AN ABSTRACT OF THE THESIS OF

Gregory R. Bean for the degree of Master of Science in Civil Engineering presented on September 28, 1989.

Title: Adsorption of Hexavalent and Trivalent Chromium to a Clayey Silt Soil: Batch Kinetic and Equilibrium Studies

Abstract approved: Redacted for Privacy

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Chromium, an element of widespread use, is toxic in some forms. Improper disposal of waste chromium products has resulted in contamination of many sites throughout the United States, including the United Chrome Products Superfund site in Corvallis, Oregon. A better understanding of chromium chemistry is needed to facilitate the remediation of these contaminated sites.

The purpose of this study was to investigate the characteristics of adsorption of hexavalent and trivalent chromium (Cr(VI) and Cr(III), respectively) to a clayey silt soil similar to that found at the United Chrome Products site. The effects of pH on adsorption rates and magnitudes, and the effectiveness of selected extractant solutions in removing adsorbed chromium from soil, were evaluated. Simple mathematical models were used to describe adsorption kinetics and equilibrium, and the chemical nature of the adsorption reactions were postulated.

Cr(VI) adsorption magnitudes and rates increased as pH decreased. Neither distilled water or groundwater were effective extractants of adsorbed Cr(VI); an 0.02 molar orthophosphate solution was a moderately successfull extractant. Cr(VI) adsorption kinetics were diphasic in nature, and could be described with an irreversible two-site adsorption reaction model. Cr(VI) uptake by the soil was thought to be adsorbed to metallic oxide surfaces rather than reduced to insoluble Cr(III).

Trivalent chromium (Cr(III)) was most effectively adsorbed between pH values of four and five. At lower pH values, Cr(III) adsorption magnitudes decreased proportionally with hydrogen ion concentration; at higher pH values, the decrease in Cr(III) adsorption was probably due to complexation with soluble and colloidal organic matter released from the soil. EDTA was only moderately effective in extracting adsorbed Cr(III) from soil.

Adsorption of Hexavalent and Trivalent Chromium to a Clayey Silt Soil: Batch Kinetic and Equilibrium Studies

by

Gregory R. Bean

A THESIS

submitted to
Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed September 28, 1989
Commencement June 1990

APPROVED:

Redacted for Privacy

Professor of Civil Engineering in charge of major

Redacted for Privacy

Head of department of Civil Engineering

Redacted for Privacy

Dean of Graduate School

Date thesis is presented: September 28, 1989

Presented by: Gregory R. Bean

ACKNOWLEDGEMENTS

I'd like to acknowledge Dr. Peter O. Nelson, my major professor, who provided invaluable guidance and assistance. I also thank Mohammad Azizian, who conducted a great deal of the analytical work for this study. Most of all, I thank my wife Karla, for her love and encouragement, especially during the times when it seemed the writing would never end.

Financial support for this study was provided by the U.S. Department of Interior, U.S. Geological Survey, through a Program Grant to the Oregon State University Water Resources Research Institute.

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ADSORPTION OF HEXAVALENT AND TRIVALENT CHROMIUM TO A CLAYEY SILT SOIL: BATCH KINETIC AND EQUILIBRIUM STUDIES

1. INTRODUCTION

Chromium is a metallic transition element which, in various chemical forms, has long been employed in a variety of applications. The name of the element, which is derived from the Greek "chroma" (literally, "a color"), refers to its many colorful solutions and solid compounds, some of which are used as pigments in paints and inks. Chromium is also used as a biocide in industrial cooling water systems, it is the principle chemical agent in leather tanning, and it is a key additive to several important metal alloys, including stainless and chrome steels. It is probably best known for its use as a decorative and corrosion resistant plating material for automobile parts and other metal products.

Due to its toxicity, chromium has also earned a place on the United States Environmental Protection Agency's Priority Pollutant list. Low doses damage kidney tissues in a manner similar to mercury, and prolonged exposure to chromate compounds has been shown to cause lung tumors and cancers (Doull et al, 1980). Unfortunately, like many other chemical compounds of long and widespread use, chromium compounds and waste products have often been improperly or recklessly "disposed of". These wastes now contaminate or threaten to contaminate many of our soil, groundwater, and surface water resources (Stollenwerk and Grove, 1985; Dugan et al, 1984; Jan and Young, 1978; Mason and Leonard, 1984; Davids and Lieber, 1951). In many cases, remedial action is necessary to protect against further contamination and resource loss (Dugan et al, 1984; Mason and Leonard, 1984; Ecology and Environment, Inc., 1985).

One reclamation scheme that has been proposed for chromium contaminated soils is aqueous extraction, or "soil flushing", followed by collection and treatment of the chromium laden elutriate. The extraction solution may be pure water, or it may contain additives which enhance the extraction process, such as acid, base, or competing ion salts (USEPA, 1984). The extraction may be performed in-situ by flooding the contaminated area and collecting the elutriate in a series of shallow wells, or batch slurries of excavated soil may be used. The latter has been implemented, with only limited succes, for treatment of contaminated soil at the Pearl Harbor Naval Shipyard (Dugan et al, 1984). The former method, sometimes referred to as the "pump and treat" method, has been approved by the USEPA for remedial action at the United Chrome Products "Superfund" site in Corvallis, Oregon (Corvallis Gazette Times, 11/1/87); this method has also been proposed for at least one other chromium contamination site in the U.S. (Mason and Leonard, 1984).

Design of such remedial treatment schemes requires an understanding of the chemical processes likely to effect chromium fate in the soil-groundwater system (USEPA, 1984). Failure to recognize significant processes may cause failure of otherwise well-designed treatment plans. For example, water flushing of a contaminated Hawaiian soil by a batch slurry process initially reduced EP-extractable chromium to acceptable levels (less than 5 mg/L), but after time and disposal in a sanitary landfill, EP-extracts of treated soil had tripled, with seven of 20 samples above legal limits of toxicity (Dugan et al, 1984). This result was attributed to soil moisture loss causing higher contaminant concentrations in soil water, but slow desorption of chromium may have been responsible. In either case, inadequate understanding of chromium behavior in the soil led to the failure of an extensive and expensive treatment process.

The literature indicates that chromium behavior in soil-groundwater systems is quite complex, and will vary markedly with environmental conditions such as pH, pE, ionic composition of groundwater, and physical/chemical characteristics of the soil (see Literature Review). It is clear, then, that varying the composition of the soil flushing solution may greatly enhance or impair the extraction process.

However, specific information is still lacking regarding the environmental chemical processes which would effect treatment by soil flushing. The USEPA has identified the need for greater study of adsorption and precipitation processes under conditions that might be encountered at remedial action sites (USEPA, 1984). Chromium was listed among the metals for which specific information regarding chemical reactions in soil was needed, especially regarding the reduction of Cr(VI) to Cr(III).

The general objectives of this research were to investigate the kinetics and equilibrium of chromium adsorption in soils. Batch adsorption experiments were performed in aqueous suspensions of a soil similar to that at the United Chrome Products Superfund site, Corvallis, Oregon, using chromium concentrations similar to those at the site. Specifically, the objectives of this study were to:

1. Determine the effect of pH on the kinetics and equilibrium of Cr(III) and Cr(VI) adsorption to soil;

2. Determine the effectiveness of selected extractant solutions in recovering Cr(III) and Cr(VI) from the soil;

3. Describe the behavior of Cr(III) and Cr(VI) in the soil/groundwater system using simple kinetic and

equilibrium models;

4. From the information gathered in meeting objectives one, two and three, infer the chemical nature of Cr(VI) and Cr(III) adsorption to the Dayton soil.

2. LITERATURE REVIEW

2.1 Introduction: The Environmental Chemistry of Chromium

The element chromium is a transition metal of group VIB, with atomic number 24 and atomic weight of 52.00. The uncharged metal has $4s^1$, $3d^5$ electron configuration; the highest oxidation state, +6, results from removal of these six electrons. While all oxidation states from -2 to +6 have been reported, only three are important; these are the uncharged metal, Cr(0), and the trivalent and hexavalent oxidation states, Cr(III) and Cr(VI), respectively (Cotton and Wilkinson, 1972; Mertz, 1969). Of these three, only the latter two are of interest in natural environmental systems (Schmidt, 1984).

Chromite ($FeCr_2O_4$), a spinel, is the principle ore of chromium, though other spinel forms such as magnesio-chromite ($MgCr_2O_4$) also occur (Schmidt, 1984). These mineral forms are all in the trivalent oxidation state, which is generally regarded as the most stable state (Cary et al, 1977; Cotton and Wilkinson, 1972). The stability field diagram in Figure 2.1 (from Schmidt, 1984) shows that this is indeed the case

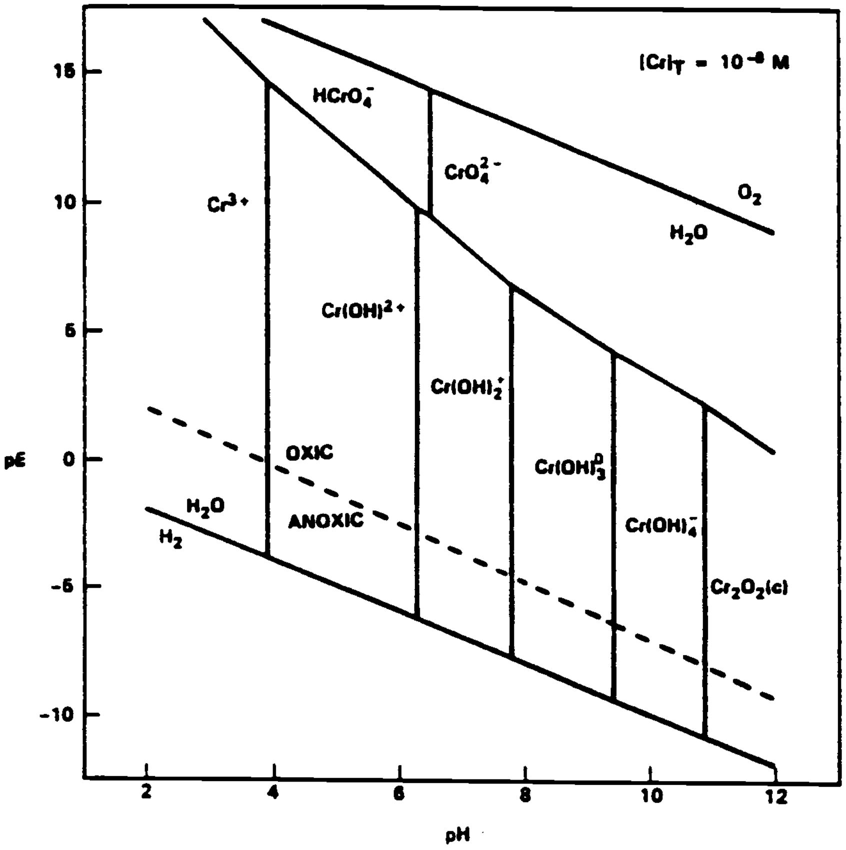

Figure 2.1: Stability field diagram, from Schmidt (1987).

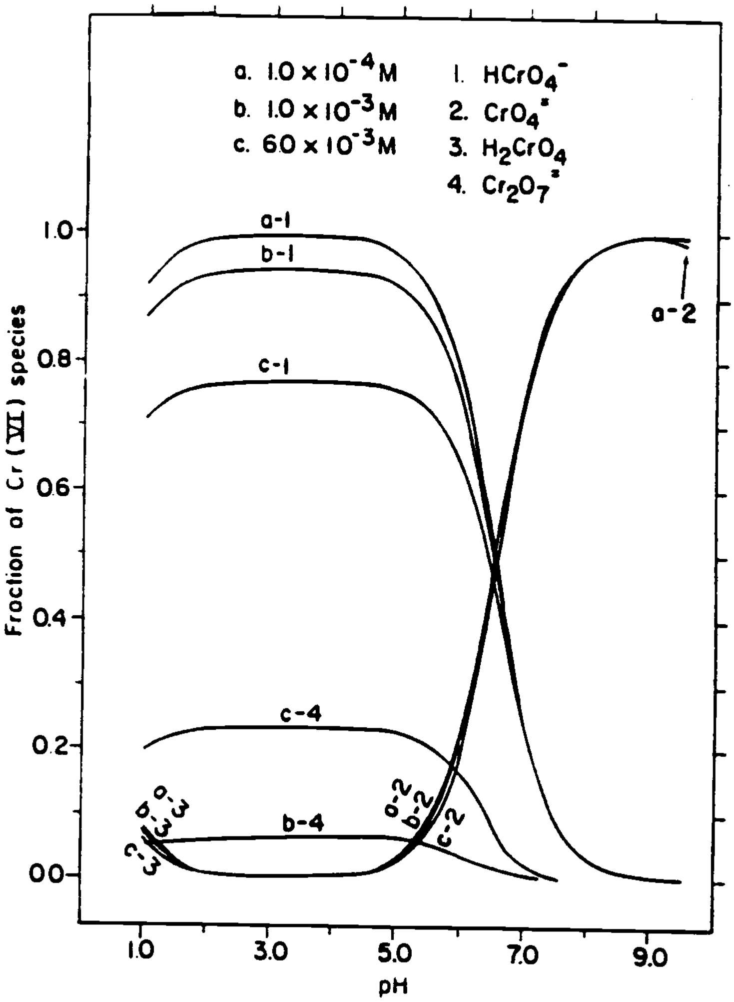

Figure 2.2: Cr(VI) speciation vs. pH at three total Cr(VI) concentrations, from Griffin et al (1977).

over a great range of the pH and Eh conditions possible in aqueous environmental systems. Robertson (1975) shows that Cr(III) is favored over the strongly oxidizing Cr(VI) in most natural waters and almost all groundwaters; in well aerated waters, the hexavalent state is favored thermodynamically. However, thermodynamically unstable chromium species are often encountered in environmental systems, as will be shown below.

The chemistry of Cr(III) and Cr(VI) are strikingly different. An understanding of the environmental behavior of chromium requires a knowledge of the solution and solid phase chemistry of both oxidation states, as well as the redox chemistry controlling the system.

2.2 Cr(VI) Chemistry

Aqueous Speciation of Cr(VI): Hexavalent chromium always exists as an oxo species, such as CrO_3, CrO_4^{2-}, or CrO_2X_2, where X is Cl or F. In water, Cr(VI) solids dissolve and/or hydrolyze to form the weak base oxyanions CrO_4^- (chromate), $HCrO_4^{-2}$ (bichromate) and $Cr_2O_7^{2-}$ (dichromate). Chromate and bichromate are tetrahedral in shape, with the four oxygens surrounding the central Cr(VI) atom. In dichromate, oxygen atoms are also oriented tetrahedrally around each of the two Cr(VI) atoms, which are connected by a shared oxygen (Cotton and Wilkinson, 1972).

As shown in Figure 2.2 (from Griffin <u>et al</u>, 1977), Cr(VI) speciation is dependent on both pH and total soluble chromium concentration ($C_{t,cr}$) in aqueous solution at standard temperature and pressure (STP). Three species dominate the figure: dichromate, bichromate, and chromate. Diprotonated chromate and the protonated forms of dichromate do not form to an appreciable extent at the pH and concentration ranges shown.

Some inorganic complexes have been reported for Cr(VI) (Schmidt, 1984), but they are generally considered to be of little importance in dilute aqueous solutions (Griffin et al, 1977). Yet Cotton and Wilkinson (1972) report that in solutions of hydrochloric and sulfuric acid, hydrogen chromate is converted almost entirely to chlorochromate (CrO_3Cl^-) or the sulfato complex ($(CrO_3(OSO_3)^{2-})$).

Cr(VI) Precipitation/Controlling Solid Forms: The sodium and potassium salts of chromate and dichromate have quite high solubilities in water (Schmidt, 1984). However, the calcium salt of chromate is only moderately soluble; Cr(VI) also forms salts of moderate to low solubility with several transition and "heavy" metal cations, including silver, barium, cesium, copper, mercury, and lead (Cotton and Wilkinson, 1972; Schmidt, 1984). In most natural systems, of course, concentrations of these species will be quite low. At sites where chromium contamination is a problem, however, other heavy metals are likely to be present as well. Such is the case at the United Chrome Products site, where elevated levels af lead were also detected (Ecology and Environment, Inc., 1985).

Adsorption of Cr(VI): It is difficult to differentiate precipitation, co-precipitation and adsorption reactions in heterogeneous media (Veith and Sposito, 1977; Sposito, 1982). In addition, accurate distinction between Cr(VI) and Cr(III) may not be possible in some solid media (Dreiss, 1986). Stollenwerk and Grove (1985) used the term "adsorption" to refer to any removal of chromium from solution; the same convention will be used here when the specific reaction mechanism is not evident.

Cr(VI) adsorption studies have been conducted with a variety of solid media. Equilibration times reported for batch Cr(VI) adsorption tests in suspensions of the following materials were: iron oxyhydroxide, 30 minutes (Zachara et al, 1987); activated carbon, 24 hours (Huang and Wu, 1977); mineral alluvium, within three days (Stollenwerk and Grove, 1985); kaolinite and montmorillonite, two weeks, assuming Cr(VI) equilibration coincides with pH equilibration (Griffin et al, 1977). Typically, similar batch reaction tests with metal cations and organic pollutants in soil suspensions equilibrate in minutes to hours (Wu and Gschwend, 1986; Aringhieri et al, 1985; Harter and Lehmann, 1983). However, equilibration was quite slow for orthophosphate, an oxyanion, in soil suspensions (Enfield et al, 1981).

The effect of pH on Cr(VI) adsorption varies with the adsorbent. In soils, Cr(VI) adsorption generally increases as pH decreases (Bartlett and Kimble, 1976b; Grove and Ellis, 1980; Cary et al, 1977). Equilibrium adsorption edges have been presented in the literature for suspensions of: kaolinite and montmorillonite in distilled water and landfill leachate solutions (Griffin et al, 1977); amorphous iron oxyhydroxide in the presence of a variety of common groundwater species (Davis and Leckie, 1980; Zachara et al, 1987); amorphous aluminum oxide in KNO_3 solutions (Davis and Leckie, 1980); and activated carbon in solutions with and without CN^- (Huang and Wu, 1977). In general, adsorption decreased as pH was raised in the mineral suspensions; these results are typical for anions adsorbing to hydrous oxide solids whose surface charge decreases with increasing pH due to OH^- adsorption and/or H^+ desorption (Davies-Colley et al, 1982; Sposito, 1984; Stumm and Morgan, 1981). However, in the clay suspensions at low Cr(VI) concentrations, adsorption decreased slightly at low pH (Griffin et al, 1977). Distinct adsorption maxima were observed between pH 5 and 6 in activated carbon suspensions (Huang and Wu, 22).

