

YEAR 2

**Effect of Specific Chemical Reactions on the
Transformation and the Transport of Chromium in
the Soil-Water System and in Concrete Walls**

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by

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ABSTRACT

Leaching behavior of chromium in chromium-contaminated soil (Cr-soil) derived from chromium ore processing residue (COPR) and the transport of chromium in concrete material were studied. Physico-chemical properties of Cr-soil were characterized. Cr-soil is a highly alkaline material containing a large amount of calcium, presumably in the form of CaCO_3 . By X-ray diffraction analysis, the major Cr form in the Cr-soil was identified as chromite. HF is the most effective extractant of Cr from Cr-soil derived from COPR.

Leaching experiments were conducted using simulated rainwater as the leaching solution. Leaching of chromium and other metals with synthetic rainwater is highly pH sensitive. Low pH promotes Cr(VI) reduction to Cr(III), and thereby decreases the mass of Cr(VI) leached. Approximately 1% of total Cr (25 mg/g) is in the form of Cr(VI) which is readily leachable at pH between 4 and 12. The bulk of the remaining chromium mainly contains nonleachable trivalent chromium. Removal of the organic matter from the Cr-soil increases the amount of Cr(VI) leached over the entire pH range, suggesting that the organic matter can reduce Cr(VI) during the leaching process. The mass of Cr(VI) leached is the same under either aerobic or anaerobic conditions. The amount of Cr(III) leached was controlled by the solubility of Cr(III) precipitates, the extent of Cr(VI) reduction, and the magnitude of Cr(III) adsorption onto the soil surface. The absence of detectable Cr(III) between pH 4.5 and 12 can be attributed to the presence of insoluble precipitates such as $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ and the adsorption of Cr(III) species onto the soil particle surface.

Adsorption, redox, and precipitation reactions are the major processes affecting the

concentration and speciation of chromium in the chromium-concrete interface, and solution pH is the crucial parameter affecting these chemical interactions. Below pH 3.5, the concentration of Cr(VI) is controlled by reduction reactions. Cr(VI) is reduced to Cr(III) by reaction with aqueous Fe(II) derived from Fe(II)-containing concrete materials. The concentration of Cr(III) is then governed by the $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ and/or $\text{Cr}(\text{OH})_3(\text{s})$ precipitates. At pH 4 to 9, adsorption is mainly responsible for Cr(VI) removal. Prediction of the Cr(VI) adsorption density for different sizes of concrete particle can be made by knowing the specific surface area of the concrete particle. The adsorption of Cr(VI) onto concrete particles can be described by surface complex formation model. Because the magnitude of favorable electrostatic energies and the adverse solvation and lateral interaction energy which contribute to the total adsorption are relatively small in comparison with the favorable specific chemical energy, I conclude that the specific chemical interaction is the major mechanism.

An interactive spreadsheet program written with Lotus 1-2-3 macros for one-dimensional contaminant transport in porous media coupled with adsorption and decay reactions was developed. The program is used to simulate the leaching of Cr(VI) from Cr-soil and the transport of Cr in concrete material. The simulation results support the suggestion that the Cr(VI) leaching process is mainly governed by the adsorption/desorption, precipitation, and redox reactions. Possible dissolution of COPR might exist during the leaching process, but no direct evidence was found throughout this work.

Transport of Cr in the concrete is highly dependent on the solution pH. Cr(VI) is mobile in the concrete because Cr(VI) is not favorably adsorbed by concrete at high pH. Thus the transport of Cr(VI) in the concrete block is mainly caused by dispersion and advection only. Cr(III), however, can strongly be adsorbed by concrete at high solution

pH. As a result, the transport of Cr(III) in the concrete is drastically retarded by the adsorption process. It is possible that when acidic chromate solutions are in prolonged contact with the concrete, the concrete will gradually lose its buffering capacity. As a result, the transport of Cr(VI) under such conditions should include adsorption and deca (hence redox) reactions. Dissolution of the Ca or other alkaline material in the concrete by H^+ or by exchanging with ions in the leachate results in loss of its buffering capacities, and thereby more Cr(VI) will be adsorbed on the concrete and weaken the concrete strength.

Chapter 1

INTRODUCTION

Soil contamination by heavy metals is extremely pernicious because these contaminants are environmentally persistent. Unlike most organic contaminants, metals are generally refractory and can not be degraded or readily detoxified biologically. Toxic metals pose a particularly difficult long term pollution problem. Chromium is one of the most commonly found metal contaminants in U.S soils (Ellis et al. 1984).

Chromite ore processing residue (COPR) has been used as construction or landfill material in several countries, including England, Japan, West Germany, and the United States (McKee 1988). In the United States, major chromium producing regions are Maryland, New Jersey, Ohio and New York (Public Health Service 1953). Between 1905 and 1976, there were three chromite-processing facilities in Hudson County, New Jersey. During this time period approximately 2.75 million tons of processing waste containing 2% to 5% chromium was generated (ESE 1989; Hsieh 1988). Over 400 industrial and residential chromium contaminated sites in Hudson County and other areas of northeastern New Jersey have been identified (MEMT 1990). Since a portion of the chromium is in the hexavalent form, which is a known lung carcinogen, and also a toxin via dermal and oral exposure (ESE 1989), there has been great public concern over potential exposure by workers and residents in these areas to dust, dirt and contaminated water. Chromium salts can deteriorate concrete

structures in chromium contaminated areas (Hsieh et al. 1988; MEMT 1990). Yellow crystals of chromate salts have been found on the surface of concrete blocks of many buildings (Stricharchuk 1990). The enormous volume of contaminated soil and the extent of urban development in these areas make excavation an impractical means for exposure reduction. Remediation of these sites is necessary since they are hazardous to public health. Knowledge of the chromium leaching behavior in the soil derived from COPR, the chemical interactions between chromium and concrete materials, and the transport of chromium in the soil as well as concrete is essential to the establishment of a clean-up strategy. Although substantial research has been conducted pertaining to chromium behavior in soils, some of this information may not be applicable to the specific sites, since the contaminated material is actually "soil" derived from weathered chromium processing waste. The material is highly alkaline and contains high levels of carbonates and other salts not normally found in soils of the northeastern United States. Moreover, little is known about the chemical interactions between chromium and concrete in the aqueous system.

This thesis focuses on studying the characterization of Cr-soil derived from COPR, behavior of chromium leached from Cr-soil, chemical interaction between chromium and concrete, and transport of chromium in concrete. The major portion of data in chapters 3 and 4 has been published (Weng et al. 1994a; Weng et al. 1993). Chapter 2 states the chemical properties and the problems of COPR wastes. Literature review of chromium reactions with soil and the contaminant transport in the porous medium are also presented in this chapter. The specific objectives of this research are addressed in this chapter. Chapter 3 shows the characterization of COPR and the concrete materials. Major physico-chemical properties such as total chromium, chemical composition, specific surface area, particle size distribution, pH_{zpc} , soil pH,

and organic matter content are included. Chapter 4 presents the chromium leaching behavior in soil derived from COPR. Factors, such as pH, temperature, and organic matter, that may affect the leaching behavior are included in this chapter. Chapter 5 explores the chemical interaction between chromium and concrete materials. Parameters, such as pH, chromium concentrations, and particle size, which may affect the chemical interactions were studied. Adsorption/desorption, redox, and precipitation processes, that affect the concentration of chromium in its interaction with concrete, were also investigated. Determination of surface acidity of hydrous concrete using electrophoretic mobility measurements was made. A surface complex formation model (SCFM) originally developed by Huang and Stumm (1973) was used to describe the adsorption of chromium onto concrete particles. Chapter 6 presents the development of a user-friendly interactive spreadsheet computer program for modeling the contaminant transport through porous medium. Manual for this program is shown in appendix B. Verification of this program with the analytical solution was demonstrated. This chapter also shows the use of the numerical model to simulate the chromium leaching from Cr-soil and the transport of chromium through concrete materials. Chapter 7 summarizes the research results and gives recommendations for future study.

Chapter 2

LITERATURE REVIEW

2.1 Problems of Chromium

Chromium (Cr) is a transition metal that exists primarily as Cr(III) and Cr(VI) in the environment (Udy 1956). Cr(III) is less toxic than Cr(VI) and is relatively immobile in the aqueous environment due to its strong adsorption onto soils (Amacher and Baker 1982). Because of its inability to cross cell membranes, it is not readily bioavailable and is a relatively inactive genotoxic agent. In contrast, Cr(VI) is relatively mobile since it is only weakly adsorbed to soil under natural conditions. Cr(VI) compounds are irritants due to their high solubility and diffusivity in tissue that allow them to cross biological membranes easily. Therefore, Cr(VI) compounds are readily adsorbed by inhalation, ingestion, and through the skin (Finkel 1983). Unlike Cr(III), which is a Lewis acid and can form insoluble chromium hydroxide $\text{Cr}(\text{OH})_3(\text{s})$, Cr(VI) is a Lewis base that exists in aqueous solution as an anion. The current limit for soluble Cr in drinking water is 0.05 mg/l (10^{-6} M) (U.S.EPA 1984).

The public health consideration of chromium is mostly related to hexavalent compounds. Hexavalent chromium compounds have been reported to produce hemorrhage, dermatitis, respiratory problems, and liver and kidney damage. Symptoms are generally gastrointestinal such as repeated vomiting, diarrhea, and anorexia. The dosage of $\text{K}_2\text{Cr}_2\text{O}_7$ fatal to human is 0.5 g to 1.5 g (Casarett and Doull 1980). Studies have showed that the worker in chromate-producing industry and

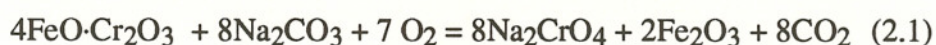
chromium-plating factories has increased occupational exposure and risks. In particularly, the risk of lung cancer was found to be abnormally high for the chromate workers (Alderson et al. 1981; Hayes et al. 1979). It is documented that certain hexavalent compounds, i.e., calcium chromate, are known lung carcinogens (U.S.EPA 1984).

2.2 Chemical Properties of Chromite Ore Processing Residue (COPR)

The first generations of large scale chromite ore processing plants were built in the late nineteenth and early twentieth centuries and had life spans ranging from 5 to 75 years. These plants were distributed in countries such as England, Germany, Japan, and the United States. They were shut down and replaced with more modern facilities over the last thirty years. The COPR produced from these old plants were usually dumped untreated or used as a fill material near the old factory sites. Some of these chromium-contaminated sites continuously bleed chromate salts even after decades of weathering (McKee 1988; Gemmell 1973).

In the U.S. there are six plants which were directly involved in the manufacture of chromates and dichromates from chromite ore (Public Health Service 1953). These plants are located in the states of Maryland, New Jersey, New York, and Ohio. Chromite ore as observed in the chromate-producing and the refractory industries, is a hard, granular material before processing and is chemically inert. The theoretical formula of the mineral chromite is $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, but the ores rarely conform. The iron in the chromite ore may be partially replaced by magnesium and the chromium by aluminum and the ferric iron.

Basically the same chromate manufacturing process operated in all of the plants: roasting the finely ground ore with soda ash (Na_2CO_3) or with a soda ash and lime (CaO) mixture to produce a water soluble chromium compound, sodium chromate. The roasting process is operated under an oxidizing atmosphere at temperatures from 1,800 to 2,200 °F depending upon the composition of the mix. The reaction for this process with sodium carbonate only:



When chromite ore is roasted with lime, calcium oxide may produce calcium chromate (CaCrO_4), as well as calcium chromite ($\text{CaO}\cdot\text{Cr}_2\text{O}_3$). The reactions are as follow:



The roast is followed by a leaching process which can generate “yellow liquor”: sodium chromate solution. The end products are sodium chromate (Na_2CrO_4), yellow rhombic crystals and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), orange-red monoclinic crystals. These products are widely used by tanners in making tanning compounds. They also are used in the manufacture of pigment used in paints, printing inks, and ceramics, for corrosion control in metal systems, as a wood preservative, for textile mordants and dyeing, and in the manufacture of chemical catalysts. Sodium dichromate can be further processed to chromic acid (CrO_3) used in electroplating, and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) used in photographic processing (Diamond Shamrock Co. 1979).

The residues from chromite ore processing plant include calcium chromate (CaCrO_4 , $3\text{CaO}\cdot\text{CrO}_4$), calcium chromate-chromite complex ($\text{CaCrO}_4\cdot\text{Cr}_2\text{O}_3$), calcium aluminochromate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCrO}_4$), tribasic calcium chromate ($\text{Ca}_3(\text{CrO}_4)_2$), and basic ferric chromate ($\text{Fe}(\text{OH})\text{CrO}_4$) (Gancy and Wamser 1976; Public Health Service 1953). These residues are very slowly soluble in water. When leached by percolating rainwater, they can produce a Cr(VI) concentration as high as 100 - 500 ppm in the leachate, posing serious environmental pollution.

2.3 State of COPR Problems

In Tokyo, Japan, the Bureau of Environmental Protection of the Tokyo Metropolitan Government (1980) found that approximately 0.26 million tons of chromite ore processing residue were produced from a plant which operated from 1915 to 1973. This residue was used as a fill material at 170 different sites throughout Tokyo. Chromate salts precipitate was found on surfaces due to up-rising of water by capillary force during the dry periods. Eventually, a brilliant yellow-green precipitate consisting largely of calcium chromate was found by evaporating water. A landfill treatment technique was employed to limit the chromate migration. Sand mixed with a slow release reducing agent was injected into the base of the landfill. Sheet piling was installed around the perimeter and the clay liner was slurred in around the side and bottom of the cell. Chromate wastes were trucked in from contaminated sites, mixed with the reducing agent, then placed in the landfill cells. This treatment process began in 1980 and was completed in 1983.

In Hudson County New Jersey, a large scale chromium contamination problem exists today which is a situation parallel to that in Tokyo, Japan. It has been reported that two to three million tons of COPR, containing 2 to 5 percent chromium were generated from three chromite ore processing plants operating from 1900 to 1970 (ESE 1989). This waste has been used as a construction fill material in areas such as parks, schools, residential sites, and around factory grounds, particularly in Jersey City and Kearny. Over hundred sites have been identified containing chromium residues. White, yellow and green crystals has been discovered growing on the surface soil around Jersey City, New Jersey. Testing by the state of New Jersey verified the crystals were chromate salts (Stricharchuk 1990). In the summer of 1993, it was claimed that chromium dust was discovered in the carpeting, dust work and vacuum cleaners of an elementary school, and in the children's blood (Stricharchuk 1990). The brown-yellow crystals were found on the concrete-block walls in some locations around contaminated sites. This kind of phenomena has been found to be hazardous to concrete structures by causing buckling of concrete floors and walls of buildings. There is a great public concern of possible exposure to the dust, soil, and water containing Cr(VI). Since the enormous volume of contaminated soil and the extent of urban development in these areas makes excavation an impractical solution for eliminating chromium exposure, a permanent in-situ treatment that eliminates exposure to chromium may be necessary. Montclair Environmental Management Team (MEMT 1990) has proposed some remediation plans for these contaminated sites, such as mining and thermal processing, mechanical encapsulation, hydraulic lagooning, and chemical treatment. Because a lot of sites contain enormous volumes of Cr-soil and they are located in urban developments, these remediation alternatives are either limited by economic reasons or practical difficulties. Therefore,

consideration of innovative and cost-effective in-situ treatment technologies is needed to reduce the risk of public health. Investigation of chromium leaching behavior and chromium interaction in concrete material is an important measure to help establishing the remediation strategies.

2.4 Aqueous Chromium Speciation

The adsorption of metal ions at the solid/aqueous solution interface is generally not only governed by the “free” (i.e., M^{z+}) metal ion, but also by the much stronger hydroxyl, sulfate, carbonate, and other metal complex species (Huang and Rhoads 1989; Stumm 1992). It has been suggested that all metal hydrolysis species $M(OH)_i^{z-i}$ should also be involved in the adsorption reaction (Huang and Rhoads 1989; Huang and Corapcioglu 1987; Huang and Elliott 1981). Thus, knowing the metal species which occur in aquatic systems and understanding the behavior of metal adsorption onto solid/liquid interface is important.

The free metal ions in solutions are actually aquo complexes, the water itself is a ligand that binds metals, and every complexation reaction in water is effectively a ligand-exchange reaction (Stumm 1992). The hydrolysis equilibrium of metals can be described as:



The equilibrium constant K_i for the reaction is defined as:

$$K_i = \frac{\{M(OH)_i^{z-i}\}}{\{M^{z+}\}\{(OH)^-\}^i} \quad (2.5)$$

where $\{ \}$ stands for the activity of the dissolved species, e.g., $\{M_j\}$. The activity of an ion can be calculated by

$$\{M_j\} = [M_j] \cdot \gamma_i \quad (2.6)$$

where $[M_j]$ is the measured metal concentration, and γ_i is the activity coefficient. γ_i can be determined from ionic strength, I , temperature, and other parameters. For ionic strength less than 0.5 M, each individual activity coefficient, γ_i , in equation (2.6) can be obtained from the Davies ion activity coefficient equation (Stumm and Morgan 1981):

$$\log \gamma = -AZ^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)^{-3/2} \quad (2.7)$$

where $I = 0.5 \sum C_i Z_i^2$; $A = 1.82 \times 10^6 (\epsilon T)^{-3/2}$ (where ϵ is the dielectric constant of solution); $A \approx 0.5$ for water at 25 °C and $\epsilon = 78.5$; Z = charge of ion.

The total soluble metal concentration, M_T , can be expressed as a total free metal concentration $[M^{z+}]$, plus the sum of soluble hydroxyl metal complexes:

$$M_T = [M^{z+}] + \sum [M(OH)_i^{z-i}] \quad (2.8)$$

The metal species in water are primarily governed by pH. At any specific pH value, the fraction of metal present in any species, α_i , can be calculated by:

$$\alpha_o = \frac{\{M^{z+}\}}{\{M_T\}} = \left(1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^3} + \frac{K_4}{[H^+]^4} \right)^{-1} \quad (2.9)$$

$$\alpha_i = \frac{\{M(OH)_i^{z-i}\}}{\{M_T\}} = \alpha_o \cdot \frac{K_i}{[H^+]^i} \quad (2.10)$$

The equilibrium constants of Cr(III) and Cr(VI) species at various ionic strength conditions are listed in Table 2.1. The speciation diagrams of Cr(III) and Cr(VI) species as a function of pH are shown in Figures 2.1 and 2.2, respectively.

Table 2.1 Equilibrium constants [log K] for Cr(VI) and Cr(III) hydrolysis reactions.

Equilibria	I = 2.5 x 10 ⁻² M ^a log K	I = 1 x 10 ⁻² M ^b log K	I = 0 M ^c log K
$\text{Cr(OH)}_3(\text{s}) + 3 \text{H}^+ = \text{Cr}^{3+} + 3\text{H}_2\text{O}$	< 9.89	< 9.76	
$\text{Cr(OH)}_3(\text{s}) + 2\text{H}^+ = \text{Cr(OH)}^{2+} + 2\text{H}_2\text{O}$	6.00	5.96	
$\text{Cr(OH)}_3(\text{s}) + \text{H}^+ = \text{Cr(OH)}_2^+ + \text{H}_2\text{O}$	< -0.44	< -0.44	
$\text{Cr(OH)}_3(\text{s}) = \text{Cr(OH)}_3^0$	< -6.84	< -6.84	
$\text{Cr(OH)}_3(\text{s}) + \text{H}_2\text{O} = \text{Cr(OH)}_4^- + \text{H}^+$	-12.80	-18.25	
$\text{H}_2\text{CrO}_4(\text{aq}) = \text{HCrO}_4^- + \text{H}^+$	0.33		0.20
$\text{HCrO}_4^- = \text{CrO}_4^{2-} + \text{H}^+$	-6.58		-6.51
$2\text{HCrO}_4^- = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	1.59		1.53

^aUsed for this study. Activity coefficients, γ , for I = 2.5 x 10⁻² M are calculated from Davies equation (Stumm and Morgan 1981).

^bSource from Rai et al. (1987).

^cSource from Martell and Smith (1976).

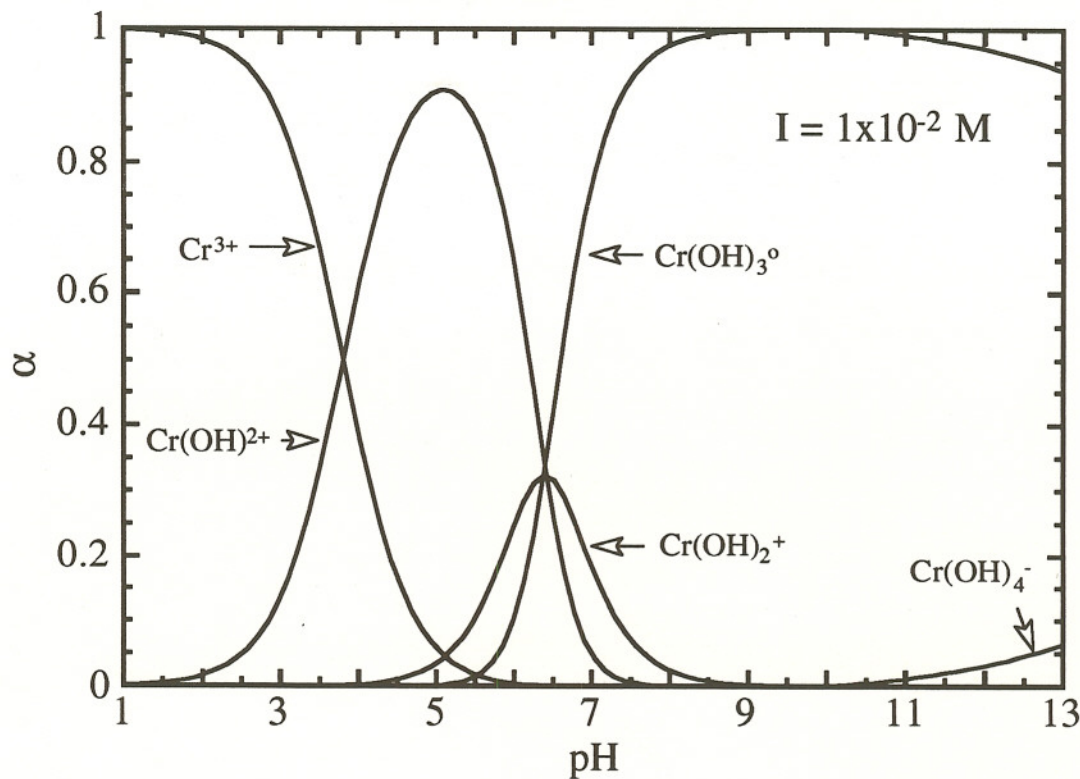


Figure 2.1 The Cr(III) speciation diagram as function of pH at ionic strength 10^{-2} M

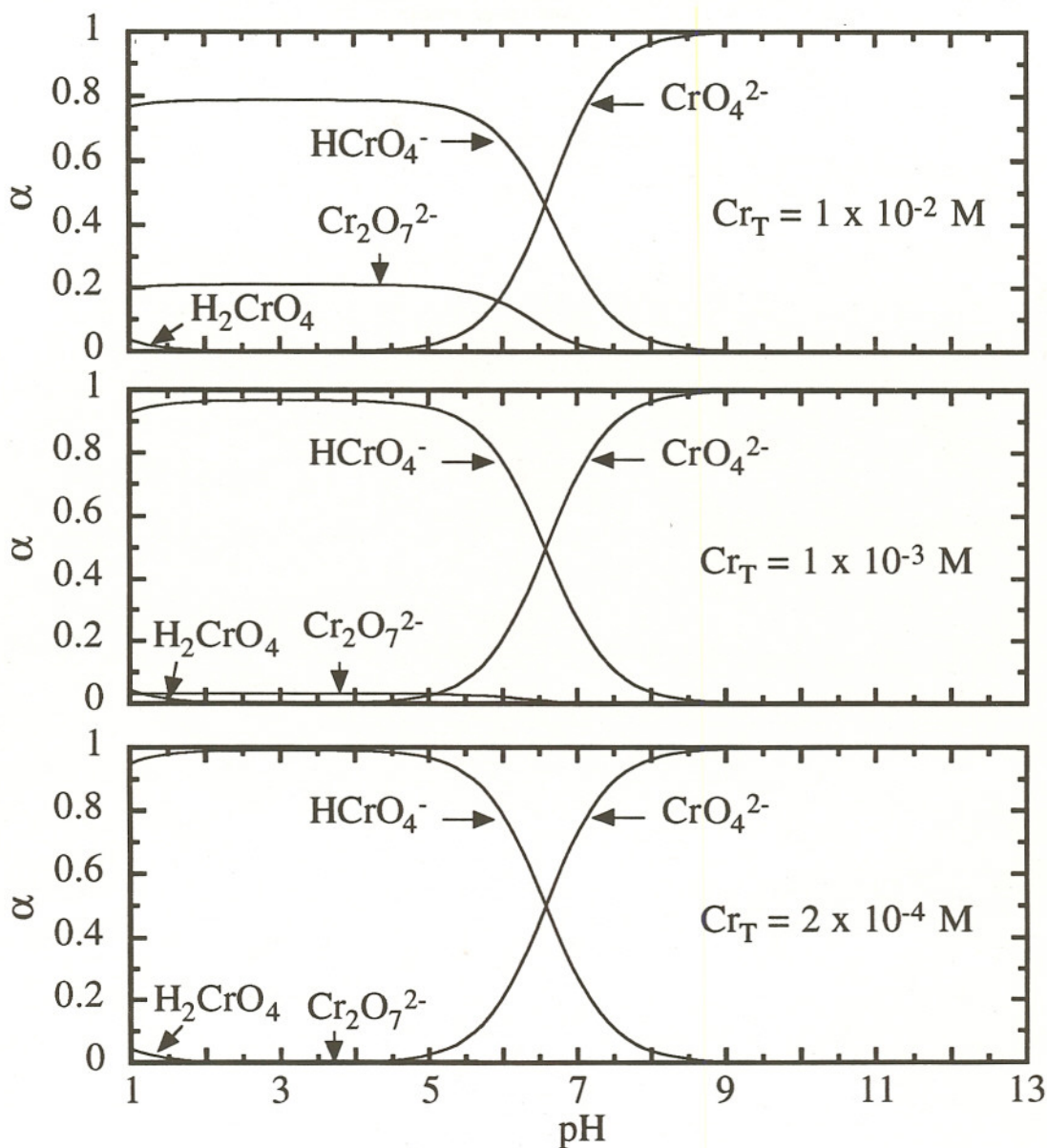


Figure 2.2 The Cr(VI) speciation diagram as function of pH and total Cr(VI) concentration.

2.5 Chromium Reaction in Soil and Concrete

While little or no information is available pertaining to chromium behavior with concrete, useful information is available with regard to its behavior in soil. Adsorption and desorption reactions play a significant role in controlling the aqueous concentration of Cr species in soils, and therefore their mobility. Chromate can be adsorbed by soil colloids such as ferric oxide, aluminum oxide, kaolinite, and montmorillonite (Rai et al. 1989; Zachara et al. 1988; Zachara et al. 1987; Stollenwerk and Grove 1985; Griffin et al. 1977; MacNaughton 1977). Hsieh et al. (1988) have studied Cr(VI) adsorption onto soil particles at low pH. Mayer and Schick (1981) have shown that Cr(VI) can be removed from the sediment/water interface by a two-step reaction scheme; reduction followed by adsorption on kaolinite or alumina oxide surfaces. Zachara et al. (1988) indicated that the Cr(VI) adsorption edge onto kaolinite is at about pH 7.3. They proposed a pH_{zpc} of 7.3 for kaolinite edge surface which is about the same value as reported by Rand and Melton (1977) and Wieland (1988). MacNaughton (1977) has found that adsorption of Cr(VI) from aqueous solution onto Al_2O_3 is pH-dependent. They have also suggested that a strong electrostatic attraction takes place between the Al_2O_3 surface and the anionic Cr(VI) species. As the pH increases above 4.0, Cr(VI) adsorption decreases reaching approximately zero at pH between 8.0 and 9.0, which is near the pH_{zpc} of Al_2O_3 . Zachara et al. (1987) have reported that amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or ferrihydrate, which is a common surface coating of subsoil particles, has a particularly high Cr(VI) adsorption capacity. Adsorption of CrO_4^{2-} onto $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ decreases as the pH increases. Apparently, the adsorption of chromate under acidic conditions can be attributed to the favorable electrostatic interaction. The extent of anionic chromate

adsorption increases as pH decreases due to a more favorable electrostatic interaction. Surface complexation model has been successfully used to describe Cr(VI) ion onto some solid surfaces. Davis and Leckie (1980) have reported that CrO_4^{2-} ion adsorption onto amorphous iron oxyhydroxide can be described by a surface complexation model. It has been suggested that CrO_4^{2-} adsorbs onto soil colloids as an outer sphere complex (Zachara et al. 1988). Generally, outer-sphere complexes give weak adsorption onto the soil particle surface. Thus, the CrO_4^{2-} ion is not held onto soil particles strongly. Intuitively, CrO_4^{2-} can be readily leached from the soil surface. Zachara et al. (1988) have reported that chromate binding is reversible with respect to pH and is inhibited by the presence of SO_4^{2-} and carbonates, which can compete for adsorption sites.

The study of Cr(III) adsorption onto soil and soil components has received little attention due probably to the fact that it is not perceived as an environmental hazard. However since the bulk of chromium in the New Jersey chromium-contaminated soil (Cr-soil) is in the trivalent form, it is important to know the adsorption behavior of this species. In general, the adsorption characteristics of Cr(III) onto hydrous solids are similar to those of divalent metals (Griffin et al. 1977; James and Healy 1972). Adsorption characteristics of cationic metals adsorption onto various type of solids have been extensively studied (Weng and Huang 1994, Lee et al. 1994; Weng and Huang 1990; Huang et al. 1990; Huang and Rhoads 1989; Huang and Hao 1989; Huang and Coracioglu, 1987; Huang et al., 1986; Elliott and Huang 1986; Huang and Blankenship 1984; Huang and Elliott 1981). Dzombak and Morel (1990) have also reported that the characteristics of Cr(III) adsorption onto hydrous ferric oxide is the same as that of divalent metal ions such as Pb(II), Cu(II), Cd(II),

Zn(II), Ni(II), and Ca(II); the amount of metal adsorbed increases with increasing solution pH. Recently, Crawford et al. (1993) and Charlet and Manceau (1992) have shown that the sorption of Cr(III) by hydrous Fe oxides involved adsorption, surface precipitation, and coprecipitation phenomena. They also reported that the adsorption of a Cr(III) ion onto goethite or hydrous ferric oxide occurs via the formation of strong inner-sphere surface complexes.

Redox reactions are also important processes that affect the aqueous speciation of Cr in soils. The oxidation of Cr(III) to Cr(VI) by Mn-oxides is thermodynamically possible in soils (Fendorf and Zasoski 1992; Amacher and Baker 1982; Bartlett and James 1979). The Cr(III) oxidation by δ -MnO₂, however, can be inhibited at pH values greater than 4 due to the formation of Cr(OH)₃(s) precipitate on the surface of δ -MnO₂ (Fendorf et al. 1992). Reduction of Cr(VI) to Cr(III) with subsequent precipitation of the adsorbed Cr(III) species may occur in the presence of reductive solids (Music et al. 1986). Huang and Bowers (1978), and Huang and Wu (1977) have demonstrated that the reduction of Cr(VI) to Cr(III) by activated carbon occurs only under acidic conditions. It has been reported that Cr(VI) can be rapidly reduced to Cr(III) by both Fe(II) and/or organic matter under acidic conditions (Eary and Rai 1991; Amacher and Baker 1982; Bartlett and Kimble 1976). Bartlett and James (1988) have suggested that in most surface soils, organic compounds can be expected to be the primary reductant for Cr(VI) reduction. Eary and Rai (1989) have reported that Cr(VI) can be reduced to Cr(III) by Fe(II) ions from dissolution of the Fe(II) components of hematite and biotite in acidic media. A two-step reaction was proposed for chromate reduction in the presence of the hematite and biotite. First, the Fe(II) is released to solution by dissolution or surface redox reactions. Second, the

released Fe(II) is rapidly oxidized to Fe(III) by reaction with Cr(VI) in the aqueous phase. The remaining Fe(III) aqueous species can spontaneously be reduced back to Fe(II) by a coupled-cation electron transfer reaction at the biotite-water interface, but not at the hematite-water interface; the Fe(II) produced from this reaction is then free to react again with the Cr(VI), resulting in additional chromate reduction.

2.6 Solute Transport Model

Nonequilibrium model has recently attention been applied to simulate some organic contaminants transport (Hatfield and Stauffer 1992; Sardin et al. 1991; Mahinthakumar and Vigneswaran 1990; Bouchard et al. 1989). Simulation of the flow and reaction of solutes through porous media is however more easily accomplished through the assumption that local chemical equilibrium rather than a rate controls the reaction between the solute and the porous media (Grove and Stollenwerk 1985). For the contaminant transport, linear, Freundlich, and Langmuir sorption isotherms are commonly applied to be used as the equilibrium adsorption constants which are incorporated into the governing equation and are expressed a retardation coefficient.

Many analytical solutions are now available for one-dimensional transport with different boundary and initial conditions (Javandel et al. 1984; Lai and Jurinak 1972; Gershon and Nir 1969; Lindstorm et al. 1967; Ogata and Banks 1961). Only small number of analytical solutions with different initial and boundary conditions are available for two- and three-dimensional solute transport. (Leij et al. 1991; Wexler 1989; Carnahan and Remer 1984; Javandel et al. 1984). Generally, the analytical

solution is often limited by the nonideal nature of initial and boundary conditions and the complexity of the passage of transport process. The analytical solution can be used to predict the large time and distance scales and to validate the numerical results.

Application of numerical methods to the simulation of solute transport has received great attention recently (Roy et al. 1994; Hatfield and Stauffer 1992; Mahinthakumar and Vigneswaran 1990; Hsieh 1988; Srinivasan and Mercer 1987; Grove and Stollenwerk 1985; Pandey et al. 1982). Generally, the program used to simulate the transport process have more than one of the following disadvantages: require high-level language compiler, unavailability of the hardware, user-unfriendly, output data untransferable or uneditable, require huge computer memory, and unable to simulate the transport conditions (such as adsorption and decay). The commercialized software BIO1D (Srinivasan and Mercer 1987) is able to simulate the biodegradation and sorption in contaminant transport. It can runs on an IBM PC only with an installed mathcoprocessor. Some 486 PC's even with installed mathcoprocessor have been found incompatible to run the program. The output data and graph can only be printed out. It is not editable or directly copied to other graphical software. The quality of the output graph is poor. Even the new release BIO1D version 1.2 did not improve the quality of the output graph. For some conditions, such as, when a high partition coefficient for adsorption reaction was chosen, the program is terminated. In general, with this program it is not easy to simulate the chromium leaching process or the transport of chromium through concrete material.

Development of a user-friendly computer program that can run in the PC and for which the output data is copy-editable, is deemed innovative and necessary for

simulating the chromium leaching from the chromium contaminated soil and the transport of chromium in the concrete.

2.7 Objectives

Migration of Cr through subsurface and concrete materials is a highly complex and poorly understood phenomenon. Transport mechanisms may depend on the variable geologic formation conditions (i.e., heterogeneous, anisotropy, and fractured subsurface materials), and from characteristics of the chromite ore processing residue (COPR) waste itself. As such, this complexity often increases the difficulty of research work on determining transport mechanisms. In the COPR contaminated sites, Cr continually leached even after decades of weathering process and chromate salt crystals formed on the surface of concrete wall posing a serious environmental problem. Although Cr behavior in soil has been studied over several decades, little is known about the Cr leaching behavior and Cr in concrete material at many COPR contaminated sites. Besides, the available information from literature may not be suitable for a specific contaminated site.

The main objective of this study is to obtain information pertaining to chromium migration behavior in these contaminated areas, to determine the chromium leaching characteristics from Cr-soil and the extent of chromium ion interactions with concrete block material, and to develop a quantitative model to predict the chromium concentration in the soil-water and concrete domains. Through numerical modeling, the amount of chromium concentration leached from Cr-soil, transport of chromium in the soil-water system, and the chromium concentration distribution in the concrete

block will be determined. This information is important to help in the design and the implementation of clean-up strategies.

In order to understanding the fate of chromium in the soil derived from COPR and the transport of chromium in the concrete material, this research is designed to achieve the following objectives:

1. Characterize the chromium contaminated soil (Cr-soil) derived from COPR.
2. Study the chromium leaching behavior in soil derived from COPR.
3. Investigate the chemical reaction between chromium and concrete.
4. Develop a quantitative model to predict the chromium leaching from Cr-soil and to simulate transport in the concrete materials.

Chapter 3

CHARACTERIZATION OF CHROMIUM CONTAMINATED SOIL DERIVED FROM COPR AND CONCRETE SAMPLES

3.1 Introduction

In this chapter I present the characterization of Cr-soil and the concrete materials. Major physico-chemical properties such as total chromium, chemical composition, specific surface area, particle size distribution, pH_{zpc} , soil pH, and organic matter content are included. Characterization of Cr-soil and the concrete materials are important in order to help establish remediation strategies. The results of this chapter are also useful with respect to the interpretation of the behavior of chromium leaching from Cr-soil and the chemical interaction between chromium and concrete.

3.2 Materials and Experimental

3.2.1 Chemicals, Soil Samples, and Concrete Materials

All chemicals used were ACS (American Chemical Society) certified grade and obtained from Fisher Scientific Company, Springfield, NJ or Aldrich Chemical Company, Milwaukee, WI.

Samples of soil derived from chromite ore processing waste (Cr-soil samples) were collected from the Liberty State Park, Hudson County, NJ (Figure 3.1). Composite Cr-soil samples were taken to a depth of approximately 6 cm at three different locations.

Concrete blocks were purchased from Yardville Supply, Co. (Yardville, New Jersey). After air drying, the concrete block was crushed by a compressive testing machine (Tinius Olsen Testing Machine Co., Willow Grove, PA). The crushed concrete particles were then passed through ASTM standard sieves and used as adsorbent material without treatment unless otherwise noted. Four particle size categories, < 0.18 mm, 0.18 mm - 0.5 mm, 0.5 mm - 1.0 mm, and 1.0 mm - 2.0 mm, were prepared. Except for the study of the particle size effect on chromium reaction with concrete, the 0.18 mm - 0.5 mm fraction was used for all batch equilibrium experiments.

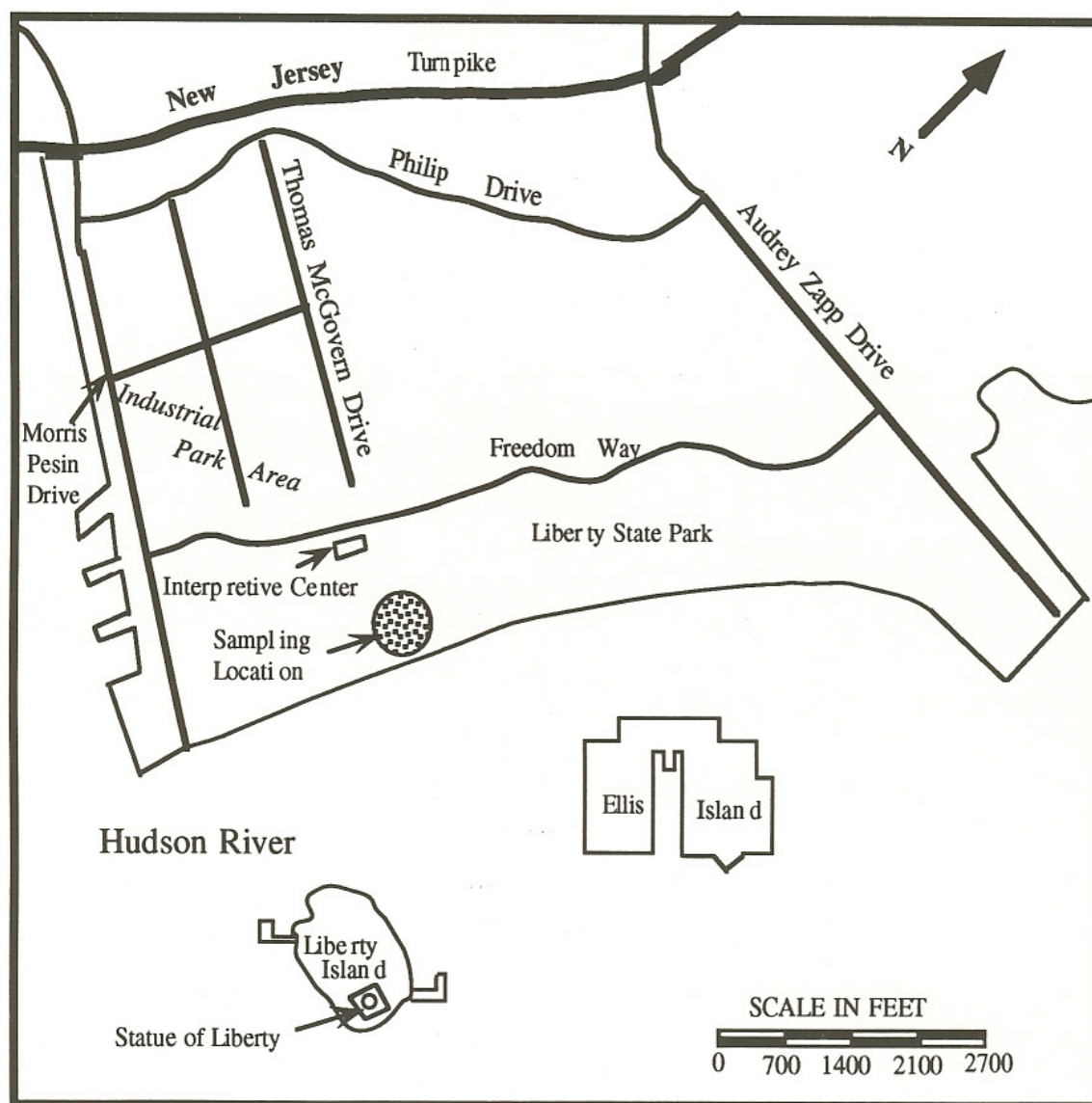


Figure 3.1 Map of Cr-soil sampling locations.

