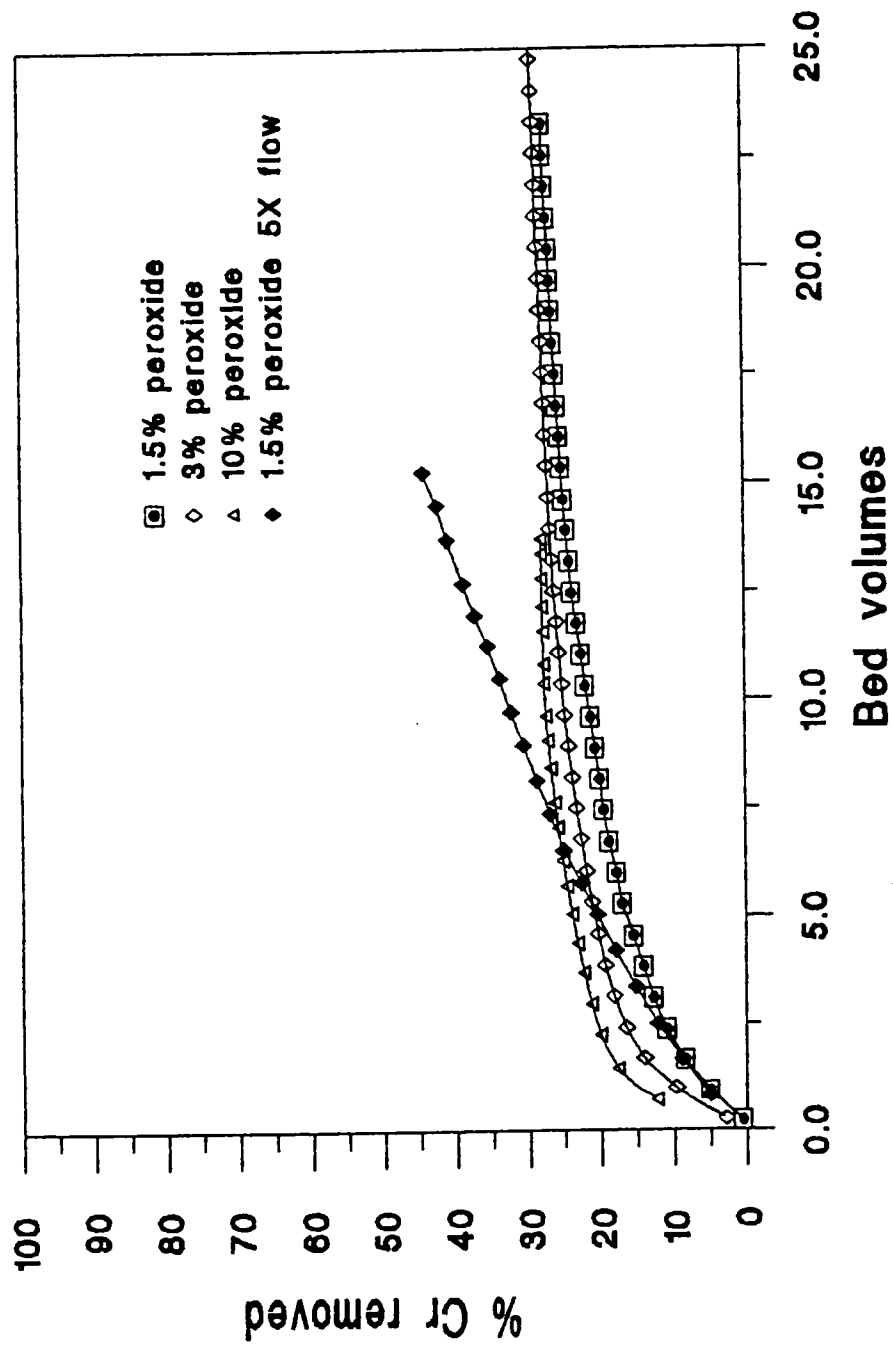


Figure 30: Percent Cr removed vs. bed volumes at varying hydrogen peroxide concentrations and flow rates.

compared to 60% in batch. The faster flow rate then allows peroxide to contact a larger volume of the column. (2) There may be a greater opportunity for chromium peroxide(s) to decompose to Cr(III) in column experiments, via contact with soil, compared to batch ones.