Solution composition also effects adsorption, but the effects of specific solution species varies with the adsorbent and with pH. In iron oxyhydroxide suspensions, concentrations of $CO_2(g)$, SO_4^{2-} and $H_4SiO_4(aq)$ in the mM range caused adsorption to decrease, while adsorption increased slightly on addition of 2.5 mM concentrations of Ca^{2+} and Mg^{2+} (Zachara et al, 1987). Adsorption to alluvium also decreased dramatically in the presence of mM concentrations of SO_4^{2-} and $H_2PO_4^-$ (Stollenwerk and Grove, 1985). In soils, the effect of orthophosphate apparently varied with soil organic matter content; excess orthophosphate in solution prevented any adsorption to a silty clay (less than 0.05% organic matter), but caused adsorption to increase in soils of higher organic content (Bartlett and Kimble, 1976b). Anionic extraction solution efficiencies also vary with soil properties; these have often been used to indicate the nature of adsorption reaction mechanisms (Bartlett and Kimble, 1976b; Grove and Ellis, 1980a; Cary et al, 1977).

There has been some debate in the literature regarding the mechanism of Cr(VI) adsorption to soil and mineral surfaces. Griffin et al (1977) concluded that adsorption to clay minerals was primarily due to $HCrO_4^-$ anion exchange because of the good agreement of adsorption data with the Langmuir equation. The increase in adsorption with decreasing pH was therefore explained by the increasingly positive charge of hydrous oxide surfaces in the clays. Decreasing adsorption densities at very low pH values were attributed to the increasing tendency to form neutral, non-adsorbing H_2CrO_4. At high pH, where CrO_4^{2-} is dominant, no adsorption occurs (see Figure 2.2). An anion exchange mechanism was also indicated by the work of Stollenwerk and Grove (1985) with Cr(VI) and alluvium of low organic matter content (0.10%). Adsorption decreased significantly in the presence of competing anions, dropping more than ninety percent in 0.02 M orthophosphate solution, and most of the adsorbed chromium was desorbed by water. Cr(VI) adsorption to the alluvium also provided good agreement with the Langmuir equation. Anion competition for Cr(VI) adsorption sites has also been observed in iron oxyhydroxide batch suspensions (Zachara et al, 1987).

Reduction of Cr(VI) to insoluble trivalent forms has been cited by several other workers as the primary cause of Cr(VI) "adsorption" to soils. Cary et al (1977) observed very little exchange of adsorbed $^{51}CrO_4^{2-}$ on addition of unlabeled 0.02 M K_2CrO_4. After one day of incubation, percentages extracted by this procedure were quite similar to those for soils to which $^{51}CrCl_3$ was applied, implying that hexavalent species were quickly reduced to trivalent forms. An ammonium chloride extraction procedure used by Grove and Ellis (1980) to determine the exchangeable fraction of Cr(VI) applied to soils removed negligible amounts of chromium. The successive extraction procedure performed in that study also indicated that Cr(VI) was converted to insoluble forms of Cr(III) with time, and that reduction was favored at low pH. The authors postulated the equation

$$H_2CrO_4 + 6\ H+ + 3\ e- = Cr^{3+} + 4\ H_2O \qquad \text{(Eq. 2.1)}$$

to illustrate the pH dependency of the reduction reaction. They asserted that, under the anaerobic conditions maintained by Griffin <u>et al</u> (1977), reduction of Cr(VI) to insoluble Cr(III) forms probably occurred, rather than the anionic exchange mechanism originally proposed. The pH dependence of Cr(VI) adsorption to the clays, they stated, was probably due to enhanced reaction by the above mechanism rather than increased soil surface charge. The mass of organic carbon present in the clays (5.1 mg/g in kaolinite and 9.2 mg/g in montmorillonite) was more than ten times the maximum Cr(VI) adsorption density, thus there was likely a sufficient source of electrons for the reduction reaction of Equation 2.1 to take place.

Results presented by Bartlett and Kimble (1976b) for tests in several different soils indicate that either or both the exchange reaction and reduction reactions may occur, depending on the characteristics of the soil system. After four weeks of incubation following addition of chromium to soil at field moisture, high percentages of adsorbed Cr(VI) were removed from a soil of very low organic content with an 0.10 M orthophosphate extraction solution. However, no Cr(VI) was extracted by this procedure from three soils of 5-10% organic matter content. Reduction of Cr(VI) did not occur when manure was added to the inorganic soil at a pH of 6, but did occur when the pH of the soil-manure system was reduced to a value of 3 with HCl. The presence of Cr(III) in extraction solutions of these soils confirmed that reduction of Cr(VI) was occurring in the soil. Also, extractable Cr(VI) increased when lime was added to raise soil pH.

2.3 Cr(III) Chemistry

Aqueous Speciation of Cr(III): Trivalent chromium has a 3d3 electronic configuration, with six vacant outer shell orbitals forming an octahedran around the cation (Mertz, 1969; Cotton and Wilkinson, 1972). These orbitals are responsible for the strong complexing power of the trivalent cation, as they are able to accept free electron pairs from complexing ligands (Mertz, 1969); thousands of Cr(III) complexes reportedly exist (Cotton and Wilkinson, 1972). These complexes have relatively slow ligand exchange rates, with typical half-times of several hours. As a result, many species persist for relatively long times, though they may be quite unstable thermodynamically (Cotton and Wilkinson, 1972). Because of its strong complexing ability, Cr(III) solubility and speciation in aqueous solution vary greatly with solution composition.

Essentially all aqueous forms are octahedrally complexed (Cotton and Wilkinson, 1972). The free cation does not exist in water; six waters of hydration surround the Cr^{3+} cation; one to four hydroxide ions may replace hydrating water groups. Figure 2.3 shows the solubility "envelope" formed by the concentrations of these hydroxide species as a function of pH in equilibrium with $Cr(OH)_3(s)$ (Schmidt, 1984). Monomeric hydroxide complexes are stable in acidic solution, but above pH=4 they will hydrolyze to form polynuclear complexes. Once formed, these will continue to grow and will ultimately precipitate out of solution (Mertz, 1969), complicating quantitative speciation calculations (Cary et al, 1977). See discussion below on precipitation of Cr(III).

Cr(III) also complexes with a number of other inorganic anions, including all of the halides, ammonia, sulfate, phosphate, and thiocyanate (Schmidt, 1984; Cotton and Wilkinson, 1972). A number of organic compounds have also been shown to form stable complexes with Cr(III), though thermodynamic data are not as numerous as for the inorganic species. Martell and Smith (1974, 1977) list complexation constants for acetate and EDTA, but few other organic ligands are included. Sposito (1981) describes a general method for estimating metals complexation constants by natural organic ligands using the Misono softness parameter (Huheey, 1978). Estimated complexation constants derived in this manner can be used to show that, given sufficient concentrations of natural organic matter, organic complexes may dominate Cr(III) in a variety of aqueous environments. Examples of Cr(III) complexes observed in environmental systems will be discussed below in the Oxidation/Reduction Chemistry section.

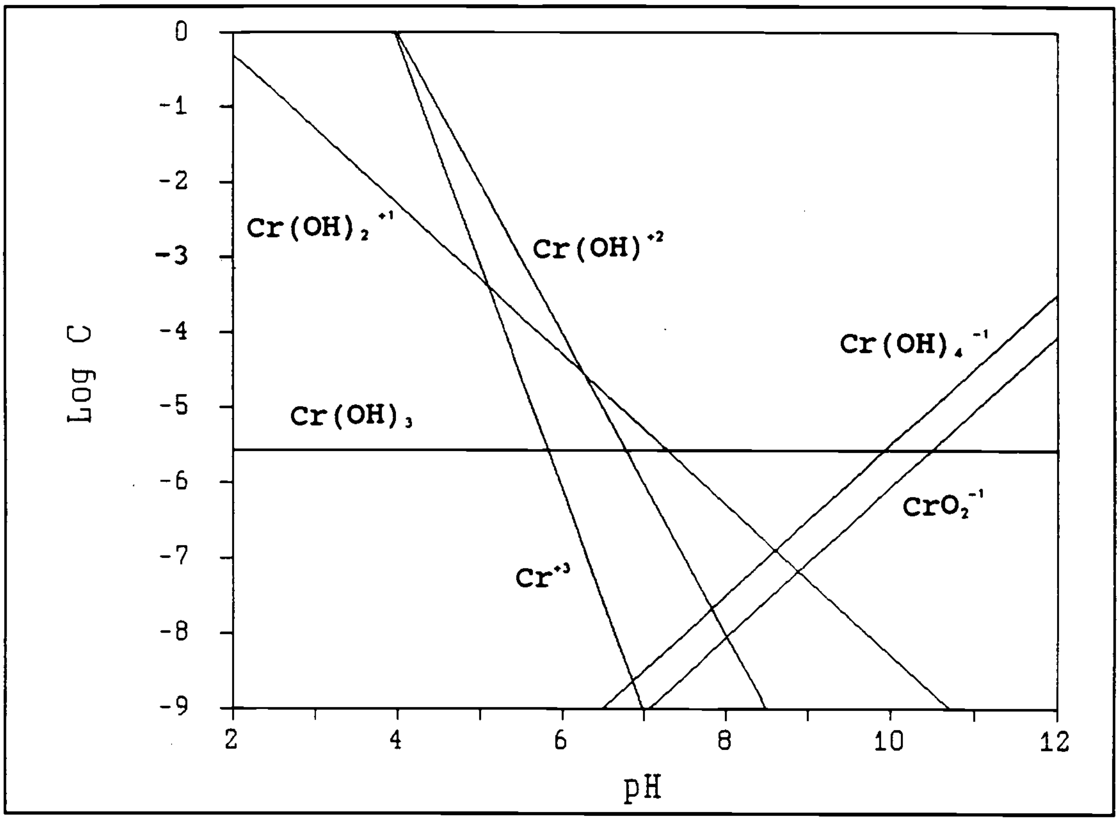

Figure 2.3: Cr(III) solubility in equilibrium with Cr(OH)3 solid (Schmidt, 1984).

Cr(III) Precipitation/Controlling Solid Forms: As stated earlier, the primary mineral source of chromium is chromite, $FeCr_2O_4$; magnesio-chromite, $MgCr_2O_4$, is less common (Bowen, cited by Schmidt, 1984). In the absence of solubilizing ligands, $Cr(OH)_3(s)$ and polynuclear hydroxides readily precipitate from neutral and alkaline solutions; these solid hydroxides may slowly transform to the more stable chromic oxide, Cr_2O_4 (Schmidt, 1984). Depending on environmental conditions, any of these solids might control Cr(III) solubility. Jan and Young (1978) successfully predicted total Cr(III) concentrations off the coast of Southern California within 15% using the simple mononuclear hydroxide speciation model described above for systems controlled by $Cr(OH)_3(s)$.

Figure 2.4 shows the solubility of Cr(III) as a function of pH for systems controlled by chromite, magnesio-chromite, and the amorphous tri-hydroxide solid precipitate, using the formation constants of Schmidt (1984). Only the mono-nuclear complexes (those shown in Figure 2.3) were included in the calculation of total soluble Cr(III) ($C_{T,Cr(III)}$). The magnesio-chromite line was constructed assuming Mg^{+2} concentration to be fixed at 1.1 mM, which was the concentration determined in the groundwater used in adsorption experiments (see "Experimental Materials"). For chromite controlled systems, Fe^{2+} concentrations were calculated at two pE values, 2 and 8, assuming ferrous iron solubility to be determined by the presence of ferric hydroxide solid. Fe^{2+} concentrations determined in this manner became unrealistically high below pH values of 7 and 4, respectively, in the pE 2 and 8 systems, thus the curves indicate artificially low Cr(III) solubilities in acidic solutions. However, in solutions containing as low as 0.02 mM Fe^{2+}, chromite is more likely to form above pH 3 than is amorphous Cr(III) hydroxide. Magnesio-chromite becomes the determining solid phase above pH 8.5.

Adsorption of Cr(III): Adsorption of Cr(III) to soil, clay and hydrous oxides differs from Cr(VI) adsorption in that adsorption increases with pH (Bartlett and Kimble, 1976a;

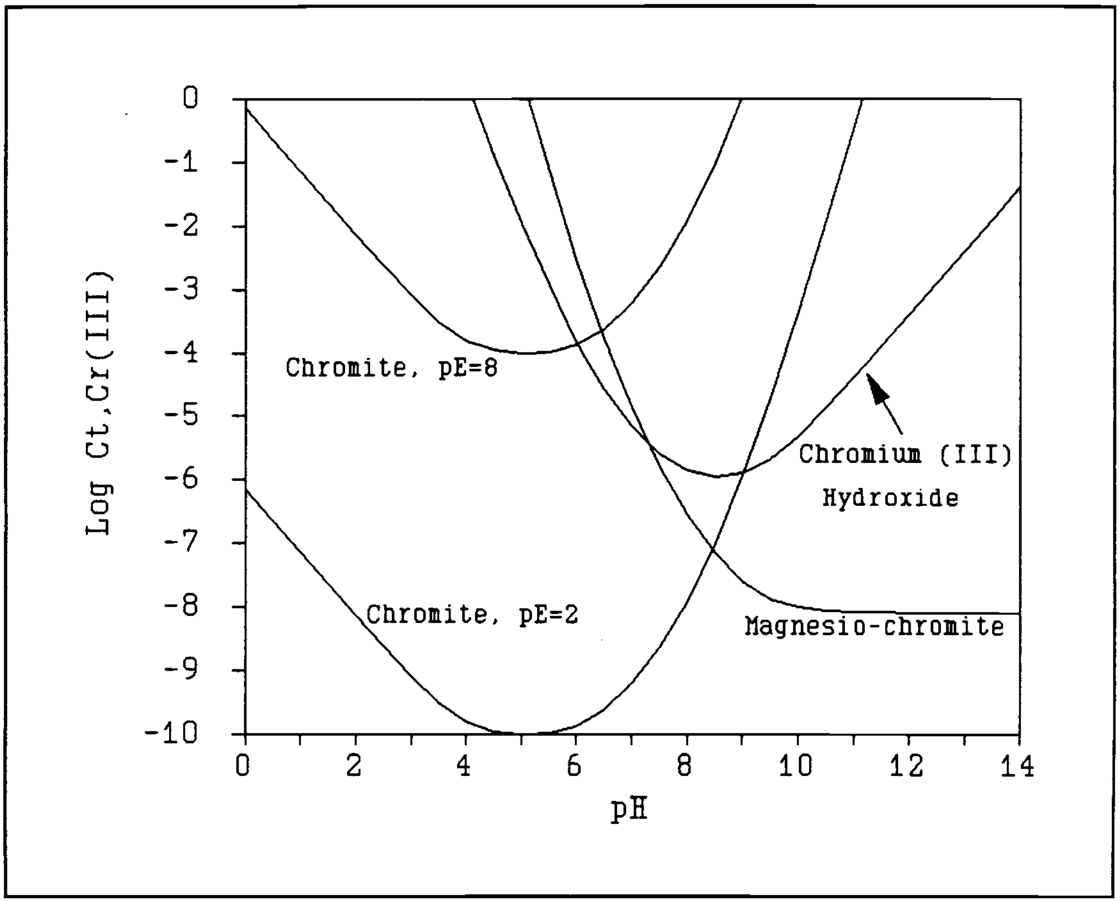

Figure 2.4: Controlling solid phases of Cr(III).

Griffin et al, 1977; Schultz et al, 1987). This is typical for cation adsorption to oxyhydroxide surfaces, where the number of negatively charged soil surface sites increases as OH^- is adsorbed or H^+ is desorbed from the oxide surface (Davies-Colley et al, 1981; Sposito, 1984; Stumm and Morgan, 1972). Like adsorbed Cr(VI), Cr(III) adsorbed by certain soils are partially extractable by oxalate solutions, with the remainder of the adsorbed fraction being completely extractable by citrate/dithionate solutions (Grove and Ellis, 1980). These extractions were designed to indicate amorphous precipitated and crystalline iron hydroxides (Mehra and

Jackson, 1960; McKeague and Day, 1966), and were thought to indicate association of adsorbed chromium with these phases (Stollenwerk and Grove, 1985; Grove and Ellis, 1980).

Complexing organic ligands can protect soluble Cr(III) from precipitation or adsorption in soil systems (James and Bartlett, 1983a,b) and in suspensions of iron oxyhydroxide in seawater (Nakayama et al, 1981a-c). Cr(III) adsorption to clays was also moderately lower in a municipal landfill leachate solution than in distilled water (Griffin et al, 1977). Cationic competition was cited as the cause of the decreased adsorption in the leachate, but competive complexation of Cr(III) by ammonia and organic acids in the landfill leachate may have been more significant.

2.4 Oxidation/Reduction Chemistry

The stability-field diagram of chromium in Figure 2.1 shows the species and oxidation state most favored thermodynamically at a given pH and Eh. The diagram shows that the hexavalent oxidation state is only favored under highly oxidizing conditions. Cr(III) is favored by lower pH and lower oxidation potentials. Predictions of chromium oxidation state from the diagram are only accurate, however, when chromium in the system approaches thermodynamic equilibrium.

Local chemical processes greatly influence the redox chemistry of chromium in natural systems. As stated above, soluble organic matter complexes and protects Cr(III) from precipitation or adsorption in soil suspensions and iron oxyhydroxide suspensions in seawater. Soluble organics also reduce Cr(VI) to Cr(III) in acidic soils and seawater (James and Bartlett, 1983b,c; Nakayama et al, 1981a-c).