3.2.2 Analytical Methods

Most metals in the aqueous leachates were determined with an atomic absorption spectrophotometer (AA) (Perkin-Elmer, Model Zeeman 5000, Norwalk, CT) following procedures described in standard methods (APHA 1985). Fe(II), Fe(III), Cr(VI), and Cr(III) were analyzed by the colorimetric method. Two methods were used to determine total Fe and Cr in the extraction solution: atomic absorption spectrophotometry and colorimetry. Fe(II) was analyzed by the 1,10-phenanthroline method at a wavelength of 510 nm (APHA 1985). Total Fe was analyzed by the ferrover method using Hach ferrover iron reagent (510 nm, APHA 1985). Fe(III) was determined from the difference between the total Fe and Fe(II). Cr(VI) was analyzed by the reddish-purple 1,5-diphenylcarbohydrazide chromate complex in an acidic medium at 540 nm (ASTM 1990a). Total Cr was determined by oxidizing the Cr(III) to Cr(VI) with potassium permanganate then determining the total Cr as Cr(VI) (Huang and Bower 1978). Cr(III) was determined from the difference between the total Cr and Cr(VI). Concentrations of NH_4^+ , NO_3^- , and Cl^- were determined using ion selective electrodes. The concentration of SO_4^{2-} was determined by the turbidimetric method at a wavelength of 420 nm (APHA 1985).

3.2.3 Particle Size Distribution

The particle size distribution of the Cr-soil samples was analyzed by ASTM standard sieve analysis.

3.2.4 Total Chromium

Total metal concentrations in the soils were determined by wet extraction analysis. In order to compare the Cr(VI) extraction efficiency, three wet extraction methods were used. For method I, soil samples were predigested in a 250-mL Teflon beaker with concentrated HNO_3 followed by the addition of a 25 mL solution of concentrated H_2SO_4 , HClO_4 , and HF at volume ratio of 1:2:5 for 6 hours at 60-80 °C (Reisenauer 1982). For method II, soil samples were combusted at 400 °C for 4 hours, then a 1:1 volume ratio of concentrated HCl-HF was added to the samples in a 250 mL Teflon beaker. The samples were then digested for another 6 hours at 60-80 °C (Perkin-Elmer 1982). In method III, the soil samples were combusted in a furnace (400 °C) for 4 hours, then a 1:3 volume ratio of concentrated HNO_3 -HCl was added to the samples in a 250 mL Teflon beaker and digested for 6 more hours at 60-80 °C (Delfino and Enderson 1978).

3.2.5 Soil pH and Concrete pH

The soil pH was measured in water suspensions and in 10^{-2} M CaCl_2 solutions at a 1:1 soil to solution volume ratio with a pH meter (Model 3500 digital pH meter, Beckman, Irvine, CA). The procedures followed those of ASTM method D 4972-89 (ASTM 1990b), a standard test method for soil pH. The concrete pH was measured by the method describe above except that the concrete particle size of 0.18 mm to 0.5 mm was used.

3.2.6 Organic Matter

The soil organic matter content was determined by combustion (Nelson et al. 1982). Cr-soil samples were heated at 400 °C in a furnace for 4 hours (Model 1300, Thermolyne Co., Dubuque, IA). The organic matter content was then calculated from the mass lost on combustion.

3.2.7 Specific Surface Area

The specific surface area of the concrete material and Cr-soil samples were determined by the BET-N₂ gas adsorption method using a model QS-7 Quantasorb surface area analyzer (Quantachrom Co., Greenvale, NY). The preweighted sample was outgassed at 170 °C for 8 hours with continuous purging by nitrogen gas. The quantasorb obtains the specific surface area of the samples by using the techniques of adsorbing the adsorbate (N₂ gas) from a flowing mixture of adsorbate and an inert non-adsorbable carrier gas (He gas) (Lowell 1980). Because of the adsorption signal is often accompanied by non-Gaussian tailing curves, particularly on porous samples (i.e., Cr-soil and concrete) at high N₂ concentrations, desorption signals are always preferable to used for the specific surface area analysis. The desorption signal was calibrated by injecting known volumes of nitrogen gas.

The multipoint BET method is used for calculating the specific surface area of the sample. The BET equation has a linear form:

$$\frac{1}{X\left(\frac{P_o}{P} - 1\right)} = \frac{C-1}{X_m C} \frac{P}{P_o} + \frac{1}{X_m C} \quad (3.1)$$

where

X = mass of adsorbate (N₂) adsorbed at relative pressure P/P_o,

P = partial pressure of adsorbate,

P_o = saturate vapor pressure of adsorbate,

X_m = mass of monolayer coverage of adsorbate adsorbed, and

C = a constant related to the heat of the adsorbate condensation and heat of adsorption.

The partial pressure of adsorbate, P , is obtained by:

$$P = C_{N2} \cdot P_a \quad (3.2)$$

where

C_{N2} = fraction of nitrogen in the flowing mixture,

P_a = ambient or barometric pressure in mm Hg.

The saturate vapor pressure, P_o , is estimated by

$$P_o = P_a + 15 \text{ mm} \quad (3.3)$$

The relative pressure, P/P_o , is calculated by equation (3.4):

$$\frac{P}{P_o} = \frac{C_{N2} \cdot P_a}{P_a + 15 \text{ mm}} \quad (3.4)$$

A plot of the left-hand term of equation (3.1) versus P/P_o yields a straight line of slope, $S = (C-1)/(X_m C)$, and intercept, $I = 1/X_m$, which are used to determine the mass adsorbed at the monolayer. As shown by equation (3.5), the mass adsorbed at the monolayer, X_m , can be calculated.

$$X_m = \frac{1}{S + I} \quad (3.5)$$

It is important to note that, because of the assumptions implicit in the BET equation, the linear range $0.05 \leq P/P_0 \leq 0.35$ is usually observed. Therefore, the relative pressure in the range $0.05 \leq P/P_0 \leq 0.35$ are used for determining the specific surface area. The total surface area of the sample, S_t , is determined by equation (3.6):

$$S_t = \frac{X_m N A_{cs}}{M_a} \quad (3.6)$$

where

N = Avogadro's number = 6.023×10^{23} ,

A_{cs} = cross sectional area of adsorbate molecule ($N_2 = 16.2 \times 10^{20} \text{ m}^2$; Rhodin 1953), and

M_a = molecular weight of adsorbed molecule ($N_2 = 28 \text{ g/mole}$).

The specific surface area, S (m^2/g) is determined by equation (3.7):

$$S = \frac{S_t}{\text{Weight of sample}} \quad (3.7)$$

3.2.8 SEM-EDAX and XRD Analysis

The major chemical components of the Cr-soil sample and the concrete materials are determined by energy dispersion analysis by X-ray (SEM-EDAX) (Phillips 501 scanning electron microscope and Phillips EDAX 9100). For the Cr-soil, three different particle size categories were used for the purpose of comparison. These size categories were classified according American Society for Testing Materials

(ASTM) standard sieve. Identification of major mineral phases in the soil and concrete materials were performed by X-ray diffraction analysis (XRD) (Phillips semi-automatic X-ray diffractometer).

3.2.9 pH_{zpc}

The zeta potential of Cr-soil and concrete particles was determined by a zeta meter (Laser Zee® Model 500, Pen Kem Inc., Bedford Hills, NY). To two separate 500-mL deoxygenated water samples of given ionic strength (1×10^{-2} M, and 4×10^{-3} M, 1×10^{-3} M NaNO_3), 0.1 gram powdered concrete was added with continuous bubbling of N_2 gas to remove dissolved O_2 , and the mixture was stirred. The hydration time was set at 30 minutes. While the suspension was being stirred, the initial pH was measured and recorded. The pH was adjusted by 0.1 M HClO_4 or 0.1 M NaOH to cover a range from 2.5 to 10.5 in approximately 0.5 pH unit increments. 20-mL of the suspension was introduced into the chamber of the zeta meter, and mobility of the particles was measured at the upper stationary layer of the chamber with voltage fixed at 100 mV. The zeta potential was then determined at each pH value. The calculated zeta potential (mV), ζ_{corr} , is corrected for the temperature changes by:

$$\zeta_{\text{corr}} = \zeta_{\text{meas}} [1 - 0.02 (T - 25)] \quad (3.8)$$

where ζ_{meas} is the measured zeta potential (mV) and T ($^{\circ}\text{C}$) is the operating temperature.

3.2.10 Porosity and Density

Porosity of the concrete material is determined by first immersing the concrete stick (2.5 cm x 2.5 cm x 30 cm) into a 1-L volumetric cylindrical containing 800-mL distilled water. After wetting for 1 hour, the increase in water volume V_{rise} is recorded and the stick is then taken out and records of the residual water volume in the cylinder, V_{down} and wet weight of concrete stick (g), W_{wet} are made. The amount of water in the concrete is based on volumetric measuring $(V_{\text{wc}})_v$ (cm^3) and is obtained from:

$$(V_{\text{wc}})_v = V_w - V_{\text{down}} \quad (3.9)$$

Total volume of concrete V_{tot} (cm^3) is determined by:

$$V_{\text{tot}} = V_{\text{rise}} - V_{\text{down}} \quad (3.10)$$

The dry weight of concrete stick (g), W_{dry} , is measured before wetting. The weight of water in the concrete stick W_{wc} (g) is obtained by:

$$W_{\text{wc}} = W_{\text{wet}} - W_{\text{dry}} \quad (3.11)$$

When water density, ρ_w , is 1 g/cm^3 , the volume of water, $(V_{\text{wc}})_w$ (cm^3), in the concrete stick based on weight measurement is determined by:

$$(V_{\text{wc}})_w = W_{\text{wc}}/\rho_w \quad (3.12)$$

The average volume of water in the concrete stick V_{wc} (cm^3) is obtained from

$$V_{\text{wc}} = 1/2[(V_{\text{wc}})_v + (V_{\text{wc}})_w] \quad (3.13)$$

The porosity of concrete, ϕ (dimensionless), is determined by:

$$\phi = V_{\text{wc}}/V_{\text{tot}} \quad (3.14)$$

The density of dry concrete, ρ_{dry} (g/cm^3), is obtained

$$\rho_{\text{dry}} = W_{\text{dry}} / (V_{\text{tot}} - V_{\text{wc}}) \quad (3.15)$$

3.3 Results and Discussion

3.3.1 Particle Size Distribution

Results of ASTM standard sieve analyses show that the Cr-soil samples consist predominately of sand-sized particles with a small percentage of silt-sized particles.

3.3.2 SEM-EDAX and XRD Analysis

Results of SEM-EDAX analyses indicate that indeed Cr is one of the major components in the Cr-soil with ca. 5% in the soil mass. Other elements such as Ca, Fe, Al, Si, Mg, K, and Ti were also observed by SEM-EDAX analysis (Table 3.1). Specifically, these soil samples contain, in average, 39% Ca and 33% Fe. Results from SEM-EDAX analysis, also show that the chemical composition does not vary with particle size. Cr appears to distribute uniformly in all particle size fractions. Moreover, results from XRD analysis indicate that chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, is the major Cr form (Figure 3.2). This chromite apparently can be considered as a residual chromite waste derived from chromite ore processing or a discarded low grade chromite ore. The high grade ore used in the chromate production usually contains at least 42% Cr_2O_3 (Stowe 1987). Contrary to what was suggested by some researchers, calcium chromate salts were not observed from XRD analysis. However, possibly the presence of these salts in Cr-soil cannot be ruled out because the XRD work may not be sufficiently sensitive to identify them at a low level. It has been reported that

during the early stage of a COPR disposal, the following chromate salts such as calcium chromate (CaCrO_4 , $3\text{CaO}\cdot\text{CrO}_4$), calcium chromate chromite complex ($\text{CaCrO}_4\cdot\text{Cr}_2\text{O}_3$), calcium aluminochromate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCrO}_4$), tribasic calcium chromate ($\text{Ca}_3(\text{CrO}_4)_2$), and basic ferric chromate ($\text{Fe}(\text{OH})\text{CrO}_4$) may be present (Gancy and Wamser 1976; Gemmell 1973; Breeze 1972; Public Health Service 1953). However these authors provided no XRD data in their reports. These salts were produced during the chromite ore roasting processes at temperature between 1,800 to 2,200 °F in which lime and/or soda ash were added (Public Health Service 1953). Through decades of weathering, it is expected that these chromium salts may have undergone some chemical changes.

The major chemical components of the concrete material are Si, Al, Fe, Ca, and Mg, as determined by energy dispersion analysis by X-ray (SEM-EDAX) (Phillips 501 scanning electron microscope and Phillips EDAX 9100). The major crystal phases of the concrete particles are quartz (SiO_2), calcite (CaCO_3), gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), orthopyroxene ($(\text{Fe}, \text{Mg})\text{SiO}_3$), and olivine ($(\text{Fe}, \text{Mg})_2\text{SiO}_4$) which were identified by X-ray diffraction analysis (XRD) (Phillips semi-automatic X-ray diffractometer) (Figure 4.2).

3.3.3 Total Chromium in the Cr-Soil

From the results of wet extraction analysis, generally, the amounts of metals extracted by method I and II are greater than those of method III (Table 3.2). The amount of total Cr in soil extracted by method I or II is about four times as great as that by method III. Apparently, the use of hydrofluoric acid (HF) in method I and II

significantly increases metal extraction from Cr-soil, especially for total Cr, Fe, Mg, and Al. Clearly, method III, using only HNO_3 and HCl , that is commonly used for metal extraction, does not access all Cr from Cr-soil. This is expected since the chromite ore is known to be acid resistance. The Cr form in the Cr-soil is predominantly chromite according to the result of XRD analysis. By comparing method I with method II, method I tends to extract more Cr from the Cr-soil. I therefore suggest that extraction method I, using the combination of HNO_3 , H_2SO_4 , HClO_4 , and HF , in the extraction process, can be used to estimate the total Cr in Cr-soil.

Results also show that the total Cr and Fe obtained from AA analyses are the same as those obtained from the colorimetric methods. In general, the Cr-soil contains about 2.5% Cr, 5.4% Ca, and 22% Fe by weight. Other major elements include Mg and Al. The chemical composition of these three Cr-soil samples is generally indistinguishable. For example, the Ca contents of these three Cr-soil samples are 46 g/kg for sample I, 53 g/kg for sample II, and 62 g/kg for sample III. Trace amount of metals such as Na, K, Mn, Zn, Ni, Pb, Cu, and Cd were also detected in the wet extraction analyses. Results of wet chemical extraction, especially, Cr, Fe, Mg, and Al agree with those from surface spectroscopic analysis (Table 3.2). The result of total Cr content in the Cr-soil from wet extraction analyses is higher than that of ESE (1989) which gives values ranging from 26 to 6,600 mg/kg for the same contaminated site at the sampling depths of 3, 6, and 9 ft. Apparently, different sampling depths and locations, as well as analytical method employed can yield different values. According to ESE (1989), the surface soils collected from other sites in the Hudson County, New Jersey exhibit total Cr concentration as high as 1 to 2.6% on a weight

basis. They also reported that Al, Ca, Fe, and Mg were the major components in addition to Cr.

Table 3.1 Analysis of Cr-soil chemical elements by EDAX.

Atom % element	Cr-soil sample I			Cr-soil sample II			Cr-soil sample III		
	(T)	(M)	(B)	(T)	(M)	(B)	(T)	(M)	(B)
Mg	4.42	2.69	1.43	1.25	0.83	1.63	2.70	1.86	1.27
Al	3.76	5.56	5.42	18.13	3.51	8.80	3.40	4.03	4.23
Si	1.32	2.11	16.93	52.30	4.27	18.30	1.57	4.57	5.39
K	----	----	1.54	7.71	0.93	2.68	0.50	0.79	0.80
Ca	54.37	51.75	25.38	5.28	38.66	22.47	61.96	44.56	41.89
Ti	----	0.90	1.41	2.89	1.24	1.64	0.71	1.07	1.24
Cr	4.36	4.42	4.09	2.28	6.65	5.48	3.53	5.64	5.62
Fe	35.34	32.58	33.79	10.17	43.92	39.00	25.63	37.47	39.56

Note: Based on the ASTM sieve analysis, approximately 30% by weight of total soil particles has a particle size > 4.75 mm (T), 40% of size fraction between 4.75 mm and 0.6 mm (M), 30% of size fraction < 0.6 mm (B).

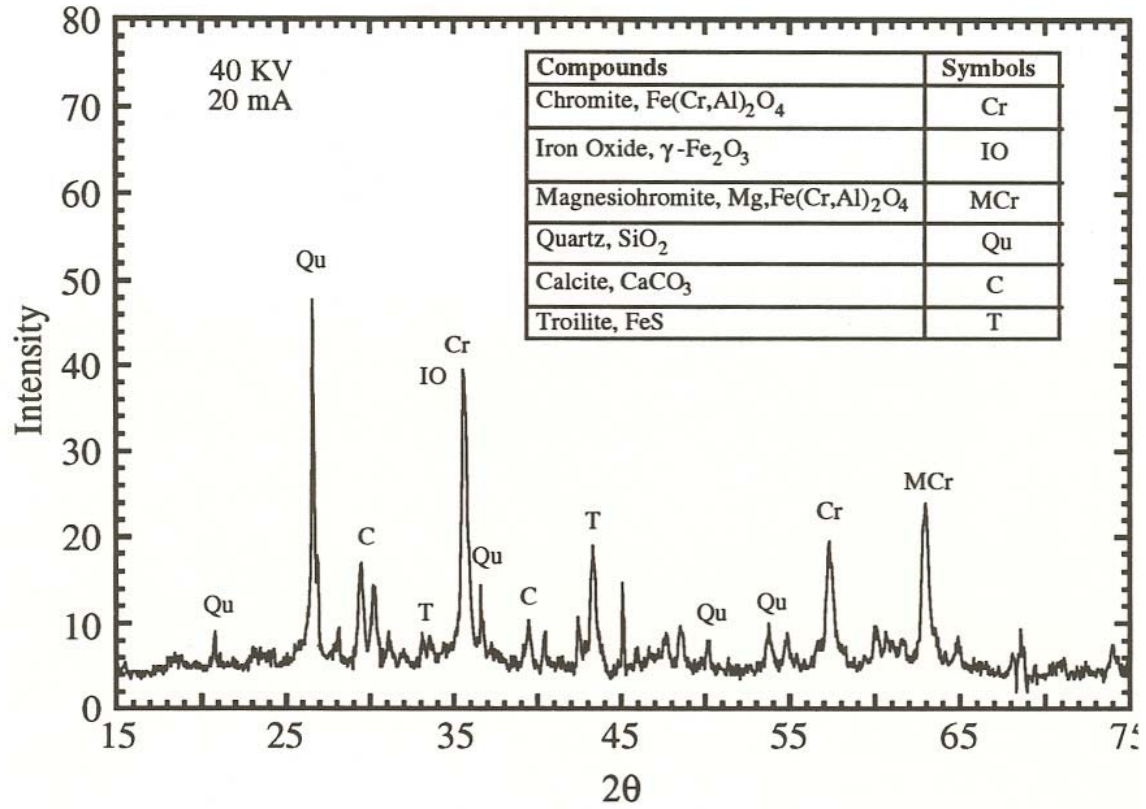


Figure 3.2 XRD patterns of Cr-soil sample. The patterns were analyzed based on the search manual published by the Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA, 1980.

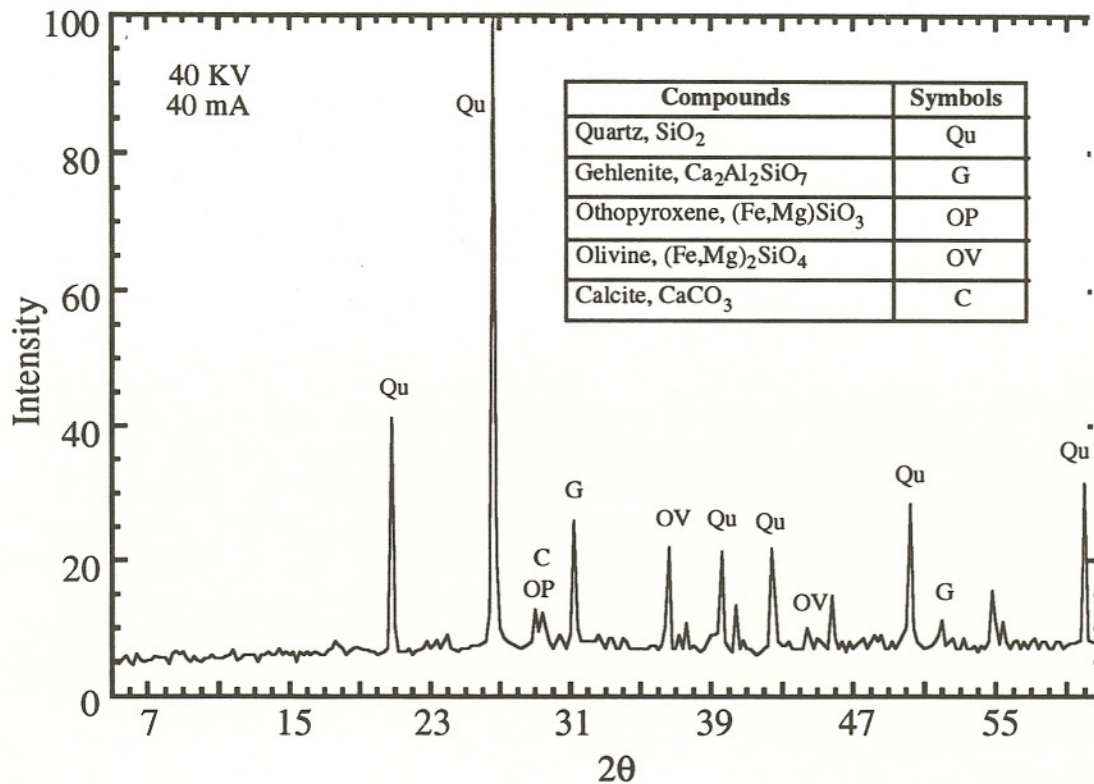


Figure 3.3 XRD patterns of concrete particles. The patterns were analyzed based on the search manual published by the Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA, 1980.

Table 3.2 Comparison of various wet extraction methods for the Cr-soil samples.

Element	Cr-soil sample I			Cr-soil sample II			Cr-soil sample III		
	Extraction Method			Extraction Method			Extraction Method		
(g/Kg)	I	II	III	I	II	III	I	II	III
Cr	25.54	23.38	5.45	24.22	21.22	6.23	33.29	27.42	6.62
Cr ^a	26.90	22.99	5.82	27.37	21.74	6.37	33.47	28.39	6.00
Fe	222.20	240.50	103.30	182.60	188.70	111.90	210.10	232.90	117.00
Fe ^b	232.00	253.50	127.20	171.10	185.50	127.20	216.00	241.50	125.30
Mg	60.35	59.72	29.55	59.78	49.17	28.33	73.24	53.17	27.44
Ca	45.86	46.46	46.21	53.10	53.70	53.79	61.55	63.36	62.76
Al	43.83	50.18	23.55	51.47	48.60	29.46	47.97	39.15	12.42
Na	4.98	3.47	0.96	3.10	2.74	1.19	2.30	2.21	1.46
K	4.17	4.50	0.36	5.01	6.89	0.40	4.17	2.59	0.42
Mn	1.49	1.69	0.90	1.49	1.60	1.07	1.72	1.88	1.11
Zn	0.88	0.86	0.62	2.06	1.00	0.70	1.08	1.01	0.73
Ni	0.97	0.87	0.56	1.07	0.80	0.63	1.17	1.02	0.68
Pb	0.57	0.42	0.34	1.04	1.32	0.63	0.84	0.70	0.51
Cu	0.18	0.16	0.17	0.21	0.22	0.15	0.21	0.17	0.24
Cd	0.05	0.05	< 0.01	0.08	0.08	0.01	0.07	0.07	0.01

All metals were analyzed by atomic adsorption spectrophotometry (AA) except as noted.

Extraction procedures for Method I, II, and III have been described in section 3.5.2.

^aBy oxidization with K_2MnO_4 and spectrophotometry.

^bBy Hach ferroVer iron reagent and spectrophotometry.

3.3.4 Soil and Concrete pH, Organic Matter, and Specific Surface Area

The results of soil pH, organic matter content, and specific surface area of Cr-soil samples are shown in Table 3.4. The high soil pH value indicates that the Cr-soil is a highly alkaline material and has a strong acid buffering capacity. The concrete pH in distilled water and in 10^{-2} M CaCl_2 is 11.7, indicating that the concrete material is a highly alkaline material and has a strong acid buffering capacity. The Cr-soil has an organic matter content of about 9%. It has been reported that high organic content may facilitate the reduction of Cr(VI) to Cr(III) under acidic conditions (Bartlett and Kimble 1976).

The specific surface area of the Cr-soil ranges from 20 to 30 m^2/g (Table 3.4). Specific surface area of coarse sized-particle categories, 12.55 mm - 19 mm, 6.3 mm - 12.55 mm, and 2 - 6.3 mm and fine sized-particle categories, 1 mm - 2 mm, 0.5 mm - 1 mm, 0.18 mm - 0.5 mm, and < 0.18 mm, are 1.7 m^2/g , 1.8 m^2/g , 2.0 m^2/g , 2.1 m^2/g , 2.3 m^2/g , 2.5 m^2/g , and 3.2 m^2/g , individually. The results indicate that the larger particles exhibit smaller specific surface area and vice versa. The relationship between specific surface area and concrete particle size is shown in Figure 3.4. A linearized logarithmic plot can be used to predict the specific surface area of concrete block.

$$\log(\text{SA})_{\text{predicted}} = 0.36 - 0.11 \log(D) \quad (3.16)$$

where $\text{SA}_{\text{predicted}}$ (m^2/g) is the predicted surface area and D (mm) is the diameter of concrete particle. For an one inch thick of concrete block, the specific surface area of the concrete block is 1.6 m^2/g according to equation (3.16). A linear ($\log(\text{SA}) - \log(D)$ plot) relationship between specific surface area and particle size was also observed for crushed quartz and quartz sand by Parks (1990).

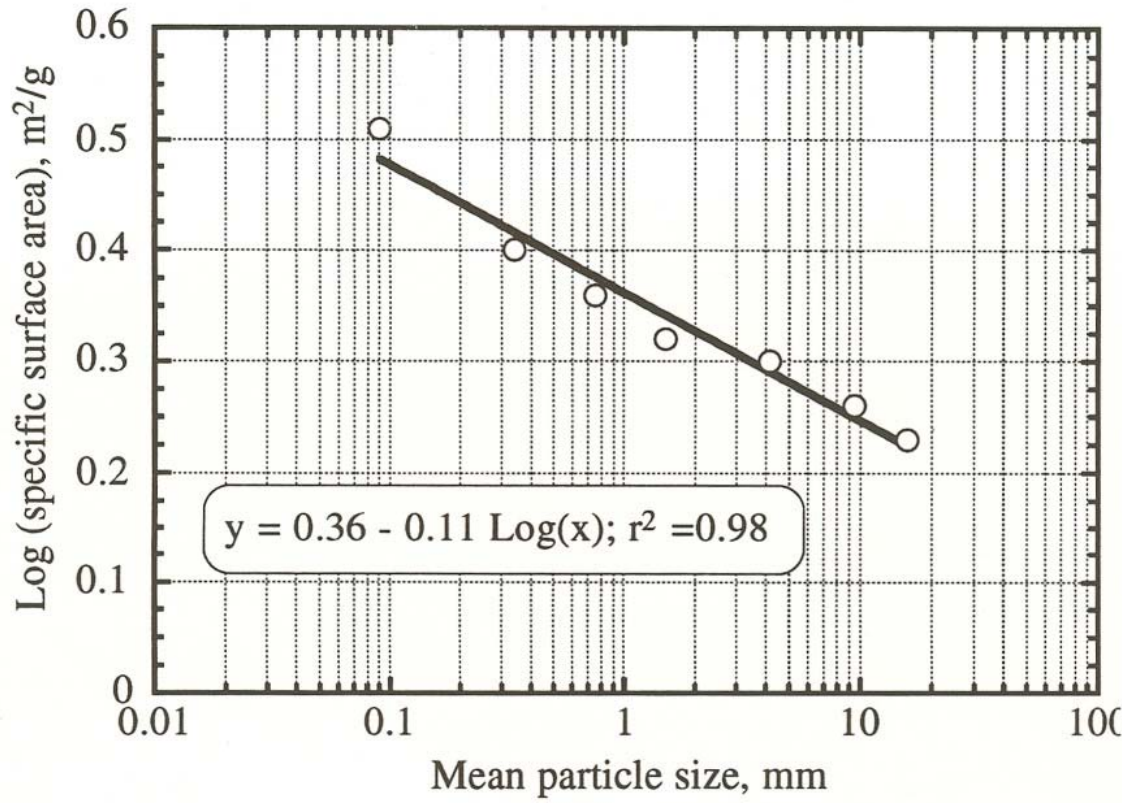


Figure 3.4 Specific surface area of concrete particles correlated to its mean particle size.

3.3.5 pH_{zpc}

Figure 3.5 shows the electrophoretic mobility of Cr-soil as a function of pH at various ionic strengths exemplified by sample I. The higher the ionic strength is, the lower the zeta potential. This is caused by electrical double layer compression. The pH at which zero zeta potential occurs is defined as the pH_{zpc} . A pH_{zpc} of 6.8 was obtained for all three Cr-soil samples. The positively charged nature of the soil is indicative of a multicomponent solid mixture (Elliott and Sparks 1981). In this study, iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) was identified in the XRC analysis (Figure 3.2). An iron content of about 22% by weight (Table 3.2) was observed for the Cr-soil samples. Iron, presumably in the oxide form, can exhibit a marked effect on pH_{zpc} , since the Fe-oxides generally have pH_{zpc} values in the neutral pH range. For example, pH_{zpc} 's for $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , amorphous $\text{Fe}(\text{OH})_3$, and $\gamma\text{-FeOOH}$ are 6.7, 6.5, 8.5 - 8.8, and 5.9 - 6.7, respectively (Stumm and Morgan 1981; Park 1965). It is speculated that the neutral pH_{zpc} value of Cr-soil particles is attributable to the high iron content of the Cr-soil. The pH_{zpc} of concrete particles was determined to be 5.9.

3.3.6 Porosity and Density

The average porosity, ϕ , and soil density of Cr-soil are 0.3 and 2.64 g/cm^3 , respectively. The average porosity and dry density of concrete are 0.084 and 2.28 g/cm^3 , respectively (Table 3.3).

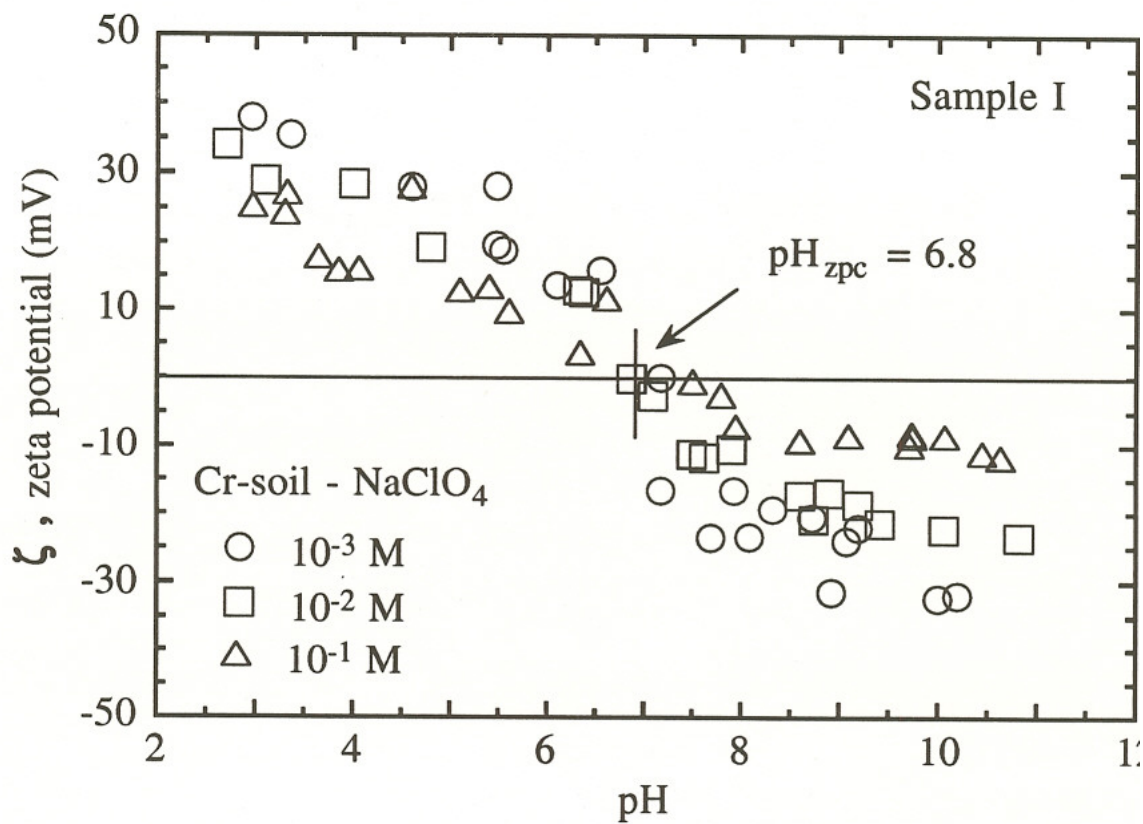


Figure 3.5 The zeta potential of Cr-soil as a function of pH in different concentration of electrolyte.

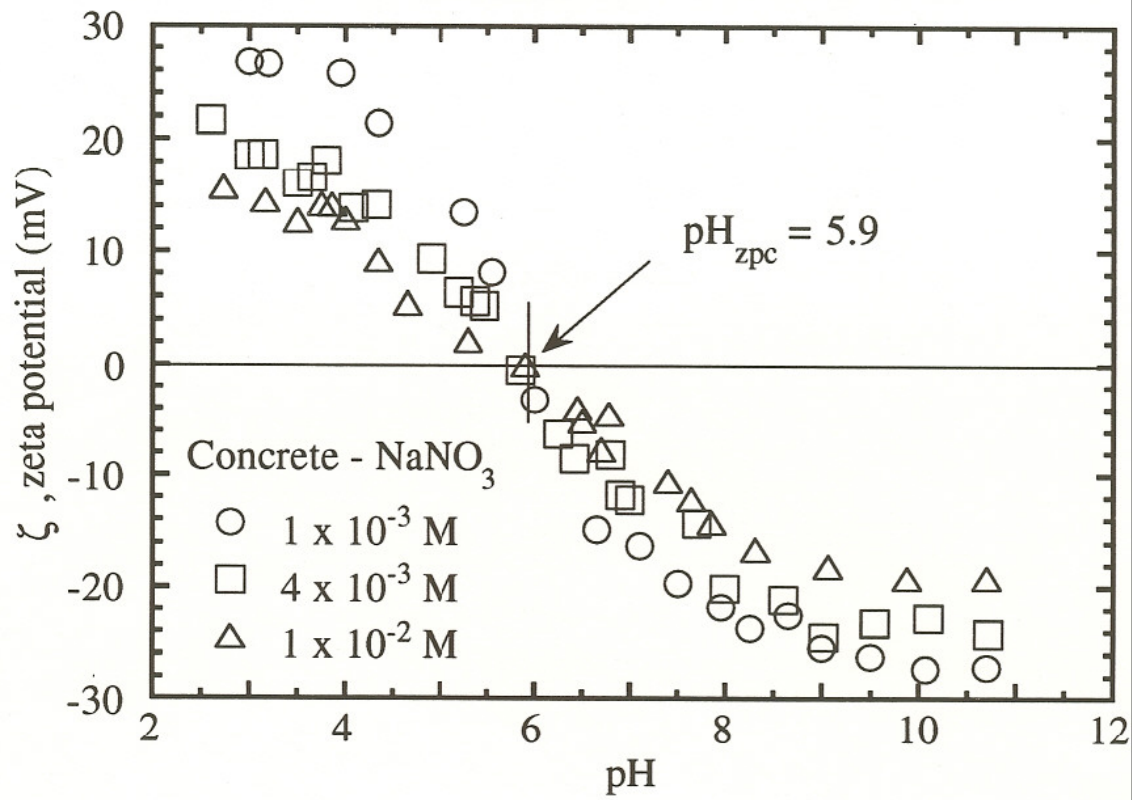


Figure 3.6 The zeta potential of hydrous concrete as a function of pH in different concentrations of electrolyte.

Table 3.3 Porosity and dry density of concrete.

	Test 1	Test 2	Test 3	Test 4	Average
$V_{\text{rise}} (\text{cm}^3)$	958.0	958.0	960.0	965.0	960.1
$V_{\text{down}} (\text{cm}^3)$	783.5	785.0	786.0	784.0	784.6
$(V_{\text{wc}})_v (\text{cm}^3)$	16.5	15.0	14.0	16.0	15.4
$V_{\text{tot}} (\text{cm}^3)$	174.5	173.0	174.0	181.0	175.6
$W_{\text{dry}} (\text{g})$	361.0	364.4	364.6	376.9	366.7
$W_{\text{wet}} (\text{g})$	376.9	377.5	378.1	391.1	380.9
$(V_{\text{wc}})_w (\text{cm}^3)$	15.9	13.1	13.5	14.2	14.2
$V_{\text{wc}} (\text{cm}^3)$	16.2	14.1	13.8	15.1	14.8
ϕ	0.092	0.082	0.079	0.083	0.084
$\rho_{\text{dry}} (\text{g/cm}^3)$	2.28	2.29	2.28	2.27	2.28

Table 3.4 Some important physical-chemical properties of the Cr-soil samples.

Properties	Cr-soil sample I	Cr-soil sample II	Cr-soil sample III
Organic matter (% by weight)	8.56	9.29	8.92
pH _{zpc}	6.8	6.8	6.8
Specific surface area (m ² /g)	21.8	19.9	31.1
Soil pH in distilled water	8.51	8.52	8.11
Soil pH in 10 ⁻² M CaCl ₂	8.27	8.25	8.00

Chapter 4

CHROMIUM LEACHING BEHAVIOR FROM SOIL DERIVED FROM CHROMITE ORE PROCESSING RESIDUE

4.1 Introduction

Remediation of chromium contaminated sites is necessary since they pose hazards to public health. It is hypothesized that during rain-fall periods, Cr(VI) will be leached from Cr-soil derived from COPR. Thus, knowledge of the chromium leaching behavior in the soil derived from COPR and of the chemical interactions between chromium and concrete materials is essential to the establishment of clean-up strategies. Although substantial research has been conducted pertaining to chromium behavior in soils, some of this information may not be applicable to the specific sites in New Jersey, since the contaminated material is actually "soil" derived from weathered chromium processing waste.

In the previous chapter, characterization of chromium contaminated soil derived from COPR has been presented. Important physico-chemical properties of Cr-soil have been obtained. In this chapter, we focus on studying the chromium leaching behavior in soil derived from COPR. Factors, such as pH, temperature, and organic matter, that may affect the leaching behavior are studied.

4.2 Experimental

4.2.1 Batch Cr-Soil Leaching Experiments

A batch reactor was used to study the equilibrium leaching properties of Cr-soil. The soil samples were air dried, ground with a ball mill (Norton, Chemical Process Products Division, Akron, OH) and sieved to less than 180 μm (ASTM #80). This particle size category allows us to obtain uniform physical-chemical properties of soil particles for the experimental work. Various amounts of Cr-soil (ranging from 1 to 10 g/L) and 100 mL of simulated rainwater (preparation of simulated rainwater is shown in the next section) were added to a series of plastic bottles. The pH value of the samples was adjusted as necessary with strong acid (1 N H_2SO_4) or strong base (1 N NaOH). The samples were shaken on a reciprocating shaker (Eberbach Co., Ann Arbor, MI) at 150 excursions per minute for 24 hours. The equilibrium pH was then recorded and aliquots of the suspensions were taken and filtered with 0.45 μm membrane filter (Supor-450, 25 mm, Gelman Sciences Co., Ann Arbor, MI). The concentrations of the metals in the supernatant were determined as described above.

4.2.2 Preparation of Simulation Rainwater

Synthetic rainwater was prepared to simulate rain of the Mid-Atlantic coastal region following the standard reference methods of the National Bureau of Standards (Koch 1986). The average values for rainwater from Lewes, Delaware and Brookhaven, New York were used (Table 4.1). Many of the average values were greater than the NBS certified SRM 2694 simulated rainwater, because rainwater in the coastal Mid-Atlantic area contains excessive sea salt (i.e., Na^+ , Mg^{2+} , Ca^{2+} , and Cl^-). The high acidity of the Mid-Atlantic rainwater may be attributed to active

regional industrial activities. However, the average pH value of 4.34 is close to the NBS reference rainwater value of 4.30.

Table 4.1 Chemical composition of rainwater and simulated rainwater.