Permanganate. Figure 31 shows the amount of chromium in solution for two potassium permanganate concentrations, 1.67 and 2.33 g/l, with the latter also performed at a faster flow rate. In all three curves, the concentration of chromium in the initial fraction was lower than that measured in the subsequent fraction. Furthermore, the initial fraction collected was colorless, indicating depletion of the oxidizing capacity of the stock solution. Subsequent fractions had a permanganate solution color approximately the same as that observed in the initial solution. Therefore, the permanganate eluent contained sufficient oxidation capacity throughout the length of the column, unlike hydrogen peroxide. This is consistent with the one time oxidation of a species, such as organic matter, present in the soil. The two curves at the lower flow rate are very similar and parallel to each other. The faster flow rate showed less chromium mobilization--the opposite that of peroxide. With peroxides, the faster flow rate allowed greater contact between the oxidant and the soil throughout the column, because of peroxide decomposition. The faster permanganate flow rate provided a shorter contact time for oxidation of chromium. The faster flow rate also showed breakthrough of chromium around 10 bed volumes (Figure 31).

Figure 32 shows the amount of chromium recovered from soil vs. bed volumes. A 1.67 g/l potassium permanganate solution removed about 80% of the chromium

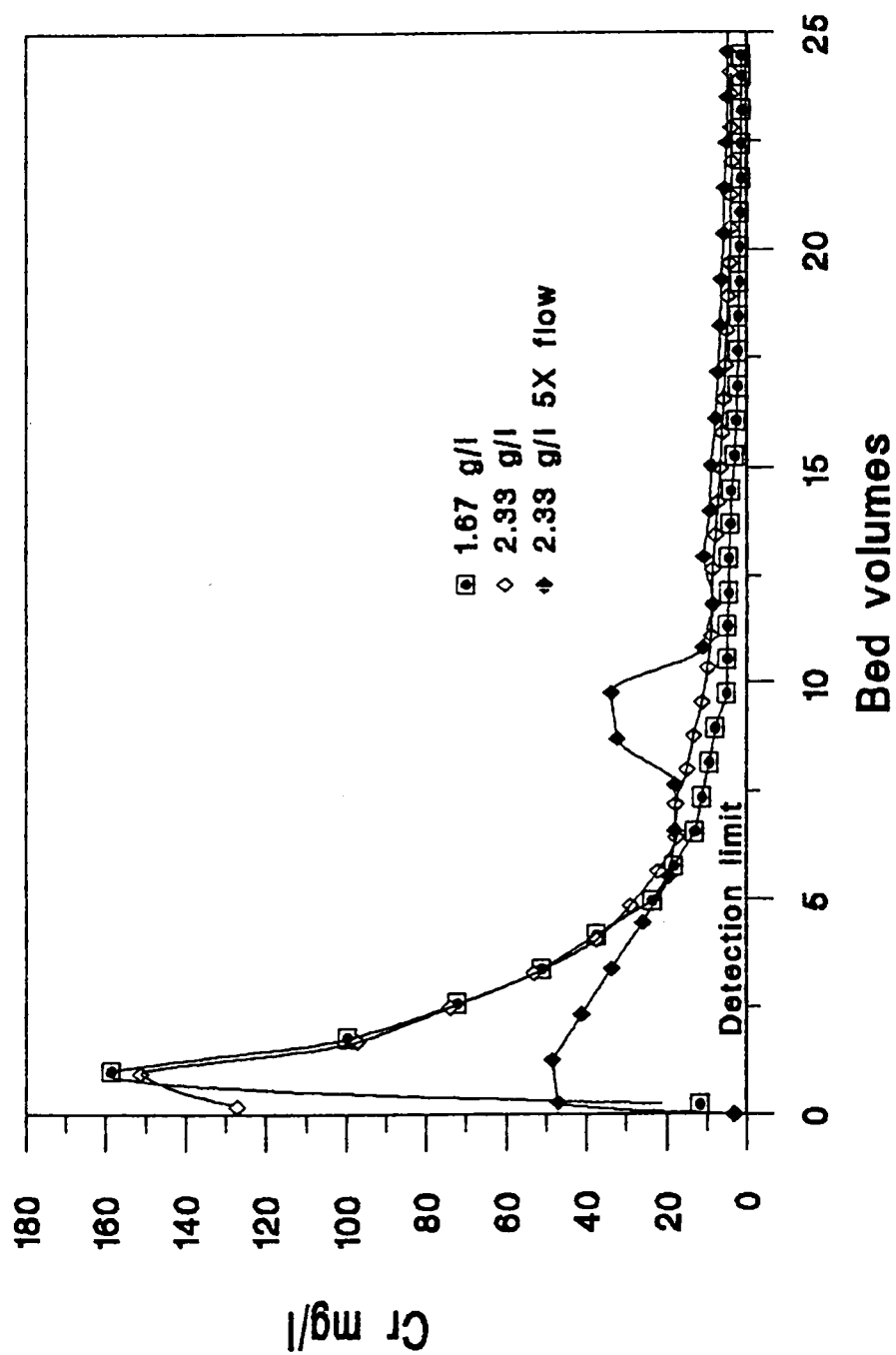


Figure 31: Cr concentration vs. bed volumes at varying potassium permanganate concentrations and flow rates.