Manganese oxyhydroxides have been shown to oxidize Cr(III) in: aerated and dearated solution (Eary and Rai, 1987); soils (Bartlett and James, 1979); and in aerated and dearated seawater (Emerson et al, 1979; Nakayama et al, 1981b). In contrast, no Cr(III) oxidation occurred in oxygen saturated seawater when manganese was absent (Nakayama et al, 1981b). Also, Emerson et al (1979) report the presence of "metastable" Cr(III) in oxic waters of Saanich Inlet, British Columbia, where diffusion of reduced chromium from deep anoxic waters exceeded the rate of Cr(III) oxidation by manganese oxide particulates in aerated upper layers.

2.5 Adsorption Models

In natural waters, adsorption plays an important role in regulating the concentrations of metals, nutrients, and organic pollutants (Mayer and Schick, 1981; Stumm and Morgan, 1981). Several models have been developed to describe these reactions.

Stumm and Morgan (1981) describe adsorption in terms of surface coordination reactions in which the role of surface functional groups is analogous to that of similar aqueous species. Thus, the adsorption of a metal cation of positive charge z (M^{z+}) to a metal hydroxide surface ($\equiv SOH$) could be described by the equation

$$\equiv SOH + M^{z+} = \equiv SOM^{(z-1)} + H^{+} \qquad \text{(Eq. 2.2)}$$

The complexation constant for this reaction is

$$^{*}K_{1}^{s} = \{\equiv SOM^{(z-1)}\}[H^{+}]/\{\equiv SOH\}[M^{z+}] \qquad \text{(Eq. 2.3)}$$

Several authors have shown the mathematical equivalence of this model and the Langmuir Equation, which has been used extensively in modeling adsorption to soils (Nelson <u>et al</u>, 1981; Harter and Smith, 1981; Veith and Sposito, 1977). Another model of widespread use is the Freundlich isotherm (Weber, 1972; Travis and Etnier, 1981). This model describes the equilibrium relationship between aqueous concentration (C) and amount of solute adsorbed per mass (or surface area) of adsorbent by the exponential equation

$$S = KC^{n} \qquad \text{(Eq. 2.4)}$$

where K and n are constants. Holding n equal to 1 reduces the Freundlich equation to a linear distribution constant equation. This simple relationship is the most commonly used model for describing the adsorption of reactive solutes to soils (Travis and Etnier, 1981).

Other more detailed adsorption models emphasize the role of electrostatic forces. Among these are the diffuse double layer model, the constant capacitance model, and the triple layer model (Sposito, 1984; Stumm and Morgan, 1981). These models, like the surface complexation model, are typically used to describe equilibrium systems. Yet many important adsorption reactions are too slow to describe with equilibrium models (Valocchi, 1985; Van Genuchten et al, 1974). Accordingly, much recent work has focused on the kinetics of adsorption reactions.

Modeling Adsorption Kinetics: Adsorption data reported in the literature often show a rapid initial phase followed by a slower reaction phase (Wu and Gschwend, 1986). As a first approximation, the slow phase is often assumed to follow first order reaction kinetics with respect to solute concentration (Harter and Smith, 1981; Aringhieri et al, 1985; Travis and Etnier, 1981). Some models incorporate both fast and slow adsorption reactions, as do the two-site kinetic models of Selim et al (1976) and Cameron and Klute (1977). These models include a rapid reaction site which equilibrates instantaneously with adsorbate, and a slow reaction site where reaction rate is limited by kinetics. Cameron and Klute model the fast reaction with a linear isotherm and the slow reaction with the first order reversible kinetic equation. Selim et al use the Freundlich isotherm for the fast reaction, and allow the slow reaction to be other than first order with respect to solute concentration.

Harter and Lehmann (1983) described the adsorption of nickel and copper to soil with a multistage reaction model. The Langmuir equation was used to model the rapid, essentially instantaneous initial reaction; subsequent adsorption was modelled as a series of first-order reactions.

3. TWO-SITE ADSORPTION MODELS

Several workers have proposed that adsorption of solutes to soils be described by a combination of equilibrium and kinetic models (Cameron and Klute, 1977; Selim et al, 1976; Harter and Lehmann, 1983). As will be shown later, adsorption of Cr(VI) to the Dayton series soil proceeds in two phases, a rapid initial uptake phase with a time scale of minutes or hours, followed by a much slower uptake phase which continues for many days without reaching equilibrium. Such adsorption behavior can be described with an equilibrium/kinetic combination model. Models that might be used to characterize each of these phases are described in the following sections. Later, the ability of each of these models to characterize the chromium adsorption data will be evaluated.

3.1 Modelling the Rapid Reaction Phase

The three combination models referred to above have each used different equilibrium isotherms to describe rapid adsorption. Selim et al (1976) and Cameron and Klute (1977) chose the Freundlich and the linear isotherms, respectively. These isotherms, when incorporated into advective-dispersive solute transport models, allowed for analytical and numerical solutions, respectively, to the transport equation. The Langmuir isotherm was chosen by Harter and Lehmann (1983) because of its good fit to rapid adsorption data.

Three isotherms-- linear, Freundlich, and Langmuir-- will be compared to the rapid, initial Cr(VI) adsorption data. Experimental results will also be used to determine whether the rapid adsorption reaction should be regarded as reversible or irreversible.

3.2 Psuedo-First Order Reaction

Adsorption of a reactive solute to soil can be described by the following general mechanism:

$$\text{Solute} + \text{Reactive Soil Surface Site} \Longleftrightarrow \text{Adsorbed Species} \qquad \text{(Eq. 3.1)}$$

If the reaction is first order with respect to both solute concentration, C and the number of reactive soil sites available per volume of solution, X; and if adsorbate desorption is first order with respect to adsorption density, S; then the net rate of reaction, r, is given by the equation

$$\begin{aligned} r &= dC/dt = \text{Rate of adsorption} - \text{rate of desorption} \\ &= -k_1C(mx) + k_2mS \\ &= -k_1CX + k_2mS \quad \text{(mol/L-hr)} \qquad \text{(Eq. 3.2)} \end{aligned}$$

where

r = Solute reaction rate (mol/L-hr)

C = Solute concentration (mol/L)

t = Time (hrs)

k_1 = Second order adsorption rate constant (L/kg*hr)

k_2 = First order desorption rate constant (1/kg*hr)

m = Mass of soil per volume liquid (kg/L)

S = Adsorption density (mol/kg)

x = Number of reactive soil surface sites per mass of soil, (mol/kg)

X = "Concentration" of reactive soil surface sites = mx (mol/L)

Reactive soil surface sites are depleted by the adsorption of solute, but if dX/dt (=dC/dt) is small relative to X, X will remain essentially constant over substantial time periods. Thus, Equation 3.2 simplifies to

$$r = -k_1'C + k_2mS_2 \quad \text{(mol/L-hr)} \qquad \text{(Eq. 3.3)}$$

where k_1' = Psuedo-first order reaction rate constant
= k_1X
= constant (1/hr)

If k_2mS is much less than $k_1'C$, the reaction is considered irreversible, and Equation 3.3 is further simplified to

$$r = -k_1'C \quad \text{(mol/L-hr)} \qquad \text{(Eq. 3.4)}$$

Separation of variables and integration of this rate equation yields the following relation:

$$\log(C/C_0) = (k_1'/2.303)t$$

or $$\log(C) = (k_1'/2.303)t + \ln(C_0) \qquad \text{(Eq. 3.5)}$$

where C_0 = Solute concentration (mol/L) at reaction time equal to zero.

As seen in Equation 3.5, solute concentration data for reactions with first order or psuedo-first order mechanisms will form a straight line when plotted as the logarithm (base 10) of the molar solute concentration versus reaction time. The slope of such a plot is equal to the reaction rate constant, k_1', divided by 2.303; the y-intercept equals the logarithm of the solute concentration at zero reaction time.

3.3 Two-Site Models

In this section, two two-site models will be described. The ability of each to characterize the adsorption of Cr(VI) to the Dayton soil will be evaluated in the Discussion of Results.

Irreversible Kinetic and Equilibrium Reactions: When an irreversible, rapid adsorption reaction phase precedes an irreversible psuedo-first order adsorption phase, both adsorption phases can be characterized using Equation 3.5. C_0 and k_1' can be determined from the concentration versus time data using Equation 3.5. If the actual initial concentration (C_i) is known, S_0 can also be determined; this value represents the amount of Cr(VI) adsorbed (irreversibly) during the rapid adsorption phase (Harter and Lehmann, 1983). Thus, a semilog plot of adsorption kinetics data can be used to determine both the pseudo-first order rate constant and to estimate the adsorption density due to rapid adsorption reaction(s).

Reversible Kinetic and Equilibrium Reactions: Other simple two-site models combine an equilibrium isotherm model for the rapid adsorption and a kinetic adsorption reaction (Selim et al, 1976; Cameron and Klute, 1977). These models require two reaction equations, one time dependent and the other independent of time, which must be solved simultaneously. Such models may be solved numerically by the finite difference method; the final form of the solution depends upon the equilibrium (rapid phase) isotherm and the kinetic reaction mechanism. One simple model of this sort combines the reversible, linear equilibrium isotherm and reversible, pseudo-first order kinetic reaction (Cameron and Klute, 1977). The numerical solution to this model is derived below; more complex models can be solved similarly.

At any given reaction time, t, C and S_1 (the adsorption density resulting from the rapid phase adsorption reaction) are related by the equilibrium relationship

$$S_1 \;=\; KC \quad (\text{mol/L}) \qquad\qquad (\text{Eq. } 3.6)$$

where K is the linear isotherm constant (L/kg), and the mass balance for the reactive species,

$$C_{max} \;=\; C + m(S_1 + S_2) \quad (\text{mol/L}) \qquad\qquad (\text{Eq. } 3.7)$$

where C_{max} is the total mass of species present, in liquid or solid phase, per volume of solution (M). Substituting Equation 3.6 into Equation 3.7 yields C as a function of C_{max}, m, K, and S_2, as follows:

$$C \;=\; (C_{max} - mS_2)/(1 + mK) \quad (\text{mol/L}) \qquad\qquad (\text{Eq. } 3.8)$$

Thus, if S_2 is known, C and S_1 may be calculated by Equations 3.8 and 3.6, respectively. S_2 varies with time, according to the kinetic equation

$$\begin{aligned} d(S_2)/dt &= -r/m \\ &= -k_1'C/m + k_2S_2 \quad (\text{mol/L-hr}) \qquad\qquad (\text{Eq. } 3.9) \end{aligned}$$

This relationship is approximated by the finite difference equation

$$\Delta S_2 = (-k_1'C/m + k_2S_2)\Delta t \qquad \text{(Eq. 3.10)}$$

for small Δt. At any time t, if the values of C and S_2 are known for time t-1, S_2 may be approximated by the equation

$$S_2(t) = S_2(t-1) + \Delta S_2 \qquad \text{(Eq. 3.11)}$$

Again, if $S_2(t)$ is known, C(t) and $S_1(t)$ can be calculated. Thus, given values for the parameters K, k_1', k_2, and m, and the initial values of the variables C, S_1, and S_2, the values of these variables can be approximated as a function of time.

4. METHODS AND MATERIALS

4.1 Experimental Approach

In order to satisfy the objectives of this study, adsorption, desorption and extraction experiments were conducted under varying conditions of pH, chromium concentration and oxidation state, and anion (exchange or extraction ion) concentration. Cr(VI) adsorption studies were performed in order to determine: (1) the effect of pH on adsorption magnitudes and rates from a groundwater solution; (2) the effect of solution composition on adsorption; and (3) isotherms describing concentration dependence of the rapid adsorption reaction(s). Adsorption studies for Cr(III) were conducted in order to: (1) Determine adsorption kinetics at pH 3.8; and (2) Construct adsorption isotherms over a range of pH values. Desorption and extraction studies were conducted on Cr(III) and Cr(VI)-reacted soils to provide evidence regarding: (1) the reversibility of the adsorption reaction; (2) the redox state of adsorbed forms; and (3) the fraction of the soil responsible for adsorption. Table 4.1 is a summary of the experiments and experimental conditions.

4.2 Experimental Materials

Soil: A soil from the Dayton silt loam soil series was collected from an uncontaminated field at the Corvallis

Table 4.1: Summary of experimental conditions.

1. Preliminary Adsorption Kinetics Experiments

	Dose, uM	X, g/L	pH	Reaction Time	Suspension
1a.	192 (VI)	200	4.7	0-240 Hours	Distilled Water
1b.	192 (VI)	40	4.8	0-150 "	" "
1c.	192 (VI)	40	4.3	0-290 "	" "
1d.	962 (VI)	40	4.1	0-800 "	" "
1e.	192 (III)	40	3.8	0-6 "	" "

2. Adsorption vs. pH

	Dose, uM	X, g/L	pH	Reaction Time	Suspension
2a.	192 (VI)	40	3-8	0.25-500 Hrs.	Groundwater
2b.	192 (VI)	40	3-7	48 & 144 Hrs.	Distilled Water
2c.	38-962*	40	3-8	1 Hour	Groundwater
2d.	19-3850**	200	2-7	120 Hours	Distilled Water

* 38, 96, 192, 384, and 962 uM Cr(VI)
** 19, 96, 192, 384, 962 and 3840 uM Cr(III)

3. Cr(VI) Adsorption/Desorption Experiment

	Dose, uM	X, g/L	pH	Reaction Time	Suspension
Ads:	962	200	3-8	168 Hours	Groundwater
Des:	192	40	3-8	0.25-500 Hrs.	"

4. Extraction and Digestion Experiments

Distilled Water/Phosphate Extractions of Cr(VI): Adsorption as in 1c. First extraction, distilled water for 15 minutes; second extraction, 0.02 M KH_2PO_4 for 24 hours.

Alkaline Digestion for Cr(VI) Recovery: Adsorption for 24 hours as in 2a; digestion in hot alkaline solution.

EDTA Extraction of Cr(III): Adsorption for 23 hours, Cr(III) dosed at 192 uM and 1920 uM, pH of about 4.0. Extracted with 0.01 M Na_2H_4EDTA solution for 26 hours.

Citrate-Dithionite Extraction/Acid Digestion: Adsorption for 24 hours as in 2a; extracted with hot citrate-dithionite solution for 30 minutes; digested with strong acid.

Airport (7-15-87), near the United Chrome Products Superfund site. Previous investigations at that site showed that most of the chromium contamination is found in a zone of clayey silt extending from the surface to roughly twenty feet of depth; there was little variation between the soil in this zone and other surface soils in the area (Ecology and Environment, 1985). The soils used in the present study should therefore be representative of much of the contaminated soil.

Enough soil was taken from a zone of roughly 2" to 14" depth to fill three five-gallon plastic containers. Field conditions were such that no drying was required before further preparation. Large clumps were broken up and pebbles and large roots were removed by mechanical grinding in a "Dynacrush" soil grinder and by screening soil with a two-mm mesh sieve. The ground, sieved soil was hand mixed and stored at field moisture and 4°C until use.

The pH point-of-zero-charge (pH_{pzc}) determination is described in the Experimental Procedures section. Free iron and manganese were determined by the citrate-dithionite extraction method of Coffin (1963); this method was designed to remove free iron oxides while removing minimal crystalline iron forms from soil. Total iron and manganese were determined by the ASTM acid digestion method (ASTM, 1986). Results from all of the above procedures are listed in Table 4.2. pH_{zpc} results are also shown graphically in Figure 4.1.

Table 4.2: Chemical characteristics of the Dayton soil.

Constituent	Weight %
Free moisture	5.6
Total moisture	6.5
Volatile Solids	4.9
Free iron	0.82
Total iron	2.4
Free manganese	0.25
Total manganese	0.22

pH_{PZC} = 3.75

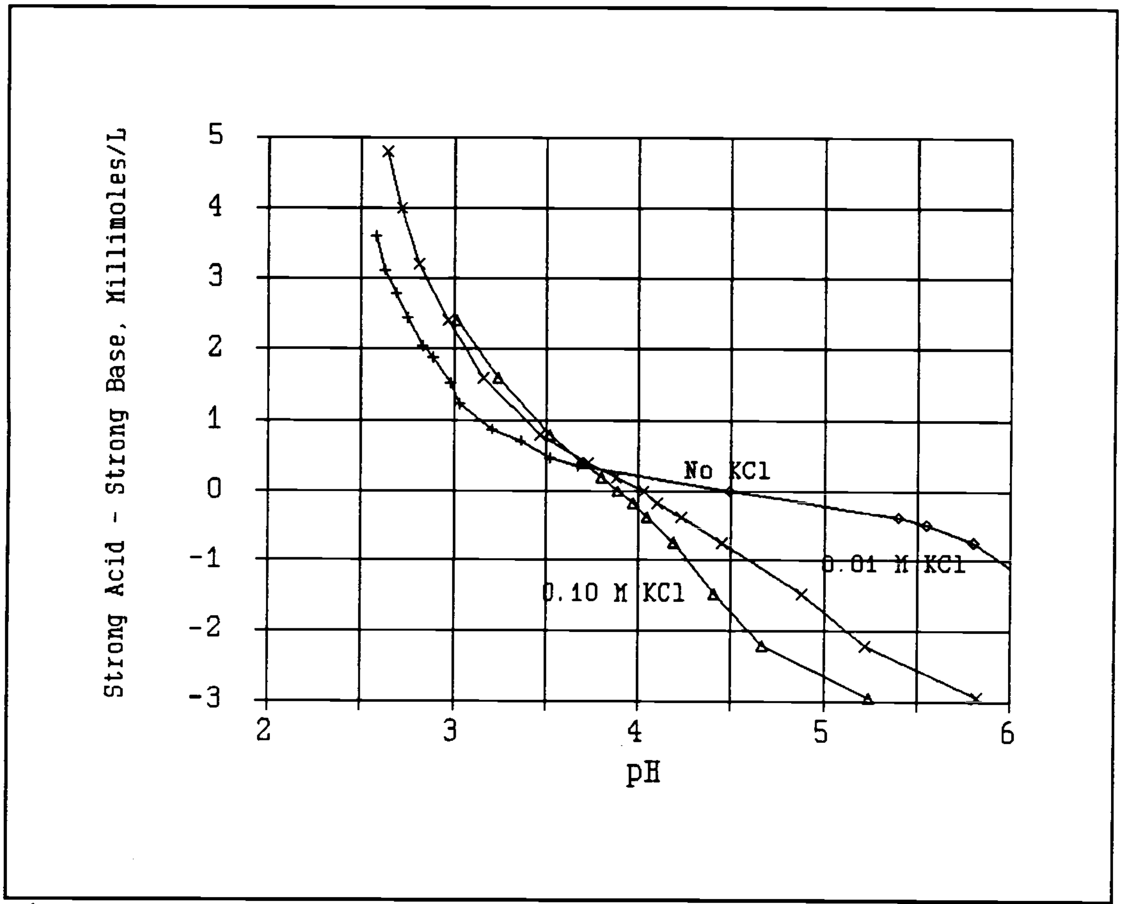

Figure 4.1: Soil titration for determination of pH point-of-zero charge.