Composition	Lewes, DE ⁽¹⁾ 1978 -1987	Brookhaven, NY ⁽¹⁾ 1973 -1983	NBS ⁽²⁾ SRM 2694	Average ⁽³⁾
Avg. Precip. (cm/yr)	104.8	116.3	----	110.5
H ⁺ (μeq/L)	47.9	42.7	----	45.3
pH	4.32	4.37	----	4.34
NH ₄ ⁺ (μeq/L)	14.0	10.3	6.2	12.1
Ca ²⁺ (μeq/L)	6.0	4.6	0.5	5.3
Na ⁺ (μeq/L)	54.2	31.3	8.7	42.7
Mg ²⁺ (μeq/L)	12.3	----	1.0	12.3
K ⁺ (μeq/L)	1.8	----	1.3	1.8
SO ₄ ²⁻ (μeq/L)	51.0	43.4	56.2	48.5 ⁽⁵⁾
Cl ⁻ (μeq/L)	64.5	35.9	13.2	50.2
NO ₃ ⁻ (μeq/L)	23.1	18.6	8.1	20.9

⁽¹⁾Unpublished data from Dr. Tom Church, College of Marine Studies,
University of Delaware, Newark, DE 19716.

⁽²⁾Koch (1986).

⁽³⁾Average of ⁽¹⁾ and ⁽²⁾ and used for the preparation of simulated rainwater.

⁽⁴⁾Church et al. (1982).

⁽⁵⁾We added 1.2 μeq/l SO₄²⁻ in order to balance the electroneutrality.

4.3 Results and Discussion

4.3.1 Effect of pH on Cr Leaching

Results of leaching batch experiments show that pH plays a significant role in the leaching of metals from the Cr-soil (Figure 4.1). At $\text{pH} < 2.5$, the amount of Cr(VI) leached is below the detection limit (0.01 mg/l) (Figures 4.1a). Between pH about 2.5 and 4.5, the amount of Cr(VI) leached sharply increases, reaching a maximum value at pH 4.5. The amount of Cr(VI) leached remains approximately constant between pH 4.5 and 12. The absence of Cr(VI) leached at $\text{pH} < 2.5$ is in excellent agreement with results reported by others. Zachara et al. (1988) have found that chromate adsorption occurs on acidic soil enriched in kaolinite and crystalline Fe oxides. Little Cr(VI) is found at $\text{pH} < 2.5$, which may be attributed to the adsorption of Cr(VI) onto the soil and reduction of Cr(VI) to Cr(III) by Fe(II) and/or the organic matter. The Cr(III) could then be coprecipitated with noncrystalline Fe oxyhydroxide (Rai et al. 1989). Under acidic conditions, the soil surface is characterized by a positive charge (i.e., a pH_{zpc} of 6.8 for Cr-soil). Electrostatic interaction favors anionic chromate species adsorption when solution pH is less than pH_{zpc} ; electrostatic chromate adsorption onto Cr-soil is not favorable at high solution pH. The leaching behavior of Cr(III) from the Cr-soil (Figure 4.1b) is similar to that of Al, Fe, and Mn (Figures 4.1c - 4.1f). Generally, the amount of metal leached increases sharply with decreasing pH. At $\text{pH} < 4.5$, the amount of Cr(III) leached increases sharply. No soluble Cr(III) was detected at $\text{pH} > 4.5$ except $10.0 < \text{pH} < 12.0$ when a small amount of Cr(III) was observed. This can be attributed to the presence of chromium hydroxide, $\text{Cr}(\text{OH})_3(\text{s})$ and/or other precipitates such as $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ in the Cr-soil (Eary and Rai 1991; Eary and Rai 1989; Eary and Rai 1988; Sass and Rai 1987;

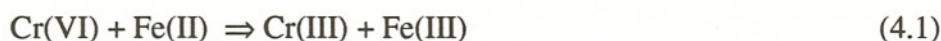
Cranstone and Murray 1978). The results of Cr(VI) and Cr(III) leaching experiments agree well with those of Hsieh et al. (1988) and Bartlett and Kimble (1976). Imai and Gloyna (1990) have reported that the removal of Cr(VI) and Cr(III) by activated sludge strictly depends on solution pH. They found that as pH increases from 4 to 9, the removal of Cr(III) increases, but the reverse is found for Cr(VI). They concluded that adsorption is the main mechanism responsible for both the Cr(III) and Cr(VI) removal.

Figure 4.1f shows the leaching of Mn(II) from Cr-soil as a function of pH. No Mn(II) is detected at pH > 6.5. The amount of leached Mn(II) was small compared to the other metals. However, the possibility of oxidation of Cr(III) to Cr(VI) by manganese oxides should not be ignored.

The leaching of Ca(II) and Mg(II) from Cr-soil samples as a function of pH was also studied (Figures 4.1g and 4.1h). The release of these two metals leached in appreciable amounts below pH 9.0 indicates that the Cr-soil is a highly alkaline soil. It is interesting to note that the amount of Ca(II) leached during leaching experiment is closely related to the total calcium content of the Cr-soil samples from wet extraction analysis. The maximum values of Ca(II) leached from leaching experiment (Figure 4.1g) are 44, 47, and 58 mg/g for sample I, II, and III, respectively compared to that of total Ca 46, 53, and 62 mg/g for sample I, II, and III, respectively from wet extraction analyses (method I) (Table 3.2). Based on these above results and the XRD analysis, it is speculated that the Ca is leached from the solid CaCO_3 phase in the Cr-soil.

Figures 4.1d and 4.1e show the amount of Fe(III) and Fe(II), respectively, leached from the Cr-soil. At pH < 3.5, the amount of Fe(III) leached is appreciable.

At pH > 3.5, no Fe(III) was detected. The same leaching pattern was found for Fe(II) except that the amount of Fe(II) leached is less than that of Fe(III) leached. The small amount of Fe(II) observed may be attributed to redox reactions. It is possible that a portion of Cr(VI) in solution is reduced to Cr(III) at pH < 6.5 by Fe²⁺ ion during the leaching experiment. The source of Fe²⁺ may be hydrolysis of ferruginous silicate materials in acidic solutions (Eary and Rai 1989). The reduction of Fe(III) silicates or Fe(III) oxides by organic acid can also bring Fe(II) into solution (Hering and Stumm, 1990). The high organic matter content (about 9%) and total Fe (about 22%) in the Cr-soil samples makes it difficult to determine the predominant species contributing to the potential reduction of Cr(VI) to Cr(III). However, in acidic aqueous solutions, the overall reduction reaction of Cr(VI) by Fe(II) can be described as:



where $[\text{Cr(VI)}] = [\text{HCrO}_4^-] + [\text{CrO}_4^{2-}] + [\text{Cr}_2\text{O}_7^{2-}]$,

$$[\text{Fe(II)}] = [\text{Fe}^{2+}] + [\text{Fe(OH)}^+],$$

$$[\text{Cr(III)}] = [\text{Cr}^{3+}] + [\text{Cr(OH)}_2^+] + [(\text{CrOH})^{2+}], \text{ and}$$

$$[\text{Fe(III)}] = [\text{Fe}^{3+}] + [\text{Fe(OH)}_2^+] + [\text{Fe(OH)}^{2+}].$$

Depending on solution pH, total Cr and Fe, the composition of the solution, and experimental conditions, the Cr and Fe species will vary. Since Fe³⁺ and Cr³⁺ have the same charge and similar ionic radii (0.64 Å for Fe³⁺ and 0.63 Å for Cr³⁺, respectively (Lide 1991), they are exchangeable between the solid phases formed by these two ions. Sass and Rai (1987) have reported that when both Cr(III) and Fe(III) are present in acidic solutions, a resulting hydroxide precipitate, Cr_xFe_{1-x}(OH)₃(s) will

occur under slightly acidic to alkaline solution conditions depending on their concentrations. They have proposed the following reaction mechanism:



where x can vary between 0 to 1. The Cr hydroxide solids, $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ can precipitate rapidly under slightly acidic to slightly alkaline solution following the following relationship:

$$\log [\text{Cr}(\text{OH})_2^+] = -2\text{pH} + 4.18 + 0.28(1-x)^2 - 1.79(1-x)^3 + \log x \quad (4.3)$$

The above equation was generated from a series of solubility data and can be used to predict the aqueous Cr(III) concentration in the range of pH 2 to 6. Sass and Rai (1987) have reported an “ x ” value of less than 0.69.

Figure 4.2 shows the solubility diagram for $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$. In this study, we have discovered a brown precipitate under acidic conditions. Precipitates of the same brown color were also reported by Eary and Rai (1988) in their study of chromate reduction with ferrous ion. Based on the experimental procedure used in this study, it is not possible to identify the brown precipitate as $\text{Cr}(\text{OH})_3(\text{s})$ or $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$. However, based on the experimental results (Figure 4.2), the concentration of Cr(III) in the leachate appears to be controlled by a solubility process rather than an adsorption/desorption reaction, since the experimental points fall near the theoretical solubility lines. The mole fraction of $\text{Cr}(\text{OH})_3(\text{am})$ in the precipitate, x , appears to be in the range of 0.01 to 0.69 according to equation (4.3) (Sass and Rai 1987). The x value is not a constant, rather it is a function of the chemical composition of solution and the aging time of the precipitate. The value of x

was found to vary from 0.01 to 0.69 because of the heterogeneous nature of leaching system and short aging time (24 hours reaction time). In a similar study, Eary and Rai (1988) have reported a Fe/Cr ratio near 3.0 and concluded that the x value is 0.25, giving the Cr-Fe precipitate a solution composition of $\text{Cr}_{0.25}\text{Fe}_{0.75}(\text{OH})_3(\text{s})$. In their study of chromate reduction by subsurface soils under acidic conditions, Eary and Rai (1991) reported that the x value is significantly less than 0.25.

4.3.2 Effect of Organic Matter on Cr Leaching

The effect of soil organic carbon on Cr(VI) leaching from the Cr-soil was studied by heating soil samples in a furnace to remove the organic matter from the soil. The amounts of Cr(VI) leached from the “treated” soils (no organic matter, Figure 4.3) is about five times as great as that from the untreated soils (Figure 4.1a). It appears that organic matter plays an important role in affecting the Cr(VI) leaching. Soil organic matter can reduce Cr(VI) to Cr(III) over a wide range of pH (Bartlett and Kimble 1976). In fact, there is a similar trend observed of Cr(VI) leaching between treated and untreated Cr-soil samples (Figure 4.1a). Between pH 2.5 and 4.5, the amount of Cr(VI) leached increases with increasing pH, while between pH 4.5 and 11, the amount of Cr(VI) leached remains constant. Different amounts of Cr(VI) leached from the untreated Cr-soil samples may be attributed to different organic matter content of the three soil samples. In contrast, no major difference in the amount of Cr(VI) leached among the three “treated” Cr-soil samples was observed. Removal of organic matter from the three soil samples did not change the leaching behavior of Cr(III), Fe(III), and Fe(II) from that shown in Figures 4.1b, 4.1d, and 4.1e. The

presence of Fe(II) both found in the leachate for the treated and untreated sample indicates that all of the Fe(II) in the soil did not become oxidized to Fe(III) during the heating process. As shown in Figure 4.4, the ratio of Fe(II)/Fe(III) leached from both treated and untreated samples follows an identical relationship. Therefore, we conclude that organic matter plays an important role in Cr(VI) leaching but not Cr(III)

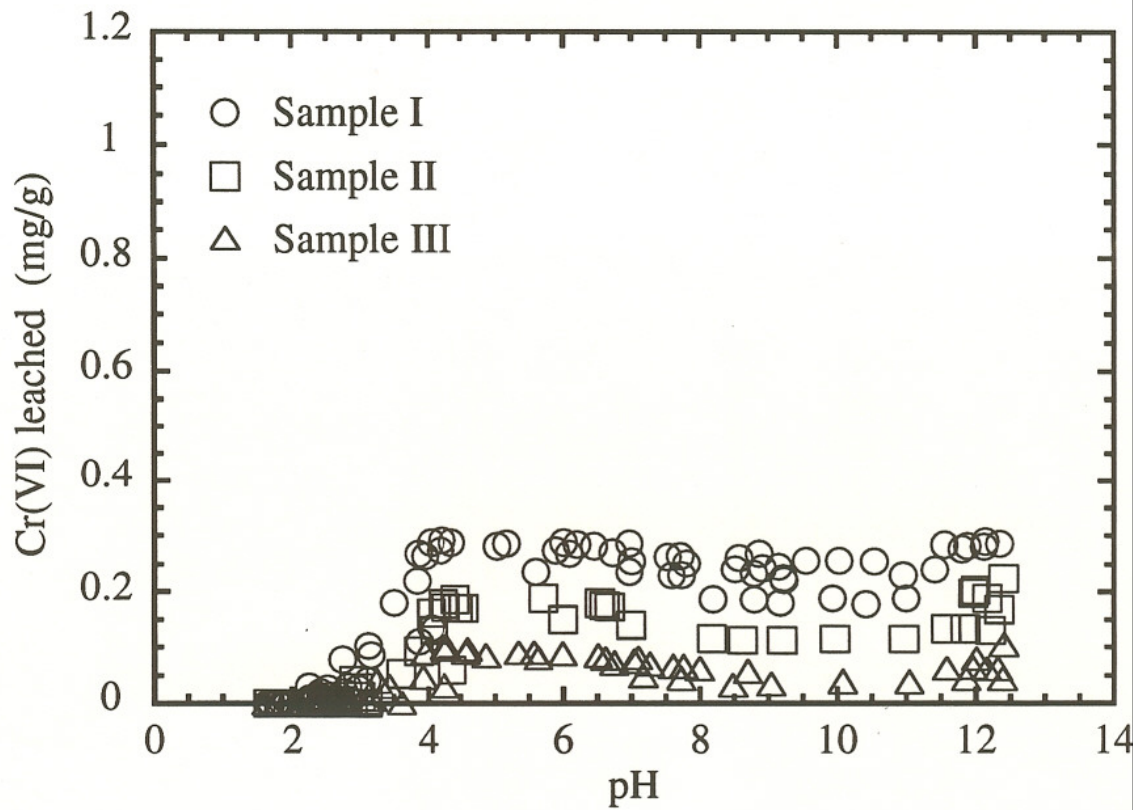


Figure 4.1a Cr(VI) leached as a function of pH. Experimental conditions were 24 hours reaction time, soil-to-water ratio 5 g/L, 25 °C.

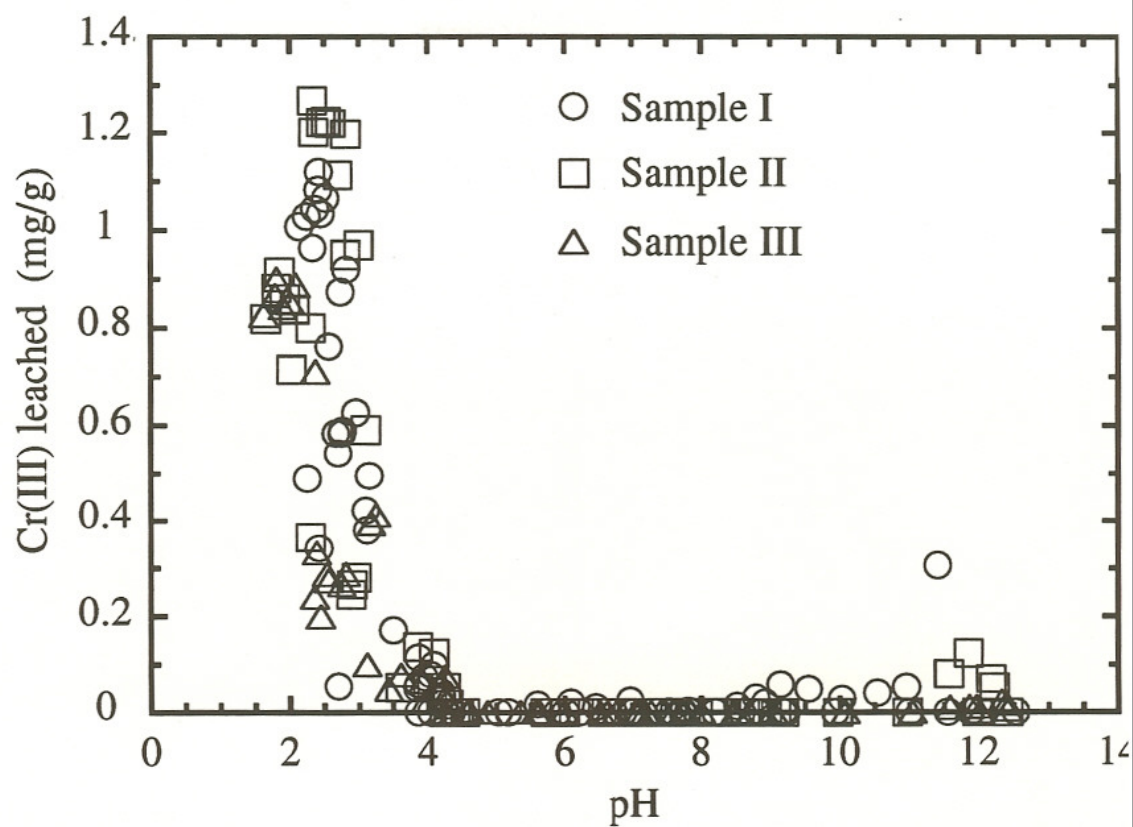


Figure 4.1b Cr(III) leached as a function of pH. Experimental conditions were 2 hours reaction time, soil-to-water ratio 5 g/L, 25 °C.

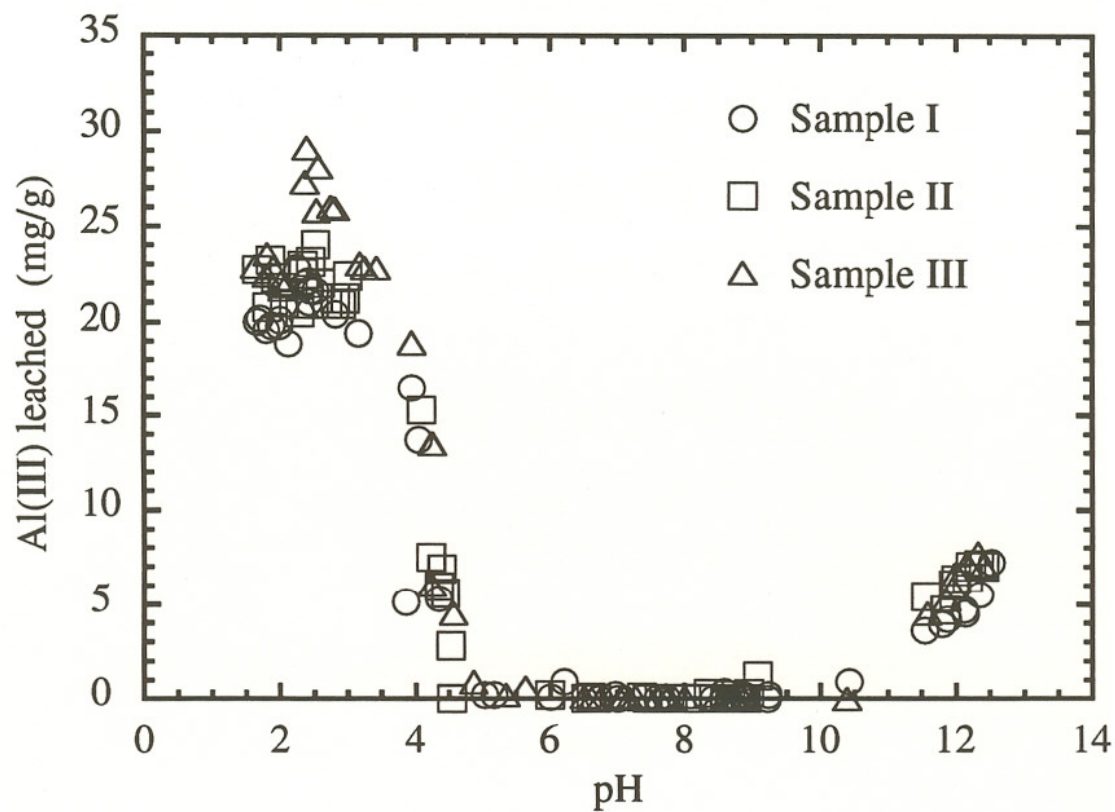


Figure 4.1c Al(III) leached as a function of pH. Experimental conditions were 24 hours reaction time, soil-to-water ratio 5 g/l, 25 °C.

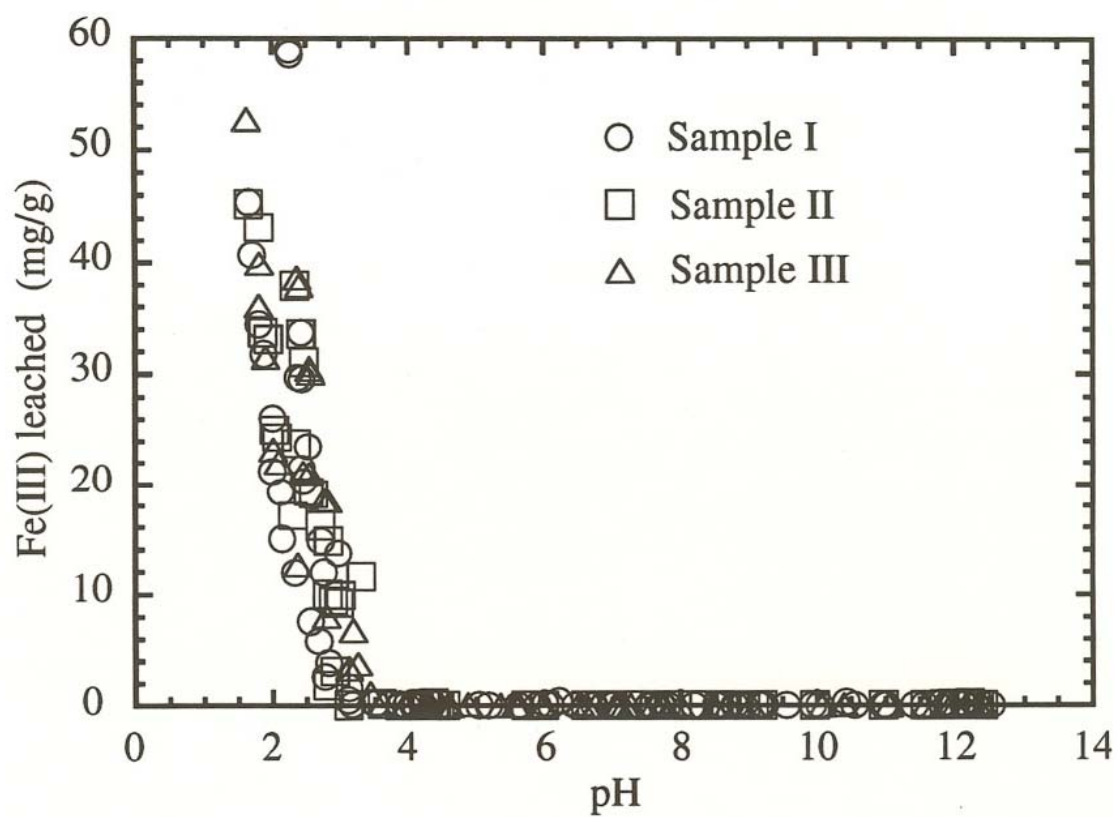


Figure 4.1d Fe(III) leached as a function of pH. Experimental conditions were 2 hours reaction time, soil-to-water ratio 5 g/L, 25 °C.

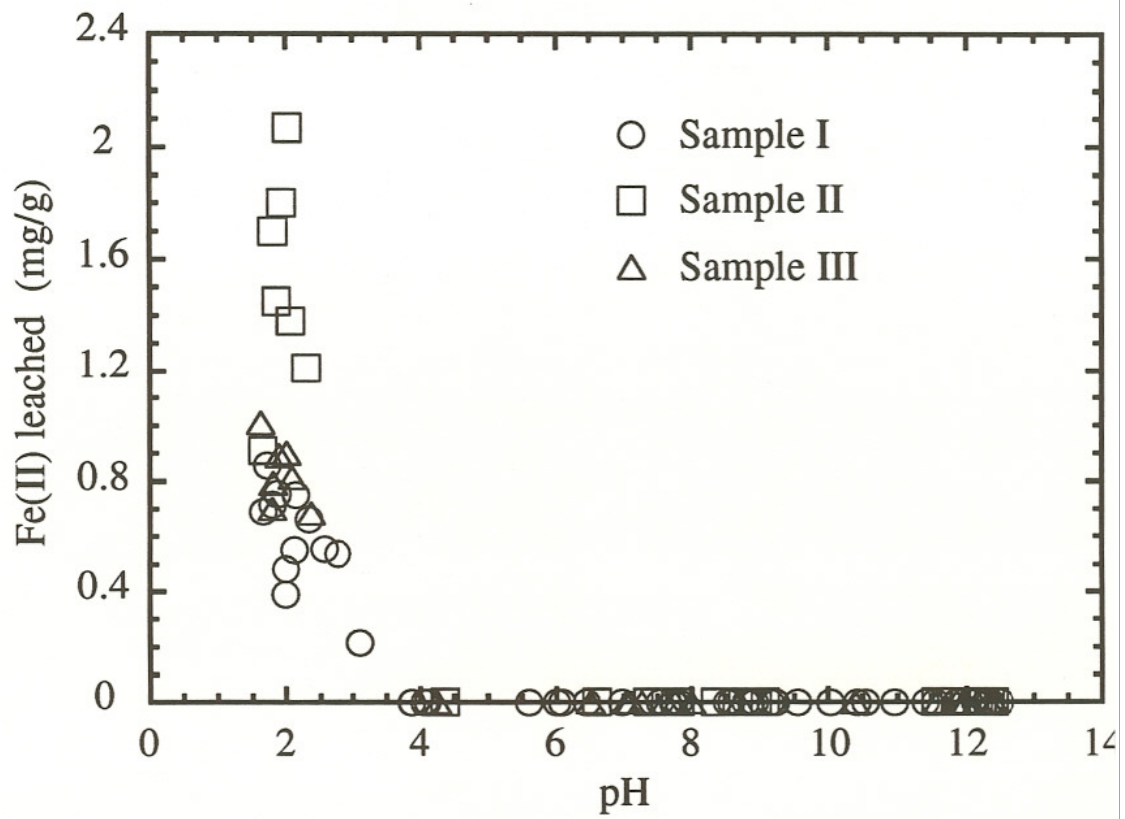


Figure 4.1e Fe(II) leached as a function of pH. Experimental conditions were 24 hours reaction time, soil-to-water ratio 5 g/L, 25 °C.

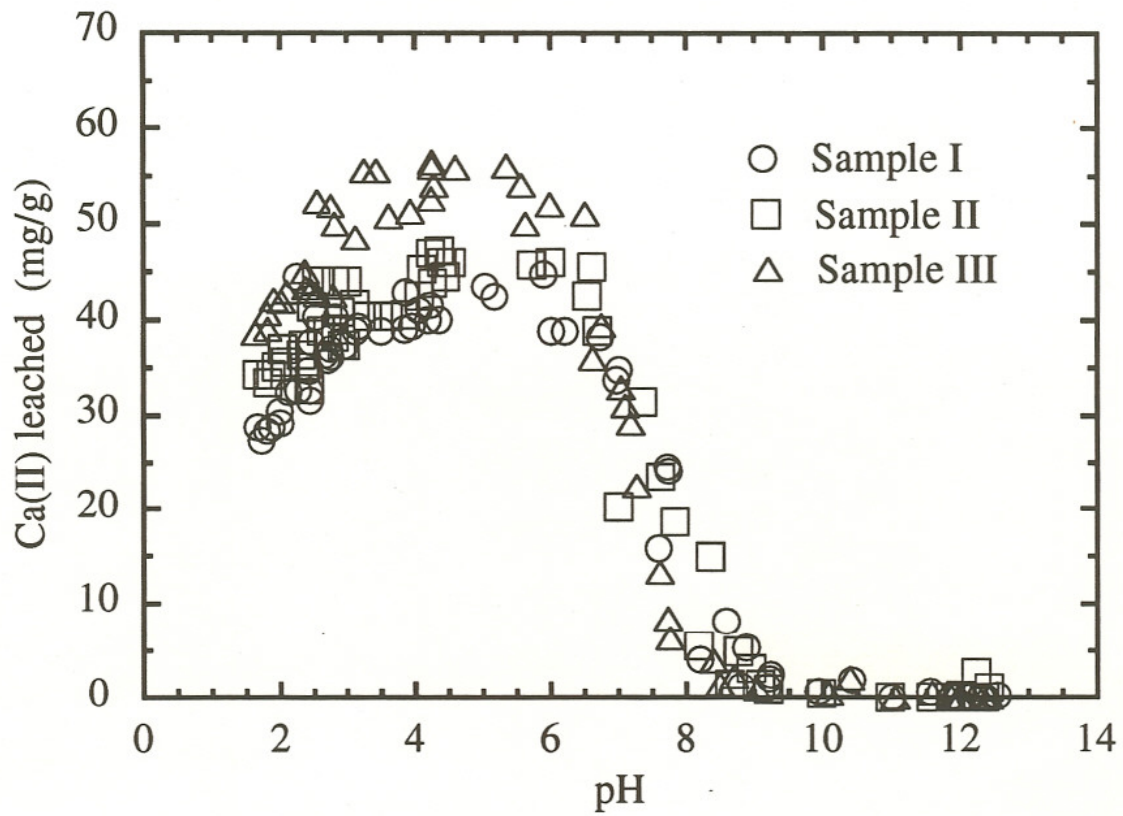


Figure 4.1g Ca(II) leached as a function of pH. Experimental conditions were 24 hours reaction time, soil-to-water ratio 5 g/L, 25 °C.

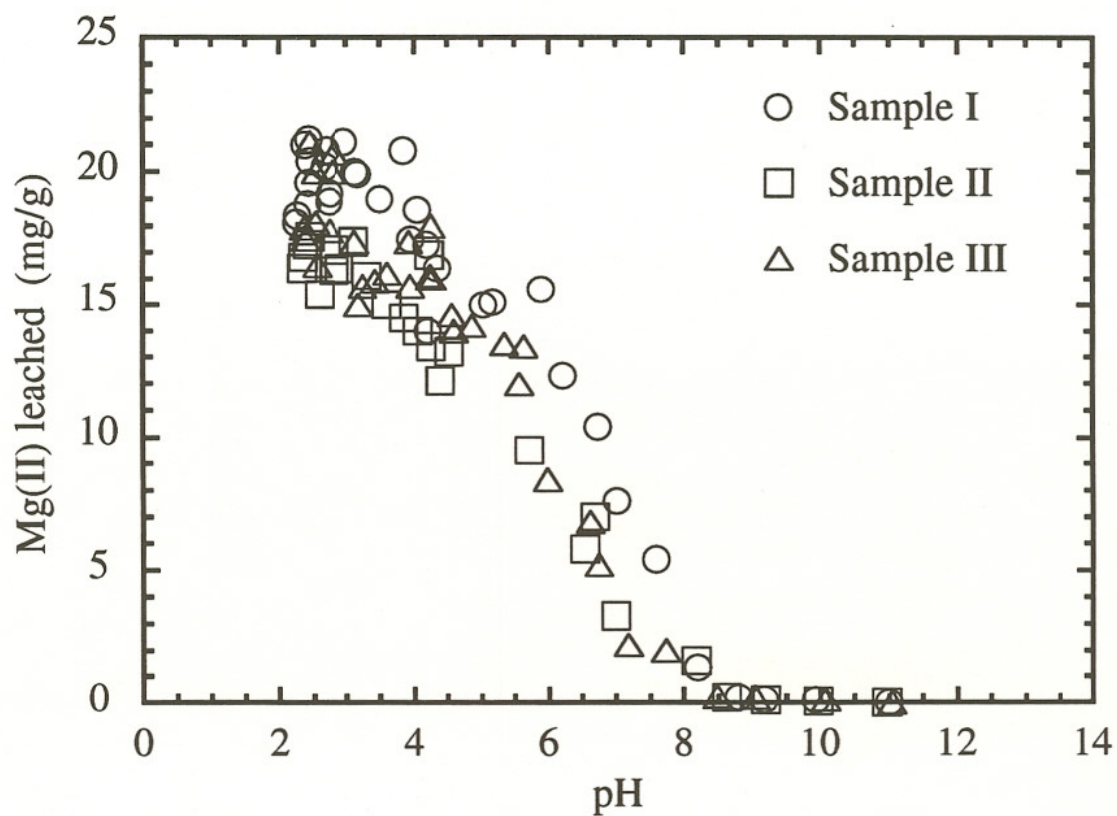


Figure 4.1h Mg(II) leached as a function of pH. Experimental conditions were 24 hours reaction time, soil-to-water ratio 5 g/l, 25 °C.

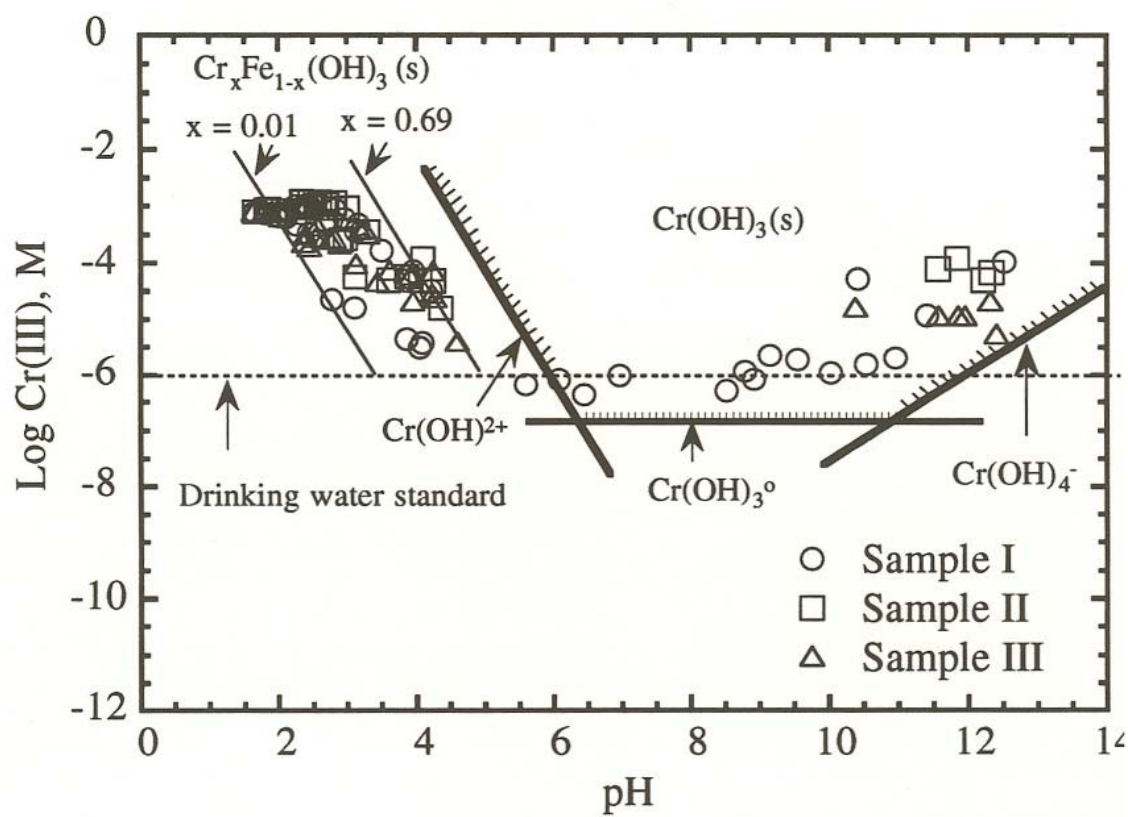


Figure 4.2 Data fitting for the solubility of $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$. Thin lines represent $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ at different values of x (mole fraction of $\text{Cr}(\text{OH})_3(\text{s})$). Bold line represent $\text{Cr}(\text{OH})_3(\text{s})$.

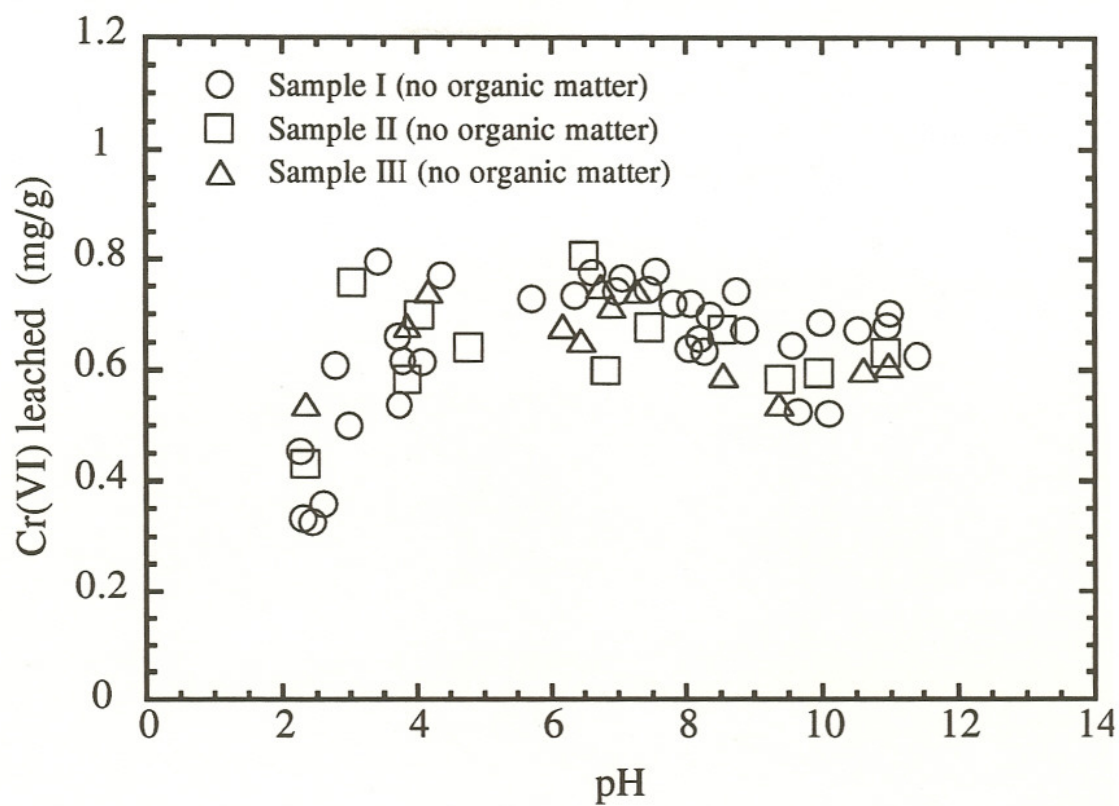


Figure 4.3 Cr(VI) leached as a function of pH. The Cr-soil samples were heated in a furnace for 4 hours to remove the organic matter content. Experimental conditions were 24 hours reaction time, soil-to-water ratio 5 g/L, and 25 °C.

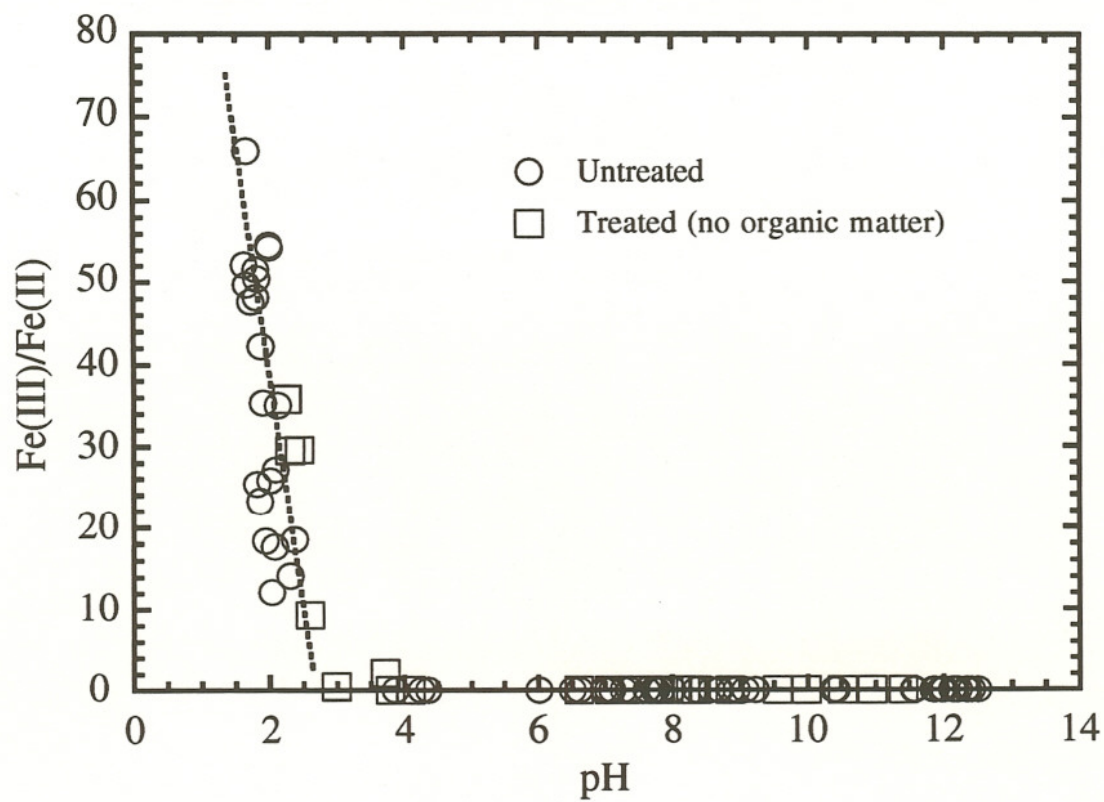


Figure 4.4 Comparison of the ratio of Fe(II)/Fe(III) leached as a function of pH for the treated and untreated Cr-soil samples.