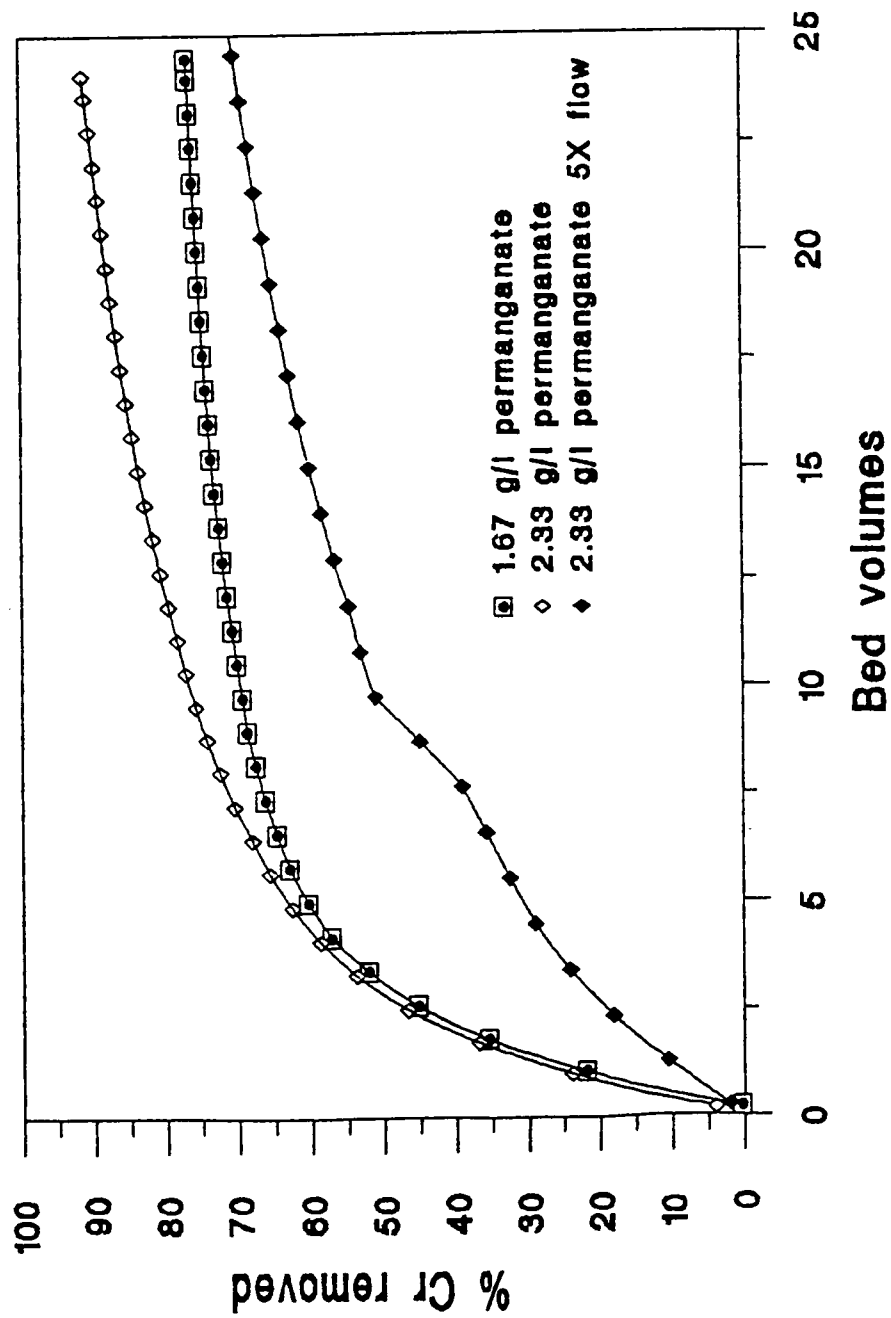


Figure 32: Percent Cr removed vs. bed volumes at varying potassium permanganate concentrations and flow rates.

initially bound to the soil, whereas the 2.33 g/l solution removed about 90%. The faster flow rate shows only about 70% removal of chromium. The faster flow rate in this case may have prevented efficient mass transfer of solution oxidant to the adsorbed chromium.

Permanganate solutions were more effective than peroxide solutions for mobilizing chromium. Chromium(III) is an easily oxidizable metal; in batch experiments both oxidants mobilized about 60% of the metal. The lower mobilization of chromium in column experiments using peroxides solution was probably due to the oxygen evolution from peroxide decomposition. This may prevent the mass transfer of chromium from solution to soil.

CHAPTER 6

Summary and Conclusions

1. Summary

Metal Adsorption

The adsorption of zinc or lead to Portsmouth and Hanford soils (untreated, peroxide and permanganate pretreated) was rapid and complete within hours to less than two days. The corresponding adsorption of chromium to the two soils was complete within an hour.

Adsorption isotherms for zinc with Hanford and Portsmouth soils are best described by the Langmuir equation (Table 4). Compared to the untreated Hanford and Portsmouth soils, the maximum zinc adsorption, $q_{\max}$, increased with