Groundwater: Groundwater for the study was also collected at the Corvallis Airport, from an uncontaminated well, one of two which were servicing the airport at the time (2-11-87). The pumping system was purged with fresh wellwater to remove any chlorine disinfectant from the lines. Water was then pumped into and stored in five gallon plastic carboys in the dark and at 4°C. The ionic constituents of this water are listed in Table 4.3.

Table 4.3: Chemical composition of Corvallis Airport wellwater.

Groundwater Constituent	Concentration, mmol/L	Equivalents, meq/L
Ca^{2+}	1.43	2.86
Mg^{2+}	1.11	2.22
Na^{+}	0.97	0.97
K^{+}	0.06	0.06
HCO_3^-	5.0	5.0
	pH = 7.4	

Chemicals: All chemicals used were ACS reagent grade. Glass and plasticware were soaked in 10% nitric acid and rinsed well with glass distilled water prior to all uses.

4.3 Experimental Procedures

Table 4.1 lists the general conditions (pH, initial chromium concentrations, soil concentration, and reaction times) of all adsorption, desorption and extraction experiments performed. More detailed descriptions of the experiments are given below.

4.3.1 Adsorption Experiments: General Procedure

Chromium solutions were reacted with soil in 50 mL, screw-top plastic centrifuge tubes. Unless otherwise noted, 25 mL of solution were reacted with one gram of soil, giving a 40 g/L soil slurry. Soil suspensions were kept well mixed by continuous shaking in a 25°C constant-temperature shaker bath. Air filled the headspace; no effort was made to control $O_2(g)$ or $CO_2(g)$ partial pressures. Solutions were made from either distilled water or groundwater. Hexavalent chromium was added as potassium dichromate solution, trivalent chromium as the chloride salt solution; stock solutions of each were prepared at concentrations 1 g/L (0.0192 M). Strong acid or base (HCl or KOH) was added to adjust pH between 2.5 and 9. After shaking for the desired reaction time, tubes were centrifuged at 10,000 rpm for 10 minutes and supernatent solutions were decanted and filtered with 0.45 um Millipore filters. Samples were stored in plastic containers at 4C until analysis for pH, total soluble Cr, and/or Cr(VI). Adsorbed chromium was determined by difference from initial and final solution concentrations by the following calculation:

$$S = (C_i - C)/m$$

where S = Adsorbed concentration (umol/kg)

C_i = Initial liquid phase chromium concentration (uM)

C = Final liquid phase chromium concentration (uM)

and m = Mass of soil per volume of solution (kg/L).

4.3.2 Specific Conditions of Adsorption Experiments

Preliminary Adsorption Kinetics Experiments (1a-1d): These were the first experiments conducted; their purpose was to determine whether significant Cr(VI) and Cr(III) adsorption would occur in the soil suspensions, and if so, to determine the reaction time necessary for equilibration. Experimental conditions were varied in the four Cr(VI) kinetics experiments (1a-1d in Table 4.1) to investigate the effects of initial solute concentration, soil concentrations, and suspension pH on adsorption magnitudes and rates.

Cr(VI) Adsorption vs. pH (Experiments 2a-2c): The effect of pH on Cr(VI) adsorption magnitudes and rates was investigated by reacting Cr(VI) in groundwater suspensions of varying pH (Experiment 2a). Experiments were conducted for reaction times of 15 minutes to 500 hours (21 days); adsorption densities were plotted against pH for each reaction time. Adsorption vs. time plots for discrete pH values were constructed from the adsorption versus pH "edges" by fitting a smooth curve to the data at each reaction time and reading the amount adsorbed from each curve at the pH of interest.

Similar experiments were conducted in distilled water-soil suspensions for reaction times of one and six days; the resulting edges were compared to the wellwater suspension data to determine the effect of solution composition on adsorption of Cr(VI).

The concentration dependence of the rapid adsorption reaction was examined in experiments of one hour reaction times (Experiment 2c). In these, both pH and initial Cr(VI) concentrations were varied, and adsorption edges were plotted for each initial concentration. Isotherms for discrete pH values were constructed from the edges by the method described above for the adsorption vs. time plots.

Cr(III) Equilibrium Adsorption Edges: Initial Cr(III) concentrations were varied from 385 uM to 1920 uM (Experiment 2d) in 200 g/L soil-distilled water suspensions. Suspensions were reacted for five days. Equilibrium was assumed, based on results of the Cr(III) kinetics experiment and on results of previous metal cation adsorption studies (Aringhieri et al, 1985; Harter and Lehmann, 1983).

4.3.3 Cr(VI) Adsorption/Desorption Experiments

Chromium was adsorbed in 200 g/L soil suspensions dosed at 960 uM Cr(VI) in groundwater (Experiment 3). pH was varied by addition of strong acid or base. After one week reaction time, some of the suspensions were analyzed to determine the amount of Cr(VI) that had adsorbed to the soil. At the same time, 20 mL of Cr-free groundwater were added to the remaining suspensions to produce 40 g/L soil suspensions in dilute Cr(VI) solutions. The intent of this step was to induce desorption of reversibly adsorbed Cr(VI) from the soil. Diluted suspensions were allowed to react for 15 minutes, one week, two weeks, and three weeks, then were analyzed for Cr(VI) and pH.

In order to maintain each suspension pH constant during dilution, dilution groundwater pH was adjusted so that each 20 mL groundwater aliquot matched the pH of the 200 g/L suspensions to which it was added.

4.3.4 Extraction Procedures

Distilled Water/Phosphate Extraction of Adsorbed Cr(VI): Soils with adsorbed Cr(VI) were sequentially extracted with distilled water and with 0.02 M KH_2PO_4 solution to determine the amounts of easily desorbed and anion exchangeable Cr(VI) as a function of reaction time. Adsorption conditions were those listed for Experiment 1c. The extraction was conducted by the following stepwise procedure:

(1) Adsorb Cr(VI) to soil as in Experiment 1c.
(2) Centrifuge, then decant, filter and analyze supernatant for total Cr, Cr(VI) and pH.
(3) Wash soil with 25 mL distilled water by resuspending centrifuge plug.
(4) Repeat step 2.
(5) Add 25 mL of 0.02 N KH_2PO_4 extraction solution to soil plug and mix for 24 hours to desorb Cr(VI);
(6) Repeat step 2.

The aqueous Cr(VI) retained in the pore water after decantation (steps 2 and 4) was calculated from the gravimetrically determined pore water volumes and analytically determined aqueous Cr(VI) concentrations. Masses of Cr(VI) extracted by the distilled water and by the phosphate solution were determined by subtracting this retained Cr(VI) from the mass of Cr(VI) in the solution after steps 4 and 6, respectively.

Cr(III) Extraction by EDTA: The objective of this test was to develope a method for determining the presence of adsorbed Cr(III) that could be used to demonstrate whether or not adsorbed Cr(VI) had been reduced. EDTA was chosen because it is known to strongly complex trivalent chromium (Chaberek and Martell, 1969; Martell and Smith, 1974).

Cr(III) solutions of 192 and 1920 uM were reacted with suspensions of 40 g soil/L (doses of 4.81 and 48.1 umol/g). After one day (23 hours) reaction time, suspensions were centrifuged and supernatants were decanted, filtered, and analyzed for pH, total Cr, Cr(VI), and Fe. Centrifuged soil plugs were resuspended with 25 mL of 0.010 M Na_2H_4 EDTA and mixed for one day (26 hours). Suspensions were then centrifuged and supernatants decanted, filtered, and analyzed as before.

The volume of pore water retained by the soil plug after decantation was assumed to be one mL (gravimetric analyses in other experiments supported this assumption). The mass of soluble Cr(III) in the pore water of the centrifuged soil plug just before resuspension with EDTA solution was estimated from the assumed pore water volume and the analytically determined Cr(III) concentration. EDTA extractable Cr(III) was calculated by subtracting the estimated "carryover" Cr(III) mass from the mass of Cr(III) in the final extraction solution.

Citrate-Dithionite Extraction (Mass Balance Verification, Part 1): The citrate-dithionite extraction method of Coffin (1963) was used to determine what fraction of adsorbed chromium was associated with amorphous iron and manganese oxides. This extraction was performed on four soil samples that had been reacted with Cr(VI) for 24 hours (initial Cr(VI) concentration, 192 uM; 40 g soil/L). Two samples were reacted at pH 2.7, the other two at pH 7. After centrifugation and decantation, soil plugs were resuspended with one gram of sodium dithionite and 25 mL of citrate buffer solution (0.15 M sodium citrate + 0.05 M citric acid) and shaken for 30 minutes in a water bath at 50°C. The amount of chromium extracted was determined as in the phosphate extraction.

Subsequently, these samples were digested with acid as described below, in order to verify the mass balance assumptions used in the adsorption experiments.

4.3.5 Digestion Procedures

Alkaline Digestion: This experiment (4b) was conducted to determine the mass of adsorbed Cr(VI). The digestion procedure was a modification of EPA Method 3060 in "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods" (USEPA, 1986). The digestion in hot, alkaline solution (2% sodium hydroxide, 3% sodium carbonate mixture prepared in distilled water) is designed to quantitatively extract hexavalent chromium from solid phases. The elevated pH suppresses the reduction of soluble Cr(VI) and, along with the near boiling temperatures, prevents Cr(III) from coming into solution (Mertz, 1969).

Soils were dosed with 192 uM Cr(VI) at pH 3 and pH 6.6, in 40 g/L suspensions of soil in groundwater. Suspensions were centrifuged after 24 hours of reaction, then supernatants were decanted, filtered and analyzed as in adsorption experiments. Twenty five mL of digestion solution were then used to wash and quantitatively transfer soil plugs from the tubes into 50 mL pyrex beakers. Soil-digestion solution mixtures were then heated to near boiling for one hour, cooled, and filtered into 100 mL pyrex volumetric flasks, brought to volume, and analyzed for Cr(VI) and total Cr. Duplicate samples and blanks were carried through the entire procedure at both adsorption pH values.

Colorimetric analysis for Cr(VI) was complicated by high concentrations of humic matter which were liberated from the soil during the digestion. See "Analytical Methods".

Acid Digestion (Mass Balance Verification, Part 2): In order to verify the mass balance technique used to determine masses of chromium adsorbed (initial mass in solution minus final mass in solution equals mass adsorbed), the nitric acid-sulfuric acid digestion (ASTM, 1986), was used to recover all adsorbed chromium from four soil samples.

These soils had previously been reacted with Cr(VI) for 24 hours (initial Cr(VI) concentration, 192 uM; 40 g soil/L; two suspensions at pH 2.7, two at pH 7.0), then run through the citrate-dithionite extraction procedure.

4.3.6 Soil Titration Analysis for Determining pH_{pzc}

The pH point-of-zero-charge (pH_{pzc}) is defined as the pH value at which the total net charge on the surface of a solid particle is zero (Sposito, 1984). This value is commonly estimated by soil titration tests performed in background electrolyte solutions at two or more ionic strengths (Sposito, 1984; Stumm and Morgan, 1972). When the net surface charge is nil, the activity of adsorbed species is unaffected by ionic strength. Therefore, plots of proton or hydroxide surface densities vs. pH intersect at the pH_{pzc}.

The pH_{pzc} of the Dayton soil was determined in this manner, using solutions of 0, 0.01, and 0.10 M KCl. As in the adsorption experiments, soil-electrolyte suspensions were prepared with one gram soil and 25 mL of solution. Suspension pH values were adjusted by strong acid or base (HCl or KOH). A plot of strong acid added to suspension versus pH is shown in Figure 4.1; the pH_{pzc} is shown to be 3.75.

4.4 Analytical Methods

4.4.1. Chromium Concentration Determinations

Hexavalent chromium concentrations in solution were determined by the colorimetric method of Bartlett and Kimble (1976a). One mL of an s-diphenylcarbazide reagent solution was mixed with 1 mL of sample or standard plus 7 mL H_2O and measured for absorbance at 540 nm on a Bausch and Lomb

Spectronic 88 spectrophotometer. The reagent solution was prepared by:

i. Dissolving 200 mg s-diphenylcarbazide in 100 mL of 95% EtOH;
ii. Adding 120 mL 85% H_3PO_4 in 280 mL distilled H_2O;
iii. Adding $KMnO_4$ until pink color developed;
iv. Heating at 60°C until color disappeared.

This solution was stored at 4°C in a dark glass bottle.

This technique gave excellent standard curves, with r^2 values typically better than 0.999 when four to ten standard solutions were used. Results were repeatable within 2 uM (0.10 mg/L) for clear aqueous solutions.

Colloidal and dissolved organic material greatly decreased the precision and increased the detection limit, as the organics absorbed a significant amount of light at 540 nm. The standard additions method was used for samples with high concentrations of organic matter.

Total soluble chromium concentrations were determined by flame atomic absorption spectroscopy (AAS) using a Perkin Elmer Model 360 atomic absorption spectrophotometer. The detection limit was 1 uM (0.050 mg/L), the same as that reported by USEPA (1979). Standard curves were quite linear for concentrations below 200 uM, with r^2 values typically greater than 0.999 using four standards. Results were typically repeatable within 10% error in the optimum concentration range (10-100 uM).

Trivalent chromium concentrations were calculated by difference, by subtracting hexavalent from total concentrations. Selected solutions were digested with strongly oxidizing hot nitric and sulfuric acid solutions (ASTM, 1986) and analyzed both for Cr(VI) and total soluble Cr. Results obtained by the two analyses agreed within the limits of AAS precision, verifying the consistency of the colorimetric and AAS techniques.

4.4.2. pH

Solution pH was measured with an Orion research grade Ag/AgCl glass combination electrode (Model 91-02) with an Orion model 601a digital analyzer. The system was calibrated daily using pH 4 and pH 7 buffer solutions.

4.4.3. Other Aqueous Concentrations

Concentrations of all metals other than chromium were determined by flame AAS. Bicarbonate in the wellwater was determined by titration with 0.1 N H_2SO_4 to pH 4.8, assuming all buffering in the middle pH range to be due to inorganic carbon.

5. RESULTS

The results of the experiments described in Chapter 4 are presented in this Chapter. The presentation of results is broken up into Cr(VI) Experiments (adsorption, desorption, and extraction) and Cr(III) Experiments (adsorption, extraction). Interpretation of the results is given in Chapter 6, Discussion of Results.

5.1 Cr(VI) Experiments

5.1.1 Adsorption

Kinetics (General): Cr(VI) adsorption kinetics exhibited a diphasic behavior in which Cr(VI) was initially removed from solution relatively rapidly, then continued to be removed at a slower rate for hundreds of hours without reaching equilibrium (Figure 5.1). Cr(VI) adsorbed most rapidly within the first few minutes of reaction, and adsorption continued at relatively rapid rates for the first several hours of reaction. After 24 hours of reaction time, the removal rate had become constant, or first order, with respect to Cr(VI) concentration. This second (slow) reaction phase lasted for at least 500 hours, as shown in Figure 5.2; the logarithm of Cr(VI) concentration forms a straight line when plotted against reaction time, indicating agreement with Equation 3.5.

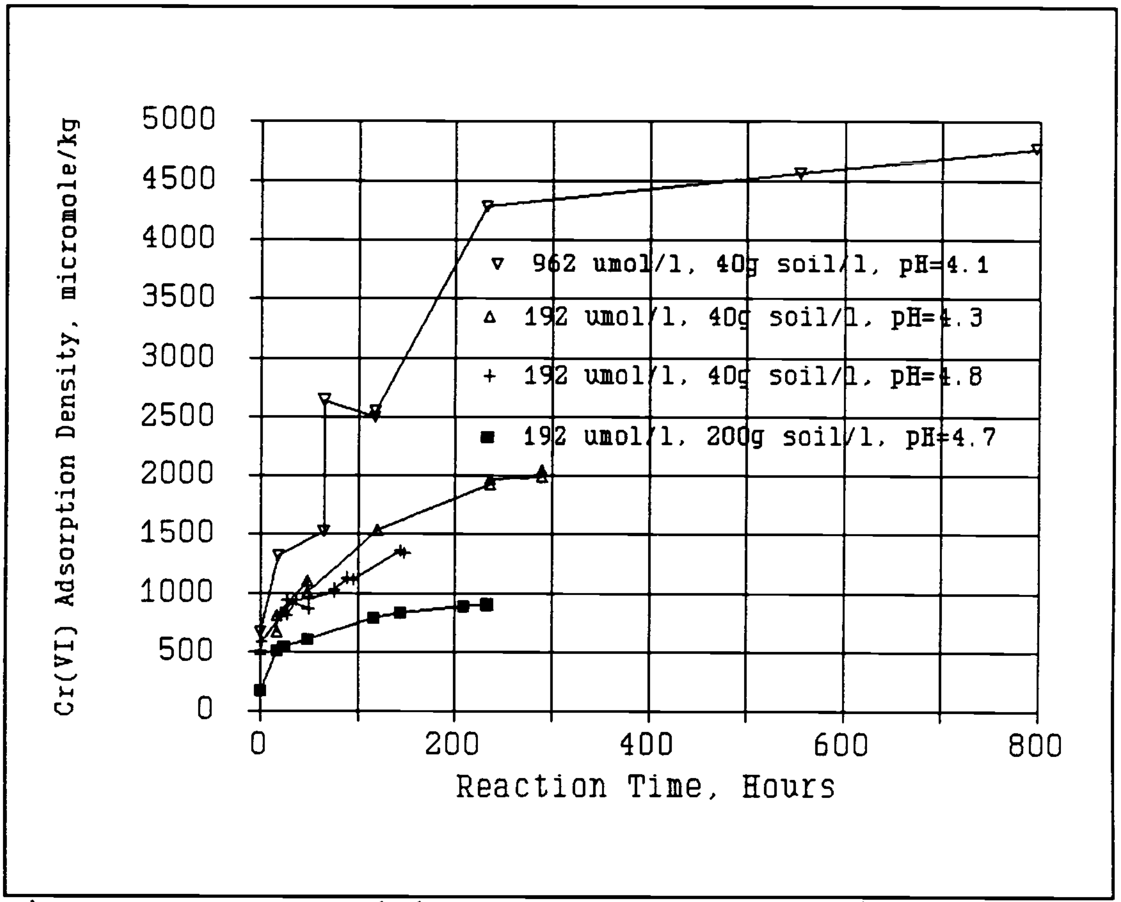

Figure 5.1: Preliminary Cr(VI) adsorption kinetics experiments: Adsorption densities vs. time in distilled water suspensions.