4.4 Summary

Leaching of chromium and all of the other metals with synthetic rainwater is highly pH sensitive. Low pH (< 4) promotes Cr(VI) reduction to Cr(III), and thereby decreases the mass of Cr(VI) leached. No Cr(VI) was detected in the leachate at low pH (< 2.5). This may be attributed to adsorption of Cr(VI) onto the soil surface and/or reduction of Cr(VI) to Cr(III) by organic matter and/or by ferrous iron (two other major components of the soil); these processes are favored at low pH. Significant amounts of Cr(VI) were leached between pH 4.5 and 12. Results from leaching experiments indicate that approximately 1% of total Cr (25 mg/g) is readily leachable. The bulk of the remaining chromium mainly consists of trivalent chromium which is nonleachable between pH 4 and 12. The major chromium form in Cr-soil was identified as chromite by XRD analysis. The forms of leachable chromium can not be identified. It can only be hypothesized that Cr(VI) is leached by a dissolution of the chromate salts and attenuated by adsorption/desorption, precipitation, and redox processes that may occur in the soil-water system. Removal of the organic matter from the Cr-soil increases the amount of Cr(VI) leached over the entire pH range, suggesting that the organic matter can reduce Cr(VI) present in the solution. Cr(III) leaching behavior was also investigated as a function of pH. Cr(III) was found in solution at pH < 4.5 . The amount of Cr(III) leached was controlled by the solubility of Cr(III) precipitates, the extent of Cr(VI) reduction, and the magnitude of Cr(III) adsorption onto the soil surface. No Cr(III) was detected between pH 4.5 and 12 which can be attributed to the presence of insoluble precipitates such as $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ and the adsorption of Cr(III) species onto the soil particle surface.

Chapter 5

CHEMICAL INTERACTIONS BETWEEN CR(VI) AND HYDROUS CONCRETE PARTICLES

5.1 Introduction

Although results from a number of research are available for the behavior of chromium in soil, oxides, activated carbon, and sediments (Rai et al. 1989; Hsieh et al. 1988; Zachara et al. 1988; Zachara et al. 1987; Stollenwerk and Grove 1985; Mayer and Schick 1981; Davis and Leckie 1980; Huang and Bowers 1978; Griffin et al. 1977; MacNaughton 1977), no information is available pertaining to chromium interaction with concrete in the aqueous system. It is hypothesized that during wet periods, Cr(VI) leached from Cr-soil derived from COPR, will react with concrete. Therefore, chemical interaction between concrete is deemed important. Information from this study is useful for the establishment of remediation strategy.

In this chapter, I describe the chemical interaction between chromium and concrete materials. Parameters, such as pH, chromium concentrations, and particle size, which may affect the chemical interactions were studied. Adsorption/desorption, redox, and precipitation processes, that affect the concentration of chromium in its interaction with concrete, were also investigated. Determinations of surface acidity of hydrous concrete using electrophoretic mobility measurements was made. A surface complex formation model (SCFM) originally developed by Huang and Stumm (1973) was used to describe the adsorption of chromium onto concrete particles.

5.2 Experimental

5.2.1 Batch Chromium Reaction With Concrete Experiments

The study of Cr(VI) reaction with concrete materials was conducted with batch equilibrium experiments in synthetic groundwater (except as mentioned otherwise) at room temperature (25 °C). To a series of plastic bottles containing different amount of Cr(VI) concentrations (0.5-10 mg/L) in 100 mL of synthetic groundwater (preparation of synthetic groundwater is shown in the next section), the initial pH was adjusted by 1N NaOH and/or HNO₃, then a given amount of the sorted concrete particles was added. The samples were shaken on a shaker (Eberbach Co., Ann Arbor, MI) at a 150 excursions per minute. After shaking for 24 hours (24-hour reaction time was found to be adequate to reach equilibrium), the final pH was recorded and an aliquot of the suspensions was taken and filtered (Gelman, 0.45 µm). The concentration of chromium in the supernatant was determined. The concentrations of other metals in the supernatant were analyzed with AA, except for Fe(II) and Fe(III) ions, which were analyzed with the colorimetric method as described previously.

5.2.2 Preparation of Synthetic Groundwater

It is hypothesized that during wet periods, Cr-contaminated groundwater transports Cr(VI) ions into concrete block. Therefore, synthetic groundwater was prepared and used as the solution matrix throughout the study of chromium reaction with concrete material. To determine appropriate groundwater constituents, that would be derived from Cr-soil, 50 g Cr-soil was added to 50 mL of simulated

rainwater (initial pH 4.3) in a plastic bottle. The samples were then placed on an orbital shaker (Model G33, New Brunswick Scientific, Edison, NJ) at a slow speed (50 rpm) at room temperature (25 °C) for 15 days. The equilibrium pH was then recorded and aliquots of the suspension were filtered through 0.45 µm Gelman filters. The concentrations of the major metal ions and other constituents in the supernatant were analyzed as described above. Results of major ion species leached from Cr-soil are shown in Figure 5.1. The high amount of leachable NO_3^- may pose a severe groundwater contamination problem. The concentration of Cr(III) in the leached solution, which was below the detection limit (0.01 mg/L), is controlled by $\text{Cr}(\text{OH})_3(\text{s})$ precipitate and/or the adsorbed Cr(III) species onto soil. The high concentration of Ca(II) is attributed to the moderately soluble CaCO_3 in the Cr-soil. Synthetic groundwater was prepared based on the amount of major ions i.e., Ca(II), Mg(II), Na^+ , K^+ , NO_3^- and Cl^- leached from the Cr-soil supplemented with an amount of HCO_3^- appropriate to maintain the electroneutrality (Figure 5.1). Other ions such as Cr(VI) (0.13 mmole/L) and SO_4^{2-} (0.01 mmole/L) also found in the leachate are not included in the recipe. The synthetic groundwater has an ionic strength of ca. 10^{-2} M and pH 7.8.

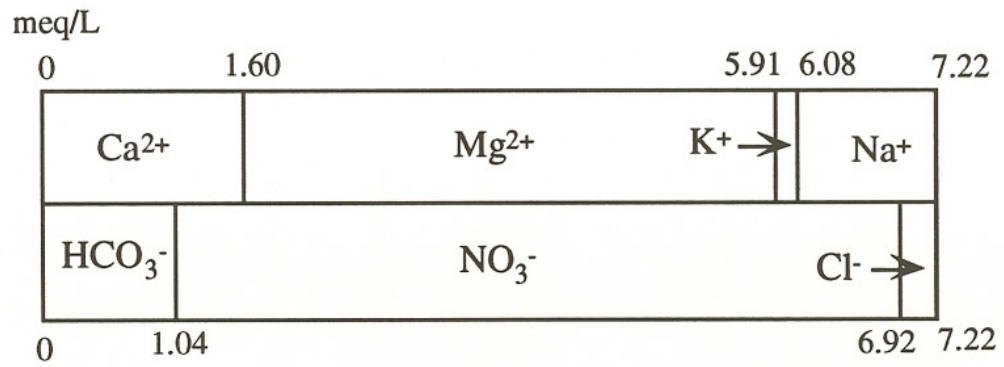


Figure 5.1 Major ions leached from Cr-soil were used as the recipe for synthetic groundwater preparation.

5.3 Results and Discussion

5.3.1 Effect of pH and Cr(VI) Concentration on Cr(VI) Removal

Figure 5.2 shows the residual Cr(VI) in the solution as a function of pH after 24-hour reaction time. Cr(III) was found below pH 4.5 and above pH 10.0, indicating that Cr(VI) was reduced to Cr(III) at this pH range. There was no apparent difference in the chromium concentration between synthetic groundwater and 0.01 M NaNO₃ as the aqueous phase. This clearly indicates that the composition of synthetic groundwater does not affect the percentage of Cr(VI) removal. Zachara et al. (1987) have reported that adsorption of Cr(VI) onto amorphous iron oxyhydroxide was affected by the presence of anionic constituents such as SO₄²⁻ because these anionic constituents compete for adsorption sites. This effect, however, was not observed in the present study.

The total amount of Cr(VI) removed by concrete materials can be expressed as:

$$\text{Cr(VI)}_{\text{rem}} = \text{Cr(VI)}_{\text{added}} - \text{Cr(VI)}_{\text{sol}} \quad (5.1)$$

where

$\text{Cr(VI)}_{\text{added}}$ = the amount of Cr(VI) present in the solution at the beginning of the experiment,

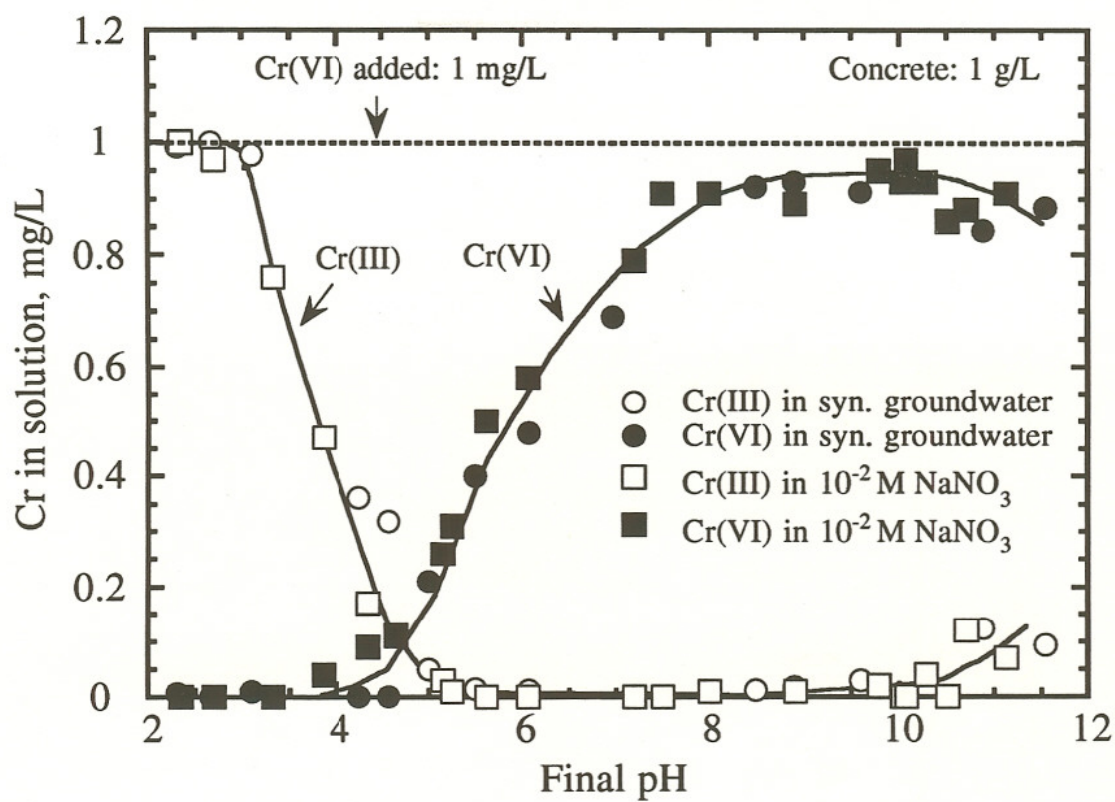


Figure 5.2 The remaining concentration of Cr(VI) and Cr(III) as a function of pH in the synthetic groundwater and 0.01 NaNO_3 solutions.

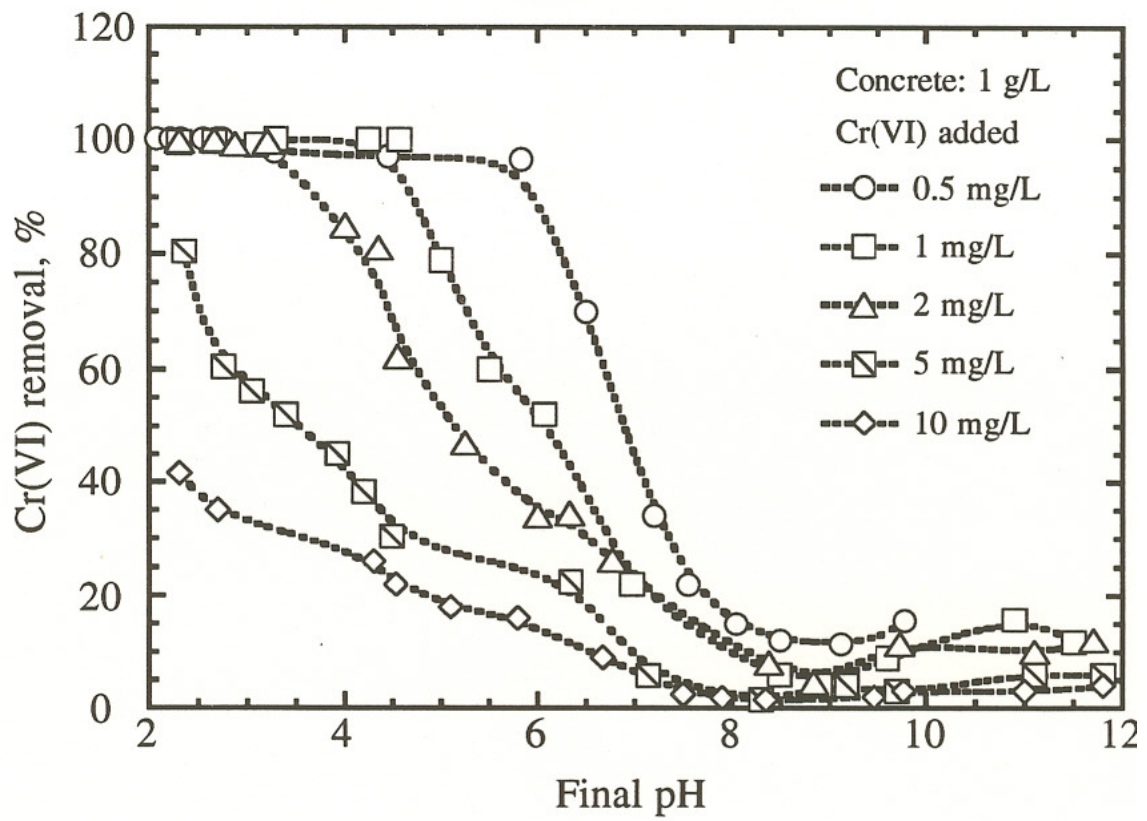


Figure 5.3 Cr(VI) removed determined as difference of initial and final Cr(VI) solution concentration.

$\text{Cr(VI)}_{\text{sol}} = \text{Cr(VI)}$ remained in the solution after experiment, and

$\text{Cr(VI)}_{\text{rem}} = \text{Cr(VI)}$ removed from the solution after experiment.

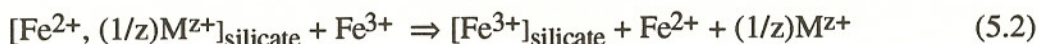
Figure 5.3 shows the percent of Cr(VI) removed at different initial Cr(VI) concentrations as a function of pH. The results indicate that the removal of Cr(VI) by concrete materials was greatly affected by pH and the Cr(VI) concentration. In general, the percent Cr(VI) removed increases with decreasing pH and Cr(VI) concentration. Nearly 100% Cr(VI) removal was observed under acidic conditions ($\text{pH} < 4.0$).

5.3.2 Redox Reaction

The observed concentrations of Cr(III), Fe(II) and Fe(III) are shown in Figures 5.4a, 5.5a, and 5.6a, respectively. At lower pH values, a significant amount of Cr(III) was found in the solution, indicating that reduction of Cr(VI) had occurred. The behavior of Cr(III) produced as a function of pH is similar to that of Al(III), Fe(III), and Cr(III) leached from the Cr-soil reported in chapter 5, in that the amount of metals leached increases sharply with decreasing pH. It appears that pH has a significant effect on the formation of Cr(III) resulted from Cr(VI) reaction with the concrete material. At $\text{pH} < 4.0$, the amounts of Cr(III) and Fe(III) produced increase sharply with decreasing pH. The concentration of Cr(III) is governed by the solubility of $(\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(\text{s})$ precipitates. No soluble Cr(III) and Fe(III) were detected at neutral pH, which may be attributed to the formation of hydroxide precipitates, $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Fe}(\text{OH})_3(\text{s})$ or other precipitates such as $(\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(\text{s})$. Cr(III)

is produced primarily from the reduction of Cr(VI) by aqueous Fe(II) in acidic solution. Evidence of Fe(II) presence in the concrete suspension is shown in Figure 5.5a. Up to 4 mg/g of Fe(II) was leached at pH 3.0 with no addition of Cr(VI) to the concrete suspension. Under acidic conditions, with increasing amount of Cr(VI) added from 0.5 to 10 mg/L in a 1 g/L of concrete particles solution, the amount of Fe(II) leached decreases (Figure 5.5a) while Fe(III) increases at a fixed pH value (Figure 5.6a). Apparently, Cr(VI) is reduced to Cr(III) by Fe(II) derived from the concrete material. As shown in Figure 5.3, there is a 100% Cr(VI) removal at pH ca. 6.0 when 0.5 mg/L of Cr(VI) is added. It is interesting to note that the amount of Cr(VI) removed is equal to the Cr(III) produced (Figure 5.4b). Stoichiometrically, the reduction of one mole of Cr(VI) requires three moles of Fe(II), yielding one mole of Cr(III) and three moles of Fe(III). It has been reported by Eary and Rai (1988) that the theoretical stoichiometric relationship must be maintained for the reduction of aqueous Cr(VI) with aqueous Fe(II) ions. In this study, the stoichiometric relationships among Cr(VI), Cr(III), Fe(II), and Fe(III) are presented in Figures 5.4b, 5.5b, and 5.6b. From Figure 5.4b, the molar ratio of Cr(III)/Cr(VI) is consistently equal to 1 below pH 3.5; all the Cr(VI) added was reduced to Cr(III). Apparently, at pH less than 3.5, oxidation/reduction is the dominant reaction between Cr(VI) and the concrete interface, and this reaction is responsible for Cr(VI) removal. Aqueous Fe(II) is the major agent for Cr(VI) reduction. As depicted in Figure 5.5a, the Fe(II) concentration dropped when Cr(VI) was added in the solution. No Fe(II) ions were found in the solution when 5 and 10 mg/L of Cr(VI) were added. Apparently, all Fe(II) present in the solution was used for Cr(VI) reduction. An insufficient amount of Fe(II) for Cr(VI) reduction led to a portion of Cr(VI) still remaining in the solution after equilibration.

The ratio of Fe(II) oxidized to Cr(VI) reduced, Fe(II)/Cr(VI), and the ratio of Fe(III) produced to Cr(III) produced, Fe(III)/Cr(III), are approximately equal to 1 which is lower than the theoretical homogeneous reduction value of 3 (Figures 5.5b and 5.6b). It appears that an additional amount of Cr(VI) was reduced, resulting in these ratios being lower than the value of 3. I speculate that the coupled electron-cation transfer (CECT) reactions involving Fe(II) in the silicate minerals and aqueous Fe(III) was important as discussed below. According to White and Yee (White and Yee 1985) the CECT reactions that occur on the surface of Fe(II)-containing silicates can be described as follow:



where brackets represent the solid surface and M represents non-involved cation of charge $z+$. The sources of Fe(III) are either from the dissolution of the Fe(III)-containing component of concrete or from the oxidation of aqueous Fe(II) in the presence of Cr(VI). Dissolution of Fe(II)-oxide, Fe(II)-silicates, and Fe(III)-oxide minerals has been documented (Suter et al. 1991; Hering and Stumm 1990; White 1990; Eary and Rai 1989; White et al. 1986; White and Yee 1985). The CECT reaction can produce Fe(II) ions (equation 5.2) and cause the aqueous Fe(III) to be reduced to Fe(II). This Fe(II) ion will be utilized as a reducing agent for Cr(VI) reduction. Consequently, additional Cr(VI) was reduced and lowered the Fe(II)/Cr(VI) ratio with respect to the theoretical homogeneous reduction value of 3. Evidence of Fe(II)-containing silicates were found in the concrete from XRD work (Figure 3.3).

Brown precipitates observed under acidic condition are believed to be $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ precipitate. Similar observations have also been reported in the Fe-Cr reaction system (Sass and Rai 1987; Eary and Rai 1988; Eary and Rai 1989). Under acidic conditions, the Cr(III) concentration in the concrete particle suspension is less than that from the solubility of pure $\text{Cr}(\text{OH})_3(\text{s})$, but follows the solubility of $(\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(\text{s})$. The concentration of Cr(III) is generally oversaturated with respect to pure $\text{Cr}(\text{OH})_3(\text{s})$. The oversaturated condition in the heterogeneous suspension has also been observed by others (Eary and Rai 1989). At neutral pH, the ratio of Fe(II) reduced to Cr(VI) oxidized can not be determined because of the formation of both $\text{Fe}(\text{OH})_3(\text{s})$ and $\text{Cr}(\text{OH})_3(\text{s})$ precipitates.

Based on the experimental results presented above, I propose a mechanism for the reduction of Cr(VI) in concrete suspension under acidic conditions: (1) Fe(II) ions are released from Fe(II)-containing concrete materials by dissolution. (2) Aqueous Fe(II) reacts with dissolved Cr(VI), producing Fe(III) and Cr(III). The reaction products can be $\text{Fe}(\text{OH})_3(\text{s})$, $\text{Cr}(\text{OH})_3(\text{s})$, and/or $(\text{Cr,Fe})(\text{OH})_3(\text{s})$ precipitates. (3) Aqueous Fe(III) ions produced from oxidation of Fe(II) ions and/or dissolution of Fe(III)-containing concrete materials react with Fe(II)-containing silicates to produce additional Fe(II) through coupled electron-cation transfer (CECT). (4) The Fe(II) produced from CECT reaction results in additional Cr(VI) reduced.

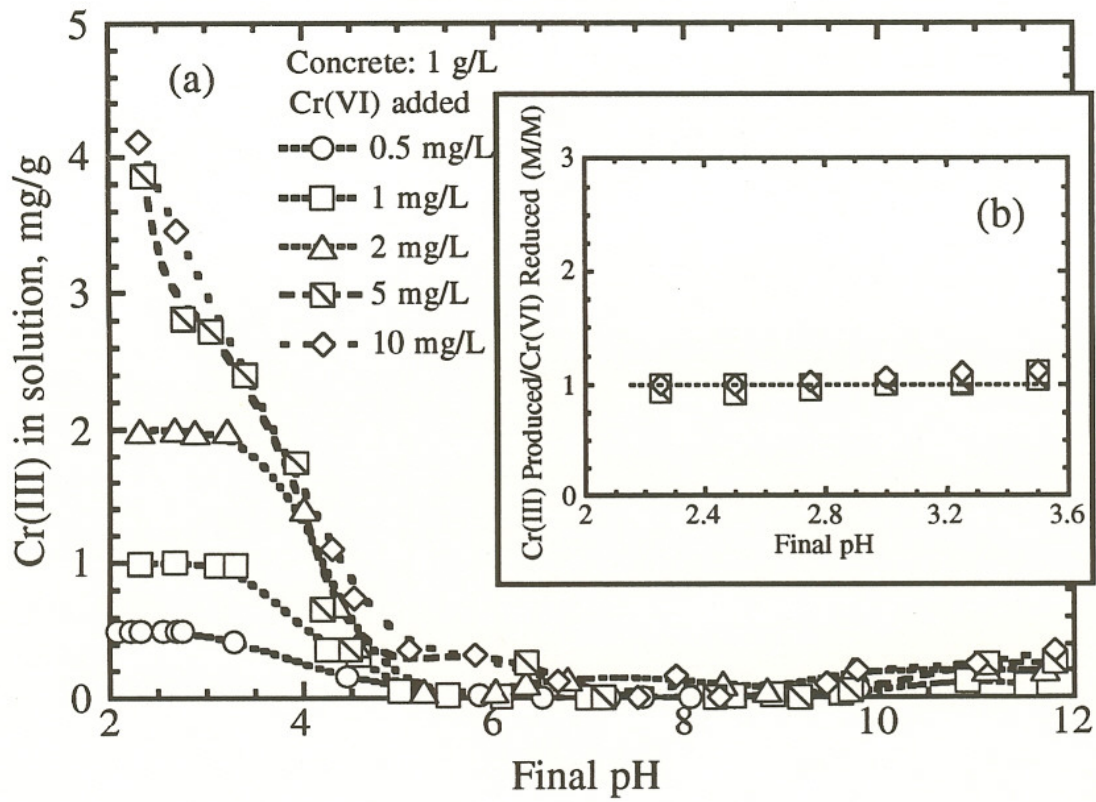


Figure 5.4 (a) Cr(III) in the solution as a function of pH and different Cr(VI) concentrations added. (b) The ratio of Cr(III) produced to Cr(VI) reduced as a function of pH.

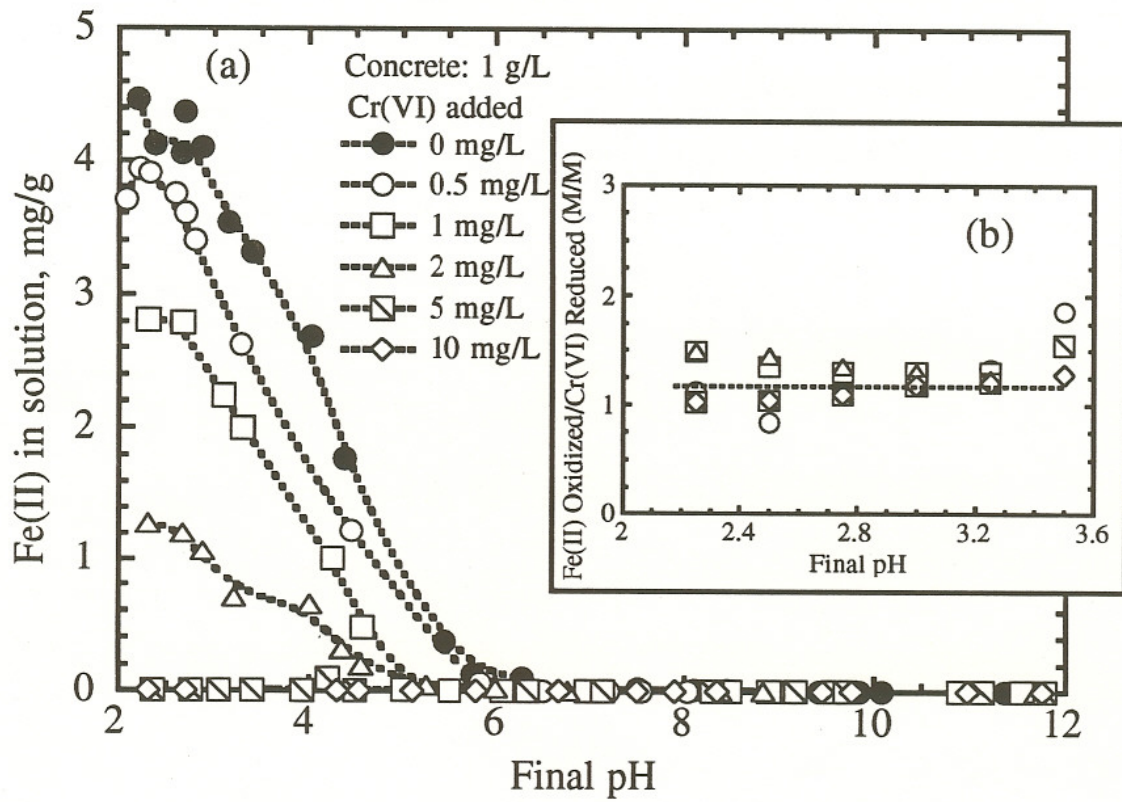


Figure 5.5 (a) Fe(II) leached as a function of pH and different Cr(VI) concentrations added. (b) The ratio of Fe(II) oxidize to Cr(VI) reduced as a function of pH.

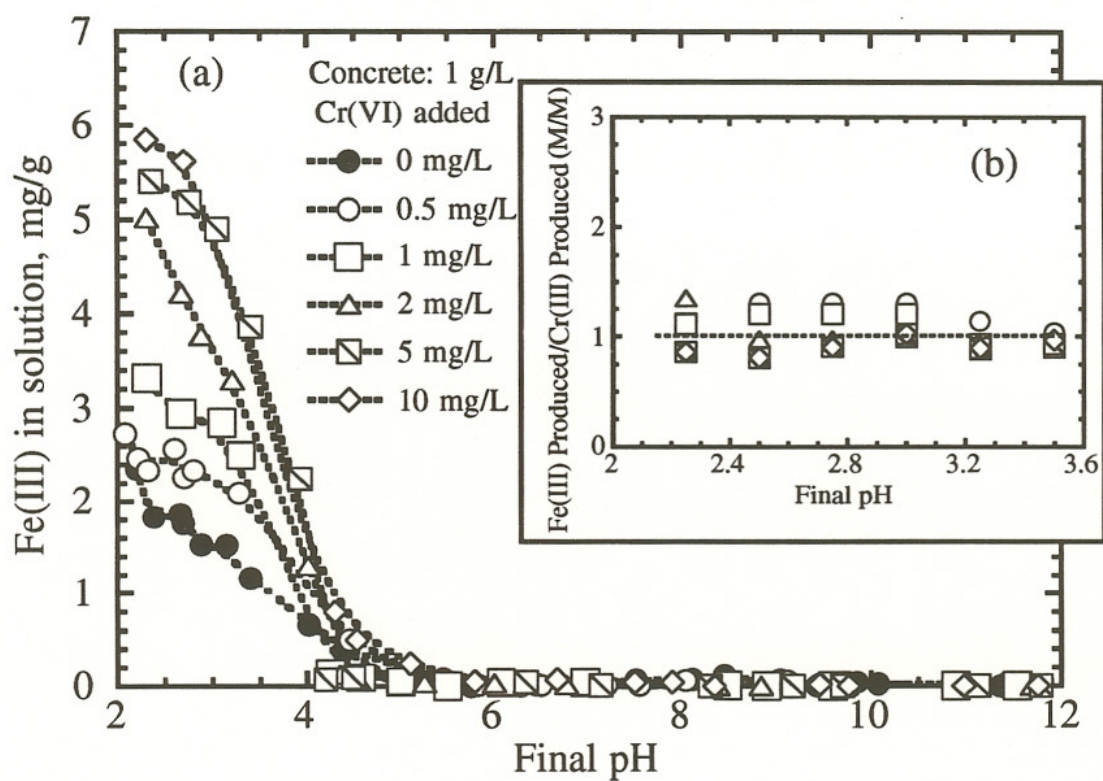


Figure 5.6 (a) Fe(III) leached as a function of pH and different Cr(VI) concentrations added. (b) The ratio of Fe(III) produced to Cr(III) produced as a function of pH.

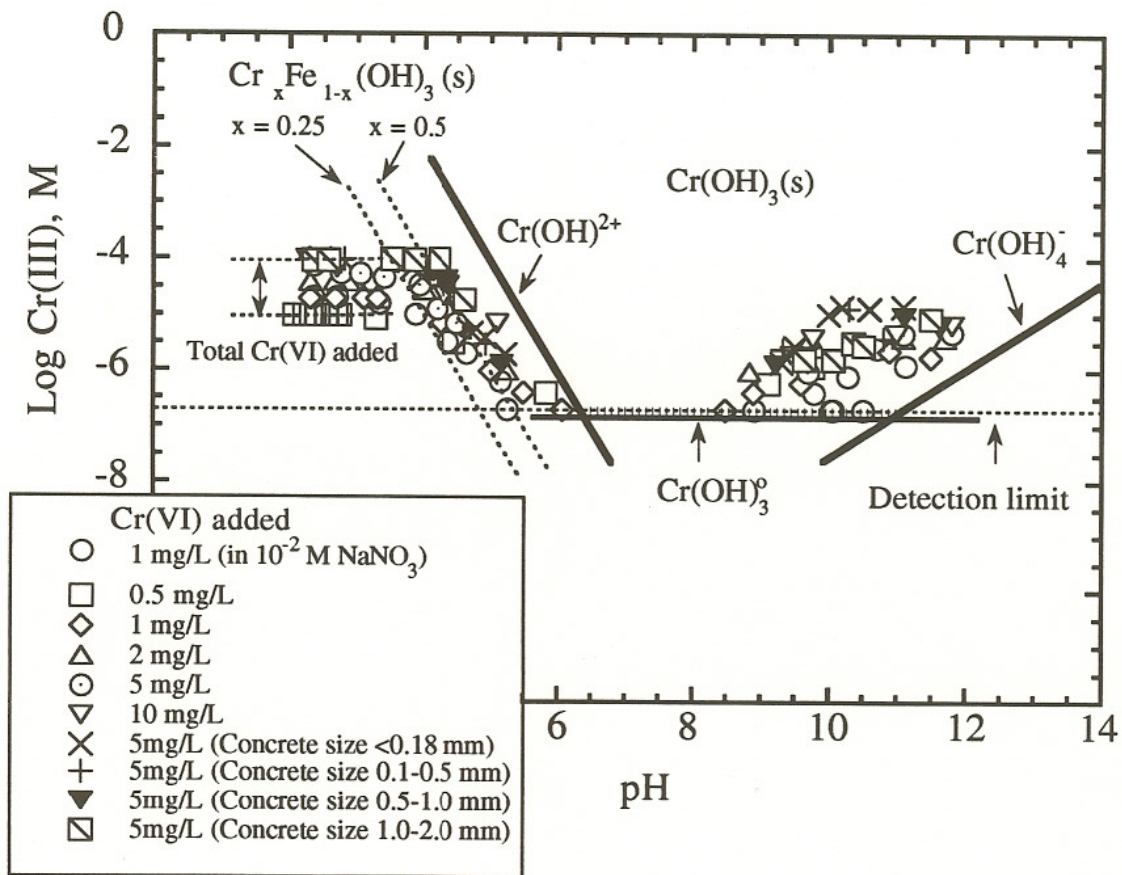


Figure 5.7 Comparison of $\text{Cr}(\text{OH})_3(\text{s})$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ precipitates. Synthetic groundwater and particle size 0.1-0.5 mm were used in the experiments except those mentioned in the legend.

5.3.3 Adsorption Reaction

In addition to the removal of Cr(VI) due to reduction, adsorption also plays an important role in chemical interaction of the Cr(VI)-concrete suspension. The total amount of Cr(VI) adsorbed was determined from:

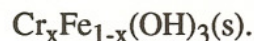
$$[\text{Cr(VI)}]_{\text{ads}} = [\text{Cr(VI)}]_{\text{add}} - [\text{Cr(VI)}]_{\text{sol}} - [\text{Cr(III)}]_{\text{sol}} - [\text{Cr(III)}]_{\text{ads}} - [\text{Cr(III)}]_{\text{precip}} \quad (5.3)$$

where

$[\text{Cr(III)}]_{\text{sol}}$ = Cr(III) remaining in the solution,

$[\text{Cr(III)}]_{\text{ads}}$ = Cr(III) adsorbed on the concrete particles, and

$[\text{Cr(III)}]_{\text{precip}}$ = primary hydroxide precipitates, i.e., $\text{Cr(OH)}_3(\text{s})$ or



Quantitatively, it is not possible to differentiate the amount of Cr(VI) adsorbed, Cr(III) adsorbed, Cr(VI) reduced, and Cr(III) precipitated by the analytical techniques used for this study. As shown in Figure 5.7, the concentration of Cr(III) is governed by the formation of $\text{Cr(OH)}_3(\text{s})$ and/or $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ precipitates. In order to simplify the calculation of Cr(VI) adsorbed, I assumed that the amount of Cr(VI) reduced to Cr(III) is not significant compared to the total amount of Cr(VI) removed at $\text{pH} > 4.0$; hence it was neglected. Thus, at solution $\text{pH} > 4.0$, chromium (both Cr(VI) and Cr(III)) not found in the solution was assumed to be adsorbed by concrete material, i.e., no redox occurring. Equation (5.3) is rewritten as:

$$[\text{Cr(VI)}]_{\text{ads}} = [\text{Cr(VI)}]_{\text{rem}} - [\text{Cr(III)}]_{\text{sol}} \quad (5.4)$$

The amount of Cr(VI) removed from solution, $[\text{Cr(VI)}]_{\text{rem}}$, is calculated from equation (5.1). The results of $[\text{Cr(VI)}]_{\text{rem}}$ and $[\text{Cr(III)}]_{\text{sol}}$ in the right-hand-term of equation (5.4), are correspondence to Figures 5.3 and 5.4, respectively. The results of Cr(VI) adsorption onto concrete materials calculated, $[\text{Cr(VI)}]_{\text{ads}}$, from equation 5.4 are shown in Figure 5.8. Results indicate that pH plays a significant role in Cr(VI) adsorption onto concrete material. At low pH (< 3.0), the amount of Cr(VI) was less than the detection limit (< 0.01 mg/L). Maximum adsorption was observed at pH 5.0. At pH > 5.0, the amount of Cr(VI) adsorbed decreases with increasing pH.

Below pH 3.0, Cr(VI) adsorption could not be assessed because the reduction of Cr(VI) is dominant in this pH region. Electrostatically, a positively charged concrete particle surface is dominant below pH 5.9, and it can enhance the anionic HCrO_4^- adsorption under acidic conditions (Figure 3.5). However, the fact that the amount of Cr(III) produced is equal to that of Cr(VI) added (Figure 5.4b) confirms the proposed overall Cr-Fe reaction stoichiometrically and the overall Cr-concrete reaction was controlled by redox reaction below pH 3.0.

Within the pH region 4.0 to 9.0, adsorption is mainly responsible for Cr(VI) removal. The percentage of Cr(VI) adsorption increases with decreasing pH. This result is in excellent agreement with those reported by others. Zachara et al. (1988), Hsieh et al. (1988) and Zachara et al. (1987) have also reported that adsorption of chromate onto soil enriched in kaolinite and crystalline Fe oxides and amorphous iron oxyhydroxide increases with decreasing pH. I speculate that the adsorption behavior of Cr(VI) onto concrete materials can be attributed to surface adsorption processes. It

is also noted that the extent of Cr(VI) removal by adsorption is highly pH-dependent. At high pH ($\text{pH} > 8$), Cr(VI) is almost no or minimally adsorbed onto concrete particles (Figure 5.8). The anionic chromate species is favorably adsorbed on positively charged sites of concrete particles when solution pH is less than pH_{zpc} . Decreasing solution pH will increase positive surface sites, resulting in increasing extended Cr(VI) adsorption. By plotting $\log q$ (adsorption density) versus $\log C_e$ (equilibrium concentration), the Freundlich adsorption constants can be determined. Appendix A shows the results of Freundlich plots for Cr(VI) adsorption onto concrete at pH 5 and 6.

5.3.4 Effect of Concrete Particle Size on Cr(VI) Removal

In order to evaluate the effect of particle size on Cr(VI) removal, four different concrete particle sizes, < 0.18 mm, $0.18 - 0.5$ mm, $0.5 - 1.0$ mm, and $1.0 - 2.0$ mm, were chosen for this study. Results of the effect of soil particle size on the removal of Cr(VI) are presented in Figure 5.8a. At $\text{pH} < 4.0$, the Cr(VI) removal has reached nearly 100% and particle size shows no effect on Cr(VI) removal, but at $\text{pH} > 4.0$, the percentage of Cr(VI) removal by all four different size particles decreases with increasing pH and particle size. Below pH 4.0, all 5 mg/L of Cr(VI) added is totally reduced to Cr(III) and particle size exhibits no effect on Cr(VI) reduction throughout the pH region studied (Figure 5.9b). As discussed previously, the removal of Cr(VI) below pH 4.0 is likely due to reduction reaction. The major reductant for Cr(VI) reduction is Fe(II) (data not shown, but similar to that of Figures 5.5a and 5.6a). The

amount of Fe(II) in the solution and the Cr(III) produced did not change with particle sizes.

Based on equation 5.4, the amount of Cr(VI) adsorbed by different concrete particle sizes can be determined. Figure 5.9c shows the amount of Cr(VI) adsorbed which is essentially the difference between Cr(VI) removed (Figure 5.9a) and Cr(III) remaining (Figure 5.9b). Peak Cr(VI) adsorption was observed at pH 5.0. The amount of Cr(VI) adsorbed decreases with increasing particle size because the larger particles have smaller specific surface areas available for Cr(VI) adsorption. The results of specific surface area of concrete indicate that larger particles exhibit smaller specific surface area and vice versa. A logarithmic plot can be used to predict the specific surface area of concrete block.

$$\log(\text{SA})_{\text{predicted}} = 0.36 - 0.11 \log(d) \quad (5.5)$$

where $\log(\text{SA})_{\text{predicted}}$ (m^2/g) is the predicted surface area in logarithmic scale and d (mm) is the diameter of the concrete particle. A linear $\log(\text{SA})$ - $\log(d)$ relationship between specific surface area and particle size was also observed for crushed quartz and quartz sand by Parks (1990). The Cr(VI) adsorption density as a function of particle size is shown in Figure 5.10. The adsorption density is related to the specific surface area of concrete materials. By knowing the adsorption density with respect to the specific surface area, it is possible to predict the adsorption density of other sizes of concrete particles as long as the surface area is provided. From Figure 5.10, one can predict the linear adsorption constant, K_L (L/Kg), for a specific size of concrete. For example, for a concrete particle 2.5 cm in diameter, the surface area is $1.6 \text{ m}^2/\text{g}$ according to equation 5.5. The adsorption density at pH 5.0, 6.0, and 7.0 will be 0.083

mg/g, 0.056 mg/g, and 0.036 mg/g, respectively. Accordingly, K_L (L/Kg) for this particle size at pH 5.0, 6.0, and 7.0 and equilibrium concentration, C_e (mg/L), are $0.083/C_e$, $0.056/C_e$, and $0.036/C_e$.