permanganate and peroxide pretreatment. The binding or 'b' value for the Hanford soil was relatively unaffected by peroxide or permanganate pretreatment compared to the untreated soil. The 'b' value for the Portsmouth soil, especially peroxide pretreatment but also with permanganate, declined compared to the untreated soil.

Adsorption of lead to Hanford and Portsmouth soils was best described by linear isotherms. For both soils, the partitioning of lead from solution to soil increased in the following order: untreated < peroxide < permanganate. The large increase in binding to permanganate may be due to the precipitation of manganese dioxide and subsequent adsorption of metal to this material.

Adsorption isotherms for chromium to Hanford and Portsmouth soils were best described by the Langmuir equation. An isotherm was obtained from the peroxide pretreated Hanford soil, but not one for the corresponding Portsmouth soil. The Hanford and Portsmouth permanganate pretreated soils gave positive tests for the conversion of Cr(III) to the chromate anion. Consequently, no useful adsorption isotherm could be produced for Cr(III) using permanganate pretreated Hanford and Portsmouth soil. The value of $q_{\max}$ for Cr(III) (2180 to 3000 mg/kg) was about the same as for Zn(II) (1990 to 2740 mg/kg). However, the binding or 'b' value for Cr(III) was an order of magnitude greater than for Zn(II) (Table 4).