Slopes of the log-concentration vs. time data and log-concentration axis intercepts were determined by linear regression for each of the kinetics experiments. Psuedo-first order rate constants (k) and theoretical Cr(VI) concentrations for zero reaction time (C_0) were calculated according to Equation 3.5, and are listed in Table 5.1. Theoretical adsorption densities for zero reaction time (S_0) were calculated from C_0 values and are also given in Table 5.1. Though C_0 and S_0 are not the actual initial Cr(VI) concentration and adsorption density values, they are useful

Table 5.1: Results of linear regression of logarithmic Cr(VI) concentrations vs. reaction time. S_0 calculated from C_0 (see Equation 3.5). Actual adsorption densities after one hour reaction time (S_{1h}) included for comparison.

Cr(VI) Dose, umol/l	Cr(VI) Dose, umol/kg	pH	r^2	1000x k_1', 1/Hr	S_0, umol/kg	S_{1h}, umol/kg
192 (DW)	962	4.7	0.9990	9.74	423	---
192 "	4808	4.8	0.9754	1.06	756	---
192 "	4808	4.3	0.9765	1.61	827	582
962 "	24040	4.1	0.8916	0.64	1044	---
192 (GW)	4808	3.0	0.9985	7.56	940	624
192 "	4808	4.0	0.9994	1.55	1147	545
192 "	4808	5.0	1.0000	0.88	815	466
192 "	4808	6.0	0.9999	0.47	559	387
192 "	4808	7.0	0.9999	0.20	324	307
192 "	4808	8.0	0.9999	0.05	131	228

DW = Distilled Water, GW = Groundwater

in characterizing the systems. In those cases where data were available, experimentally determined (actual) adsorption densities after one hour of reaction time (S_{1h}) were also included in Table 5.1 for comparison with the calculated S_0 values.

k_1', C_0, and S_0 varied with Cr(VI) dose, soil concentration, and pH. k_1' increased 1000%, but S_0 decreased by 33%, when soil concentration increased 500% (same Cr(VI) dose and pH). Conversely, k_1' decreased by 60% and S_0 increased by 26% when Cr(VI) dose was increased 500% (same soil concentration, similar pH values). Both k_1' and S_0 increased as pH decreased (same soil concentration and Cr(VI) dose). In all systems of pH less than seven (7), S_0 was greater than S_{1h}; above pH=7, S_{1h} was slightly greater than S_0.

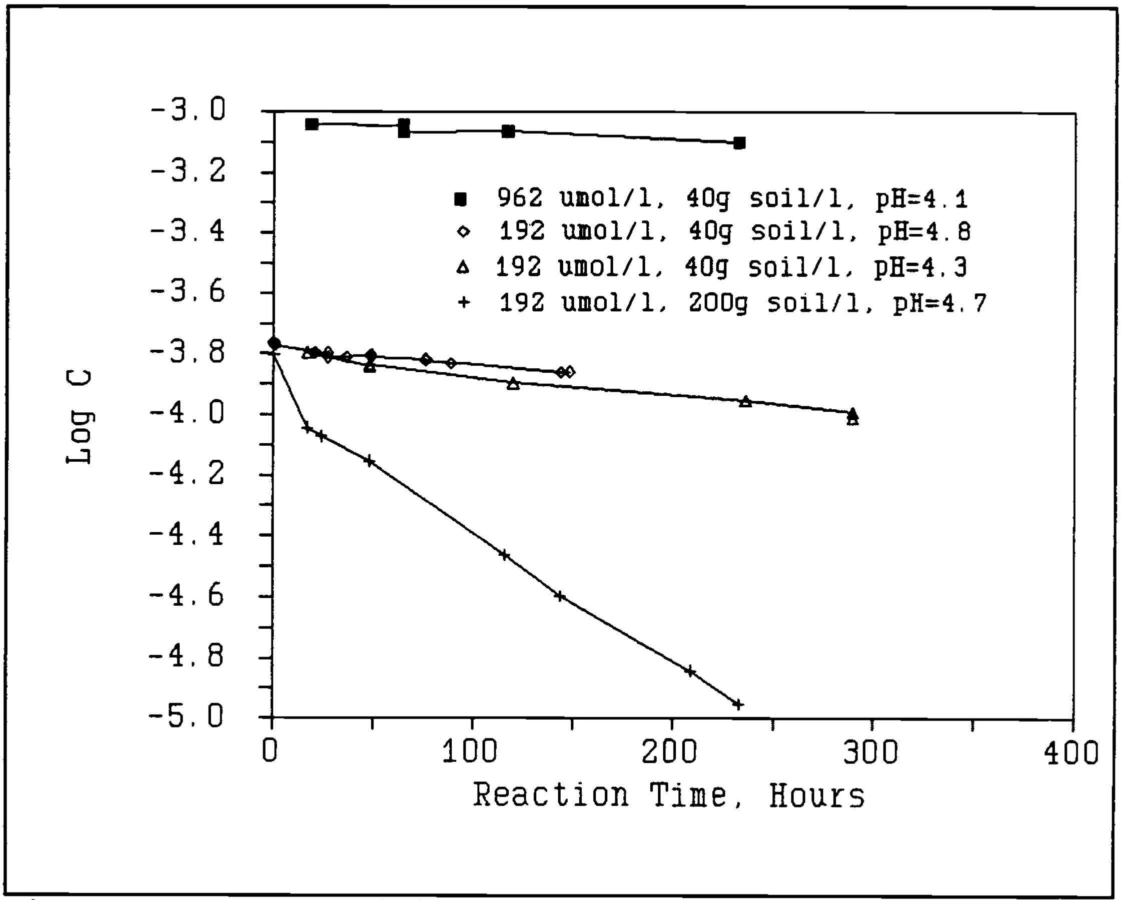

Figure 5.2: Preliminary Cr(VI) adsorption kinetics experiments: Log-concentration vs. time.

In Experiment 1d, Cr(VI) uptake continued for 796 hours, but adsorption densities after 554 and 796 hours of reaction time were significantly lower than predicted by extrapolation of 18-233 hour reaction time data using Equation 3.5.

Effect of pH: As pH increased, both the rate and mass of Cr(VI) adsorbed (adsorption density) decreased. This is illustrated in Figure 5.3, which shows Cr(VI) adsorption density vs. pH for reaction times ranging from 15 minutes to 500 hours.

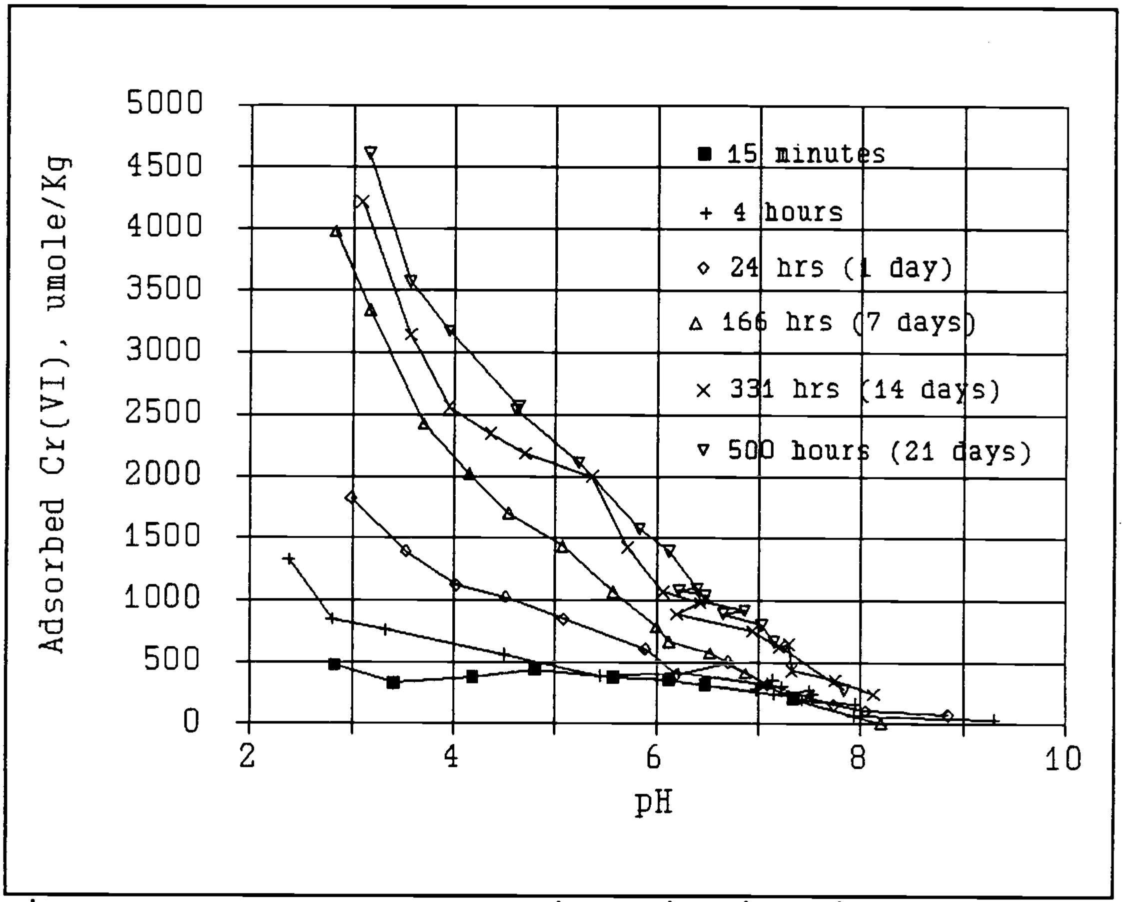

Figure 5.3: Cr(VI) adsorption kinetics in groundwater suspensions: Adsorption vs. pH at various reaction times.

Adsorption density and solution concentration values were determined for selected pH values and at various reaction times values by interpolation of adsorption edges. Figure 5.4 shows Cr(VI) adsorption as a function of time at several pH values. As in the general kinetics experiments, adsorption at each of the selected pH values followed first order kinetics. k, C_0, and S_0, and S_{1h} were determined as in the general kinetics experiments, and are given in Table 5.1.

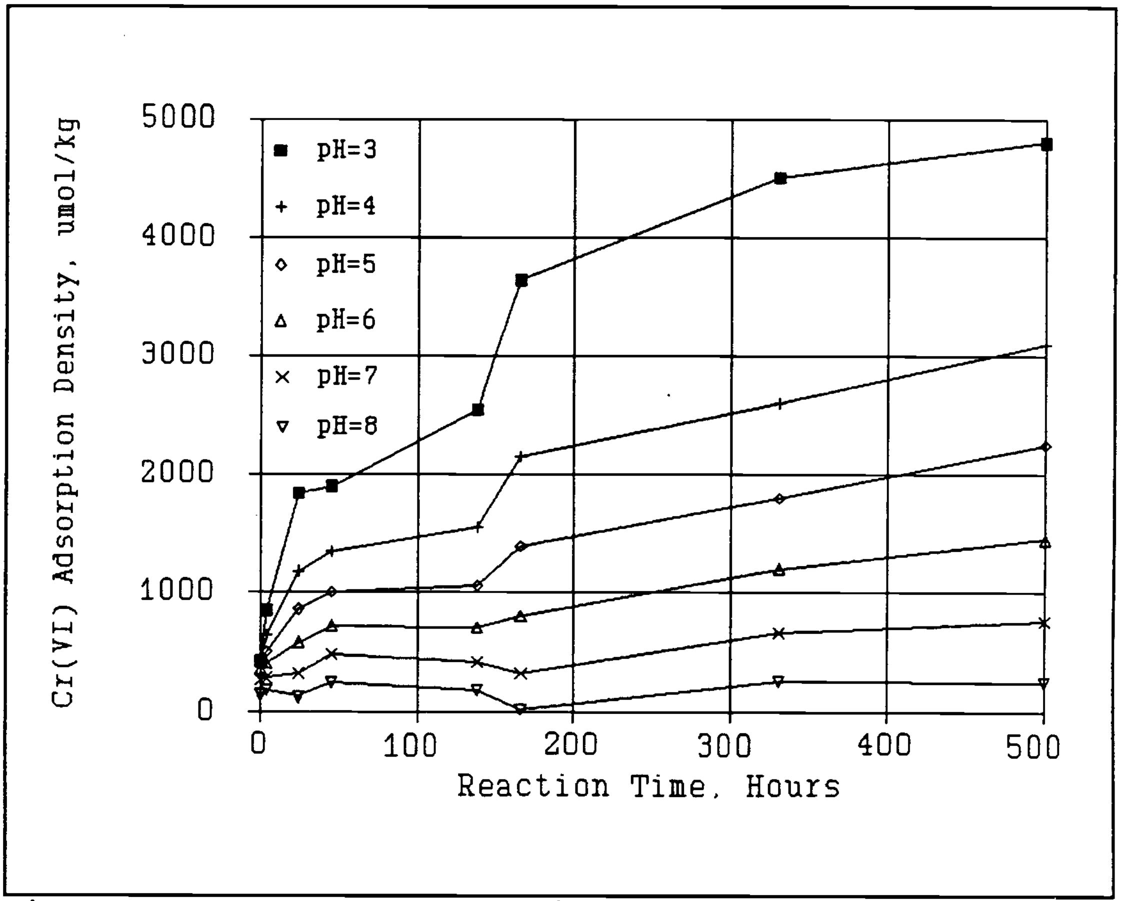

Figure 5.4: Cr(VI) adsorption kinetics in groundwater suspensions: Adsorption vs. time at selected pH values.

Effect of Cr(VI) Concentration on Rapid Phase Adsorption: Figure 5.5 shows adsorption edges for the five systems of varying Cr(VI) dose after one hour reaction time. Adsorption density vs. Cr(VI) concentration data were interpolated from these edges at selected pH values and fitted to the linear, Freundlich, and Langmuir isotherms. Best-fit parameters are listed for each model in Table 5.2, at a number of selected pH values. The linear equation (S=KC), with one fitting parameter, had the lowest r^2 values, indicating a better fit to the data than either of the two-parameter models.

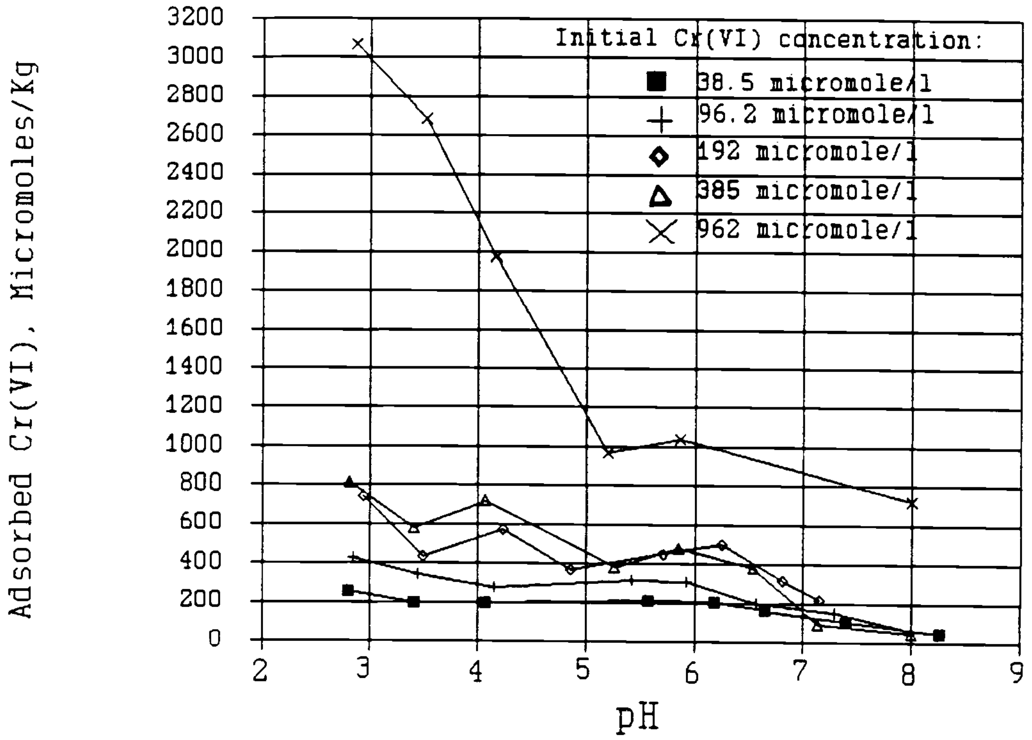

Figure 5.5: Cr(VI) adsorption after one hour reaction time in groundwater suspensions and at varying Cr(VI) doses vs. pH.

Figure 5.6 illustrates the fit of the three models to the data at pH 4. As Cr(VI) concentration increases from 0 to 400 uM, the ratio of adsorption density to Cr(VI) concentration decreases, and the slope "flattens out". In this concentration range, the data are best described by the Langmuir equation. But at higher concentrations, adsorption density increased sharply with increasing Cr(VI) concentration, in marked contrast to both Langmuir and Freundlich isotherms. Similar results were observed at all

Table 5.2: Linear, Freundlich and Langmuir isotherm parameters: One-hour reaction time for Cr(VI) in groundwater-soil suspensions.