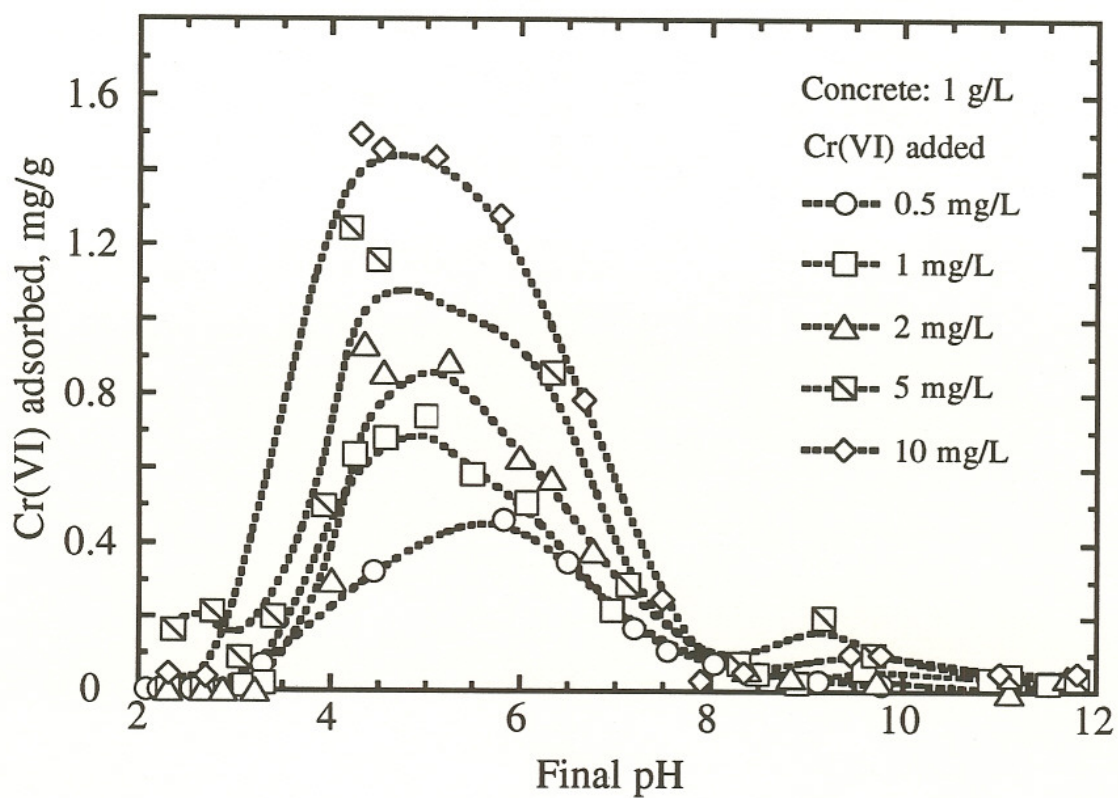


Figure 5.8 Cr(VI) adsorbed as a function of pH and different Cr(VI) concentrations added. At low pH (< 3.5), I assume that the reduction of Cr(VI) is dominant over adsorption.

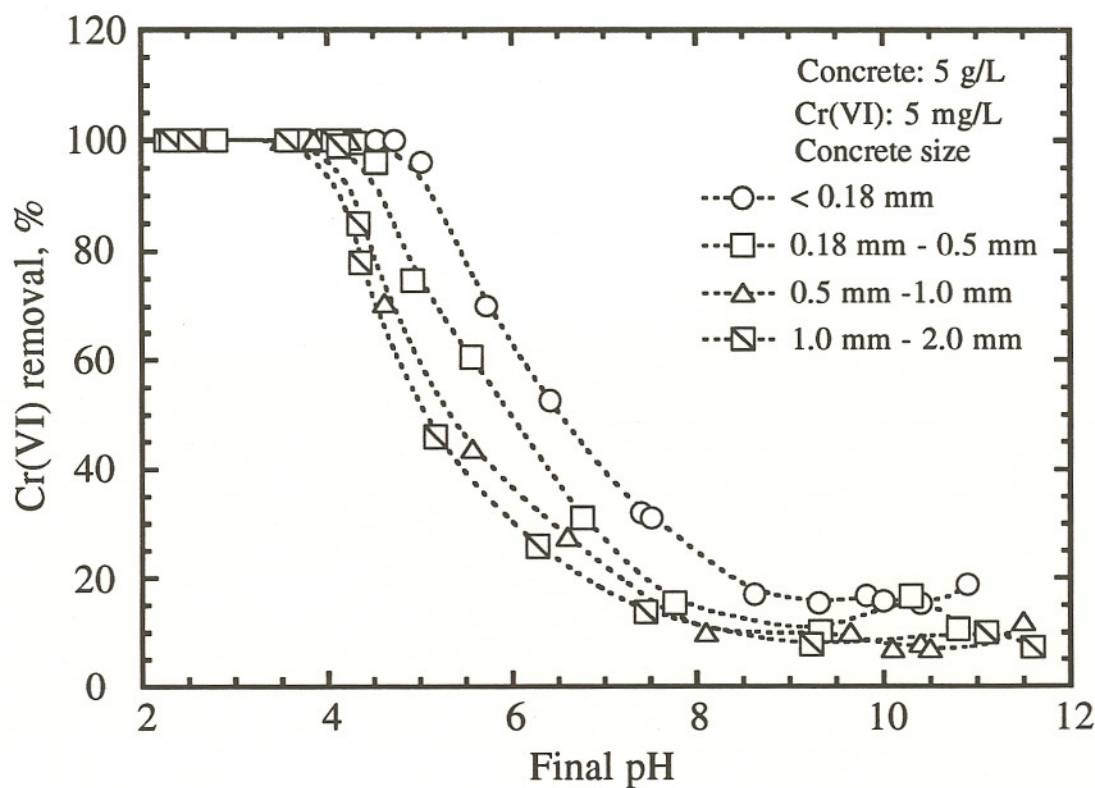


Figure 5.9a Effect of concrete particle size on Cr(VI) removal as a function of pH.

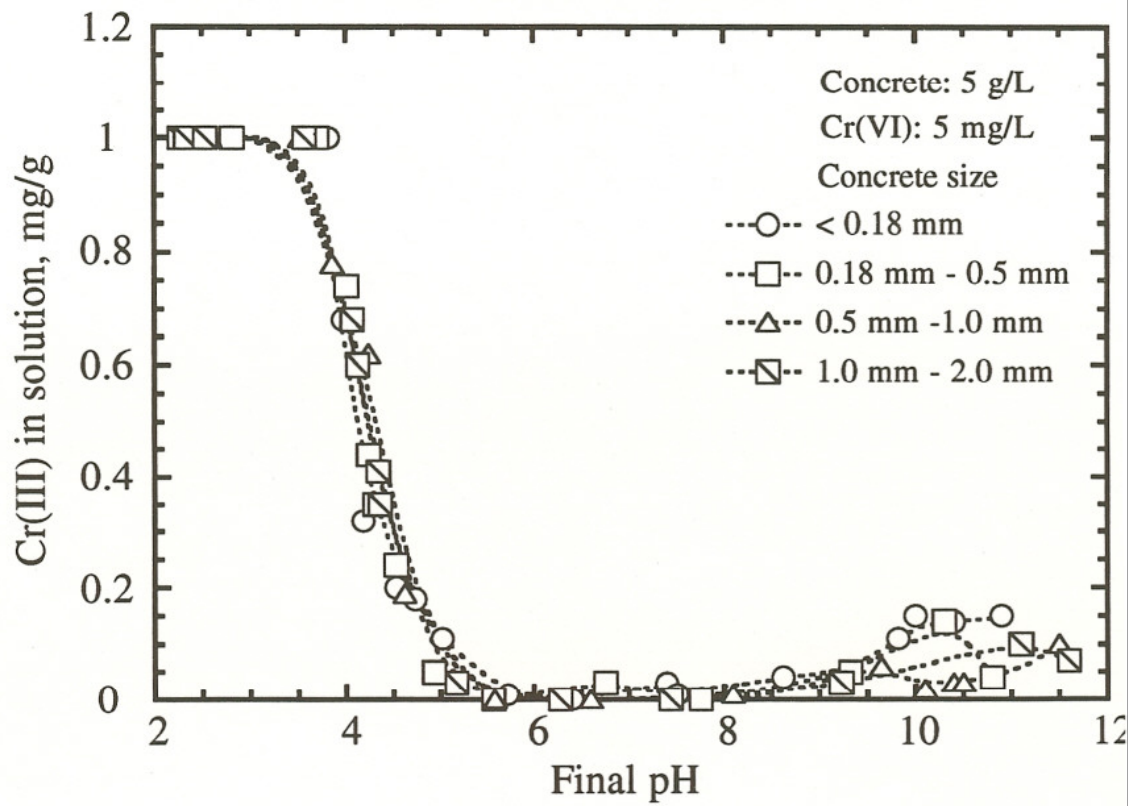


Figure 5.9b Effect of concrete particle size on Cr(III) produced as a function of pH.

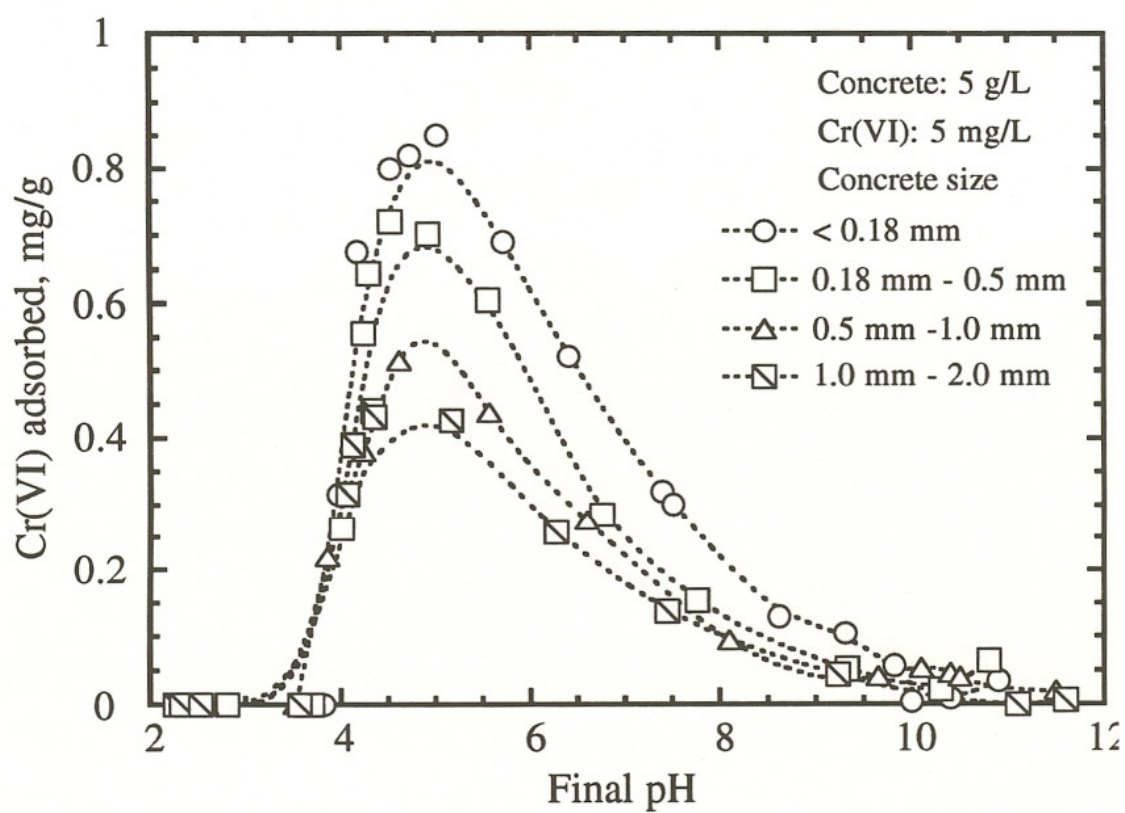


Figure 5.9c Effect of concrete particle size on Cr(VI) adsorbed as a function of pH.

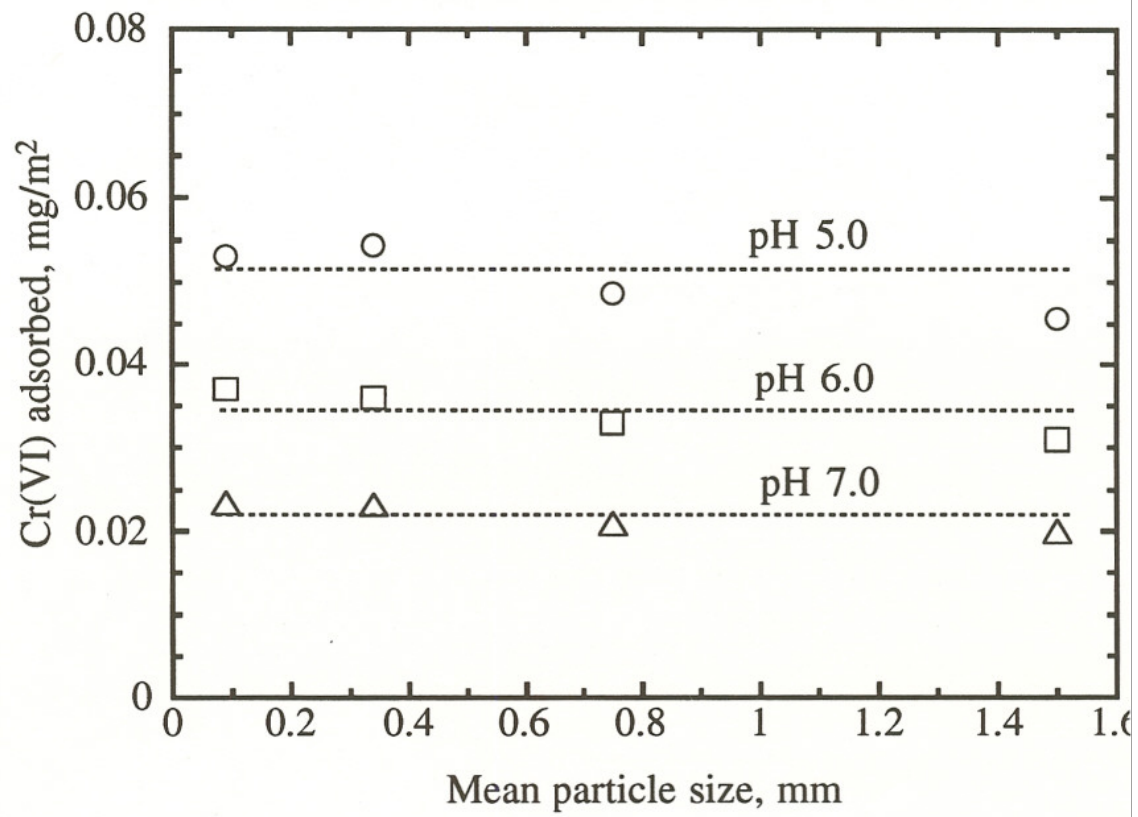


Figure 5.10 Cr(VI) adsorption density as a function of concrete particle size.

5.4 Modeling Cr(VI) Adsorption onto Concrete Particles

5.4.1 Surface Acidity of Hydrous Concrete Particles

Upon hydration, the surface of solid develops surface hydroxyl groups which behave amphotERICALLY (Huang et al. 1986):



where $\underline{SOH}_2^+$, $\underline{SOH}$, and $\underline{SO}^-$, represent protonated, neutral, and ionized surface hydroxyl groups, respectively. The various surface hydroxyls formed may not be structurally and chemically fully equivalent (Stumm 1992) but to facilitate the reaction equilibria, we consider a single hydroxyl group in the chemical reaction. The deprotonated surface group, $\underline{SO}^-$, behaves as Lewis base. For a constant ionic strength solution, which implies that the activity coefficients or surface concentration of the surface species are equal, the strength of the surface groups is expressed by the surface acidity constants (pK_{a1}^{int} and pK_{a2}^{int}):

$$K_{a1}^{int} = \frac{\{\underline{SOH}\}\{H^+\}}{\{\underline{SOH}_2^+\}} \quad (5.8)$$

$$K_{a2}^{int} = \frac{\{\underline{SO}^-\}\{H^+\}}{\{\underline{SOH}\}} \quad (5.9)$$

where $\{i\}$ stands for the surface concentration of the $\{i\}$ species. The surface proton concentration, $\{H^+\}$, is related to the bulk phase concentration, $[H^+]$, which can be directly measured, by the Boltzman distribution,

$$\{H^+\} = [H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right) \quad (5.10)$$

where F = Faraday constant, 96490 C/mol,

R = molar gas constant, 8.314 J/mol-°K,

T = absolute temperature (°K), and

ψ_o = surface potential (mV).

The surface potential, ψ_o , can not be directly measured quantitatively. An approximation has been established for determination of ψ_o , by the Nernst equation (James and Parks 1982; James and Healy 1972). For a potential-determining ion of “H⁺”, and a known pH_{zpc} , ψ_o can be determined:

$$\begin{aligned} \psi_o &\cong \frac{2.3RT}{ZF} (pH_{zpc} - pH) \\ &\cong 59.2 (pH_{zpc} - pH) \text{ (at } 25^\circ\text{C and 1:1 electrolyte)} \end{aligned} \quad (5.11)$$

where Z is the valence of electrolyte. The point at which the positive surface charge equals the negative surface charge, i.e., $\{SOH^{2+}\} = \{SO^-\}$, is called the isoelectric point (IEP). The pH value of IEP is defined as pH_{zpc} (Hunter 1981). This approximation (equation 5.11) is valid only for the very low ionic strength aqueous phase and in the vicinity of pH_{zpc} . Near-Nernstian response, for which the surface potential changes by ≈ 59.2 mV per pH unit, was found experimentally for some oxides (Sprycha and Matijevic 1989) under dilute aqueous solution ($I < 10^{-3}$ M). When high electrolyte concentration was applied, the surface potential greatly deviated from Nernstian response. It has been reported that the Nernst equation was

not fulfilled for the surface potential of some oxides at electrolyte concentrations greater than 10^{-2} M (Hohl et al. 1980; Hohl and Stumm 1976). For example, for a solid of $\text{pH}_{\text{zpc}} 2.0$ in a 10^{-3} M electrolyte concentration, it is difficult to obtain the true value of ζ -potential in the vicinity of pH_{zpc} since the $[\text{H}^+] = 10^{-2} > 10^{-3}$ M.

The Gouy-Chapman theory can be used to determine surface potential. According to this theory, the relationship between the potential at any distance from the surface within the diffuse double layer, ψ_x , and the potential at the surface, ψ_0 are related by:

$$\ln \tanh\left(\frac{Ze\psi_x}{4kT}\right) = \ln \tanh\left(\frac{Ze\psi_0}{4kT}\right) - \kappa d \quad (5.12)$$

where the reciprocal thickness of the diffuse electrical double layer, κ (in meters), is defined by:

$$\kappa = \left(\frac{2F^2 I \cdot 10^3}{\epsilon \epsilon_0 RT} \right)^{1/2} \quad (5.13)$$

and where

e = the electronic charge (1.6×10^{-19} C),

k = the Boltzmann constant (1.38×10^{-23} J/°K),

I = ionic strength (M),

ϵ = dielectric constant of water (78.5 at 25 °C) (CRC 1988), and

ϵ_0 = permittivity in vacuum (8.854×10^{-12} C/V-m).

For a 1:1 electrolyte solution (e.g., NaClO_4) at 25 °C , equation (5.13) can be simplified as:

$$\kappa = 3.29 \cdot 10^9 \cdot I^{1/2}, \quad (5.14)$$

If “d” is defined as the distance from a particle surface to the shear plane; then at the shear plane, a zeta potential, ζ , can be determined from electrophoretic measurements (Figure 3.5). By substituting $\psi_x = \zeta$ into equation (5.12) and rearranging as for a 1:1 electrolyte at 25 °C:

$$\log \tanh\left(\frac{\zeta}{102.8}\right) = \log \tanh\left(\frac{\psi_o}{102.8}\right) - 0.143\sqrt{I}d \quad (5.15)$$

A plot of “ $\log \tanh(\zeta / 102.8)$ ” versus “ $I^{1/2}$ ” at different electrolyte concentrations gives an intercept of “ $\log \tanh(\psi_o / 102.8)$ ” and a slope of “ $0.143 d$ ”. The plot of $\log \tanh(\zeta / 102.8) - I^{1/2}$ is shown in Figure 5.11 for the concrete particles in NaN_3 electrolyte. In Figure 5.11, the Nernst potential is used to extrapolate to $I=0$, which is determined from equation (5.11). The distance of the slipping plane, “d”, calculated was 7.2 Å from the slope of this plot. Once the value of “d” is determine, with the help of zeta potential obtained from experiments, it is possible to determined the surface potential ψ_o , using equation (5.15). The relationship between ψ_o and pH is shown in Figure 5.12.

The total number of surface sites available for adsorption, N_t ($\mu\text{C}/\text{cm}^2$), is the sum of three hydroxo groups:

$$N_t = \{\underline{\text{SOH}}_2^+\} + \{\underline{\text{SOH}}\} + \{\underline{\text{SO}}^-\} \quad (5.16)$$

From equations (5.6) and (5.7). one has

$$pH_{zpc} = \frac{1}{2} (pK_{a1}^{int} + pK_{a2}^{int}) \quad (5.17)$$

At $pH < pH_{zpc}$, $\{\underline{SOH}_2^+\}$ and $\{SOH\}$ groups are the predominant species on the particle surface, i.e.,

$$N_t \cong \{\underline{SOH}_2^+\} + \{\underline{SOH}\} \quad (5.18)$$

and at $pH > pH_{zpc}$, the predominant species are $\{SOH\}$ and $\{SO^-\}$, i.e.,

$$N_t \cong \{\underline{SOH}\} + \{\underline{SO}^-\} \quad (5.19)$$

The quantity of surface concentration (in mole/g), $\{\underline{SOH}_2^+\}$ and $\{\underline{SO}^-\}$, is converted from the surface charge density (in C/cm²), σ^- (at $pH < pH_{zpc}$) and σ^+ (at $pH > pH_{zpc}$), respectively, i.e.,

$$\{\underline{SOH}_2^+\} = \frac{S_A}{F} \sigma^+ \quad (5.20)$$

and

$$\{\underline{SO}^-\} = \frac{S_A}{F} \sigma^- \quad (5.21)$$

where S_A is the specific surface area (in m²/g). According to the Graham equation derived from Gouy-Chapman electrical double layer theory, in the absence of specific adsorption, the surface charge density, σ , can be related to the surface potential, ψ_0 (mV) for a 1:1 electrolyte:

$$\sigma = \sqrt{8\epsilon\epsilon_0 kT} \cdot I^{1/2} \sinh\left(\frac{|Z|F\psi_0}{2RT}\right) \quad (5.22)$$

In aqueous solution at 20 °C, equation (5.22) can be simplified as

$$\sigma = 0.117 \cdot I^{1/2} \sinh(19.46 \cdot \psi_o) \quad (5.23)$$

The surface charge density as a function of pH calculated from equation (5.23) is shown in Figure 5.13. From equations (5.8), (5.9), (5.18), and (5.19), one has

$$\frac{1}{\sigma^+} = \frac{K_{a1}^{int}}{N_t} \frac{1}{\{H^+\}} + \frac{1}{N_t} \quad \text{for the positive charge surface} \quad (5.24)$$

and

$$\frac{1}{\sigma^-} = \frac{1}{N_t K_{a2}^{int}} \{H^+\} + \frac{1}{N_t} \quad \text{for the negative charge surface} \quad (5.25)$$

From equations (5.24) and (5.25), it is possible to determine the acidity constants. By plotting $1/\sigma^+$ versus $1/\{H^+\}$ and $1/\sigma^-$ versus $1/\{H^+\}$, the intrinsic acidity constants, i.e., pK_{a1}^{int} , pK_{a2}^{int} , and N_t , can be determined from the intercept and the slope (Figure 5.14).

A comparison of the results with those resulting from using Noh and Schwarz's method (1990) to determine the surface acidity constant is made. Noh and Schwarz (1990) applied the concept of Nernst equation and modified the method that was originally proposed by Huang and Stumm (1973) to determine the surface acidity constants. According to Noh and Schwarz (1990), the equation for the determination of surface acidity can be expressed as:

$$\cosh(y_N - y_o) = eN_t \frac{\sinh(y_N - y_o)}{\sigma} - \frac{1}{\delta} \quad (5.26)$$

where
$$\delta = 2 \sqrt{\frac{K_{a2}^{int}}{K_{a1}^{int}}} = -\frac{1}{\text{intercept}} \quad (5.27)$$

$$DPK = pK_{a2}^{int} - pK_{a1}^{int} = -2 \log \left(-\frac{0.5}{\text{intercept}} \right) \quad (5.28)$$

$$N_t = \frac{\text{slope}}{e} \quad (5.29)$$

By plotting $\cosh(y_N - y_0)$ versus $\sinh(y_N - y_0)/\sigma^-$ for the negatively charged surface and $\cosh(y_N - y_0)$ versus $\sinh(y_N - y_0)/\sigma^+$ for the positively charged surface, the intrinsic acidity constants of the particle, i.e., pK_{a1}^{int} , pK_{a2}^{int} , and N_t , can be determined from the slope and the intercept using equations (5.28-5.30) (Figure 5.15). The results of surface acidity of hydrous concrete particles determined using Huang and Stumm's (1973) method and Noh and Schwarz's (1990) method are summarized in Table 5.1. Acidity constants determined from these two methods have no apparent difference and have high correlation coefficient, indicating that either of these two methods can be used to determine the acidity constants. The average values of N_t ($0.51 \mu\text{C}/\text{cm}^2$), pK_{a1}^{int} (5.15), and pK_{a2}^{int} (6.65) from Huang and Stumm's method were employed in the model fitting.

The speciation of the hydrous concrete particle is defined as:

$$\alpha^+ = \frac{\{\underline{SOH}_2^+\}}{\{\underline{SOH}\}_{TOT}} = \frac{\{H^+\}^2}{\{H^+\}^2 + K_{a1}^{int}\{H^+\} + K_{a1}^{int}K_{a2}^{int}} \quad (5.30)$$

$$\alpha^0 = \frac{\{\underline{SOH}\}}{\{\underline{SOH}\}_{TOT}} = \frac{K_{a1}^{int}\{H^+\}}{\{H^+\}^2 + K_{a1}^{int}\{H^+\} + K_{a1}^{int}K_{a2}^{int}} \quad (5.31)$$

$$\alpha^- = \frac{\{\underline{SO}^-\}}{\{\underline{SOH}\}_{TOT}} = \frac{K_{a1}^{int}K_{a2}^{int}}{\{H^+\}^2 + K_{a1}^{int}\{H^+\} + K_{a1}^{int}K_{a2}^{int}} \quad (5.32)$$

where α^+ , α^0 , and α^- , are the fractions of the positive, neutral, and negative surface hydroxyl groups, individually. $\{\text{SOH}\}_{\text{TOT}}$ is the total of hydroxyl groups which is the sum of $\{\text{SOH}_2^+\}$, $\{\text{SOH}\}$, and $\{\text{SO}^-\}$. Using Boltzman distribution (equation 5.10) to relate the surface proton concentration, $\{H^+\}$, and the solution proton concentration measured, $[H^+]$, equations (5.30-5.32) can be rewritten as:

$$\alpha^+ = \frac{[H^+]^2}{\left([H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right)\right)^2 + K_{a1}^{\text{int}} \cdot [H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right) + K_{a1}^{\text{int}} K_{a2}^{\text{int}}} \quad (5.30a)$$

$$\alpha^0 = \frac{K_{a1}^{\text{int}} [H^+]}{\left([H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right)\right)^2 + K_{a1}^{\text{int}} \cdot [H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right) + K_{a1}^{\text{int}} K_{a2}^{\text{int}}} \quad (5.31a)$$

$$\alpha^- = \frac{K_{a1}^{\text{int}} K_{a2}^{\text{int}}}{\left([H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right)\right)^2 + K_{a1}^{\text{int}} \cdot [H^+] \cdot \exp\left(-\frac{F\psi_o}{RT}\right) + K_{a1}^{\text{int}} K_{a2}^{\text{int}}} \quad (5.32a)$$

Knowing the acidity constants, $\text{p}K_{a1}^{\text{int}}$ and $\text{p}K_{a2}^{\text{int}}$, bulk proton concentration, $[H^+]$, and the surface potential ψ_o , the distribution diagram of surface hydroxyl groups as a function of pH can be constructed (Figure 5.16).

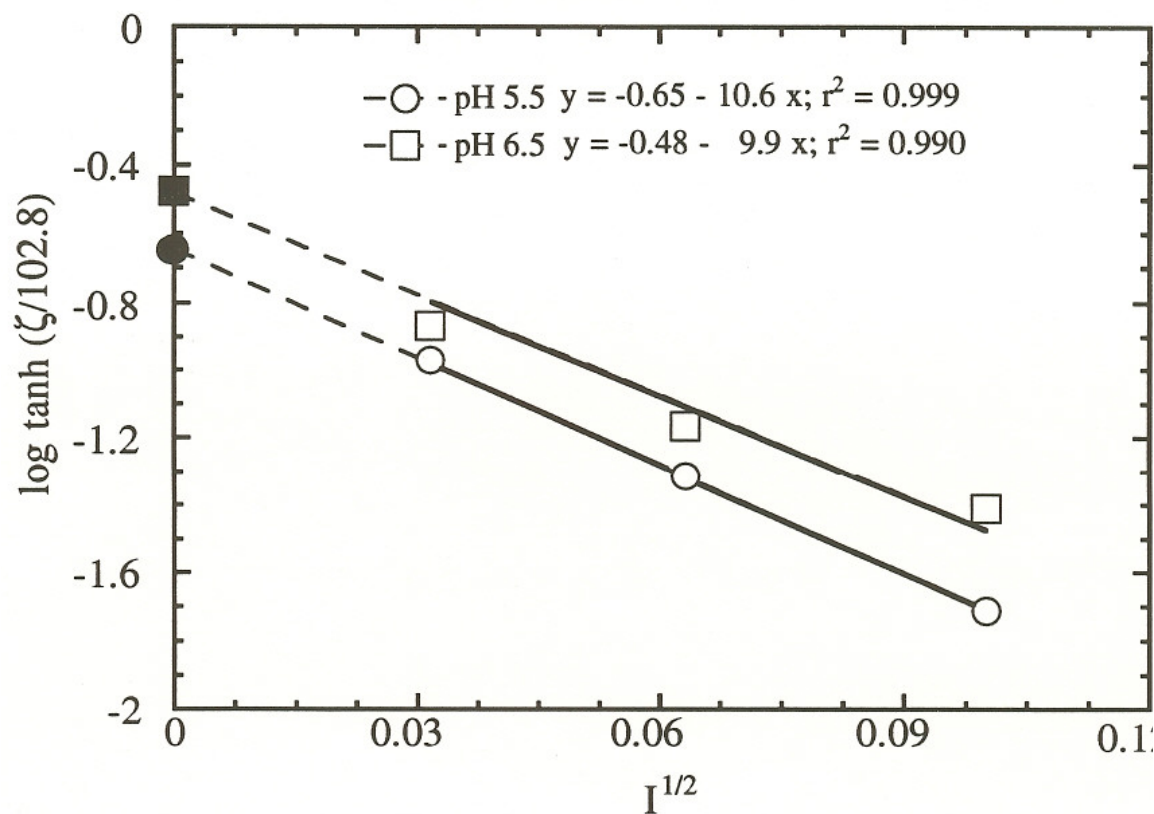


Figure 5.11 The plot of $\log \tanh(\zeta/102.8)$ as a function of $I^{1/2}$ for concrete particles NaNO_3 electrolyte (solid symbols were calculated from the Nernst equation).

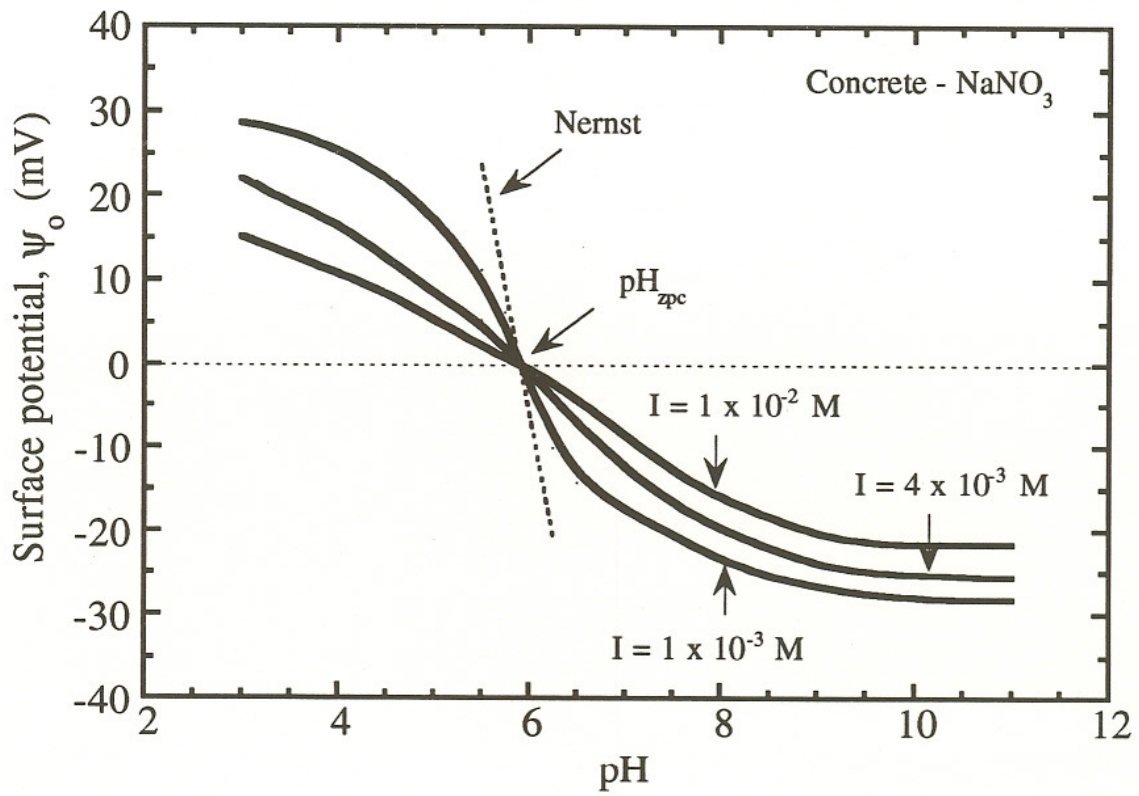


Figure 5.12 Surface potential (ψ_0) of concrete particles as a function of pH at different ionic strengths.

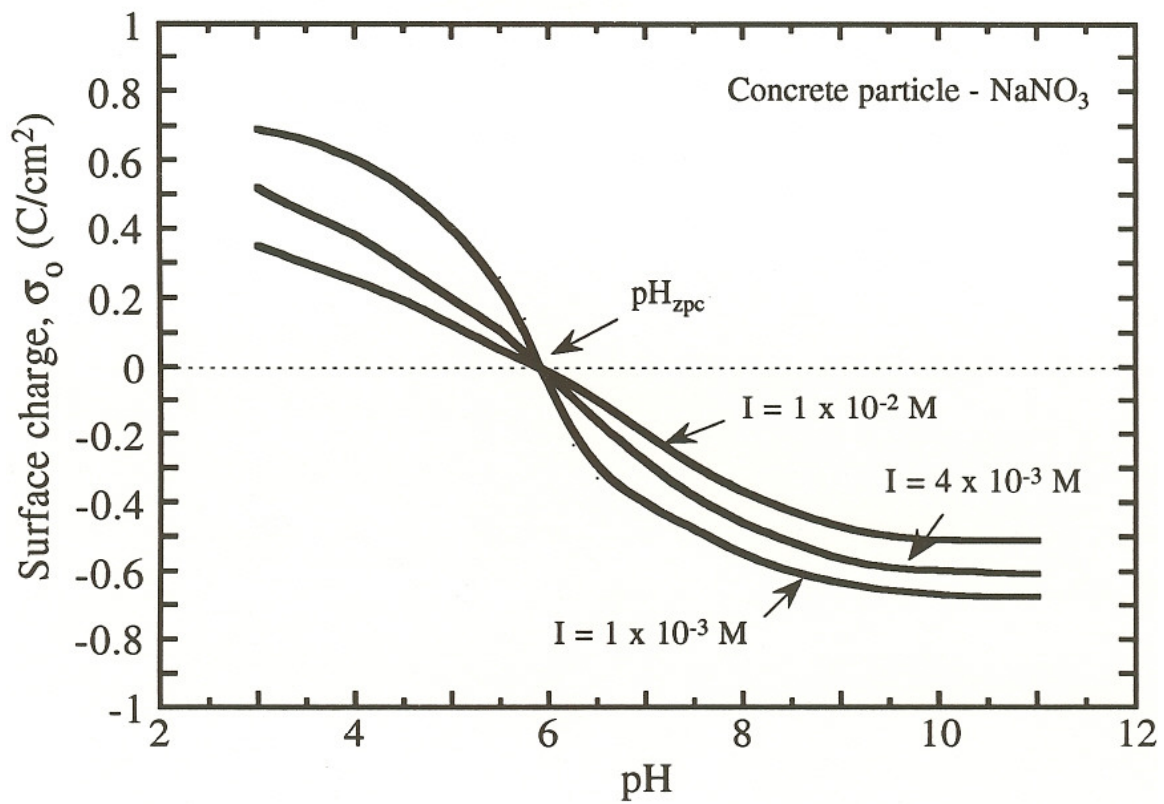


Figure 5.13 Surface charge (σ_0) of concrete particles as a function of pH at different ionic strengths.

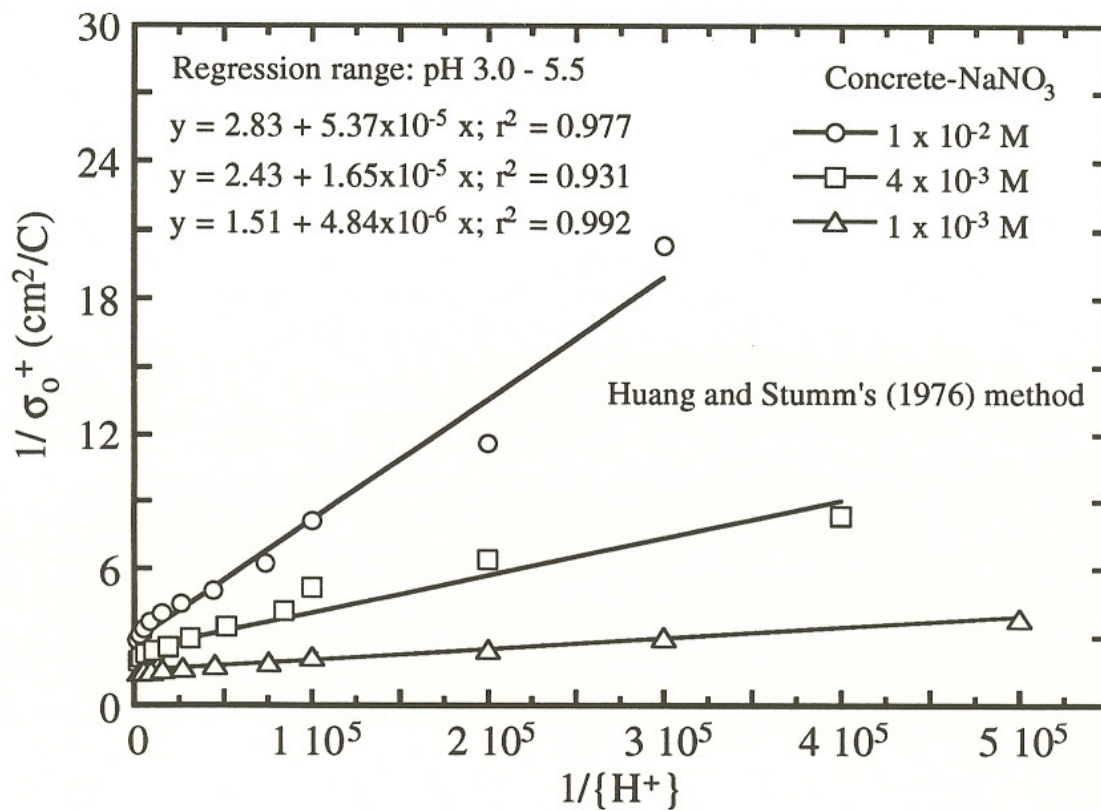


Figure 5.14a Regression plot for determination of surface acidity using Huang and Stumm's (1976) method (a) for positive surface, (b) for negative surface.

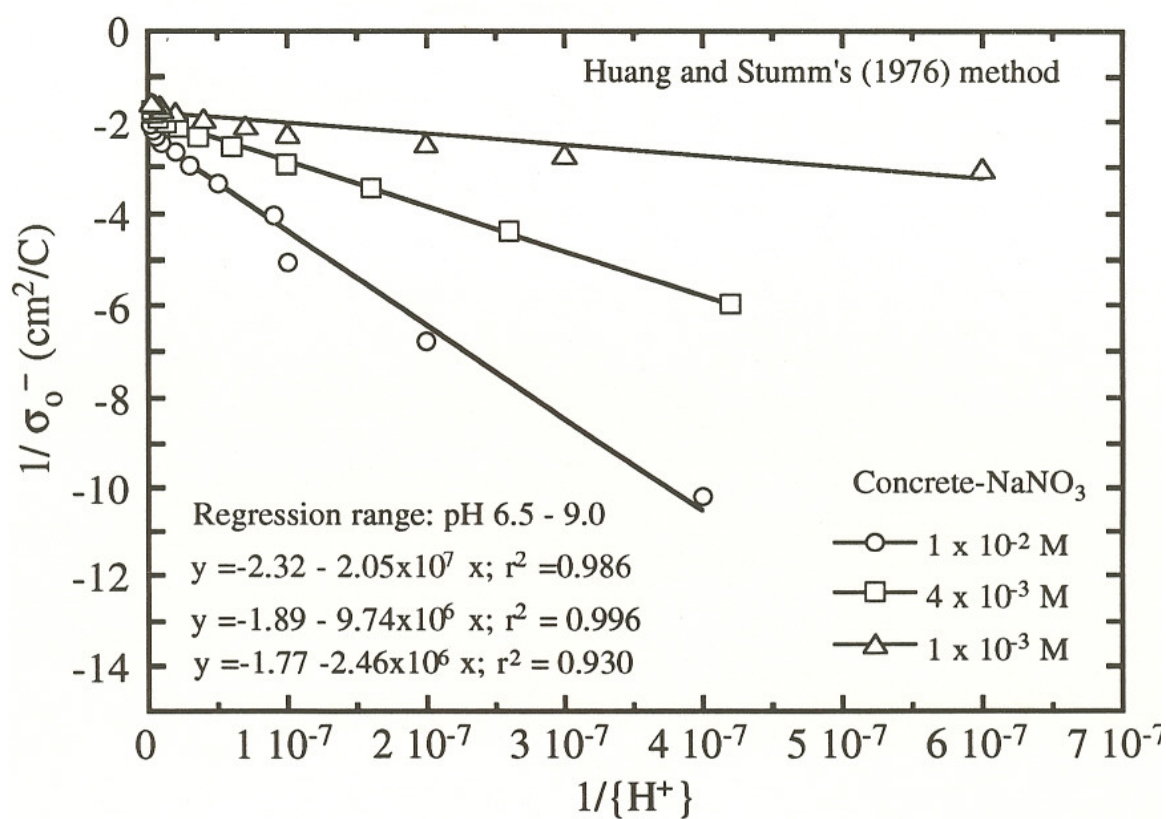


Figure 5.14b Regression plot for determination of surface acidity using Huang and Stumm's (1976) method (a) for positive surface, (b) for negative surface.