For untreated Hanford and Portsmouth soils the partitioning ($q_{\max}b$) of the three metals (zinc, lead and chromium) is: Portsmouth > Hanford. For both peroxide and permanganate pretreated Hanford and Portsmouth soils, the partitioning of the two metals (zinc and lead) is: Hanford > Portsmouth.

Metal Mobilization--Batch Experiments

For water alone (no oxidant) with untreated or pretreated Hanford and Portsmouth soils zinc was detected (>0.05 mg/l), except with peroxide pretreated Portsmouth soil which showed no detectable zinc. For water alone with untreated and pretreated Hanford and Portsmouth soils, no lead was detected (> 1 mg/l). For water alone with untreated and pretreated Hanford and Portsmouth soils chromium was not detected (> 0.5 mg/l), except with peroxide pretreated Portsmouth soil. The chromium detected in the peroxide pretreated Portsmouth soil was likely caused by oxidation of Cr(III) to Cr(VI).

The reaction of peroxide with untreated Hanford soil showed up to 4% zinc mobilization. The reaction of peroxide with peroxide pretreated Hanford and untreated and peroxide pretreated Portsmouth soils showed no detectable zinc mobilization. The reaction of peroxide with untreated and pretreated Hanford soils showed 30% to 60% chromium mobilization, except with peroxide pretreated Hanford soil which showed no detectable chromium.

The reaction of permanganate with untreated and permanganate pretreated Hanford and Portsmouth soils showed detectable zinc mobilization in only Hanford soil. The reaction of permanganate with untreated and pretreated Hanford and Portsmouth soils showed no detectable lead mobilization. The reaction of permanganate with untreated and pretreated Hanford soil showed about 45% to 70% of the chromium mobilized. The reaction of permanganate with untreated and pretreated Portsmouth soil showed about 60% to 95% of the chromium mobilized. Overall, permanganate mobilized more chromium than peroxide with Hanford and Portsmouth soils.

Metal Mobilization--Column Experiments Hanford Soil

For water alone (no oxidant) and Hanford soil there was no detectable mobilization of zinc lead or chromium.

For peroxide solutions the amount of zinc mobilized, as a function of peroxide concentration, decreased in the order: 1.5%(high flow rate) > 1.5% > 3% > 10%. The total amount of zinc mobilized varied from 1.8% to 0.2%. The amount of zinc mobilized was smaller in column experiments compared to batch experiments (6%).

Like batch experiments, there was no detectable lead mobilization with peroxide solutions. Using 1.5% hydrogen peroxide and high flow rate, about 45% of the chromium was mobilized. Using 1.5%, 3%, or 10% peroxide solution and regular flow rate, about 30% of the chromium was mobilized. The amount of chromium mobilized was smaller in column experiments compared to batch experiments.

For permanganate solutions with Hanford soil there was no detectable zinc mobilization at regular flow rates, and only a trace at high flow rate. The amount of zinc mobilized was smaller in column experiments compared to batch experiments. Like batch experiments, there was no detectable lead mobilization in column experiments. The amount of chromium mobilized, as a function of permanganate concentrations, decreased in the order: 2.33% > 2.33% (high flow rate) > 1.67%. The amount of chromium mobilized varied from 70% to 90%. The amount of chromium mobilized was slightly larger in column experiments compared to batch experiments (70%).

2. Conclusions

The purpose of this research was to determine whether the mobilization of zinc, lead, and chromium increased in the presence of oxidants (hydrogen peroxide or potassium permanganate) compared to water.

Water alone will not mobilize chromium(Cr(III)) in soils in detectable quantities. Either peroxide or permanganate will mobilize most of the Cr(III) by oxidation to the very mobile Cr(VI) in the soil.

Water alone will not mobilize lead in soils in detectable quantities (> 1 mg/l).