	Linear			Freundlich		
pH	k, l/kg	b, umol/kg	r^2	K_f, l/kg	n	r^2
3	3.34	26	0.976	51.9	0.47	0.994
4	2.25	98	0.981	49.2	0.45	0.985
5	1.01	142	0.893	46.3	0.42	0.973
6	0.90	141	0.974	45.8	0.37	0.926
7	0.82	80	0.947	55.8	0.26	0.750
8	0.70	26	0.898	----	----	----

	Langmuir, All Data			Langmuir, Omitting 962 umol/l Dose Data		
pH	K_L umol/l	Smax, umol/kg	r^2	K_L, umol/l	Smax, umol/kg	r^2
3	1270	5940	0.443	99.7	992	0.996
4	883	3580	0.587	88.7	796	0.996
5	389	1492	0.869	72.1	602	0.993
6	461	1297	0.768	48.5	414	0.986
7	650	1169	0.529	11.8	233	0.971
8	1073	841	0.219	-45.9	71	0.998

pH values. A multi-layer isotherm such as the B.E.T. might describe the data better, but there are not sufficient data at the higher concentrations to justify the use of this complex model.

Effect of Solution Composition: Below pH 5, adsorption was equivalent in distilled water-soil suspensions and groundwater-soil suspensions. Above pH 5, Cr(VI) adsorption densities were lower in the distilled water systems. Comparative adsorption edges are shown in Figure 5.7.

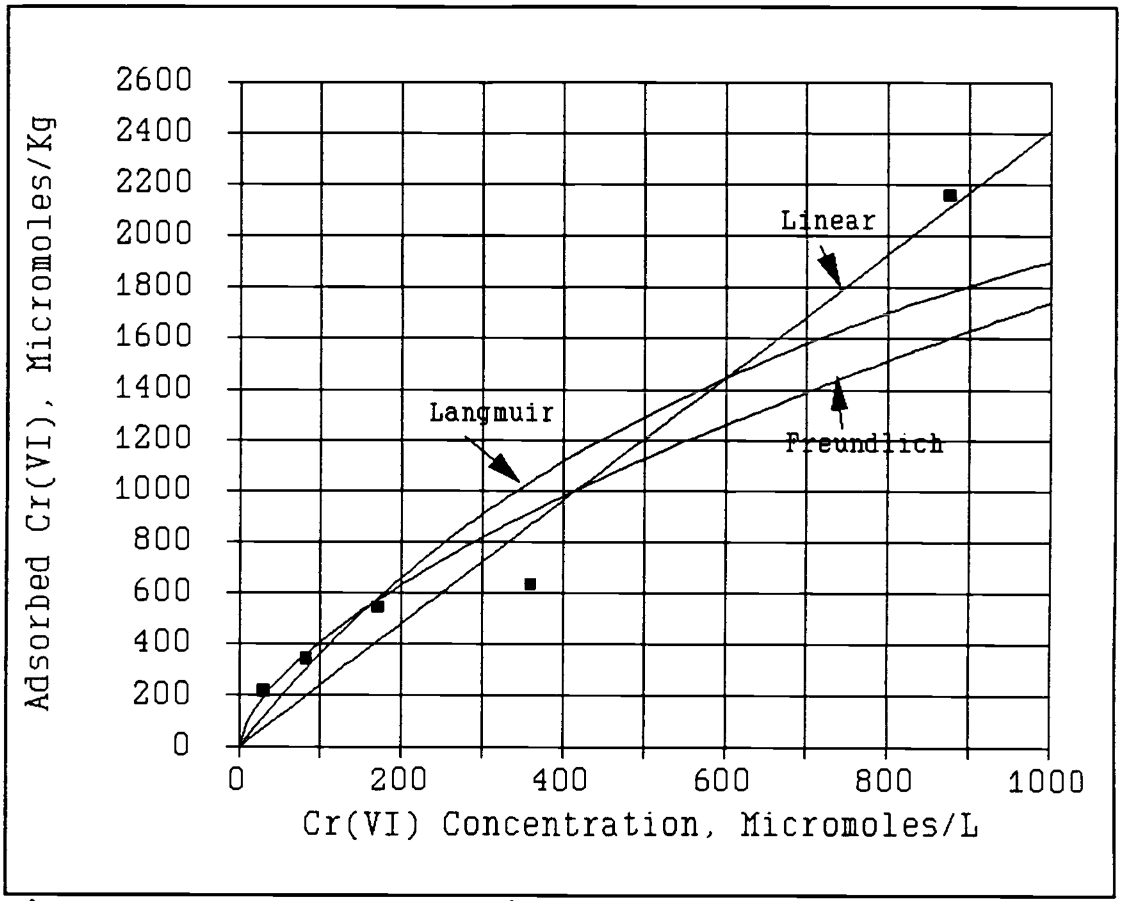

Figure 5.6: Cr(VI) adsorption after one hour reaction time in groundwater suspensions at pH 4: Best fit of Linear, Freundlich, and Langmuir isotherms.

5.1.2 Desorption

As shown by the adsorption edges in Figure 5.8, Cr(VI) adsorption density did not decrease at any pH value when suspensions were diluted with wellwater. Adsorption densities in all of the diluted suspensions were equal to or higher than the adsorption density in the 200 g/L suspensions at the same pH values. Adsorption densities were somewhat higher in suspensions that had reacted for 14 or 20 days after dilution than those which had reacted for 15 minutes or for 7 days

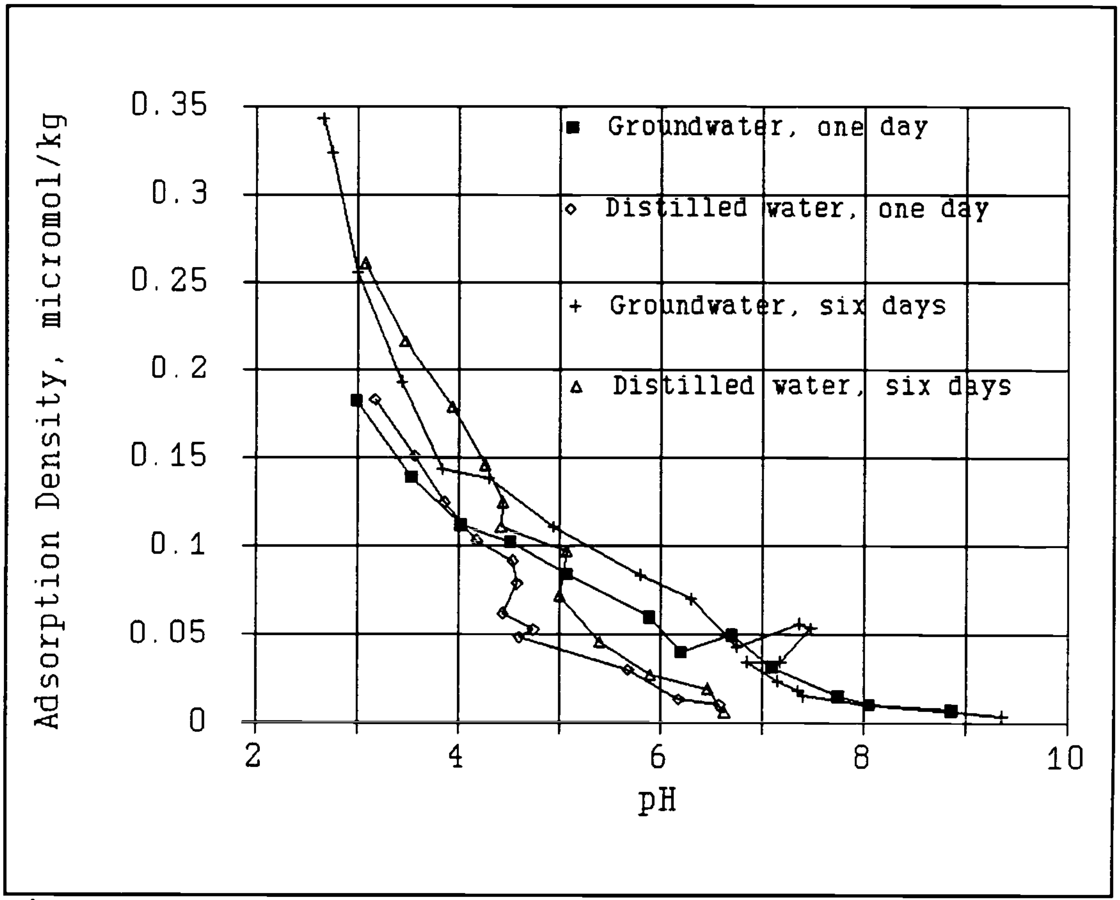

Figure 5.7: Cr(VI) adsorption: Distilled water suspensions compared to groundwater suspensions.

after dilution, indicating that Cr(VI) adsorption continued to occurr after dilution.

Suspension pH values varied to some degree when diluted with groundwater, and they continued to change during the desorption phase (after dilution) of the experiment. pH values increased immediately when dilution water was added, then decreased slowly with time during the desorption phase. As was shown earlier, the Cr(VI) adsorption rate varies with pH. Thus, the sharp pH change that occurred during dilution, along with the slow pH drift afterwards, complicates analysis

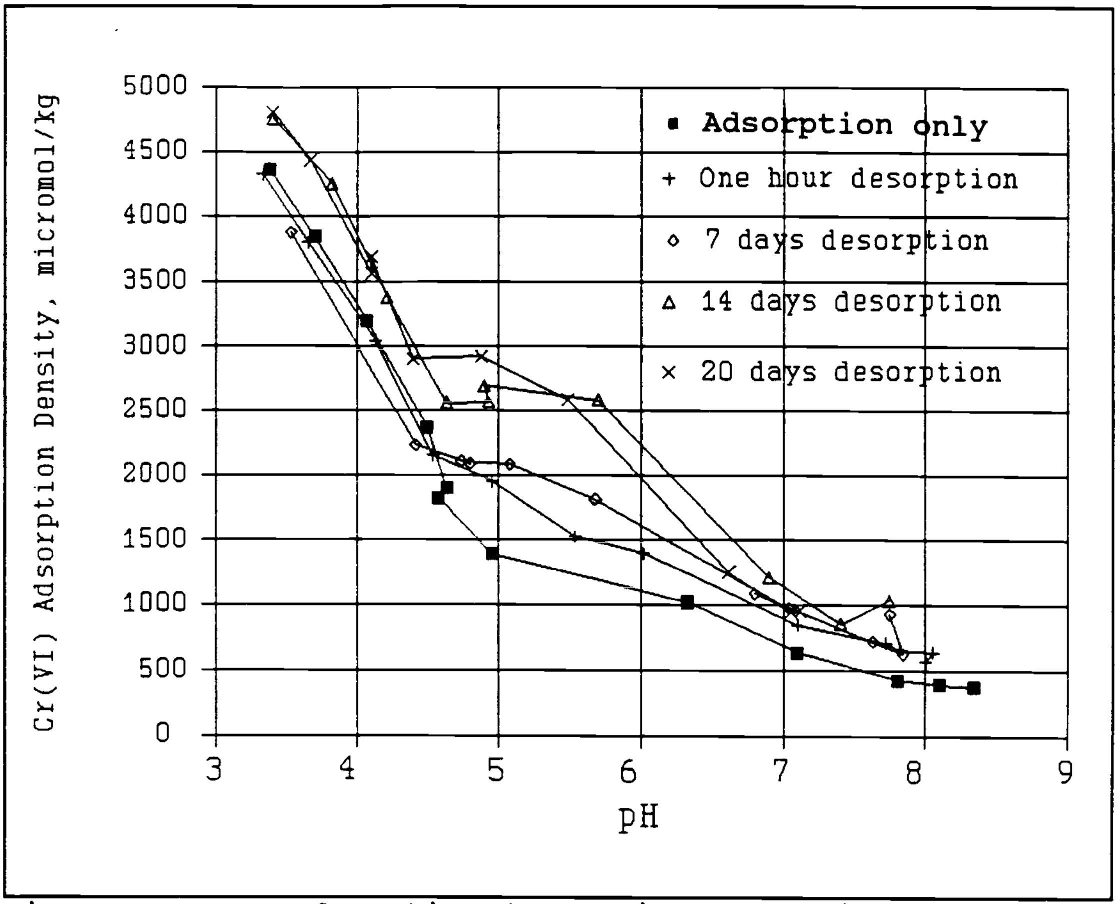

Figure 5.8: Adsorption-desorption experiment: Cr(VI) adsorption densities before and after dilution.

of the desorption experiment data.

5.1.3 **Distilled Water/Phosphate Solution Extraction**

The distilled water extraction removed very little Cr(VI) from the soil. More significant amounts of Cr(VI) were extracted by the phosphate solution. While the total Cr(VI) adsorption density increased with reaction time, the density of phosphate extractable Cr(VI) remained roughly constant at about 250 umol/kg (5% of the total chromium present) over the duration of the experiment (Figure 5.9). Thus, as a percent

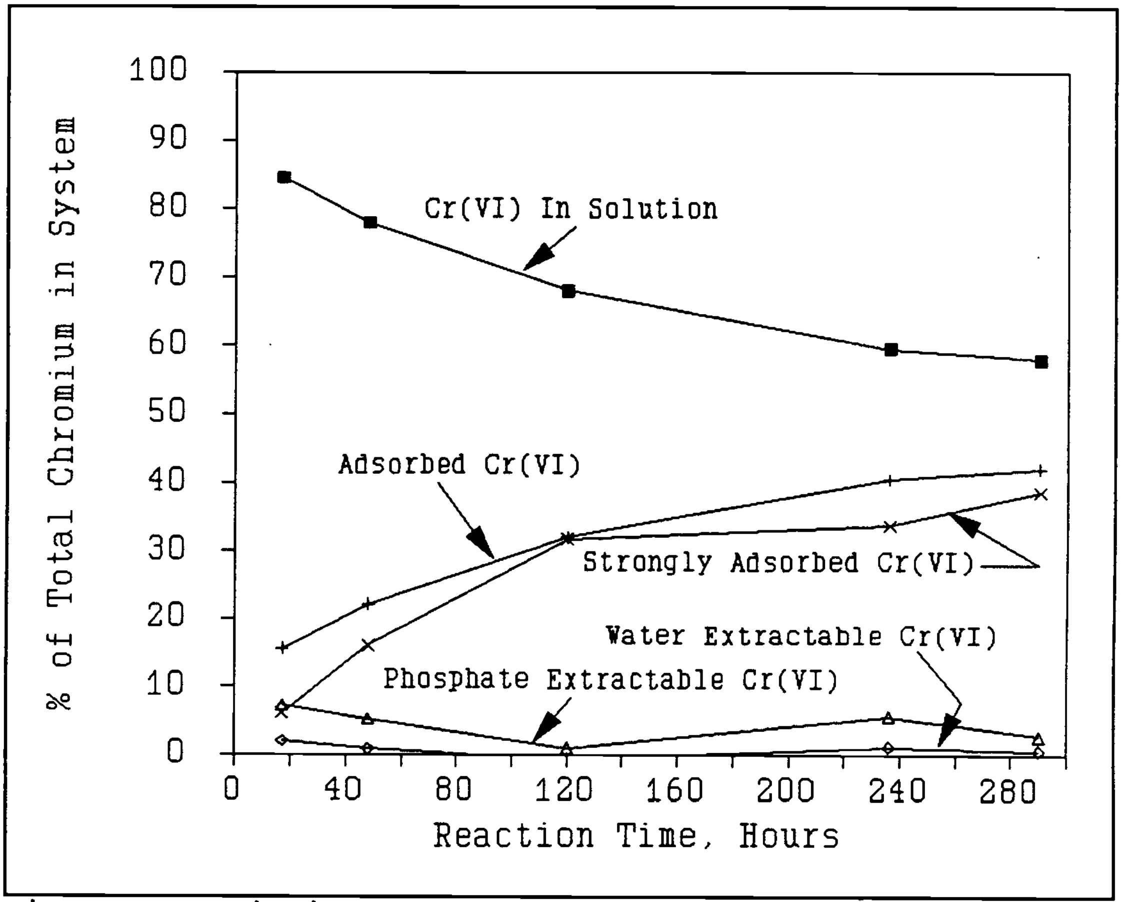

Figure 5.9: Distilled water/phosphate extraction of Cr(VI).

of the total mass of Cr(VI) adsorbed, the phosphate extractable fraction decreased with time. At 17 hours reaction time, over 50% of the adsorbed chromium was extractable by either water or phosphate. At 290 hours reaction time, only 12.5% of the adsorbed chromium was distilled water or phosphate extractable.

5.1.4 Alkaline Digestion

Little Cr(VI) or total Cr was detected in the digestion solutions, and most of this was attributed to soluble Cr(VI) and Cr contributed by the pore water carried over with the soil plugs after decantation (see Table 5.3). These results indicate that little Cr(VI) was removed from the soil by the alkaline digestion procedure.

Table 5.3: Alkaline digestion experiment. Cr(VI) was dosed at 4,800 umol/kg soil (192 umol/l).

	Cr(VI) Adsorbed, umol/kg	Cr(VI) Removed, umol/kg	Digestion % Removal Efficiency
Sample 1 (pH=3)	1540	100	6
Sample 2 "	1590	40	2
Sample 3 (pH=6)	410	20	5
Sample 4 "	330	0	0

5.1.5 Citrate-Dithionite Extraction/Acid Digestion

The citrate-dithionite extraction removed two thirds of the adsorbed Cr(VI) from the soils reacted at pH 2.7; the acid digestion removed all the remaining chromium. All of the Cr(VI) that had adsorbed at pH 7.0 was extracted in the citrate-dithionite procedure. The sum of the masses (unreacted Cr(VI) + dithionite extractable + acid digested chromium) came within 2% of the initial Cr(VI) dose (Table 5.4). These results verify the mass balance assumptions used for determining masses of chromium adsorbed.