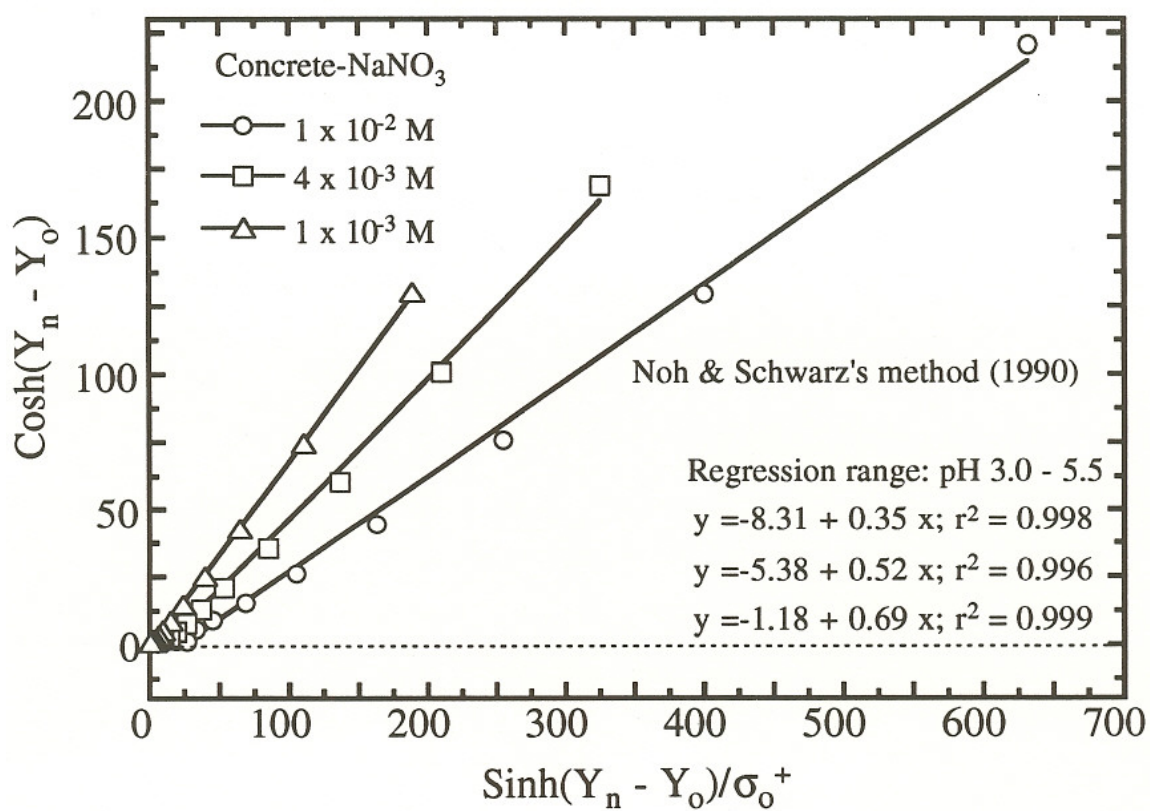


Figure 5.15a Regression plot for determination of surface acidity using Noh and Schwarz's (1990) method (a) for positive surface, (b) for negative surface.

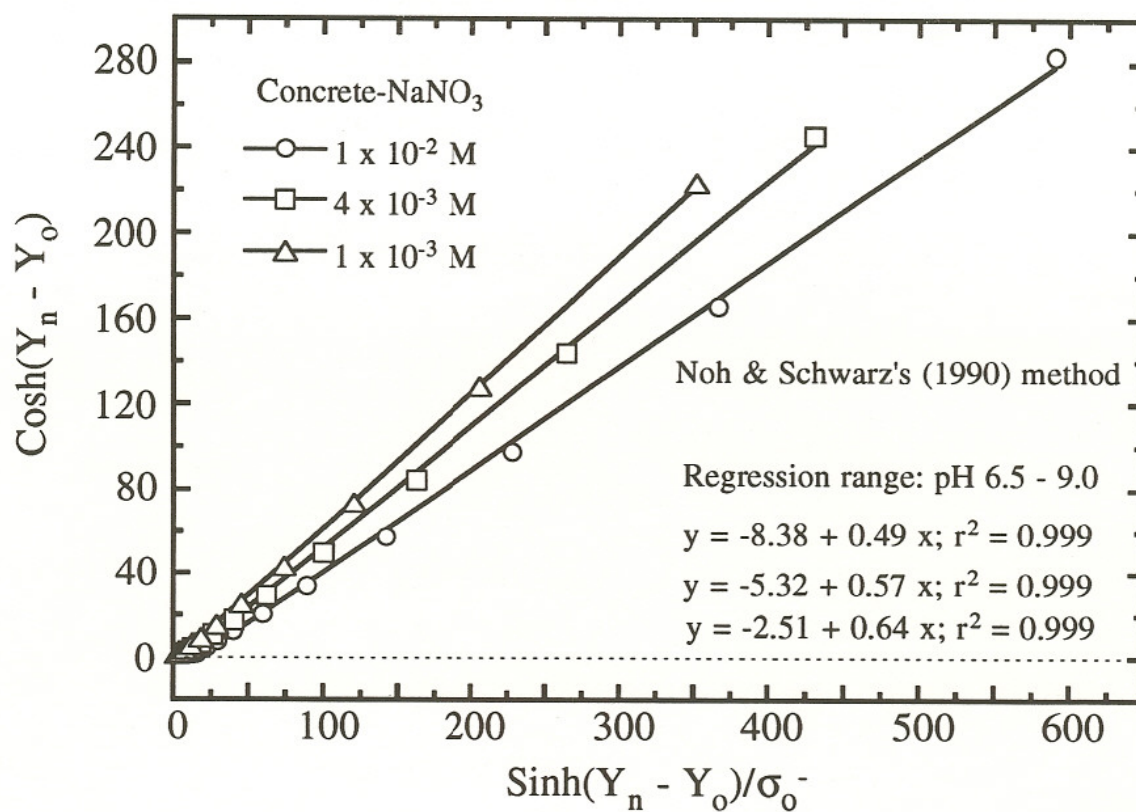


Figure 5.15b Regression plot for determination of surface acidity using Noh and Schwarz's (1990) method (a) for positive surface, (b) for negative surface.

Table 5.1 Summary of surface acidity constants of hydrous concrete particles determined from Huang and Stumm's (1976) method and Noh and Schwarz's (1990) method.

Ionic strength	Regression pH range	Huang & Stumm's method				Noh & Schwarz's method			
		pK_{a1}^{int}	pK_{a2}^{int}	N_s^*	r^2	pK_{a1}^{int}	pK_{a2}^{int}	N_s^*	r^2
1×10^{-2} M	3.0-5.5	4.72	7.08	0.35	0.977	4.68	7.10	0.35	0.998
4×10^{-3} M	3.0-5.5	5.17	6.63	0.42	0.931	4.83	6.97	0.52	0.996
1×10^{-3} M	3.0-5.5	5.49	6.31	0.66	0.993	5.45	6.35	0.69	0.999
1×10^{-2} M	6.5-9.0	4.85	6.95	0.43	0.986	4.68	7.12	0.49	0.999
4×10^{-3} M	6.5-9.0	5.09	6.71	0.53	0.996	4.87	6.93	0.57	0.999
1×10^{-3} M	6.5-9.0	5.66	6.14	0.56	0.930	5.20	6.60	0.64	0.999
Average	-----	5.15	6.65	0.51	-----	4.96	6.84	0.54	-----

* N_s unit in $\mu\text{C}/\text{cm}^2$

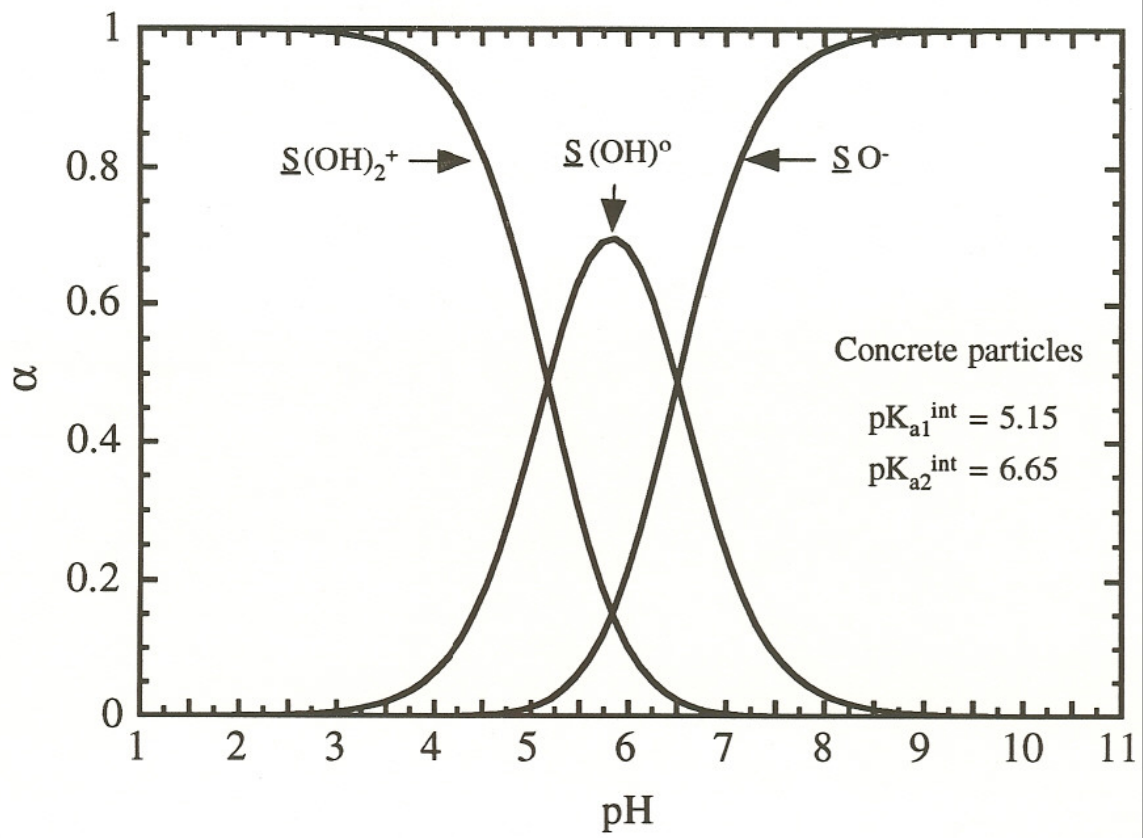


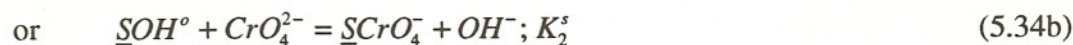
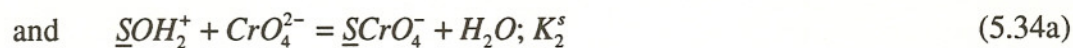
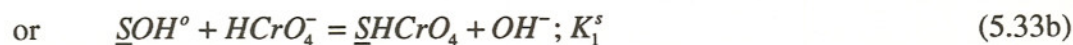
Figure 5.16 The speciation diagram of the hydrous concrete particle as a function of pH.

5.4.2 Surface Complex Formation Model

At low metal concentration, metal adsorption onto hydrous solids, such as metal oxides, is mainly a surface coordination process which can be modeled thermodynamically as a complexation reaction between surface sites and adsorbates (Stumm 1992). Surface complex formation model (SCFM) has been successfully used in describing the adsorption reactions at oxide-water interfaces (Cox and Ghosh 1994; Zhang et al. 1994; Reed and Matsumoto 1993; Weng 1990; Zachara et al. 1989; Park and Huang 1989b; Hayes and Leckie 1987; Davis and Leckie 1980; Huang and Stumm 1973) with excellent predictability.

For the sake of simplicity, a SCFM originally proposed by Huang and Stumm (1973) was employed to describe the adsorption reaction. Huang and his coworkers have used this model to describe the metal adsorption onto many adsorbates, such as fly ash, γ -Al₂O₃, activated carbon, metal sulfide (Weng and Huang 1990; Park and Huang 1989b; Coracioglu and Huang 1987b; Hao and Huang 1986).

The possible surface complex reactions for Cr(VI) adsorption onto hydrous concrete are expressed as follows:



where K_1^s , and K_2^s represent the intrinsic stability constants of the concrete complex with chromate ions and $\underline{S}$ refers to surface sites. Equations 5.33a and 5.34a therefore are formulated in term of mass expressions:

$$K_1^s = \frac{\{\underline{S}HCrO_4\}}{\{\underline{S}OH_2^+\}[HCrO_4^-]} \quad (5.35)$$

and

$$K_2^s = \frac{\{\underline{S}CrO_4^-\}}{\{\underline{S}OH_2^+\}[CrO_4^{2-}]}$$

The total amount of Cr(VI) adsorbed, Γ_t (mole/g) is the sum of $\{\underline{S}HCrO_4\}$ and $\{\underline{S}CrO_4^-\}$ which is expressed as:

$$\Gamma_t = \{\underline{S}OH_2^+\}(K_1^s[HCrO_4^-] + K_2^s[CrO_4^{2-}]) \quad (5.36)$$

Γ_t is obtained directly from the adsorption experiment. The chromate equilibrium concentrations, $[HCrO_4^-]$ and $[CrO_4^{2-}]$, can be obtained from:

$$[HCrO_4^-] = \alpha_1 \cdot \left(\frac{Cr_T}{W} - \Gamma_t \right) \quad (5.37)$$

and

$$[CrO_4^{2-}] = \alpha_2 \cdot \left(\frac{Cr_T}{W} - \Gamma_t \right) \quad (5.38)$$

where α_1 and α_2 are the fractions of $HCrO_4^-$ and CrO_4^{2-} species present in the equilibrium concentration, respectively, which can be determined by equations (2.9 and 2.10). W (in g/L) and Cr_T (in mole/L) are the total input solid concentration and the total input chromate, respectively. Knowing the surface acidity constants, pK_{a1}^{int} ,

pK_{a2}^{int} , N_t , ψ_0 , and the total amount of metal adsorbed, Γ_t , it is possible to calculate the stability constant of surface complex of each chromate species, K_1^s and K_2^s

5.4.3 Model Fitting

Figure 5.17 shows the model calculations and experimental data for Cr(VI) adsorption under several concentration of Cr(VI) added. The stability constants are determined from the best fitting of the experimental data. For the region of pH less than about 4.25, the removal of Cr(VI) was major resulted from the redox reaction. As such, the experimental data in this region can not be fitted in the SCFM. Detail of the redox reaction between Cr(VI) and concrete material has been discussed earlier. Under the region of $pH < 4.25$, the adsorption density was estimated by model calculations. From the results of model fitting, the current version of SCFM provides good prediction of metal adsorption onto concrete. The stability constants for the varies chromate species complexed with concrete are shown in Figure 5.18a. These constants has apparently dependence on total chromate added. In general, the pK^s values decrease as increasing the surface loading or surface coverage (Figure 5.18b).

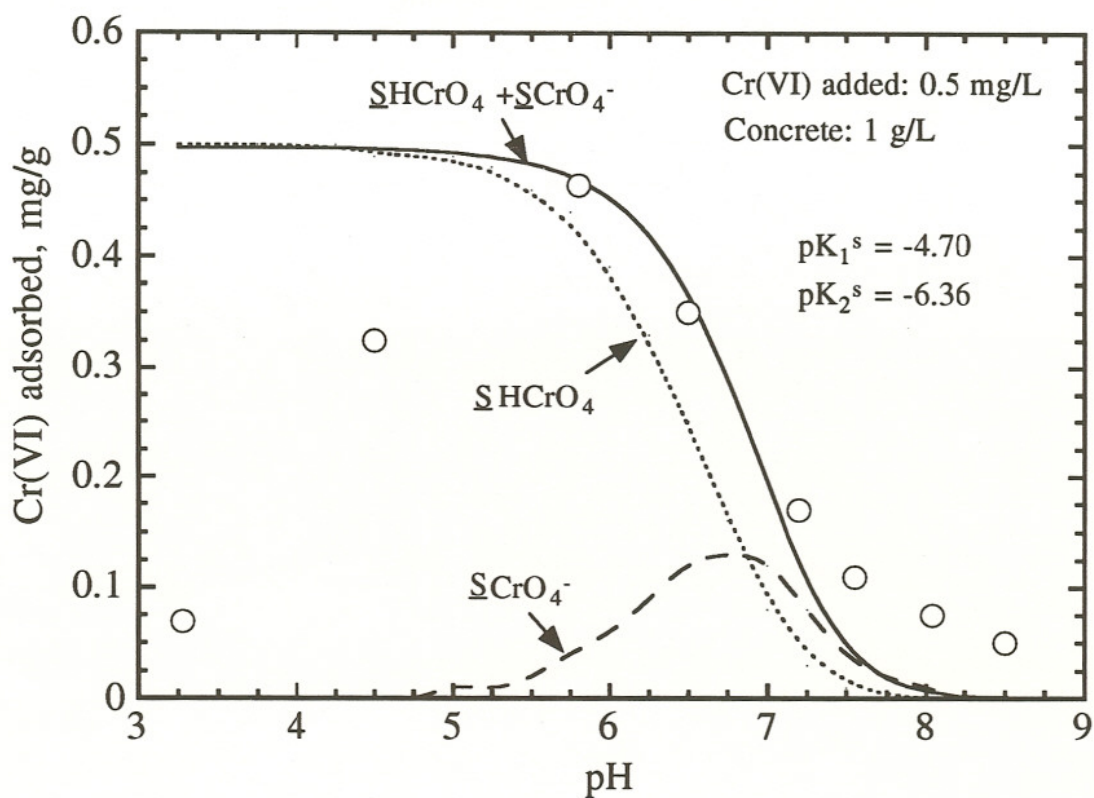


Figure 5.17a Adsorption modeling of various Cr(VI) concentrations, (a) 0.5 mg/l, (b) 1 mg/l, (c) 2 mg/l, (d) 5 mg/l, and (e) 10 mg/l, onto concrete particles. Open symbols are the experimental data. Dashed and dot lines represents model simulated species contributing to adsorption. Solid line represents the summation of model simulated species.

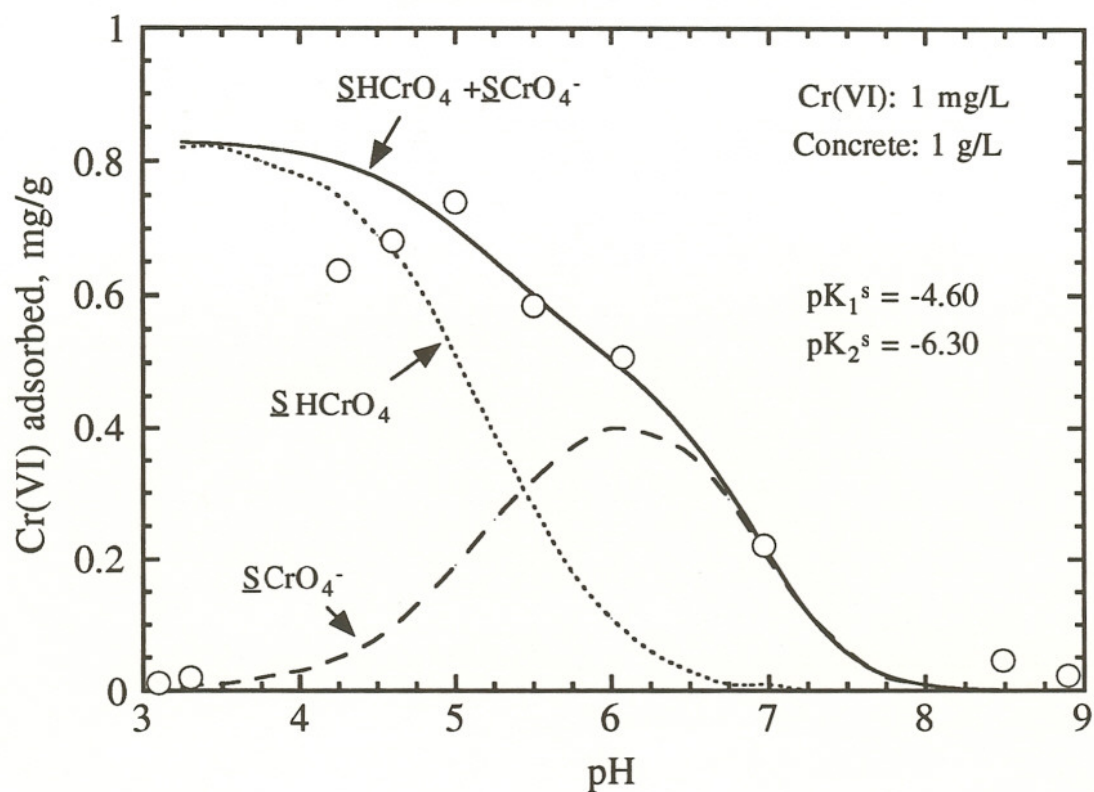


Figure 5.17b Adsorption modeling of various Cr(VI) concentrations, (a) 0.5 mg/l, (b) 1 mg/l, (c) 2 mg/l, (d) 5 mg/l, and (e) 10 mg/l, onto concrete particles. Open symbols are the experimental data. Dashed and dot lines represents model simulated species contributing to adsorption. Solid line represents the summation of model simulated species.

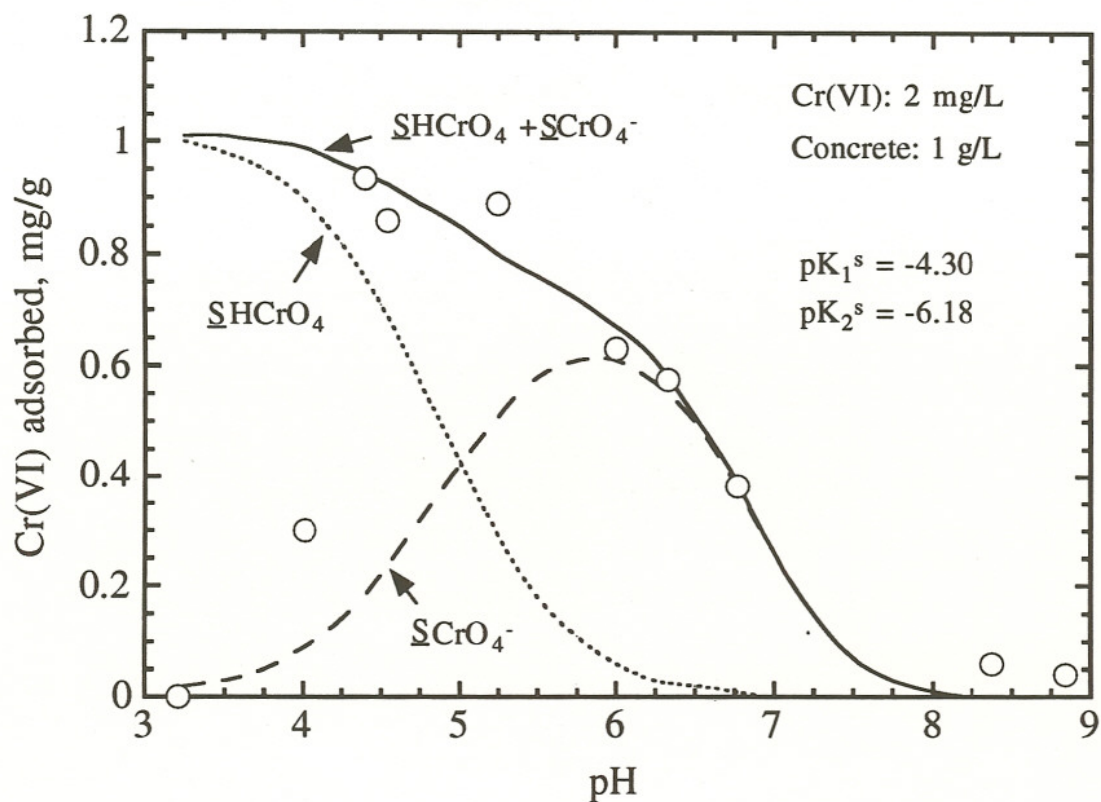


Figure 5.17c Adsorption modeling of various Cr(VI) concentrations, (a) 0.5 mg/l, (b) 1 mg/l, (c) 2 mg/l, (d) 5 mg/l, and (e) 10 mg/l, onto concrete particles. Open symbols are the experimental data. Dashed and dot lines represents model simulated species contributing to adsorption. Solid line represents the summation of model simulated species.

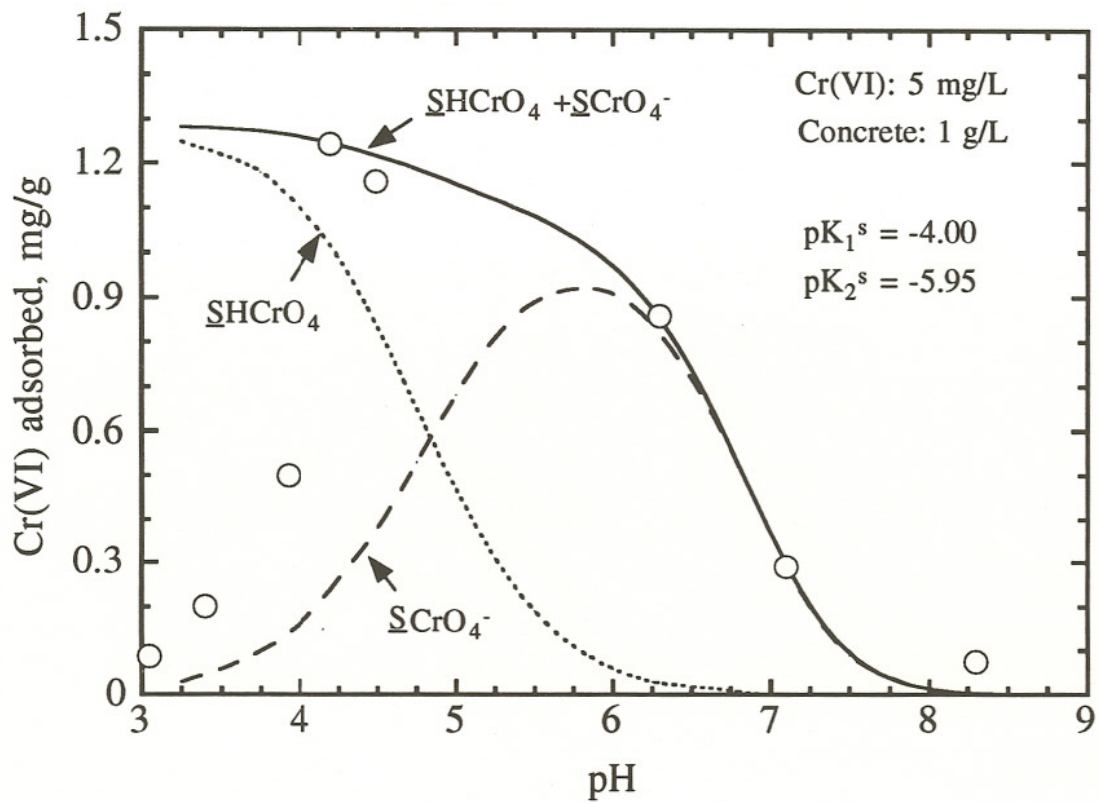


Figure 5.17d Adsorption modeling of various Cr(VI) concentrations, (a) 0.5 mg/l, (b) 1 mg/l, (c) 2 mg/l, (d) 5 mg/l, and (e) 10 mg/l, onto concrete particles. Open symbols are the experimental data. Dashed and dot lines represents model simulated species contributing to adsorption. Solid line represents the summation of model simulated species.

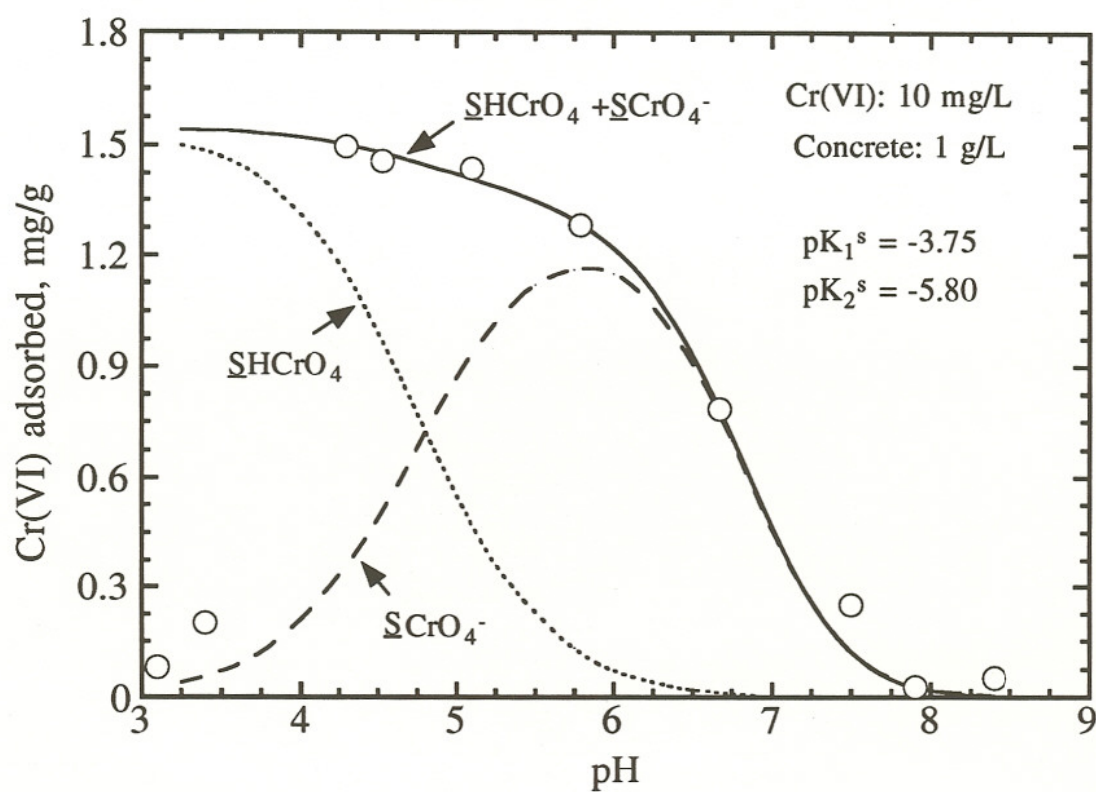


Figure 5.17e Adsorption modeling of various Cr(VI) concentrations, (a) 0.5 mg/l, (b) 1 mg/l, (c) 2 mg/l, (d) 5 mg/l, and (e) 10 mg/l, onto concrete particles. Open symbols are the experimental data. Dashed and dot lines represents model simulated species contributing to adsorption. Solid line represents the summation of model simulated species.

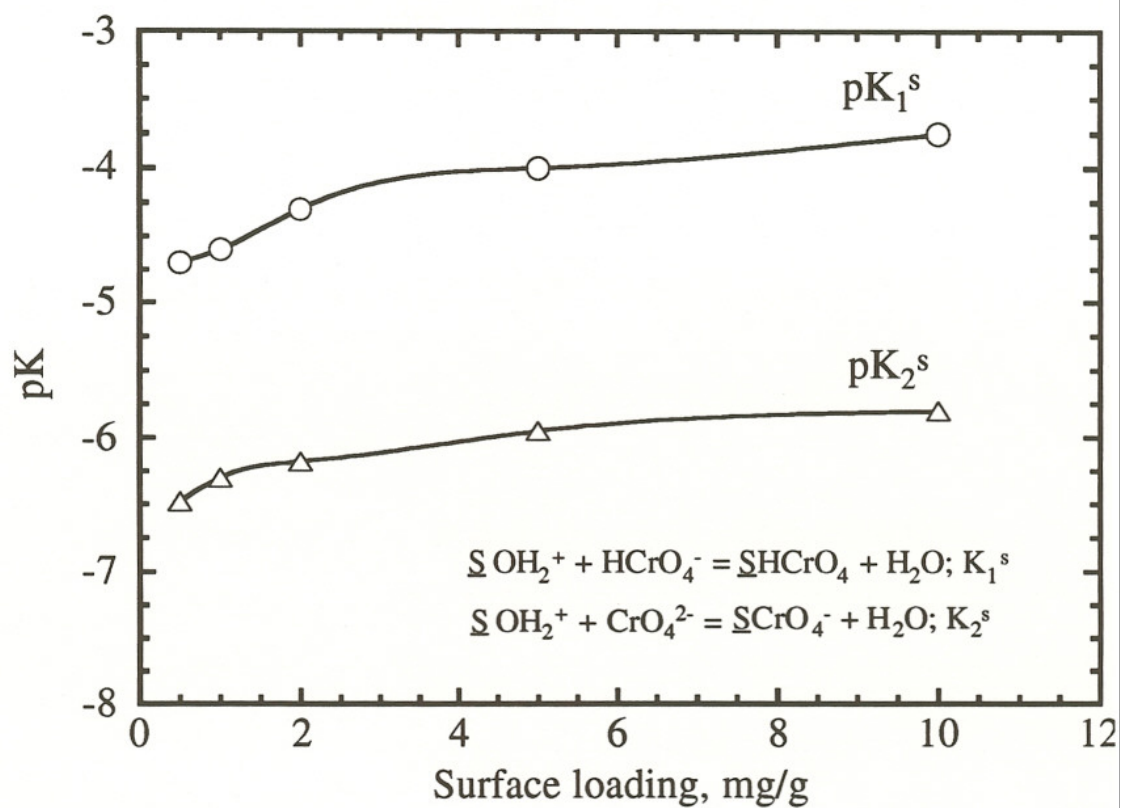


Figure 5.18a Stability constants for HCrO_4^- and CrO_4^{2-} onto concrete particle as function of surface loading.

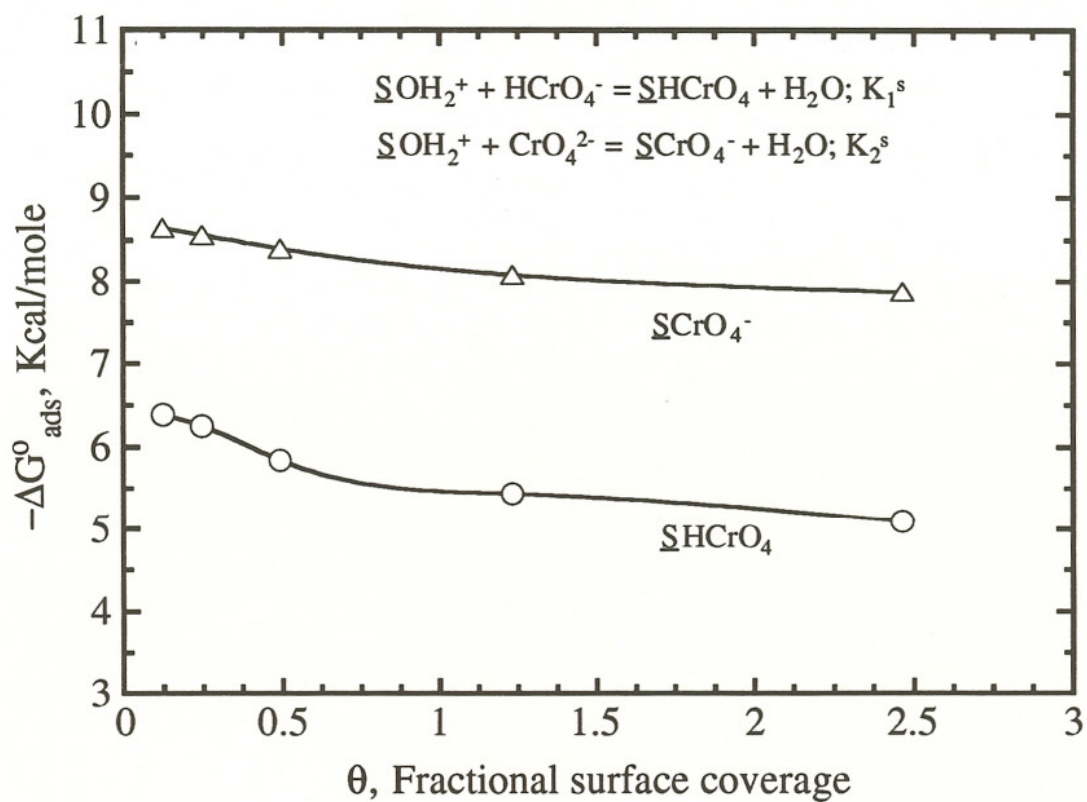


Figure 5.18b Adsorption energy for HCrO_4^- and CrO_4^{2-} onto concrete particle as a function of surface coverage. The surface coverage was calculated from mass of Cr(VI) adsorbed divided by the total available sites for adsorption.

The stability constants, pK_i^s , obtained from SCFM can be used to determined the adsorption free energy, ΔG_{ads}^o , of each chromate species:

$$\Delta G_{(ads)i}^o = 2.303 \cdot RT \cdot pK_i^s \quad (5.43)$$

The adsorption free energy of $HCrO_4^-$ ion ranges from -5.10 to -6.38 Kcal/mole and the adsorption free energy of CrO_4^{2-} specie ranges from -7.88 to -8.64 Kcal/mole for the surface loading from 0.5 to 10 mg/g. The adsorption energies of Cr(VI) species have the same magnitude found by other researchers in studying various metals onto oxides (-5 to -10 Kcal/mole) (Huang et al. 1986; Hohl and Stumm 1976; Jame and Healy 1972) and CdS(s) (Park and Huang 1989b). Thermodynamically, the negative value of ΔG_{ads}^o indicates Cr(VI) ion is favorably adsorbed onto concrete. Comparing the magnitude of the adsorption free energy, it appears that the CrO_4^{2-} specie is more favorably adsorbed onto concrete particle than $HCrO_4^-$ ion.

The total free energy of adsorption, ΔG_{ads}^o , is the sum of the specific chemical, ΔG_{chem}^o , the coulombic, ΔG_{coul}^o , the solvation, ΔG_{solv}^o , and the lateral interaction, ΔG_{lat}^o (Park and Huang 1989b), i.e.,

$$\Delta G_{ads}^o = \Delta G_{coul}^o + \Delta G_{chem}^o + \Delta G_{solv}^o + \Delta G_{lat}^o \quad (5.44)$$

For individual species energy contribution, equation (7.39) can be expressed as:

$$\Delta G_{(ads)i}^o = \Delta G_{(coul)i}^o + \Delta G_{(chem)i}^o + \Delta G_{(solv)i}^o + \Delta G_{(lat)i}^o \quad (5.45)$$

The coulombic energy, $\Delta G_{(coul)i}^o$, is determined from:

$$\Delta G_{(elec)i}^o = z_i F \Delta \psi_x \quad (5.46)$$

where ψ_x is the potential drop at the distance from surface x and it is obtained from the following equation:

$$\Delta\psi_x = \frac{2RT}{ZF} \cdot \ln \left(\frac{\left(e^{ZF\psi_o/2RT} + 1 \right) + \left(e^{ZF\psi_o/2RT} - 1 \right) e^{-\kappa x}}{\left(e^{ZF\psi_o/2RT} + 1 \right) - \left(e^{ZF\psi_o/2RT} - 1 \right) e^{-\kappa x}} \right) \quad (5.47)$$

where

$$x = r_{\text{ion}} + 2r_w ,$$

$$r_{\text{ion}} = \text{ion radius (0.69 \AA for Cr), m}^{-1},$$

$$r_w = \text{water molecule radius (1.38 \AA), m}^{-1}, \text{ and}$$

$$z_i = \text{the valence of adsorbing ion.}$$

The surface potential, ψ_o , can be obtained from equation (5.15). The calculated ΔG_{coul}^o values for adsorbing chromate ions of HCrO_4^- and CrO_4^{2-} are 0.20 and 0.42 Kcal/mole, respectively.