Neither peroxide nor permanganate will mobilize lead in detectable quantities.

Therefore, it was not determined whether oxidants increased or decreased the mobilization of lead. However if peroxide or permanganate oxidizes Pb(II) to Pb(IV), then the mobility of lead should decrease.

Zinc(II) is not oxidized by peroxide or permanganate. Therefore the effect of oxidants on zinc mobilization has indirect affects. Indirect factors that may affect zinc (or other non-oxidizable metals) mobilization using peroxide or permanganate include: type of soil, organic content of soil, pH, ionic strength, dielectric strength, and CEC. Since peroxide and permanganate are inherently unstable, soils may affect the catalytic decomposition of the oxidants, and therefore the oxidant contact time. The organic content of soil may contain bound metal ions which are released when the substrate is oxidized. Moreover, incomplete oxidation of organic matter may produce soluble ligands for metal complexation. The pH of the oxidant solution (or after oxidation) will affect metal mobilization. Generally as the pH decreases, the solubility of metals increases, resulting in increasing mobilization. The ionic strength will affect the solubility (and therefore the mobility) of compounds in water. Increasing ionic strength results in decreasing activity coefficients and lower solubility. The ionic strength may be an important consideration when using 35 g/l of potassium permanganate in the field. The dielectric strength affects reaction rates and solubilities of compounds. Hydrogen peroxide has a larger dielectric strength than water. Finally, oxidation may change the CEC of the soil. This may occur by oxidation of organic matter, or by formation of new binding sites on soil surfaces. Furthermore using potassium

permanganate will cause the formation of manganese dioxide, resulting in new binding sites for metal ions. Generally if the CEC increases after oxidation, then mobilization of zinc should decrease. Therefore water alone may or may not mobilize more zinc than peroxide or permanganate.

3. Significance and Implications--An Opinion

Hydrogen peroxide and potassium permanganate are powerful oxidants that may affect metal mobilization directly (by metal oxidation) or indirectly (by oxidation of ligands or organic material). Mobilization may occur with either metal contaminants of soil or from natural constituents (such as ores) present in soil. Oxidation of ligands may indirectly release metals in the following fashions:

1. Oxidation of reduced inorganic ligands may affect the solubility of metals. For example, the sulfur in sulfide minerals--such as copper sulfide Cu_2S , pyrite FeS , galena PbS or cinnabar HgS --may oxidize to sulfate. The solubility of metal sulfides can be substantially lower ($[\text{Cu}]^2[\text{S}] = 2.5 \times 10^{-48}$, $[\text{Fe}][\text{S}] = 6.3 \times 10^{-18}$, $[\text{Pb}][\text{S}] = 8 \times 10^{-28}$, and $[\text{Hg}][\text{S}] = 4 \times 10^{-53}$) than the solubility of the sulfates (copper(II) sulfate = 32 g/l, iron(II) sulfate = 48 g/l, $[\text{Pb}][\text{SO}_4] = 1.6 \times 10^{-8}$, and mercury sulfate which decomposes in water to mercuric oxide and sulfuric acid) (Dean, 1992).

2. Metals bound to organic material in soil, such as humic acid, may be solubilized when the organic constituents is oxidized. Moreover, the oxidized organics may produce water soluble ligands, such as oxalate for complexing with metals.

Metal mobilization may be directly affected by changes in oxidation state of the metal. Common mineral constituents (or contaminants) that are not oxidizable and,

therefore, not directly mobilized include: lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium boron, aluminum, and silicon. Many metals with more than one common oxidation state are transition metals. Generally, metals that are oxidizable fall into three categories.

1. Metals that remain "simple" cations upon oxidation and, therefore, are more insoluble and consequently become less mobile. In this case, the larger positive charge on the oxidized metal results in lower solubility because of electrostatic attraction between cations and anions causes precipitation. Metals in this category include the following: $\text{Fe(II)} \rightarrow \text{Fe(III)}$, $\text{Mn(II)} \rightarrow \text{Mn(IV)}$, $\text{Co(II)} \rightarrow \text{Co(III)}$, and $\text{Pb(II)} \rightarrow \text{Pb(IV)}$.