Table 5.4: Dithionite extraction and acid digestion (mass balance verification) results: soluble, dithionite extractable, and recoverable Cr(VI) expressed as percentages of Cr(VI) dosed.

pH	% Soluble	% Adsorbed	% Extracted by Dithionite	% Recovered by Acid	% Soluble + Extracted + Recovered
2.7	71.4	28.6	17.7	9.7	98.8%
2.7	73.0	27.0	17.6	9.9	100.5%
7.0	90.0	10.0	7.5	2.0	99.5%
7.0	90.0	10.0	7.4	1.1	98.5%

5.2 Cr(III) Experiments

5.2.1 Adsorption

No Cr(VI) was detected in any of the Cr(III) experiment solutions.

Kinetics, pH 4.8: Over 96% of the Cr(III) dosed had adsorbed within 15 minutes of reaction time in the 200 g soil/L suspensions. After 15 minutes, adsorption continued at a much slower rate. Ninety nine percent (99%) had adsorbed within six hours reaction time. Between 15 minutes and six hours reaction time, the rate of Cr(III) adsorption appeared to be first order with respect to Cr(III) concentration. Agreement with Equation 3.5 could not be verified, however, as Cr(III) concentrations (2-5 uM) were approaching the AAS detection limit (1 uM), leading to large relative errors.

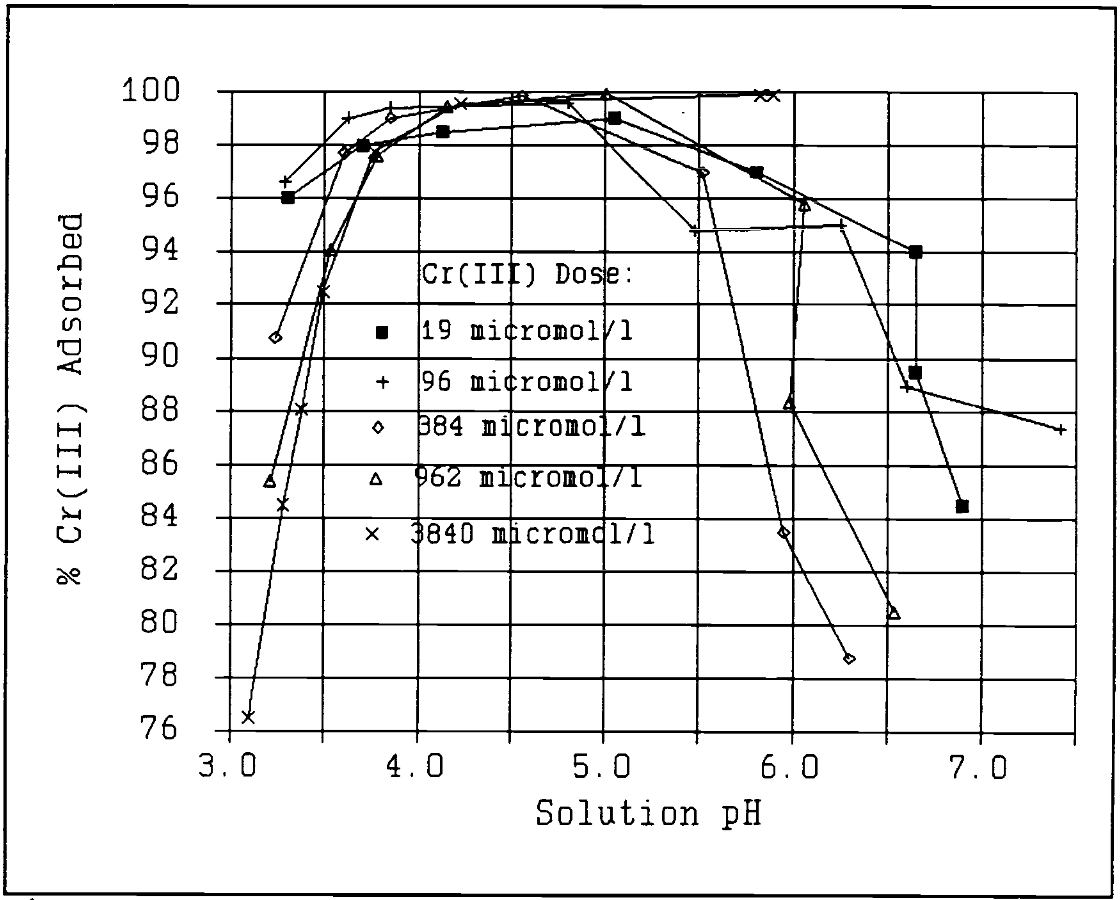

Figure 5.10: Cr(III) adsorption edges for varying Cr(III) doses.

Effect of pH: Cr(III) adsorption edges are shown in Figure 5.10. Total chromium concentrations of some samples were below the detection limit (1 uM) and could not be determined by flame AAS. In some of the suspensions dosed at 19 uM, 98% adsorption or higher (0.4 uM or less Cr(III)) was estimated, though no more than 95% adsorption could be verified within the certainty of the analytical method. Despite the uncertainty regarding the total chromium concentrations of these samples, they help illustrate the qualitative dependence of adsorption on pH.

At low pH values (< 4.5), adsorption edges for the two highest Cr(III) doses (962 and 3840 uM) were nearly indistinguishable, but at lower doses (19, 96, and 384 uM), percent Cr(III) adsorption increased as dose decreased. Between the pH values four (4) and five (5), nearly all Cr(III) was removed from solution, with at least 98% adsorbed for all Cr(III) doses. Above pH=5, percent Cr(III) adsorption decreased with increasing pH for all Cr(III) doses except perhaps the highest dose. As in other experiments, increasing color indicated increasing concentrations of organic substances were released as pH increased. This also was observed for all Cr(III) doses but the highest; no color was observed in any suspensions dosed at 3840 uM, though suspension pH values were as high as 5.9.

In Figure 5.11, the data are plotted in terms of logarithmic Cr(III) concentrations (log-C) vs. pH (recall that the Cr(III) detection limit is 1 uM, or -6 on the log-C scale; log-C values less than -6 are only estimates, but are included for qualitative analysis). Below pH=5 (and for log-C > -6), log-C vs. pH data form relatively straight lines for each experiment. The slopes of the lines best fitting the log-C vs. pH data were determined by linear regression and are as follows:

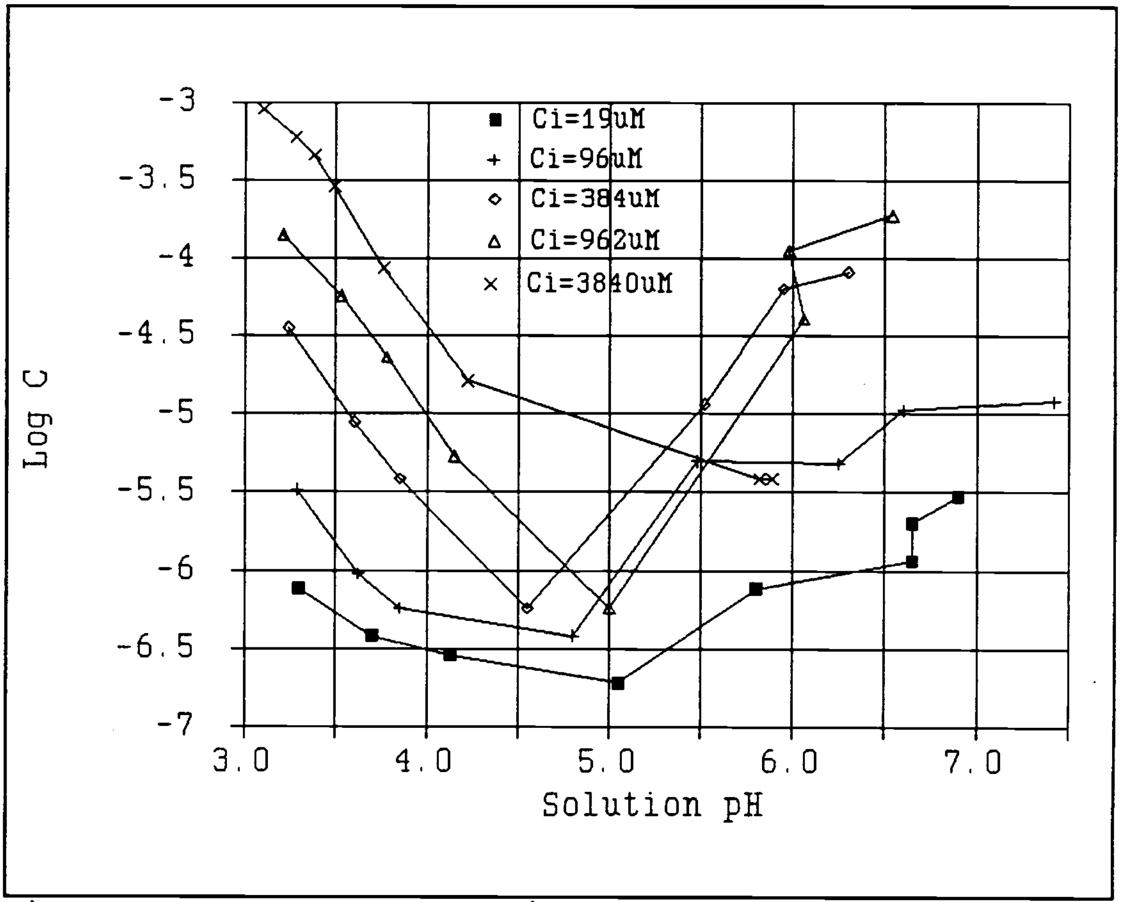

Figure 5.11: Cr(III) adsorption: Log-concentration vs. pH at various Cr(III) doses.

Cr(III) Dose	Log-C vs. pH Slope	r^2
96 uM	-1.36	0.98279
384 "	-1.35	0.99192
962 "	-1.36	0.99337
3840 "	-1.63	0.99226

An isotherm was constructed from the adsorption edge data at pH=4.0, and is shown in Figure 5.12.

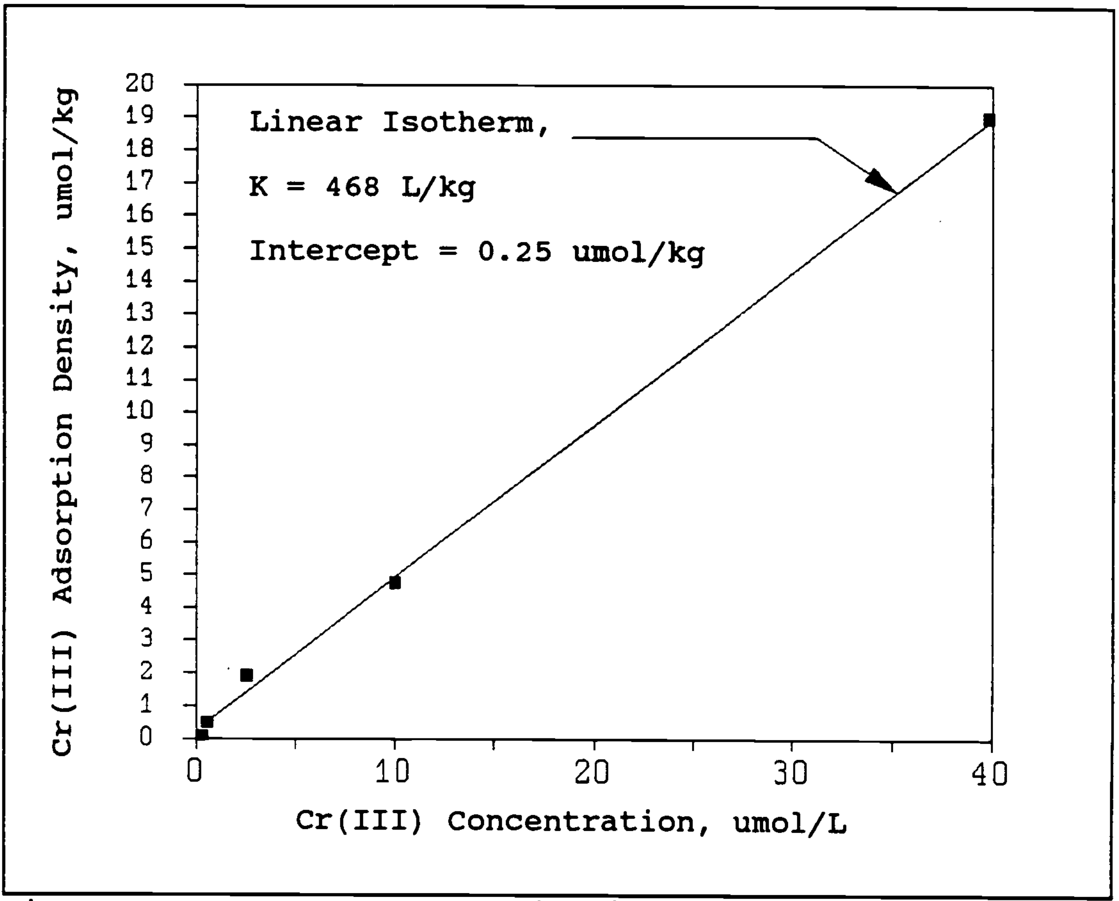

Figure 5.12: Cr(III) adsorption isotherm at pH=4 after five days of reaction time in distilled water suspensions.

5.2.2 EDTA Extraction

Table 5.5 lists the mass and percent Cr(III) adsorbed after 24 hours reaction time, the mass and percent of the adsorbed Cr(III) extracted by EDTA, and the mass of iron extracted by EDTA. At the lower Cr(III) dose (4.81 umol/g soil), 100% of the dosed Cr(III) adsorbed to the soil. Only 51.9% adsorbed at the higher Cr(III) dose (48.1 umol/g soil), yet the mass adsorbed was more than five times higher than in the low dose system. Despite these differences in mass and percent Cr(III) adsorbed, the EDTA extraction removed roughly the same fraction (5-6%) of the adsorbed Cr(III) from soil at the two Cr(III) doses.

The amount of iron EDTA extracted from the soil varied with Cr(III) dose. Thirty eight percent (38%) less iron was extracted from the high Cr(III) dosed soil than from the low dosed soil.

Table 5.5: EDTA extraction of Cr(III) from soil.

Cr(III) Dose, umol/kg	Cr(III) Adsorbed, umol/kg	% Cr(III) Adsorbed	Cr(III) Extracted, umol/kg	% Extraction Efficiency
4,810	4,810	100	250	5.2
48,100	25,000	52	1,490	6.0

6. DISCUSSION OF RESULTS

6.1 Cr(VI) Adsorption

6.1.1 Adsorption Kinetics

The adsorption kinetics data follow the two-phase sequence described by Wu and Gschwend (1986) and others (see "Modeling Adsorption Kinetics" in Literature Review), with adsorption proceeding rapidly at first, then at a slower rate at longer reaction times.

Rapid Adsorption Phase: It is likely that several reactions of varying binding energies are involved in the rapid uptake phase. Given sufficient data, this rapid phase might be described as a series of first-order adsorption reactions, as done by Harter and Lehmann (1983) with the rapid adsorption of copper and nickel to soil. However, further characterization of the rapid phase reaction kinetics would not reveal the type(s) of reaction occurring. Inclusion of additional adsorption reactions would not significantly improve the predictive value of the adsorption model.

The isotherms prepared from one-hour reaction time data did not clearly characterize the relationship between Cr(VI) concentration and rapid phase adsorption density, although it was determined that the simple linear isotherm model described the system more accurately than either the Langmuir or

Freundlich models.

Slow Adsorption Phase: The pseudo-first order adsorption reaction becomes predominant after four (4) to 24 hours reaction time, after most of the higher energy adsorption reaction sites had been occupied or had reached equilibrium with soluble Cr(VI). According to the model described in Chapter 3, this adsorption reaction is maintained at a constant rate (with respect to soluble Cr(VI) concentration) by a relatively constant "concentration" of reactive soil sites, X, of roughly equal reactivity with respect to Cr(VI).

The declining adsorption rate (with respect to soluble Cr(VI) concentration) observed in Experiment 1d can be explained using Equation 3.3. The number of reactive soil sites, X, might have decreased significantly due to reaction, causing the psuedo-first order rate "constant", $k_1' = k_1X$, to decrease as well. Alternatively, Cr(VI) adsorption density may have become high enough that the desorption term of Equation 3.3 had become significant. Either or both of these situations would decrease the adsorption rate with respect to soluble Cr(VI) concentration.

6.1.2 Chemical Nature of Cr(VI) Adsorption

Effect of pH: Both rapid and long-term adsorption of Cr(VI) increased as pH decreased. The same tendency has been reported for Cr(VI) adsorption to soil, clays, and metal hydroxides (Bartlett and Kimble, 1976b; Griffin et al, 1977; Zachara et al, 1987).

Qualitatively, the pH dependence of Cr(VI) adsorption to the Dayton clayey-silt soil (reaction times of several days to several weeks) closely resembles that of Cr(VI) adsorption to suspensions of amorphous iron oxyhydroxide with aged silica, but is significantly different than that of silica-free amorphous iron hydroxide suspensions (Zachara et al, 1986). Though Cr(VI) adsorption to silica-free iron hydroxide suspensions also decreased with increasing pH, adsorption edges had the classical "S" shape, with nearly 100% adsorption at pH 6 and practically no adsorption at pH 8. In contrast, the adsorption edges for the Dayton soil and iron hydroxide-silica suspensions are concave upward, with adsorption rising steadily as pH decreases (Figure 5.3).

Adsorption edges for the Dayton soil resembled those of kaolinite and montmorillonite quantitatively as well as qualitatively (Griffin et al, 1977). Adsorption densities in the soil after two weeks of reaction were slightly greater than in kaolinite suspensions and slightly lower than in montmorillonite suspensions at similar solids concentrations, Cr(VI) concentrations, and reaction times. Adsorption maxima were not observed at intermediate pH values, as was reported for activated carbon (Huang and Wu, 1977).

Similar adsorption tendencies with respect to pH may indicate similar adsorption mechanisms, i.e., coordination with iron oxide surfaces. Cr(VI) adsorption characteristics of the Dayton soil most closely resemble those of impure clays and amorphous iron hydroxide-silica suspensions. Each of these substrates contains amorphous iron hydroxides and silica. The soil and clays also contain some organic matter (5% in the Dayton soil, 0.51 and 0.92% for the kaolinite and montmorillonite, respectively), but the iron hydroxide-aged silica suspensions did not. Without a suitable electron donor, reduction of Cr(VI) could not have taken place in that system. The similarities of these systems indicate that Cr(VI) adsorption in each takes place by anion exchange or surface complexation with iron hydroxide surface sites, and is influenced by the presence of silica (Griffin et al, 1977; Zachara et al, 1987).