The solvation interaction arises because when an ion approaches the solid-water interface, energy has to be provided to remove the secondary solvation sheath from that ion (James and Healy 1972). Accordingly, the lower the dielectric constant of the solid, the higher the solvation energy is needed at the solid-water interface for solvation interaction. The solvation energy, $\Delta G_{(\text{solv})i}^o$, is calculated as proposed by James and Healy (1972):

$$\Delta G_{solv}^o = \left(\frac{z^2 e^2 N}{16 \pi \epsilon_o} \right) \left(\frac{1}{r_{ion} + 2r_w} - \frac{r_{ion}}{2(r_{ion} + 2r_w)^2} \right) \left(\frac{1}{\epsilon_{int}} - \frac{1}{\epsilon_{bulk}} \right) + \left(\frac{z^2 e^2 N}{32 \pi \epsilon_o} \right) \left(\frac{1}{r_{ion} + 2r_w} \right) \left(\frac{1}{\epsilon_{solid}} - \frac{1}{\epsilon_{int}} \right) \quad (5.48)$$

where ϵ_{solid} , ϵ_{bulk} , and ϵ_{int} are the adsorbent dielectric constant (assumed 50), the water dielectric constant (78.5), and the interfacial dielectric constant, respectively. ϵ_{int} can be calculated from:

$$\epsilon_{int} = \left(\frac{\epsilon_{bulk} - 6}{1 + 1.2 \cdot 10^{-17} (d\psi / dx)_x^2} \right) + 6 \quad (5.49)$$

and the rate of surface potential drop, $d\psi/dx$, is calculated from:

$$\frac{d\psi}{dx} = -2\kappa \frac{RT}{ZF} \sinh \left(\frac{ZF \cdot \Delta\psi_x}{2RT} \right) \quad (5.50)$$

The calculated ΔG_{solv}^o , values for HCrO_4^- and CrO_4^{2-} are 0.05 and 0.19 Kcal/mole, respectively.

For high surface loading, the lateral interaction (adsorbate-adsorbate interaction) contributed to the total adsorption and can not be neglected (Adamson 1982). Values of ΔG_{lat}^o for HCrO_4^- and CrO_4^{2-} estimated from Figure 5.18b by taking the average of ΔG_{ads}^o at $\theta > 1$, subtracting the average of ΔG_{ads}^o at $\theta < 1$ are 0.22, and 0.21 Kcal/mole, respectively.

With the calculated values of ΔG_{coul}^o , ΔG_{solv}^o , and ΔG_{ads}^o from equation (5.43), the ΔG_{chem}^o is therefore determined by rearranging equation (5.44):

$$\Delta G_{chem}^o = \Delta G_{ads}^o - \Delta G_{coul}^o - \Delta G_{solv}^o - \Delta G_{lat}^o \quad (5.51)$$

According to the solvation model proposed by James and Healy (1972), the adsorption energy, $\Delta G_{\text{ads}}^{\circ}$ was determined by assuming a value of $\Delta G_{\text{chem}}^{\circ}$ for the best fitting adsorption data. By their approach, the assumed value of $\Delta G_{\text{chem}}^{\circ}$ will be the same for all the adsorbing species. In my approach, $\Delta G_{\text{ads}}^{\circ}$ is obtained from SCFM, while the $\Delta G_{\text{chem}}^{\circ}$ is calculated from the known quantities (equation 5.51).

Table 5.2 summarized the values of $\Delta G_{\text{coul}}^{\circ}$, $\Delta G_{\text{solv}}^{\circ}$, $\Delta G_{\text{chem}}^{\circ}$, and $\Delta G_{\text{ads}}^{\circ}$. The magnitude of the $\Delta G_{\text{coul}}^{\circ}$ contribution to adsorption is relatively small in comparison with $\Delta G_{\text{chem}}^{\circ}$. The large $\Delta G_{\text{chem}}^{\circ}$ value indicates the formation of strong covalent bonding between surface sites and chromate ions. In general, the coulombic and specific chemical are mainly responsible for the adsorption while solvation and lateral interactions can reverse the adsorption, especially for the high valence absorbing ion and high surface loading adsorption. It is noted that the adsorption energy is approximately equal to the specific chemical energy, i.e., $\Delta G_{\text{ads}}^{\circ} \cong \Delta G_{\text{chem}}^{\circ}$. Thus, I conclude that the specific chemical interaction is the major mechanism responsible for adsorption process.

Table 5.2 The adsorption energy of surface complexes.

Equilibria	$\Delta G_{\text{coul}}^{\circ}$	$\Delta G_{\text{chem}}^{\circ}$	$\Delta G_{\text{solv}}^{\circ}$	$\Delta G_{\text{lat}}^{\circ}$	$\Delta G_{\text{ads}}^{\circ} *$
$\text{S}\text{OH}_2^+ + \text{HCrO}_4^- = \text{S}\text{HCrO}_4$	-0.21	-6.22	0.05	0.22	-6.16
$\text{S}\text{OH}_2^+ + \text{CrO}_4^{2-} = \text{S}\text{CrO}_4^-$	-0.41	-8.52	0.19	0.21	-8.53

Note: All units are Kcal/mole.

*Average of $\Delta G_{\text{ads}}^{\circ}$ at $\theta < 1$.

5.5 Summary

The study shows that adsorption, redox, and precipitation reactions are the major process affecting the concentration and speciation of chromium in the chromium-concrete interface, and that solution pH is the crucial parameter affecting these chemical interactions. Below pH 3.5, the removal of Cr(VI) is controlled by reduction reactions. Cr(VI) is reduced to Cr(III) by reaction with aqueous Fe(II) derived from Fe(II)-containing concrete materials. The concentration of Cr(III) is governed by the $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ and/or $\text{Cr}(\text{OH})_3(\text{s})$ precipitates. At pH 4 to 9, adsorption is mainly responsible for Cr(VI) removal. Prediction of the Cr(VI) adsorption density for different sizes of concrete particles can be made by knowing the specific surface area of the concrete particles. Extrapolation of linear adsorption coefficient for pulverized concrete to a whole concrete block is made. Among all parameters studied, pH appears to be the most important governing the fate of chromium in concrete. Since the pH of the Cr-soil and concrete are both high Cr(VI) is only minimally adsorbed onto concrete. The adsorption of Cr(VI) onto concrete particles can be described by surface complex formation model. Because the magnitude of favorable electrostatic energy and the adverse solvation and lateral interaction energy which contribute to the total adsorption are relatively small in comparison with the favorable specific chemical energy, I conclude that specific chemical interaction is the major mechanism responsible for the adsorption process.

Chapter 6

TRANSPORT OF CHROMIUM IN POROUS MEDIA

6.1 Introduction

This chapter focuses on the development of a numerical model for contaminant transport through porous media. The finite difference method was applied to solve the partial differential equations. A user-friendly program written with Lotus 1-2-3 macro was developed for reactive substance transport through porous media coupled with adsorption and decay reactions. The numerical solution was confirmed by exact analytical solution for specific boundary and initial conditions. Parametric analysis for the numerical solution was studied. The results of column experiments of chromium leaching from Cr-soil and chromium transport through concrete were presented in this chapter. Simulations are made to compare numerical results with effluent curves for chromium leaching from Cr-soil and the transport of chromium through concrete.

6.2 Theoretical Aspect of the Solute Transport Process

6.2.1 General Considerations for Transport Processes

The concentration distribution of a reactive substance transported through a porous medium is mainly controlled by advection, mechanical dispersion, molecular

diffusion, chemical reactions occurring between solid surface and solute (e.g., adsorption, desorption, and ion exchange), and chemical reaction within the solution (e.g., precipitation, dissolution, redox reactions, and biodegradation decay). The definitions of these factors that govern the transport process are discussed as follows (Bear and Verruijt 1990):

- (1). Advection - The transport of solutes at the same velocity as the fluid flows.
- (2). Hydrodynamic dispersion (miscible displacement) - This is the general term for the sum of molecular diffusion and mechanical dispersion. It denotes the spreading (a bell-shaped wave for pulse stimulus) resulting from both mechanical dispersion and molecular diffusion at the microscopic level. At low flow velocities, molecular diffusion has a more significant affecting on the overall dispersion than mechanical dispersion.
- (3). Mechanical dispersion - Mechanical dispersion refers to mixing and spreading resulted from variations in velocity within porous media (Figure 6.1a). It results from the solute moving at different rates through the porous media at microscopic level. Assuming zero fluid velocity on the particle surface and maximum velocity at some internal point, the velocity varies with the size of the pore and the shape of the interconnected pore space. These variations can cause the streamlines to fluctuate in space with respect to the mean direction of flow. The flow is faster in large pores than in small pores. Within a given pore, the flow is slower near the surface than in the middle. Therefore, the spreading is caused by the flow and the characteristics of the pore system through which the flow takes place.

(4). Molecular diffusion - Molecular diffusion is caused by the random movement of molecules in the solution arising from collisions between molecules. It produces additional flux of solute proportional to the concentration gradient. The flux tends to equalize the solute concentration across the pores, and thereby enhances the transverse component of mechanical dispersion at the microscopic level (Figure 6.1b). This is the phenomenon that explains the observed transverse dispersion. Molecular diffusion can take place alone in the absence of motion (water movement) both in the continuum and porous medium.

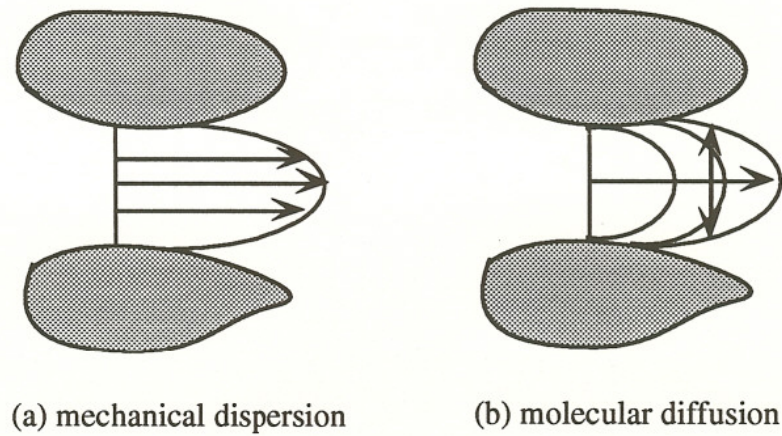


Figure 6.1 Spreading due to (a) mechanical dispersion and (b) molecular diffusion (Bear and Verruijt 1990).

6.2.2 Derivation of Advective, Dispersive, and Diffusive Fluxes Approach to Porous Media

Two common features of porous media are the void space occupied by one or more fluid phases (e.g., water and air) and the solid matrix distributed throughout the porous medium (Bear and Verruijt 1990). Typical examples of porous media are soil, sand, sandstone, rocks, limestone, activated carbon, and concrete.

As an aqueous solution passes through a porous medium, a complex network of pores and channels comprising the void space will be formed. The flow in the porous medium can be treated at a microscopic level and is bounded by the solid-water interface. Any point within the fluid can be treated as a continuum by overlooking its molecular structure. The Navier-Stokes equation may be applied to solve the variable flow at the microscopic level. However, the approach is usually impractical because of the inability to describe the configuration of the solid-water interface boundary and difficulty in verifying the mathematical solutions by measuring any values (i.e., velocity and substance concentration) at this level.

Because of these difficulties, a macroscopic level is needed to describe the phenomena. The measurable of variables can be defined and the boundary information can be determined at the macroscopic level. To approach the macroscopic level from the microscopic level, a continuum approach and the use of central point to represent any representative elementary volumes (REV) in the porous domain are adopted. This allows us to eliminate the need of specifying the microscopic configuration of the individual phases and enables using the available mathematical model to solve the problem of flow through porous media. The dispersion coefficient

is a term which depends upon the configuration of the void-solid boundary and the interface network within the average volume. Thus the properties of porous media can be expressed us to use these coefficients (i.e., molecular dispersion coefficient and mechanical dispersion coefficient) which are determined experimentally for any given porous media.

The solute concentration and velocity at the microscopic level can not be predicted because of the complexity of geometric characteristics of the void space configuration. However, we can predict the average concentration, $\underline{c}$, and the average flux, $\underline{c}\underline{v}$, at the macroscopic level. To achieve this, let us consider a REV expression as a microscopic level within a porous medium domain (Figure 6.2).

Figure 6.2 shows a solute concentration “c” and a velocity “v” at any point x' belonging to a REV centered at point X; c is the mass of the substance per unit volume of solute (M/L³). The local flux can be expressed as the product of “c·v” at point x'. The flux, “c·v” is the mass of the substance per unit of area passed per unit time. The average flux of a considered substance, $\underline{c}\underline{v}$, is equal to the sum of two macroscopic fluxes: (1) the advective flux, $\underline{c}\underline{v}$, carried by the water at the average velocity, $\underline{v}$, determined by Darcy's law, and (2) the additional flux, $(\underline{c}'\underline{v}')$ resulting from the fluctuating velocity in the vicinity of point x' within the REV:

$$\underline{c}\underline{v} = \underline{c}\underline{v} + \underline{c}'\underline{v}' \quad (6.1)$$

The additional flux, $(\underline{c}'\underline{v}')$, the flux causing spreading, is defined as the dispersive flux. This flux is a macroscopic value that represents the average of the velocity fluctuation at the microscopic level. The dispersive flux can be expressed by Fick's law in the form

$$\underline{c'v'} = -D \cdot \nabla \underline{c} \quad (6.2)$$

where D is the coefficient of mechanical dispersion and $\underline{c}$ is the average mass of the dispersing substance per unit volume of solution (Bear and Verruijt 1990).

• Molecular Diffusion

The flux, J_m due to molecular diffusion at microscopic level is expressed by Fick's law:

$$J_m = -D_m \cdot \nabla c \quad (6.3)$$

where D_m is the coefficient of molecular diffusion in a fluid continuum. In the dilute aqueous system, the flux due to molecular diffusion at macroscopic level can be expressed as:

$$J_m = -D_m T^* \cdot \nabla \underline{c} = -D_m^* \cdot \nabla \underline{c} \quad (6.4)$$

where T^* is referred to the tortuosity of the solute path in the porous media.

• Hydrodynamic Dispersion

Hydrodynamic dispersion flux can be expressed as the sum of mechanical dispersion flux, and molecular diffusion flux:

$$\underline{c'v'} + J_m = -(D + D_m^*) \cdot \nabla \underline{c} = -D_h \cdot \nabla \underline{c} \quad (6.5)$$

where D_h is the coefficient of hydrodynamic dispersion. The total mass of pollutant passing through a unit area of porous media due to advection and hydrodynamic dispersion is expressed as total flux J_T . It is written in the form:

$$J_T = \phi (\underline{c} \underline{v} - D_h \cdot \nabla \underline{c}) \quad (6.6)$$

where ϕ is the porosity of porous media for the case of saturated flow. The dispersion coefficient is generally related to the physical characteristics of the porous media and the fluid flow such as tortuosity, incomplete channel connectivity, recirculation velocity gradient eddies, and dead end pores.

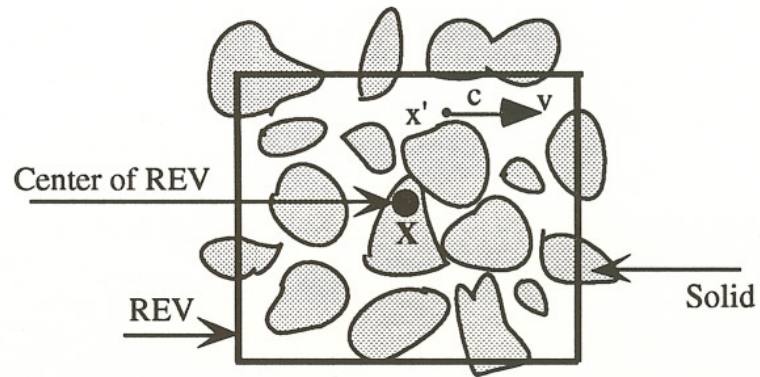


Figure 6.2 Representative elementary volume (REV) of a porous media (Bear and Verruijt 1990).

6.2.3 Governing Equation for Contaminant Transport Through Porous Media

Let C and v be the pollutant concentration and flow velocity at the macroscopic level ($C \equiv \underline{c}$ and $v \equiv \underline{v}$). Four major components can be taken into account in the construction of a macroscopic mass governing equation when a reactive chemical substance (pollutant) transports through porous media, in saturated flow (Bear and Verruijt 1990):

- (1). The amount of pollutant entering and leaving a control volume by advection, dispersion, and diffusion.

Define J_T as the total flux of pollutant due to the above mechanisms. The accumulation of that substance per unit volume per unit time due to the difference of inflow and outflow is expressed as minus the divergence of the total flux, “ $-\nabla \cdot J_T$ ”.

- (2). Chemical or electrical interactions between the pollutant and the solid surface (e.g., adsorption).

Let “ f ” denote the mass of the pollutant loss in the solution by such interactions, per unit volume of porous media, per unit time.

- (3). Chemical interactions or various decay phenomena among species inside the solution (e.g., radioactive decay, biodegradation, redox reactions, and precipitation).

Let “ $\pm Y$ ” denote the rate of pollutant gains or losses in the solution by such mechanisms, per unit mass of fluid, per unit time. With ρ denoting the solution density, the mass of pollutant gained or lost per unit volume of porous media, per unit time can be expressed as “ $\phi \rho Y$ ”.

(4). Injecting pollutant into or withdrawing pollutant from porous medium.

The total mass of pollutant added or withdrawn per unit volume of porous medium per unit time, is expressed as “I” or “W”, respectively.

For the saturated flow, the mass of a pollutant per unit volume of porous medium is denoted as “ ϕC ”. $\partial\phi C/\partial t$ is the rate at which this quantity changes within a control volume. Combining the four components described above, the (macroscopic) mass equation of hydrodynamic dispersion is:

$$\frac{\partial\phi C}{\partial t} = -\nabla \cdot J_T - f \pm \phi \rho Y - W + I \quad (6.7)$$

With no pollutant injected or withdrawn ($W = 0$, $I = 0$), and using $J_T = \phi(Cv - D_h \cdot \nabla C)$, equation (6.7) is written as:

$$\frac{\partial\phi C}{\partial t} = -\nabla \cdot \phi(Cv - D_h \cdot \nabla C) - f \pm \phi \rho Y \quad (6.8)$$

In order to express “f”, let q denote the mass of the pollutant adsorbed on the solid per unit mass of solid, ρ_s denote the density of the solid (porous media), and θ_s denote the volumetric fraction of the solid ($\theta_s = 1 - \phi$). Any advective, dispersive, and diffusive fluxes of the pollutant present in the solid are neglected. The equation for the pollutant mass balance on the solid phase is:

$$\frac{\partial(\theta_s \rho_s q)}{\partial t} = f \pm \theta_s \rho_s Y_s \quad (6.9)$$

where Y_s denotes the rate of the production or loss of the pollutant per unit of solid. This is a term arising from interaction of the adsorbed species with solid surface. It can result from biodegradation decay due to bioactivity on the solid surface or

production of pollutant from the solid owing to the transformation of pollutant by the interaction between adsorbed species and solid surface. Assuming there is no pollutant production or decay from the solid, $Y_s = 0$. Equation (6.9) is reduced to:

$$\frac{\partial(\theta_s \rho_s q)}{\partial t} = f \quad (6.10)$$

Substituting equation (6.10) into equation (6.8) for $\theta_s = 1 - \phi = \text{constant}$, equation (6.8) is reduced to

$$\frac{\partial C}{\partial t} = -\nabla \cdot (Cv - D_h \cdot \nabla C) - \frac{1-\phi}{\phi} \frac{\partial(\rho_s q)}{\partial t} \pm \rho Y \quad (6.11)$$

6.2.3.1 Sources and Sinks within the Liquid Phase

The term “ $\pm \rho Y$ ” is represented as the sources and sinks of the pollutant within the solution phase. This results from various processes such as chemical reaction among species within the solution, radioactive decay, biodegradation, and redox reactions. Consider that i -components participate in the reactions:

$$\rho Y = \sum_{i=1}^i k_i C_i^p \quad (6.12)$$

where C_i is the concentration of the i -component in moles per unit volume of solution, p indicates the order of the reaction, and k_i is the kinetic rate constant with the dimension of reciprocal time.

$$\frac{\partial C}{\partial t} = -\nabla \cdot (Cv - D_h \cdot \nabla C) - \frac{1-\phi}{\phi} \frac{\partial(\rho_s q)}{\partial t} \pm \sum_{i=1}^i k_i C_i^p \quad (6.13)$$

When the first order decay reaction takes place within the solution and only one component is considered, equation (6.13) is simplified to:

$$\frac{\partial C}{\partial t} = -\nabla \cdot (Cv - D_h \cdot \nabla C) - \frac{1-\phi}{\phi} \frac{\partial(\rho_s q)}{\partial t} - kC \quad (6.14a)$$

If we consider one-dimensional solute transport (x-direction):

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{1-\phi}{\phi} \frac{\partial(\rho_s q)}{\partial t} \pm kC \quad (6.14b)$$

The kinetic decay rate constant, k , is dependent on the experimental conditions, e.g., solution pH, temperature, and ionic strength. It may involve the dissolution of reactive species from the solid phase. Let ρ_b denote the bulk density of the solid. If ρ_b is a constant, equation (6.14b) reduces to:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho_b}{\phi} \frac{\partial q}{\partial t} - kC \quad (6.14c)$$

6.2.3.2 Adsorption Isotherms

Adsorption is the phenomenon in which the mass of a pollutant accumulates on the solid surface at the solid-liquid interface. Three types of equilibrium adsorption isotherms that express the quantity of an adsorbed component and its quantity in the solution phase are discussed (Figure 6.3).

(1). Linear isotherm

The linear isotherm has the form of:

$$q = K_L C \quad (6.15)$$

where K_L (L^3M^{-1}) is the linear adsorption constant, also known as partition coefficient or distribution coefficient. The mass of contaminant adsorbed per unit mass of adsorbate is denoted as “q” (MM^{-1}) and C (ML^{-3}) is the solute equilibrium concentration.

(2). Freundlich isotherm

The Freundlich nonlinear equilibrium isotherm was originally developed from empirical observation and is expressed as:

$$q = K_f C^n \quad (6.16)$$

where K_f and n are Freundlich adsorption constants. When n equal to 1, equation (6.16) reduces to linear adsorption form (i.e., equation 6.15).

(3). Langmuir isotherm

Langmuir nonlinear equilibrium isotherm is expressed as:

$$q = \frac{Q_m K_m C}{1 + K_m C} \quad (6.17)$$

where Q_m (MM^{-1}) is the maximum adsorbed capacity on solid surface. K_m (L^3M^{-1}) is the Langmuir adsorption constant. Q_m and K_m are empirical constants which can be determined experimentally. When the value of $K_m C \ll 1$, equation (6.17) becomes the linear form.

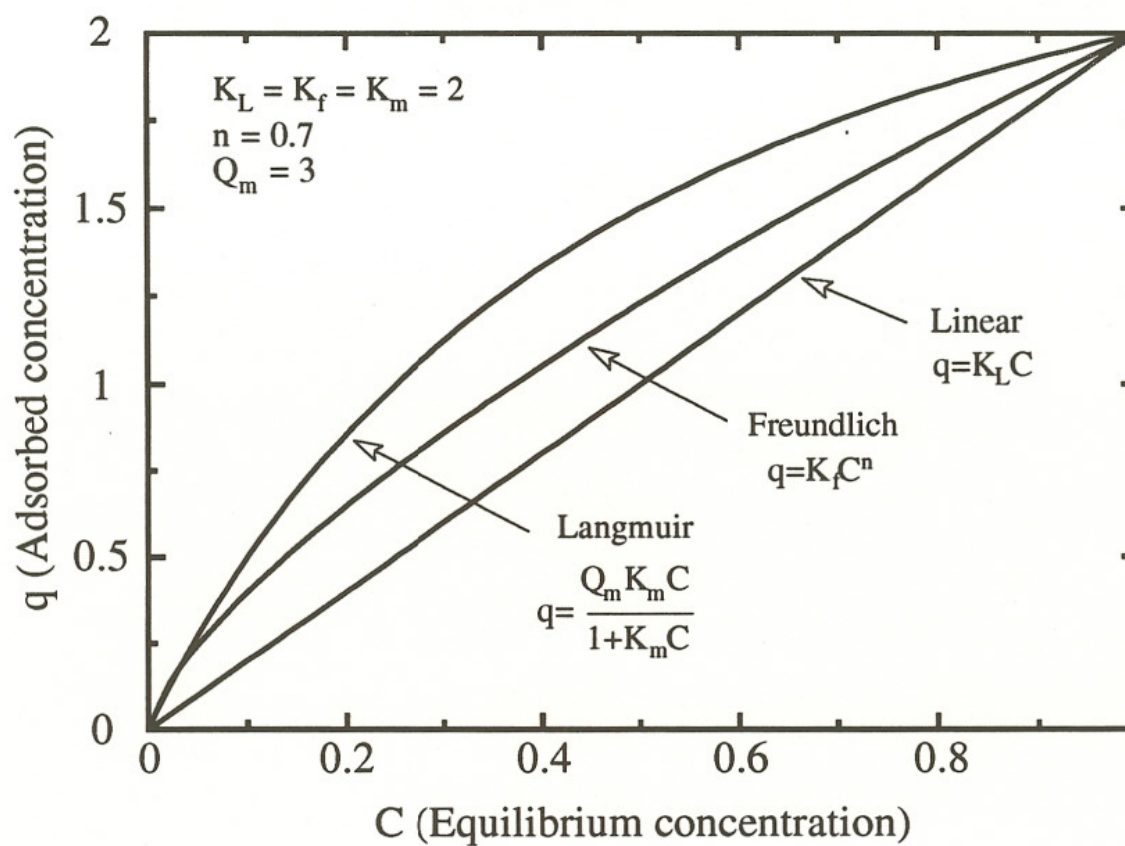


Figure 6.3 The linear, Freundlich, and Langmuir adsorption isotherms.

6.2.3.3 Mass Balance Equation with Adsorption and Decay

Consider the case of saturated flow with no external sources or sinks, i.e., $I \equiv 0$ and $W \equiv 0$, and $\partial \rho_s / \partial t = 0$ and $\partial \phi / \partial t = 0$. Assuming that the adsorption reaction obeys the linear equilibrium isotherm with $\partial K_L / \partial t = 0$. Equation (6.15) becomes:

$$\frac{\partial q}{\partial t} = K_L \cdot \frac{\partial C}{\partial t} \quad (6.18)$$

and equation (6.14c) has the form of:

$$R_d \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - kC \quad (6.19)$$

where

$$R_d = 1 + \frac{\rho_b}{\phi} K_L, \quad (6.20)$$

R_d (dimensionless) is called the coefficient of retardation or retardation factor. When the adsorption behavior is followed by the Freundlich adsorption isotherm, the slope of Freundlich adsorption isotherm is expressed as:

$$\frac{\partial q}{\partial C} = n K_f C^{n-1} \quad (6.21)$$

The retardation factor for the Freundlich form is a function of solute concentration and expressed as:

$$R_d = 1 + \frac{\rho_b}{\phi} n K_f C^{n-1}$$

When the adsorption reaction obeys the Langmuir equilibrium isotherm, equation (6.17) becomes:

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial t} \left(\frac{\Gamma_m K_m C}{1 + K_m C} \right) \quad (6.22a)$$

Equation (6.22) can be written as:

$$\frac{\partial q}{\partial t} = \frac{\Gamma_m K_m}{(1 + K_m C)^2} \frac{\partial C}{\partial t} \quad (6.22b)$$

The slope of Langmuir adsorption isotherm is expressed as:

$$\frac{\partial q}{\partial C} = \frac{Q_m K_m}{(1 + K_m C)^2} \quad (6.22c)$$

With Langmuir equilibrium isotherm, the retardation factor, R_d , in equation (6.19) becomes:

$$R_d = \left[1 + \frac{\rho_b}{\phi} \frac{Q_m K_m}{(1 + K_m C)^2} \right] \quad (6.23)$$

Let $t^* = t/R_d$

Then, equation (6.19) can be reduced to:

$$\frac{\partial C}{\partial t^*} = D_h \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - kC \quad (6.24)$$

6.2.4 Initial and Boundary Conditions

The initial condition (IC) and boundary condition (BC) for a semifinite system containing a solute with input concentration of C_f (ML⁻³) and initial concentration C_0 (ML⁻³) are discussed below. The IC is given as:

$$C(x, t = 0) = C_0(x) \quad \text{at } 0 < x \leq \infty \quad (6.25)$$

The input BC can be either the “first type (Dirichlet Type)” or the “third type (Cauchy type)”. The first type of BC assumes that the influent concentration in the inlet reservoir is ideally homogeneous on the top surface of the porous media by means of complete mixing. This type of BC can be formulated as:

$$C(x, t) = C_f \quad \text{at } x = 0 \text{ and } t \geq 0 \quad (6.26a)$$

The third type of BC assumes that the influent concentration is described by flux continuity and is a function of flow velocity, hydrodynamic dispersion coefficient, and concentration difference between the influent solute and right below the top surface of porous media. This type of BC can be stated as:

$$\frac{\partial C}{\partial x} = -\frac{v}{D_h}(C - C_f) \quad \text{at } x = 0 \text{ and } t \geq 0 \quad (6.26b)$$

The output BC applied is called the “second type (Neumann type)”:

$$\frac{\partial C}{\partial x} = 0 \quad \text{at } x = L \text{ and } t \geq 0 \quad (6.26c)$$

6.3 Numerical Solution: Finite Difference Method

6.3.1 Difference Equations

The hydrodynamic dispersion equation (equation 6.14b) can be solved using the finite difference method. The finite difference method was the first method to be used for the systematic numerical solution of partial differential equations. The

method consists of an approximation of partial derivatives by algebraic expressions involving the values of the dependent variable at a limited number of selected points. As a result of the approximation, the partial differential equation describing the problem is replaced by a finite number of algebraic equations, written in terms of the values of the dependent variable at the selected points (Bear and Verruijt 1990). Because the basic theory of this method is much simpler than finite element method, it usually requires less computer memory and computation time, for solving the hydrodynamic dispersion equation involving adsorption and decay reaction. The simplified finite algebraic equation can be written with common programming languages such as FORTRAN, C, and PASCAL. In this study, the difference equations were written with a spreadsheet software (Lotus 1-2-3 Release 4 for Windows) which runs in a PC (personal computer).

The basic idea of the finite difference method is that the region R is covered with two families of straight parallel lines, in the t- (or y-) and x-direction, respectively, which together form a grid of a rectangle network (Figure 6.4). With denoting θ as a weighted approximation factor, the basic difference equation is:

$$a_1 C_{i-1}^{j+1} + a_2 C_i^{j+1} + a_3 C_{i+1}^{j+1} = b_1 C_{i-1}^j + b_2 C_i^j + b_3 C_{i+1}^j \quad (6.27)$$

where a's and b's are functions of Δx , Δt , and θ . For any grid point (i, j) along with the known IC and BC, the derivatives of basic equations can be replaced by the finite difference forms.

$$\frac{\partial C}{\partial t} = \frac{C(x, t + \Delta t) - C(x, t)}{\Delta t} = \frac{C_i^{j+1} - C_i^j}{\Delta t} \quad (6.28)$$

$$U_i = \left[\frac{(\theta-1)D_h}{(\Delta x)^2} + \frac{(\theta-1)v}{2\Delta x} \right] C_{i-1}^j + \left[\frac{-1}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} \right] C_i^j \\ + \left[\frac{(\theta-1)D_h}{(\Delta x)^2} - \frac{(\theta-1)v}{2\Delta x} \right] C_{i+1}^j$$

, $1 \leq i \leq M$, and $1 \leq j \leq N$.

For one-dimensional solute transport coupled with adsorption and decay, equation (6.19) can be expressed as the finite difference form:

$$\frac{R_d(C_i^{j+1} - C_i^j)}{\Delta t} = \\ \theta \left[D_h \left(\frac{C_{i+1}^{j+1} - 2C_i^{j+1} + C_{i-1}^{j+1}}{(\Delta x)^2} \right) - v \left(\frac{C_{i+1}^{j+1} - C_{i-1}^{j+1}}{2\Delta x} \right) - kC_i^{j+1} \right] \\ + (1-\theta) \left[D_h \left(\frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{(\Delta x)^2} \right) - v \left(\frac{C_{i+1}^j + C_{i-1}^j}{2\Delta x} \right) - kC_i^j \right] \quad (6.34)$$

Rearrange equation (6.34) as the form of equation (6.27):

$$R_i C_{i-1}^{j+1} + S_i C_i^{j+1} + T_i C_{i+1}^{j+1} = U_i \quad (6.35)$$

where $R_i = \frac{\theta D_h}{(\Delta x)^2} + \frac{\theta v}{2\Delta x}$

$$S_i = -\frac{R_d}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2}$$

$$T_i = \frac{\theta D_h}{(\Delta x)^2} - \frac{\theta v}{2\Delta x}$$

$$U_i = \left[\frac{(\theta - 1)D_h}{(\Delta x)^2} + \frac{(\theta - 1)v}{2\Delta x} \right] C_{i-1}^j + \left[\frac{-R_d}{\Delta t} - \frac{2(\theta - 1)D_h}{(\Delta x)^2} - (\theta - 1)k \right] C_i^j + \left[\frac{(\theta - 1)D_h}{(\Delta x)^2} - \frac{(\theta - 1)v}{2\Delta x} \right] C_{i+1}^j$$

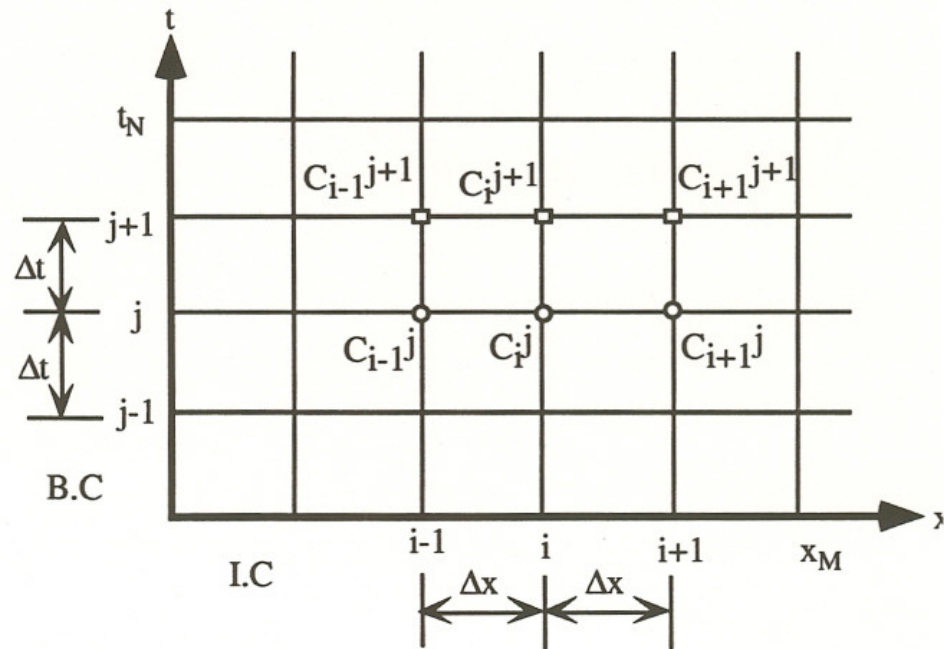


Figure 6.4 The network of finite difference method.

6.3.2 Difference Equations for Initial and Boundary Conditions

For initial condition at $t=0$ (i.e., $i=0$):

$$C_o^0 = C_f \quad \text{at } x=0 \text{ (i.e., } j=0 \text{) and}$$

$$C_o^{j+1} = C_o \quad \text{at } 0 < i < L \text{ (i.e., } 0 < x < M \text{)}$$

For the first type of boundary condition at $x=0$ (i.e., $i=0$), let

$$C_{-1}^{j+1} = C_f \text{ and therefore } C_o^j = C_f \quad (6.36)$$

Substituting equation (6.36) into equation (6.33):

$$\begin{aligned} & \left(\frac{\theta D_h}{(\Delta x)^2} + \frac{\theta v}{2\Delta x} \right) C_f + \left(-\frac{(R_d)_o}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2} - \theta k \right) C_o^{j+1} + \left(\frac{\theta D_h}{(\Delta x)^2} - \frac{\theta v}{2\Delta x} \right) C_1^{j+1} = \\ & \left[\frac{(\theta-1)D_h}{(\Delta x)^2} + \frac{(\theta-1)v}{2\Delta x} \right] C_f + \left[-\frac{(R_d)_o}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} - (\theta-1)k \right] C_o^j + \\ & \left[\frac{(\theta-1)D_h}{(\Delta x)^2} - \frac{(\theta-1)v}{2\Delta x} \right] C_{i+1}^j \end{aligned} \quad (6.37)$$

Rearranging equation (6.37):

$$\begin{aligned}
& \left(-\frac{(R_d)_o}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2} \pm \theta k \right) C_o^{j+1} + \left(\frac{\theta D_h}{(\Delta x)^2} - \frac{\theta v_x}{2\Delta x} \right) C_1^{j+1} = \\
& \left[\frac{-(R_d)_o}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} - (\theta-1)k \right] C_o^j + \left[\frac{(\theta-1)D_h}{(\Delta x)^2} + \frac{(\theta-1)v_x}{2\Delta x} \right] C_1^j \quad (6.38) \\
& + \left[\frac{-D_h}{(\Delta x)^2} - \frac{v_x}{2\Delta x} \right] C_f \\
& S_o = -\frac{R_d}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2} - \theta k
\end{aligned}$$

Equation (6.38) can be formulated as:

$$S_o C_o^{l+1} + T_o C_o^{l+1} = U_o \quad (6.39)$$

$$\begin{aligned}
T_o &= \frac{\theta D_h}{(\Delta x)^2} - \frac{\theta v}{2\Delta x} \\
U_o &= \left[\frac{-R_d}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} - (\theta-1)k \right] C_o^j + \\
& \left[\frac{(\theta-1)D_h}{(\Delta x)^2} + \frac{(\theta-1)v}{2\Delta x} \right] C_1^j + \left[\frac{-D_h}{(\Delta x)^2} - \frac{v}{2\Delta x} \right] C_f
\end{aligned}$$

For the second type of BC at $x=L$ (i.e., $i=M$), then

$$\frac{C_{M+1}^{j+1} - C_{M-1}^{j+1}}{2\Delta x} = 0 \quad (6.40)$$

From equation (6.40):

$$C_{M+1}^{j+1} = C_{M-1}^{j+1} \quad (6.41)$$

Therefore, according to equation (6.33), at $x=L$ (i.e., $i=M$), the difference equation can be written as:

$$(R_M + T_M)C_{M-1}^{j+1} + S_M C_M^{j+1} = U_M \quad (6.42)$$

For the third type of boundary condition at $x=0$ (i.e., $i=0$), let

$$\frac{C_1^{j+1} - C_{-1}^{j+1}}{2\Delta x} = -\frac{v}{D_h}(C_f - C_o^{j+1}) \quad (6.43)$$

Rearranging equation (6.43):

$$C_{-1}^{j+1} = C_1^{j+1} - \frac{2\Delta x v}{D_h} C_o^{j+1} + \frac{2\Delta x v}{D_h} C_f$$

and therefore:

$$C_{-1}^j = C_1^j - \frac{2\Delta x v}{D_h} C_o^j + \frac{2\Delta x v}{D_h} C_f \quad (6.44)$$

Substituting equation (6.44) into equation (6.33):

$$\begin{aligned} & \left(\frac{\theta D_h}{(\Delta x)^2} + \frac{\theta v}{2\Delta x} \right) \left(C_1^{j+1} - \frac{2\Delta x v}{D_h} C_o^{j+1} + \frac{2\Delta x v}{D_h} C_f \right) + \left(-\frac{(R_d)_o}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2} - \theta k \right) C_o^{j+1} + \\ & \left(\frac{\theta D_h}{(\Delta x)^2} - \frac{\theta v}{2\Delta x} \right) C_1^{j+1} = \left[\frac{(\theta-1)D_h}{(\Delta x)^2} + \frac{(\theta-1)v}{2\Delta x} \right] \left(C_1^j - \frac{2\Delta x v}{D_h} C_o^j + \frac{2\Delta x v}{D_h} C_f \right) + \\ & \left[\frac{-(R_d)_o}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} - (\theta-1)k \right] C_o^j + \left[\frac{(\theta-1)D_h}{(\Delta x)^2} - \frac{(\theta-1)v}{2\Delta x} \right] C_1^j \end{aligned} \quad (6.45)$$

Rearranging equation (6.45)

$$\begin{aligned}
& \left(-\frac{2\theta v}{\Delta x} - \frac{\theta v^2}{D_h} - \frac{(R_d)_o}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2} - \theta k \right) C_o^{j+1} + \left(\frac{2\theta D_h}{(\Delta x)^2} \right) C_1^{j+1} = \\
& \left[\frac{2(\theta-1)v}{\Delta x} - \frac{(\theta-1)v^2}{D_h} - \frac{(R_d)_o}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} - (\theta-1)k \right] C_o^j + \quad (6.46) \\
& \left(\frac{2(\theta-1)D_h}{(\Delta x)^2} \right) C_1^j + \left(\frac{-2v}{\Delta x} - \frac{v^2}{D_h} \right) C_f
\end{aligned}$$

Equation (6.46) can be formulated as:

$$S_o C_o^{l+1} + T_o C_o^{l+1} = U_o \quad (6.47)$$

$$S_o = -\frac{2\theta v}{\Delta x} - \frac{\theta v^2}{D_h} - \frac{(R_d)_o}{\Delta t} - \frac{2\theta D_h}{(\Delta x)^2} - \theta k$$

$$T_o = \frac{2\theta D_h}{(\Delta x)^2}$$

$$\begin{aligned}
U_o = & \left[\frac{2(\theta-1)v}{\Delta x} - \frac{(\theta-1)v^2}{D_h} - \frac{(R_d)_o}{\Delta t} - \frac{2(\theta-1)D_h}{(\Delta x)^2} - (\theta-1)k \right] C_o^j + \\
& \left(\frac{2(\theta-1)D_h}{(\Delta x)^2} \right) C_1^j + \left(\frac{-2v}{\Delta x} - \frac{v^2}{D_h} \right) C_f
\end{aligned}$$

6.3.3 Tridiagonal Matrix

With the BCs and the differences equation, a set of algebraic equations can be written as a matrix form:

$$\begin{aligned}
 S_0 C_0^{j+1} + T_0 C_0^{j+1} &= U_0 \\
 R_1 C_1^{j+1} + S_1 C_1^{j+1} + T_1 C_1^{j+1} &= U_1 \\
 R_2 C_2^{j+1} + S_2 C_2^{j+1} + T_2 C_2^{j+1} &= U_2 \\
 R_3 C_3^{j+1} + S_3 C_3^{j+1} + T_3 C_3^{j+1} &= U_2 \\
 &\dots\dots\dots \\
 R_{M-1} C_{M-2}^{j+1} + S_{M-1} C_{M-1}^{j+1} + T_{M-1} C_M^{j+1} &= U_{M-1} \\
 (R_M + T_M) C_{M-1}^{j+1} + S_M C_M^{j+1} &= U_M \quad (6.48)
 \end{aligned}$$

The coefficients of the discretized equations, S_0 , T_0 , R_i , S_i , and T_i are constants which are calculated by knowing the weight approximation factor θ , pore velocity v , dispersion coefficient D_h , bulk density ρ_b , porosity ϕ , retardation factor R_ϕ decay constant k , distance step Δx , and time step Δt . U_0 can be calculated from equation (6.39) for the first type of BC or equation (6.47) for the third type of BC using initial concentration, $C_0^0 = C_f$ at $x \leq 0$ and $t=0$ and $C_1^0 = C_0$ at $0 \leq x \leq L$ and $t=0$. U_i is known at previous time step j . With a known influent concentration, C_f , and initial concentration C_0 , the coefficient of dispersion equation U_i can be calculated at $t=0$ and $0 \leq x \leq L$.