2. Metals that become oxycations become more soluble after oxidation and consequently more mobile. Metals in this category include the following: $\text{U(IV)} \rightarrow \text{UO}_2^{+2}$, and $\text{VO}^{+2} \rightarrow \text{VO}_2^+$. Since the metals formed in this category have a positive charge, then they have some adsorption potential to soil.

3. Metals that become oxyanions become very soluble after oxidation and consequently more mobile. Metals in this category include the following: $\text{Cr(III)} \rightarrow \text{Cr}_2\text{O}_7^{-2}$, $\text{Tc(IV)} \rightarrow \text{TcO}_4^-$, and $\text{Mo(IV)} \rightarrow \text{MoO}_4^{-2}$. These metals, because of their negative charge, have a different sorption affinities (and mechanisms) to soils.

Metals that are surface bound may be affected (directly or indirectly) by the oxidants. Some of these metals may become more (or less) mobile in the environment. Contaminants are very likely to be found on or near the surface of soil particles and, therefore, accessible to interaction with oxidants. Metals that are components of

minerals may be less likely affected by oxidants because the oxidants may be inaccessible to the bulk of the material.

The use of oxidants is a proposed solution for the environmental remediation of organic contaminants in soils. The implications of this research include the following:

1. The oxidation of $\text{Pb(II)} \rightarrow \text{Pb(IV)}$ may present important environmental opportunities, since Pb(IV) compounds are more insoluble than Pb(II) . It *may* be possible to control the mobility of lead in the environment using powerful oxidants.
2. Soils contaminated with Cr(III) may effectively mobilize more than 50% of the chromium contamination to environmentally hazardous Cr(VI) in the presence of oxidants. It is probably unwise to use oxidants with soils contaminated by chromium. Uncontaminated soils with naturally high chromium content may produce some Cr(VI) . The potential for mobilizing chromium from soils with high chromium content should be evaluated before field testing with an oxidant.
3. The sponsor proposes to treat soils contaminated with organic compounds with oxidants at DOE plants in Hanford Washington and Portsmouth Ohio. Both DOE sites use uranium to produce fissile isotopes; Hanford produces plutonium-239, and Portsmouth produces uranium-235. Therefore, uranium is a possible contaminant at both sites, and its potential for oxidation should be evaluated. Technetium is not a naturally occurring element but is a common radioactive fission product that is a possible contaminant at both DOE sites; its potential for mobilization with oxidants should be evaluated.
4. In the absence of metal mobilization affects, the author prefers the oxidizing capabilities of permanganate solutions to peroxide. Peroxide solutions

decompose very quickly and do not have a long time for reacting with organic contaminants or penetrating soils. That is, peroxides have local and short term effects.

Permanganate solutions decompose more slowly allowing longer contact time and greater penetration into soil. The decomposition of permanganate to the possible electron acceptor Mn(IV) may provide an additional oxidizing capacity for bioremediation.

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APPENDIX

Table A.1 Summary of pH changes in equilibration time experiments.

Metal	Soil	Soil pretreatment	Initial pH	pH at 2hrs	Final pH (days)
Zn(II)	Hanford	untreated	5.5U*	8.0S**	8.5S
		peroxide	5.45U	8.04S	8.61S
		permanganate	5.52U	8.06S	8.48S
	Portsmouth	untreated	6.13U	6.51U	6.67U
		peroxide	5.82U	6.34U	6.59U
		permanganate	5.73U	6.0U	6.39U
Pb(II)	Hanford	untreated	5.05U	8.03U	8.46U
		peroxide	4.87U	7.87U	8.47U
		permanganate	4.87U	7.93U	8.51U
	Portsmouth	untreated	5.03U	6.03U	6.58U
		peroxide	5.12U	6.15U	6.49U
		permanganate	5.08U	6.04U	6.59U
Cr(III)	Hanford	untreated	5.02U	7.12S	7.81S
		peroxide	4.89U	6.23S	7.67S
		permanganate	5.05U	6.06S	7.92S
	Portsmouth	untreated	4.98U	5.87S	6.67S
		peroxide	5.0U	6.14S	6.87S
		permanganate	5.03U	5.84S	7.68S