However, as mentioned earlier, Grove and Ellis (1980) disputed Griffin's conclusion that anion exchange accounted for Cr(VI) adsorption to clays, claiming that a reductive mechanism was more likely in both soils and clays. Others conclude that both adsorption and exchange can contribute to Cr(VI) adsorption in the same soil (Bartlett and Kimble, 1976a & b; Bartlett and James, 1979; James and Bartlett, 1983a, b, & c; see Literature Review).

Ionic Effects: No differences between distilled water and groundwater suspensions were observed below pH=5. Above pH=5, adsorption was higher in soil-groundwater suspensions than in soil-distilled water suspensions (Figure 5.7), although the groundwater contained 5 uM inorganic carbon as bicarbonate ion. Bicarbonate and dissolved CO_2 compete with bichromate ($HCrO_4^-$) for coordination sites on iron oxyhydroxide (Zachara et al, 1986). Anionic competition for soil adsorption sites may have occurred, but competitive effects were not sufficient to cause net Cr(VI) adsorption to decrease. The net increase in Cr(VI) adsorption may have been caused by diffuse double layer compression by the groundwater ionic species, or by primary charge reduction of the soil by adsorbed groundwater cations (Griffin et al, 1977). Concentrations of the divalent cations Ca^{2+} and Mg^{2+} were 1.4 and 1.1 mM, respectively; similar concentrations of these ions have been shown to cause destabilization of colloidal matter in natural waters (Weber, 1972).

Desorption/Extractions: Little or no adsorbed chromium was removed by the distilled water extraction or by dilution with groundwater, indicating that the adsorbed Cr(VI) was strongly bound by the soil.

Phosphate extraction indicated that at least 200 to 300 umol of Cr(VI) per kg soil had not been reduced, but remained in anion exchangeable form after adsorption. The amount of phosphate extractable Cr(VI) remained roughly constant throughout the experiment, indicating that most or all of it had adsorbed during the rapid, initial uptake phase of reaction. In contrast with Cr(VI) adsorbed during the second phase of adsorption, most of the rapidly adsorbed Cr(VI) was phosphate extractable.

Orthophosphate ($H_2PO_4^-$) and bichromate ion ($HCrO_4^-$) are geometrically similar, and probably compete for anion exchange sites. Orthophosphate solutions of similar strength also displaced adsorbed Cr(VI) from other soils (Bartlett and Kimble, 1976b) and dramatically decreased Cr(VI) adsorption to inorganic alluvium (Stollenwerk and Grove, 1985). The fact that this strongly competitive anion removes little or none of the Cr(VI) adsorbed during the second adsorption phase suggests an irreversible reaction.

A possible mechanism for the apparently irreversible adsorption of Cr(VI) is reduction by soil organic material to insoluble Cr(III). Grove and Ellis (1980) concluded that Cr(VI) had been reduced when 1 M Cl^- and 0.1 M SO_4^{2-} solutions failed to remove it from soil. Phosphate is much more effective than these anions in inhibiting Cr(VI) adsorption and extracting it from soil (Stollenwerk and Grove, 1980; Bartlett and Kimble, 1976b), thus there is stronger evidence of reduction in the Dayton soil than in the soils used by Grove and Ellis. No Cr(III) was detected in any of the Cr(VI) experiment solutions, but this does not necessarily indicate that Cr(III) was not present in the solid phase; as shown in the EDTA extraction experiment, adsorbed Cr(III) was difficult to remove from the Dayton soil. Thus there is neither conclusive evidence for or against Cr(VI) reduction. Most of the rapidly adsorbed Cr(VI) was removed by citrate-dithionite extraction, indicating that most or all of this chromium is associated with amorphous iron and/or manganese oxides (Grove and Ellis, 1980; Coffin, 1963).

6.1.3 Modelling Cr(VI) Adsorption

Adsorption, desorption and extraction experiments indicated that both the rapid and slow adsorption reactions were irreversible. In Figure 6.1, the simple two-site model combining irreversible rapid and slow adsorption reactions described in section 3.3 is compared with the data at a pH of 5.0. Parameters for the model (k_1') were those listed in Table 5.1. The model overestimates adsorption at short reaction times (less than a day), but fits the remaining data relatively well.

The model combining reversible rapid and slow adsorption reactions, which was described in section 3.4, was also compared to the data at pH=5. The equilibrium constant (K) used in the model was that determined in the one-hour "isotherm" experiment for pH=5. The adsorption and desorption constants (k_1' and k_2) for the reversible first order kinetic reaction were determined by trial and error to obtain a good fit to the data. The comparison of the model to the data is shown in Figure 6.2.

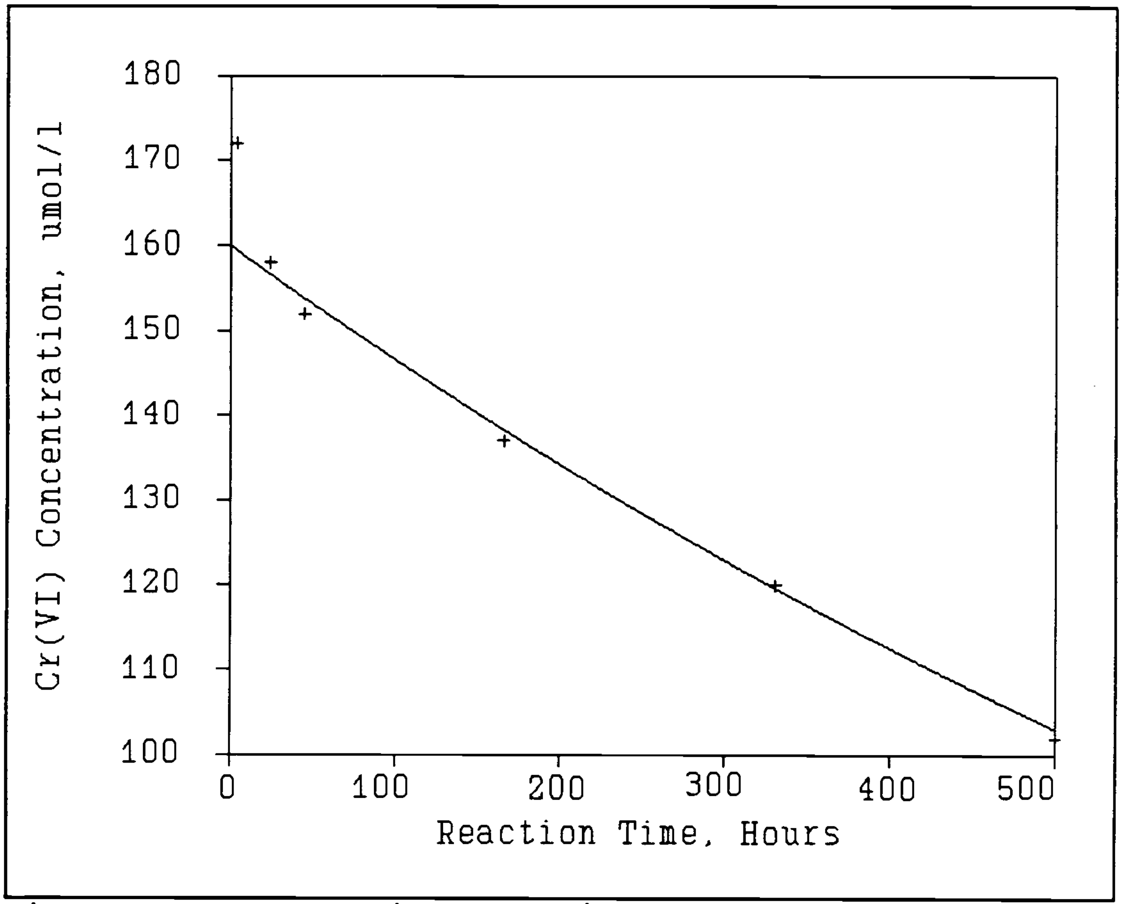

Figure 6.1: Irreversible two-site model compared to Cr(VI) adsorption data at pH=5 in groundwater supsensions.

While both models fit the data farily well, the results of the desorption and extraction experiments indicate that the model combining irreversible rapid and slow adsorption reactions is more appropriate. This model is also simpler; there are two parameters, compared to three in the model combining reversible equilibrium and kinetic adsorption reactions. Both parameters of the irreversible two-site model are derived directly from linear regression of the log-concentration versus time data, while there is not a simple way to derive the adsorption and desorption rate constants in the reversible two-site model. Based on these considerations, the irreversible two-site model is the better of the two.

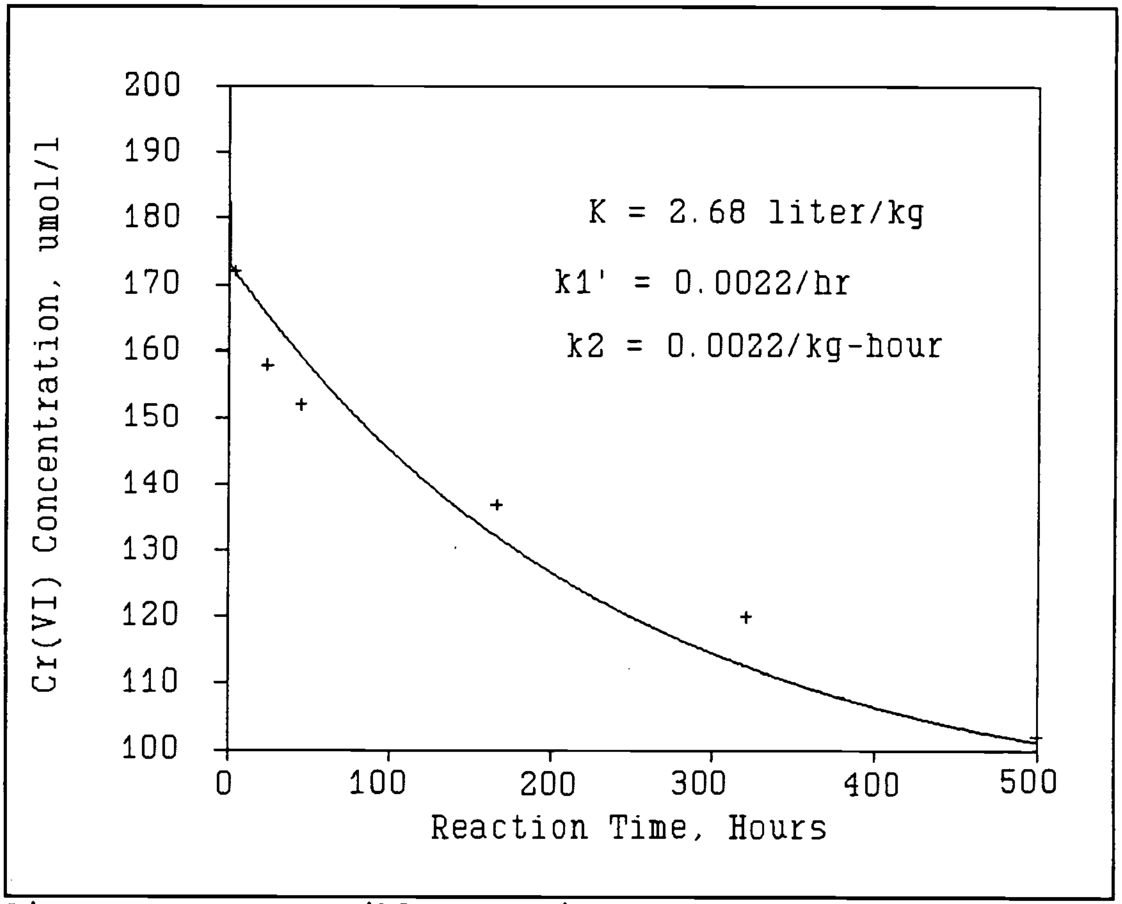

Figure 6.2: Reversible two-site model compared to Cr(VI) adsorption data at pH=5 in groundwater suspensions.

6.2 Cr(III) Adsorption

Effect of pH on Cr(III) Adsorption: The slopes of the log-C vs. pH data in the low pH range (< 5) in Figure 5.11 indicate an adsorption mechanism of the form

$$Cr(III) + Soil \Rightarrow Soil\text{-}Cr(III)\ complex + 4/3\ H^+$$

Below pH=4 (and assuming few or no organic ligands are present), the primary component of total soluble Cr(III) is Cr^{3+}; for pH values between four (4) and six (6), $CrOH^{2+}$ is the major soluble species (Figure 2.3). At these pH values, $Cr(OH)_3$ solid is not predicted to form at the Cr(III) concentrations of the adsorption edge experiments, but precipitation of a mixed ferrous-chromic hydroxide might be favored if enough Fe(II) were present. Interpreted by the surface complexation model of Stumm and Morgan (1981), the data suggest that soil oxyhydroxide surface sites adsorb roughly 4 OH^-, or releases roughly 4 protons (H^+), with every three Cr^{3+} (or $Cr(OH)^{2+}$) cations adsorbed, i.e.

$$3\ SOH_2 + 3\ Cr^{3+} = 2\ SOH\text{-}Cr^{2+} + SO\text{-}Cr^{+} + 4\ H^{+} \qquad \text{(Eqn. 6.1)}$$

Above pH 5, total Cr(III) concentrations exceed those predicted by $Cr(OH)_3(s)$ solubility calculations (Figure 2.3). The formation of anionic Cr(III)-hydroxides such as $Cr(OH)_4^-$ does not effect total Cr(III) solubility until pH is raised above 7, so the increasing Cr(III) concentrations observed above pH=5 can't be explained by such species. The soluble and colloidal organic matter observed in these samples probably complexed much of the Cr(III), protecting it from precipitation or adsorption to the soil (Nakayama et al, 1981b). The solutions of 3.84 mM initial concentrations seem to have caused flocculation and precipitation of these organics, as evidenced by the clear solutions observed in these samples at pH=5.8, suggesting that the organic material is actually colloidal in nature.

Cr(III) Extraction by EDTA: EDTA proved a relatively ineffective extractant, removing only 5% to 6% of the adsorbed Cr(III) from the soil. Iron and possibly other cationic species in the soil may have decreased the effectiveness of the extraction by competing for available EDTA; iron bound at least 10-15% of the EDTA.

Increasing Cr(III) dose decreased the amount of EDTA extractable iron. This could have been due either to competition for EDTA between Cr(III) and iron, or to Cr(III)-iron hydroxide interactions which tended to protect the iron from chelation by EDTA.

7. SUMMARY & CONCLUSIONS

7.1 Cr(VI) Adsorption

The kinetics of Cr(VI) adsorption to Dayton clayey silt soil was diphasic in nature, indicating the presence of at least two types of surface adsorption site in the soil. Adsorption was initially quite rapid, but Cr(VI) did not equilibrate with the soil even after 800 hours of reaction. The amount of Cr(VI) adsorbed during the first (rapid) and the rate of Cr(VI) adsorption during the second (slow) phase both increased as pH decreased. The presence of groundwater ions had little effect on Cr(VI) adsorption.

Much of the Cr(VI) adsorbed during the first (rapid) adsorption phase was extractable by orthophosphate and was associated with amorphous iron and manganese oxides in the soil, indicating the first phase (rapid) of adsorption phase to be a specific anion exchange reaction.

The mechanism of the second (slow) adsorption phase was not clearly identified. No net desorption of Cr(VI) was observed in either groundwater or distilled water, indicating an irreversible reaction. A strong complexation reaction with hydrous oxide soil surfaces was indicated, but Cr(VI) reduction to insoluble Cr(III) was not ruled out.

Soluble Cr(VI) did not equilibrate with suspended soil even after 800 hours of reaction time. Both the adsorption rate and the mass of Cr(VI) adsorbed increased as pH decreased.

In terms of the specific objectives listed in Chapter 1, the following conclusions were drawn:

1. Cr(VI) adsorption to the Dayton soil increases, both in rate and magnitude, with decreasing pH;

2. Little or no adsorbed Cr(VI) was removed from the Dayton soil by distilled water or groundwater, but some adsorbed Cr(VI) was extracted with a phosphate solution. Cr(VI) adsorption to the Dayton soil is not greatly effected by the presence of common groundwater ions;

3. Cr(VI) adsorption to the Dayton soil can be described by a two-site, equilibrium/kinetic adsorption model.

4. The rapid adsorption reaction was thought to be an anion exchange reaction; the slow adsorption reaction may have been either strong complexation to soil hydrous oxide surface sites or reduction to insoluble Cr(III) by soil organic matter.

7.2 Cr(III) Adsorption

When in suspension with the Dayton clayey silt soil, Cr(III) adsorption was greatest between pH=4 and pH=5. Adsorption was quite rapid in this pH range. Below pH=4, Cr(III) adsorption to the soil decreased, due to increasing soil surface charge and/or increasing concentrations of hydrogen ions competing with Cr(III) cations for adsorption sites. Above pH=5, Cr(III) adsorption decreased as pH increased because of Cr(III) complexation with colloidal organic matter. Adsorbed Cr(III) was bound relatively strongly to the soil, as indicated by the low extraction efficiency of the EDTA extraction. There was no evidence of Cr(III) oxidation to Cr(VI).

In terms of the specific objectives listed in Chapter 1, the following conclusions were drawn:

1. Cr(III) adsorption to the Dayton soil was greatest in the pH range between four and five, and decreased as pH increased or decreased outside that range. The effect of pH on adsorption kinetics was not evaluated.

2. EDTA removed very little adsorbed Cr(III) from the soil;

3. Cr(III) adsorption kinetics were too rapid to characterize fully at pH=4. Below pH=5, Cr(III) adsorption densities were linearly proportional to Cr(III) concentration and hydroxide ion concentration. Above pH=5, Cr(III) behavior was more complex and could not be described by a simple model.

4. The chemical nature of Cr(III) adsorption was not determined; either adsorption or precipitation may have been responsible.

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