U* Under saturated with respect to carbonate or hydroxide precipitation

S** Over saturated with respect to carbonate or hydroxide precipitation

Table A.2 Final solution pH of Zn adsorption isotherm experiments on untreated and pretreated Hanford soil.

untreated*			peroxide**			permanganate***		
Zinc (mg/l)		pH	Zinc (mg/l)		pH	Zinc (mg/l)		pH
initial	final		initial	final		initial	final	
230	90.8S	7.00	200	32.4U	6.96	200	60.4U	7.04
184	67.5S	7.23						
153	34.0S	7.26						
138	28.1S	7.37	133	16.8U	7.06	133	36.5U	7.10
123	17.1S	7.44	120	14.2U	7.11	120	19.5U	7.17
107	10.8S	7.53	107	8.72U	7.34	107	8.62U	7.54
92	6.51S	7.63	93	6.44U	7.37	93	11.7U	7.50
77	4.22S	7.77	80	2.40U	7.62	80	3.61U	7.70
46	1.84S	7.99	67	1.87U	7.57	67	0.217U	7.94
0	0	9.02	0	0.080U	7.57	0	.071U	7.96

*Initial solution pH for untreated = 6.49.

**Initial solution pH for peroxide pretreated = 5.70.

***Initial solution pH for permanganate pretreated = 5.15.

S Over saturated with respect to precipitation of zinc hydroxide and/or carbonate.

U Under saturated with respect to precipitation of zinc hydroxide and/or carbonate.

Table A.3 Final solution pH of Pb adsorption isotherm experiments on untreated and pretreated Hanford soil.

untreated*			peroxide**			permanganate***		
Lead (mg/l)		pH	Lead (mg/l)		pH	Lead (mg/l)		pH
initial	final		initial	final		initial	final	
183.1	18.6S	7.71	200	2.17U	7.54	200	1.49	8.10U
146.5	15.8S	7.95						
122	13.6S	8.13						
109.9	11.9S	8.18	133	1.17U	7.74	133	1.30	8.17U
97.7	10.2S	8.22	120	.51U	7.88	120	1.01	8.25U
85.4	9.59S	8.28	107	.54U	7.94	107	.49	8.36U
73.3	7.74S	8.36	93	.42U	8.14	93	.30	8.39U
61.0	6.67S	8.50	80	.68U	8.17	80	.29	8.45U
36.6	3.97S	8.70	67	.35U	8.46	67	.49	8.47U
0	0	8.90	0	0	8.87	0	0	9.46

*Initial solution pH for untreated = 5.56.

**Initial solution for peroxide pretreated = 4.95.

***Initial solution pH for permanganate pretreated = 5.33.

S Over saturated with respect to precipitation of lead hydroxide and/or carbonate.

U Under saturated with respect to precipitation of lead hydroxide and/or carbonate.

VITA

A. Andrew Carey was born April 13, 1951, in Nassau, Bahama Islands.

After graduating from Saint Augustine's School, Ramsgate, England, Mr. Carey attended the University of Notre Dame and in 1973 earned a Bachelor of Science in Chemistry. In 1976 Mr. Carey earned a Master of Science Degree in Chemistry from the Ohio State University. He subsequently earned a Ph.D. in Chemistry from the same institution in 1980.

Dr. Carey has worked as a Development Engineer for advanced isotope separation technologies in the Oak Ridge area in both the private sector and the public one. He has taught college Chemistry and worked as a consultant in the environmental field.

Dr. Carey is married to the former Julia Ann Coffey. He has two daughters, Alice and Patricia.