At $t > 0$ and $0 \leq x \leq L$, the concentration at each node in equation (6.48) can be solved through Tridiagonal Matrix Method. The general matrix form of solving concentration at time step j is:

$$\begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \\ \dots \\ C_{M-2} \\ C_{M-1} \\ C_M \end{bmatrix}_{1 \times M} = \begin{bmatrix} S_0 & T_0 & 0 & 0 & 0 & 0 & 0 & 0 \\ R_1 & S_1 & T_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_2 & S_2 & T_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & R_3 & S_3 & T_3 & 0 & 0 & 0 \\ \dots & 0 & 0 & 0 & \dots & \dots & 0 & 0 \\ 0 & 0 & 0 & 0 & R_{M-2} & S_{M-2} & T_{M-2} & 0 \\ 0 & 0 & 0 & 0 & 0 & R_{M-1} & S_{M-1} & T_{M-1} \\ 0 & 0 & 0 & 0 & 0 & 0 & R_M + T_M & S_M \end{bmatrix}_{M \times M}^{-1} \begin{bmatrix} U_0 \\ U_1 \\ U_2 \\ U_3 \\ \dots \\ U_{M-2} \\ U_{M-1} \\ U_M \end{bmatrix}_{1 \times M} \quad (6.49)$$

6.4 Development of Spreadsheet Program

Most marketed software or existing developed programs have one or more of the following drawbacks: user-unfriendly, uneditable output results, limited by the availability of hardware (such as incompatibility of the hardware for executing the program), and limited by the poor computer knowledge of high-level computer language, e.g., FORTRAN. Therefore, development of a user-friendly program to minimize the user requirement of computer knowledge, to be directly used in the PC, and to have the nature of editable or transferable output is necessary.

The idea to develop a solute transport program utilizing PC based spreadsheet software such as Lotus 1-2-3 and Microsoft-Excel is related to use of the finite difference method to solve the solute transport governing equation. In the use of finite difference method, the partial differential equation can be broken into steps by the finite

difference scheme. Since the time step and distance step are setup in the spreadsheet cell, the concentration distribution is therefore calculated through cell operation. With the help of the macro, a series of commands automates the calculation task and the governing equation can directly be solved in the spreadsheet. The choice of Lotus 1-2-3 is due to the many macro commands automating the interactive popup dialog boxes and performing programming tasks.

The flow chart of solute transport program is shown in Figure 6.5. In this program, a flow chart type of "button" similar to Figure 6.5 was set up to input data and to execute the program. When the "Start" button is clicked, the program first displays a series of dialog boxes for a user to input data such as solid density, porosity, coefficient of hydrodynamic dispersion, pore velocity, distance step, and time step. The stability of using finite difference method will be checked by the values of Pe (Peclet number) and Cr (Courant number). If the values of Pe and Cr exceed the stability criteria, a dialog box will popup for a user to reenter the value of distance and time steps or skip the advice. Details of the stability of numerical model will be discussed in section 6.4.4. Then, a menu choice of the types of the transport conditions will prompt. If the transport process includes the adsorption reaction, the user can further select the type of adsorption isotherms (i.e., Linear, Freundlich, and Langmuir isotherms). This will be followed by the input of influent solute concentration, initial solute concentration in the porous media, and the selection of boundary condition. After entering the number of total time steps, the user can select the type of output results such as plot the last step only or plot as the breakthrough curve. The "Help" button to access information for beginning users is provided. Manual for this interactive spreadsheet program is shown in appendix B.

The one-dimensional contaminant transport spreadsheet program developed in this study has the following advantages:

(1). It runs in a personal computer. In today's fast-growing highly competitive PC market, the speeds and prices of PC offered to the consumer are attractive. For a PC of 486DX2-50MHz with 8MB Ram and 340 MB hard drive, the price is around \$2000. Depending upon the configuration of the PC, the speed of running this program will be different. For a PC with 486DX2 66MHz and 8MB Ram, the running time of 2000 time steps is about 20 minutes. If the computer is installed with Intel-Pentium chip processor, the speed of running this program is even faster. To run this program, Lotus 1-2-3 Release 4 must be installed in PC Windows. Although the program is designed to be used in the IBM-PC, it is possible to run this program in Macintosh using a software called "SoftPC with Windows" which emulates an Intel processor and runs the Windows program directly in 68040 Macintosh. With a software called "SoftWindows" installed in Apple Power Macintosh, one can run this program at speed up to a 486SX-PC.

(2). Program is user-friendly. To run the program, One simply clicks the "Button" that was already set-up and follows the direction of popup dialog. With the flowchart type of layout, it not only it provides the user a general idea of this program, but it also allows the user to directly enter the different parts of this program.

(3). The output data can be copy-edited, transported to database program and printed out or transported to other presentation programs (using OS/2) or enhanced graphical software. For example, the output data can be copied to a separate data file, then linked or transferred to Macintosh Microsoft-Excel using "Apple File Exchange"

and “MacLink Plus/PC”. Section 6.5 demonstrates the output data generated from this program transferred from IBM-PC to Macintosh, and then plotted using KaleidaGraph™ 3.0 to plot the model results. The output graph generated in the Lotus 1-2-3 can be directly copy-edited. One can save and customize the graph, such as modify the axis scales, size, title, and color the graph, using Lotus 1-2-3 chart tools from the menu bars to make the output graph more presentable.

(4). Unlimited time steps for the simulation. This operation may require that the user turn off the “Undo”. To enable “Undo”, using Tools-User Setup from the menu bar in the Lotus 1-2-3 program, then choose Edit Undo or press “CTRL+Z”. When one works with the Microsoft Window and Lotus 1-2-3 Release 4 in a PC with 8 MB Ram, the program can be run up to 2300 steps without turning off the “Edit Undo”.

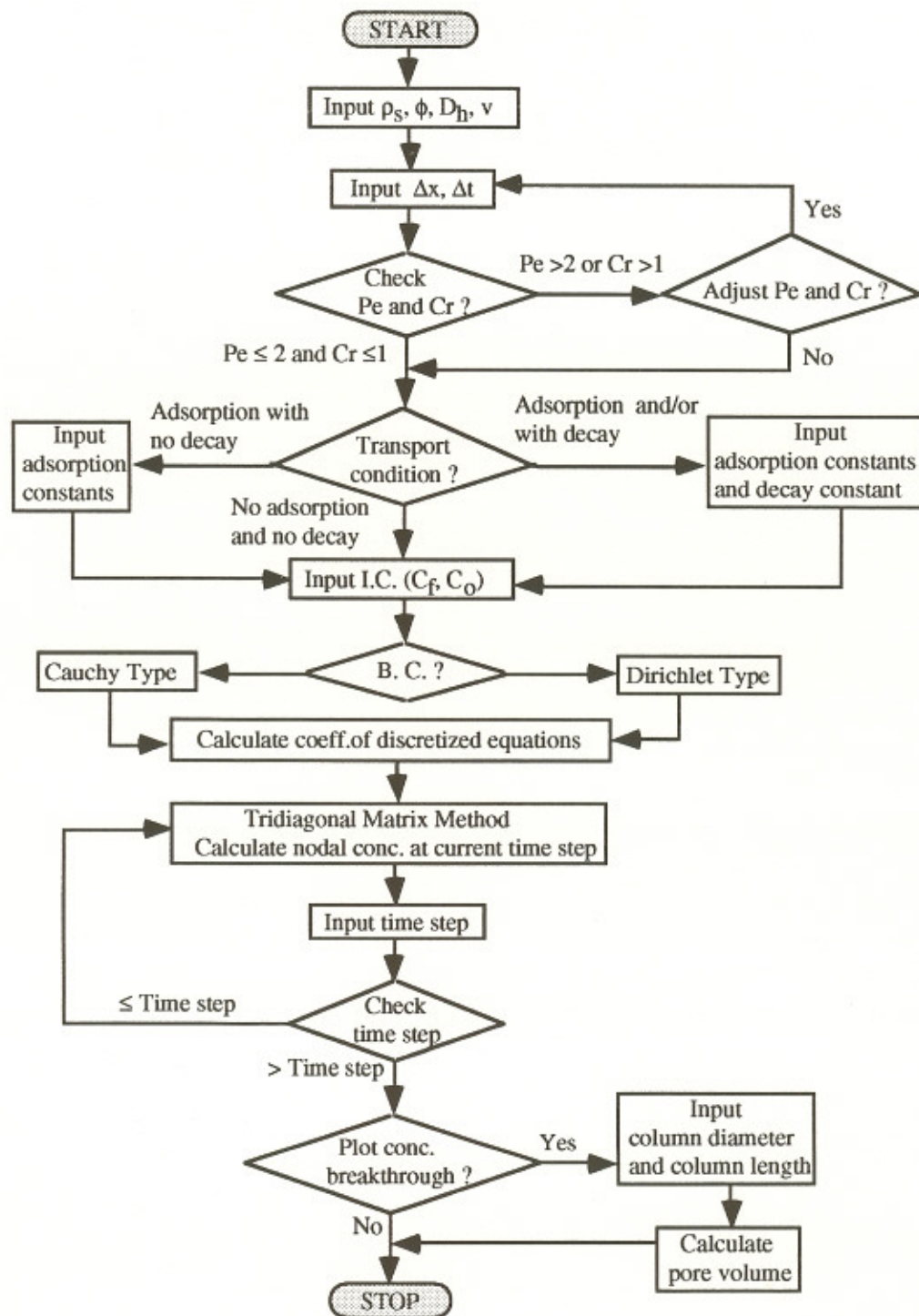


Figure 6.5 Flow chart of solute transport program.

6.5 Program Verification, Stability of Numerical Solution, and Parametric Study on Numerical Model

6.5.1 Program Verification

It is necessary to verify that the numerical model is correctly solving the governing equation before used to further applications. The known analytical solutions were compared with the calculated numerical solutions. The selected analytical solutions used for the verification of the numerical results are described below:

Case 1: Infinite column with linear adsorption (Bear 1979) (Figure 6.6a):

$$C(x, t) = \frac{C_f}{2} \cdot \operatorname{erfc}\left(\frac{x - vt}{2\sqrt{D_h t}}\right) \quad (6.50)$$

Case 2: Semi-infinite column with linear adsorption and the first type boundary condition as described in equation (6.26a) (Ogata and Bank 1961) (Figure 6.6b):

$$C(x, t) = \frac{C_f}{2} \left\{ \operatorname{erfc}\left[\frac{x - vt}{2\sqrt{D_h t}}\right] + e^{\frac{vx}{D_h}} \cdot \operatorname{erfc}\left[\frac{x + vt}{2\sqrt{D_h t}}\right] \right\} \quad (6.51)$$

Case 3: Semi-infinite column with linear adsorption and the third type boundary condition, as described in equation (6.26b) (Gershon and Nir 1969) (Figure 6.6c):

$$C(x,t) =$$

$$C_f \left\{ \frac{1}{2} \operatorname{erfc} \left[\frac{x-vt}{2\sqrt{D_h t}} \right] - \frac{1}{2} e^{\frac{vx}{D_h}} \cdot \left(1 + \frac{x+vt}{\frac{D_h}{v}} \right) \cdot \operatorname{erfc} \left[\frac{x+vt}{2\sqrt{D_h t}} \right] + \sqrt{\frac{v^2 t}{\pi D_h}} \cdot e^{-\frac{(x-vt)^2}{4D_h t}} \right\} \quad (6.52)$$

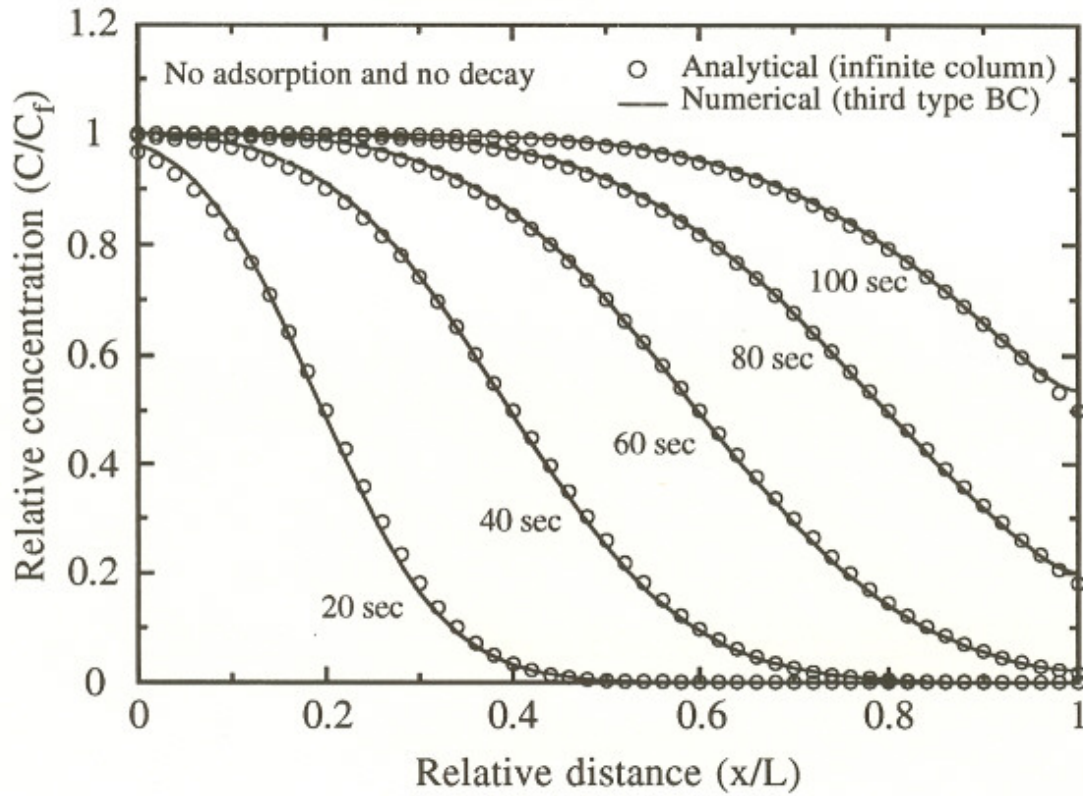


Figure 6.6a Comparison of numerical and analytical solutions for one-dimension solute transport ($D_h = 0.03 \text{ cm}^2/\text{sec}$, $v = 0.1 \text{ cm/sec}$, $\Delta x = 0.2 \text{ cm}$, $\Delta t = 2 \text{ sec}$, $C_f = 1 \text{ mg/L}$, $C_0 = 0 \text{ mg/L}$, and $L = 10 \text{ cm}$ in all cases): (a) analytical solution for infinite column (equation 6.50) and numerical solution for a third type of BC, (b) semi-finite column with first type of BC (equation 6.51), and (c) semi-finite column with third type of BC (equation 6.52).

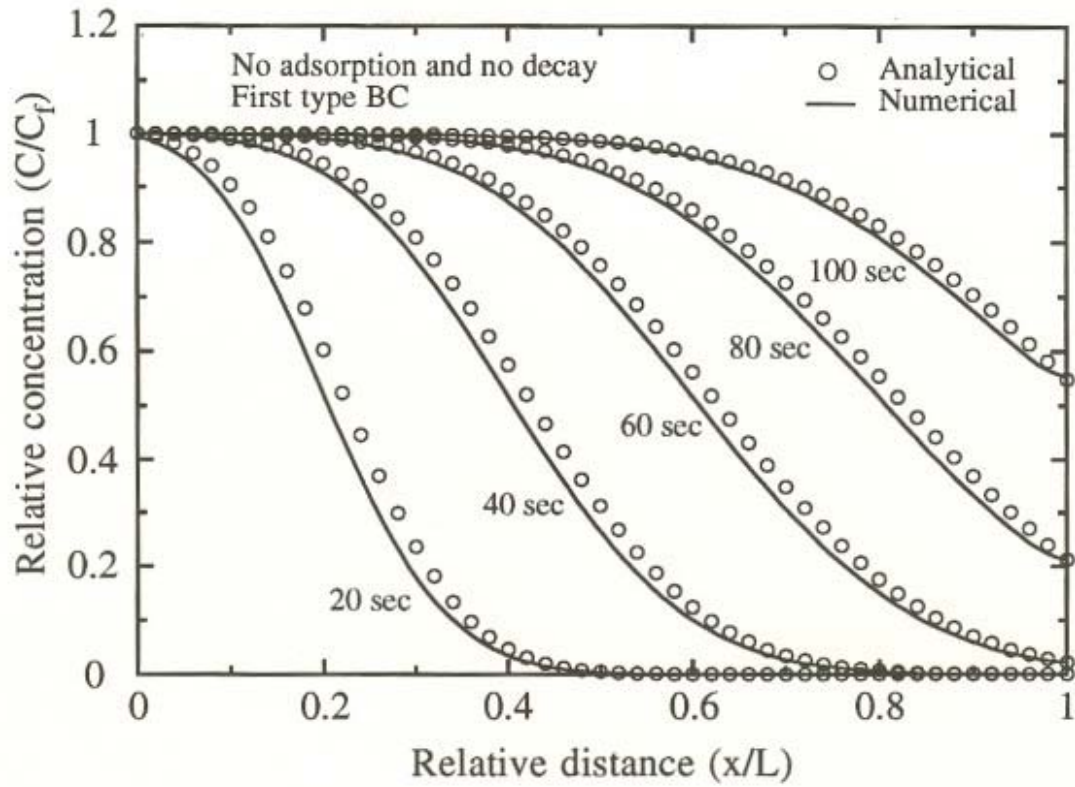


Figure 6.6b Comparison of numerical and analytical solutions for one-dimension solute transport ($D_h = 0.03 \text{ cm}^2/\text{sec}$, $v = 0.1 \text{ cm/sec}$, $\Delta x = 0.2 \text{ cm}$, $\Delta t = 2 \text{ sec}$, $C_f = 1 \text{ mg/L}$, $C_0 = 0 \text{ mg/L}$, and $L = 10 \text{ cm}$ in all cases): (a) analytical solution for infinite column (equation 6.50) and numerical solution for a third type of BC, (b) semi-finite column with first type of BC (equation 6.51), and (c) semi-finite column with third type of BC (equation 6.52).

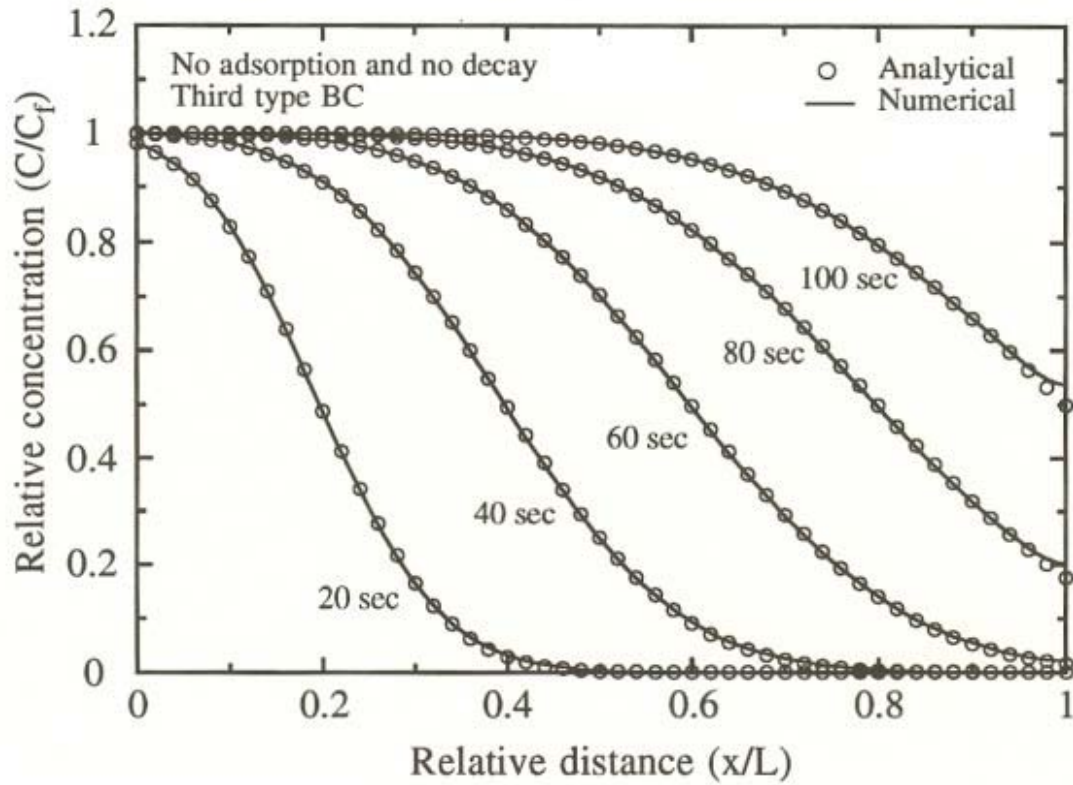


Figure 6.6c Comparison of numerical and analytical solutions for one-dimension solute transport ($D_h = 0.03 \text{ cm}^2/\text{sec}$, $v = 0.1 \text{ cm/sec}$, $\Delta x = 0.2 \text{ cm}$, $\Delta t = 2 \text{ sec}$, $C_f = 1 \text{ mg/L}$, $C_o = 0 \text{ mg/L}$, and $L = 10 \text{ cm}$ in all cases): (a) analytical solution for infinite column (equation 6.50) and numerical solution for a third type of BC, (b) semi-finite column with first type of BC (equation 6.51), and (c) semi-finite column with third type of BC (equation 6.52).

Figures 6.6a, 6.6b, and 6.6c show the comparisons of numerical solution with exact analytical solution, equations 6.50, 6.51, and 6.52, respectively. The numerical solution with first type of boundary condition shows a slight deviation with respect to the exact solution (Figure 6.6b). However, with the third type of boundary condition in the numerical model, a perfect match to the exact solution is shown in Figures 6.6a and 6.6c.

For the contaminant transport coupled with adsorption, the time, t , in the equations 6.50-6.52 is replaced to t^* , and $t^*=t/R_d$, where R_d is the adsorption retardation factor. For the case of linear adsorption isotherm, R_d can be formulated as $R_d = 1 + \rho_s K/\phi$ (equation 6.20). The verification of transport including adsorption is not made, because the similar result as shown in Figure 6.6 is expected.

It is concluded that the numerical solution generated from this program is correct and can be applied to further practices.

6.5.2 Stability of the Numerical Solution

The stability of the finite difference method used in the numerical model can be checked by Peclet number Pe and Courant number Cr :

$$Pe = \frac{v \cdot \Delta x}{D_h} \quad (6.53)$$

$$Cr = \frac{v \cdot \Delta t}{\Delta x} \quad (6.54)$$

Srinivasan and Mercer (1987) suggested $Pe < 2$ and $Cr < 1$ as a guidance for the stability criterion. If the values of Pe and/or Cr exceed these criteria, this program will prompt for the selection of an adjustment of input parameters, Δx and Δt , or skip the advice. Figure 6.7 presents the model results at various Pe and Cr values. The fluctuations in the output represent the instability of the numerical solution. It is seen in Figure 6.7 that increasing the values of Pe and Cr resulted in decreasing the stability of the output. With the values of Pe and Cr recommended by Srinivasan and Mercer (1987), the output becomes stable (no fluctuations).

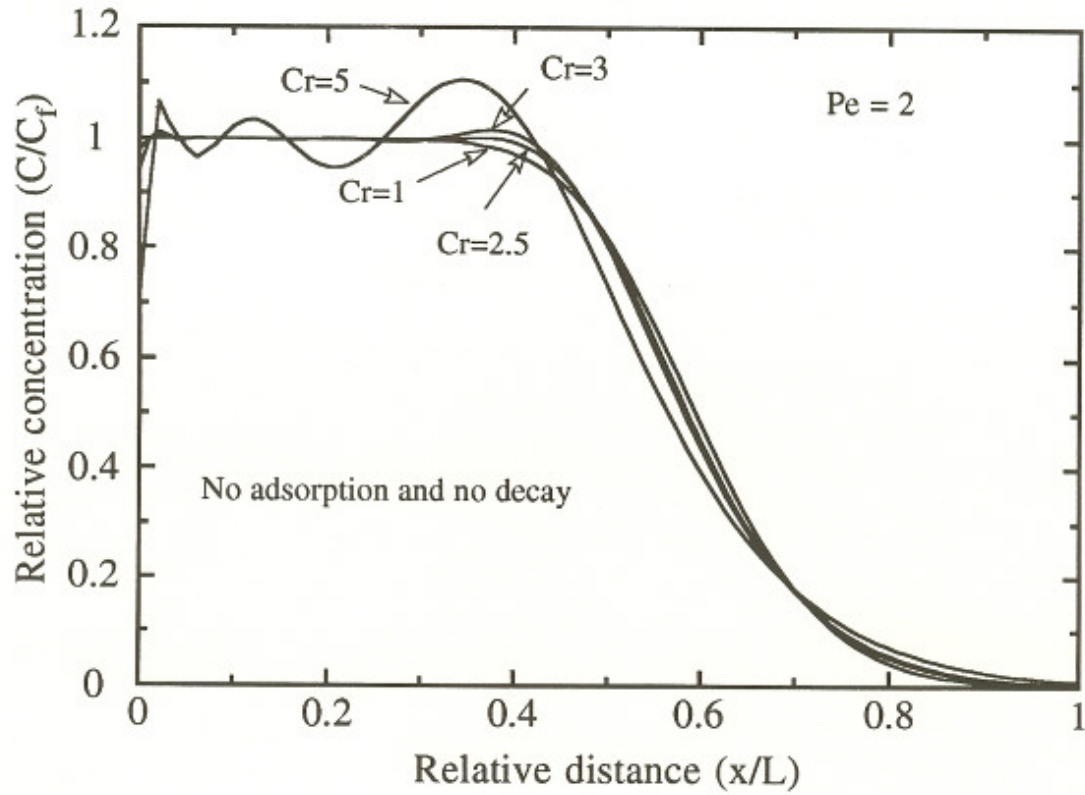


Figure 6.7 Effect of Courant number, Cr , on the stability of numerical model (the third type BC, $\Delta t = 2$ sec, 5 sec, 6 sec, and 10 sec for the calculated value of $Cr = 1$, 2.5, 3, and 5, respectively. $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $t = 60$ sec, $C_f = 1$ mg/L, $C_0 = 0$ mg/L, and $L = 10$ cm in all cases).

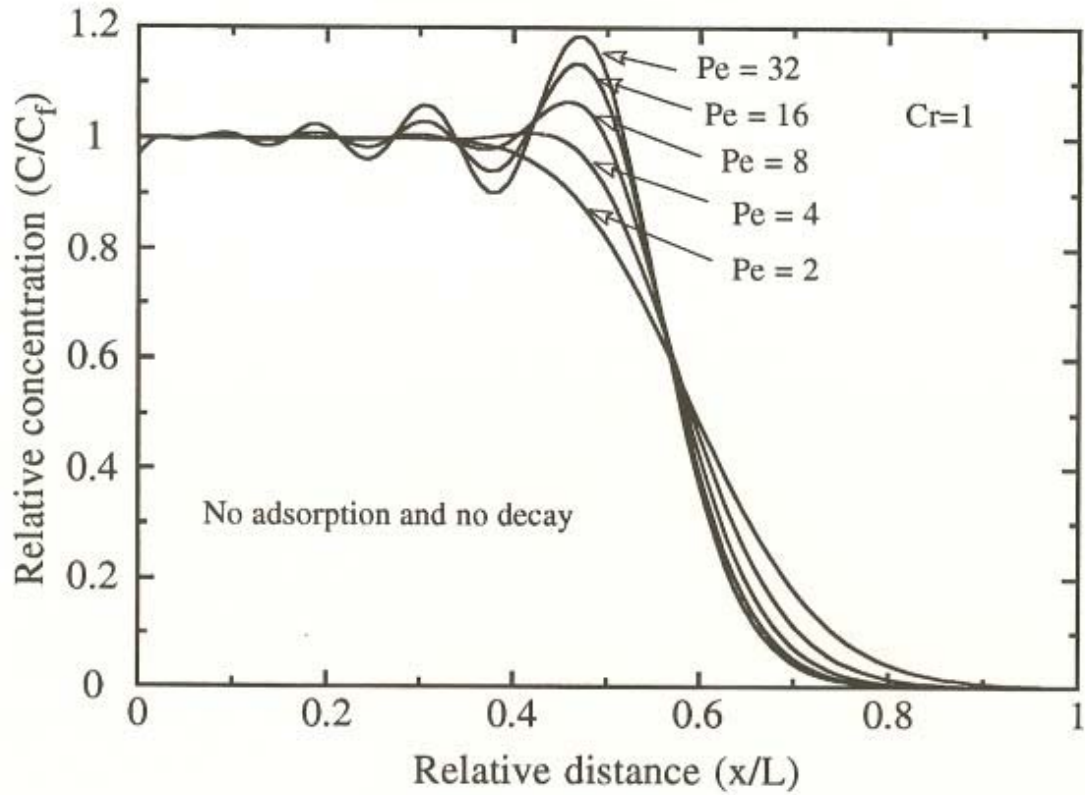


Figure 6.8 Effect of Peclet number, Pe , on the stability of numerical model (the third type BC, $D_h = 0.02 \text{ cm}^2/\text{sec}$, $0.01 \text{ cm}^2/\text{sec}$, $0.005 \text{ cm}^2/\text{sec}$, $0.0025 \text{ cm}^2/\text{sec}$, and $0.00125 \text{ cm}^2/\text{sec}$ for the calculated value of $Pe = 2, 4, 8, 16$, and 32 , respectively. $v = 0.2 \text{ cm/sec}$, $\Delta x = 0.2 \text{ cm}$, $\Delta t = 1 \text{ sec}$, $t = 60 \text{ sec}$, $C_f = 1 \text{ mg/L}$, $C_o = 0 \text{ mg/L}$, and $L = 10 \text{ cm}$ in all cases).

6.5.3 Parametric Study of the Numerical Model

In this section, the comparison of first type BC and second type of BC, the effect of various velocities and, the effect of various hydrodynamic dispersion coefficients used in the model simulation are presented. Then the effect of different transport conditions (i.e., no adsorption and no decay, adsorption with no decay, decay with no adsorption, adsorption and decay) on the concentration distribution will be followed.

6.5.3.1 Effect of Boundary Conditions, Pore Velocities, and Dispersion Coefficients

The comparison of first type and third type of BC is shown in Figure 6.9. At a fixed time for the numerical model with first type of BC, the rate of concentration transport is slightly faster than that of third type of BC. For the first type of BC, since the influent concentration just above and below the top surface of the porous media is assumed to be homogeneous, the solute transport is expected to travel faster than the third type of BC which assumes the influent concentration is governed by the continuity of the flux. Since the verification test has shown that the use of third type of BC in the numerical model exhibited an overlap to the analytical solution (section 6.3.3), therefore the third type of BC is used for the application of model simulation.

Pore velocity also plays an important role on affecting the solute transport through porous media. With the assumption of no adsorption and no decay, i.e., dispersion only, the effect of various velocities on the solute transport is shown in Figure 8.10. The greater the pore velocity applied, the faster the substance traveled.

Hydrodynamic dispersion coefficient is another factor affecting the transport process. The influence of dispersion coefficient on the concentration distribution is demonstrated in Figure 6.11. The concentration distribution tends to be dispersed by increasing the value of dispersion coefficient. It is noted that at relative concentration, $C/C_f = 0.5$, the concentration distribution is not changed by the dispersion coefficient.

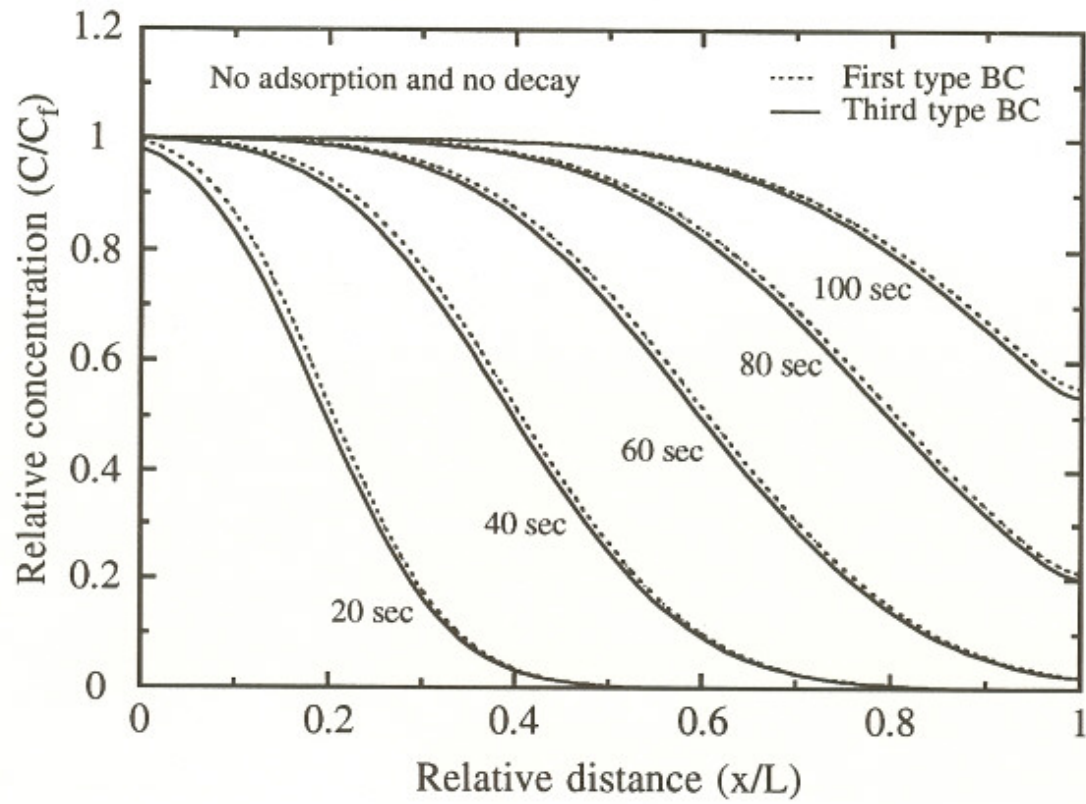


Figure 6.9 Comparison of the first type and the third type of boundary conditions applied in the numerical model ($v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $C_f = 1$ mg/L, $C_a = 0$ mg/L, and $L = 10$ cm in all cases).

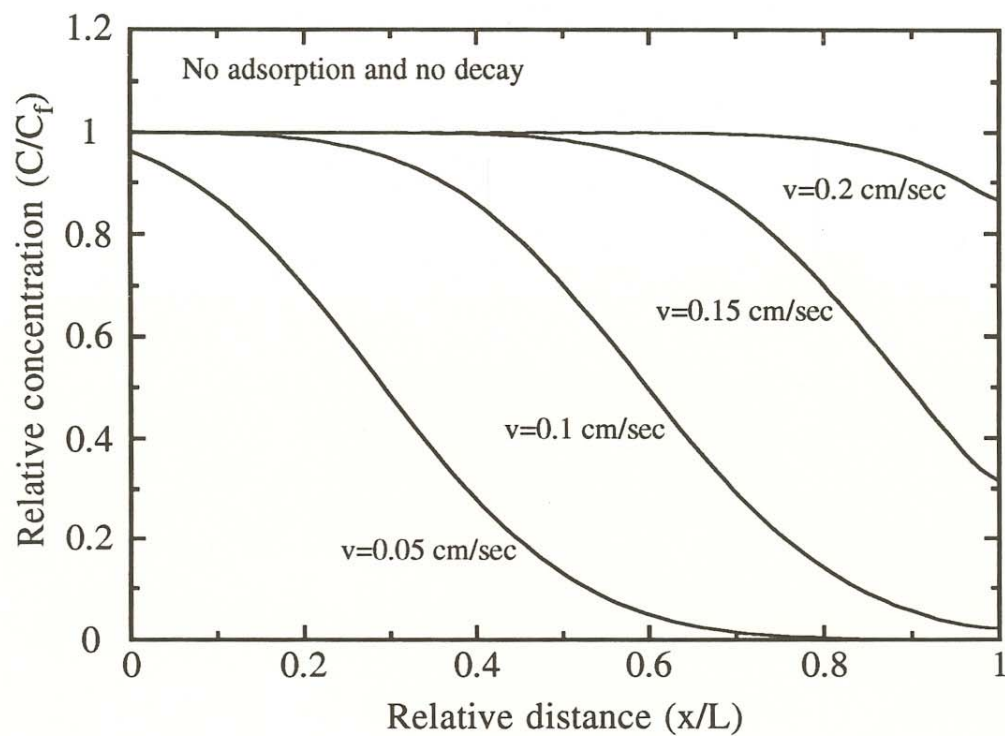


Figure 6.10 Effect of various pore velocities on the solute transport process (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $C_f = 1$ mg/L, $C_0 = 0$ mg/L, $t = 60$ sec, and $L = 10$ cm in all cases).

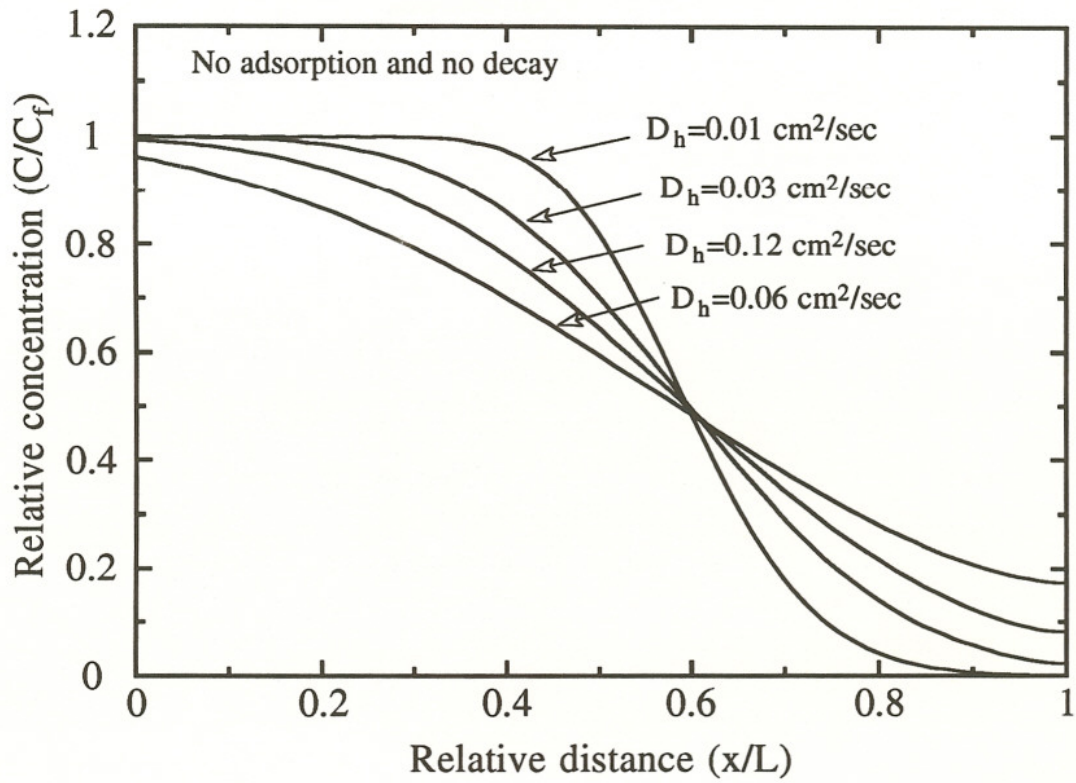


Figure 6.11 Effect of various hydrodynamic dispersion coefficients on the solute transport process (the third type BC, $v = 0.1 \text{ cm/sec}$, $\Delta x = 0.2 \text{ cm}$, $\Delta t = 2 \text{ sec}$, $C_f = 1 \text{ mg/L}$, $C_0 = 0 \text{ mg/L}$, $t = 60 \text{ sec}$, and $L = 10 \text{ cm}$ in all cases).

6.5.3.2 Adsorption with No Decay

Figures 6.12-6.14 show different adsorption isotherms applied in the model simulation for contaminant transport coupled with adsorption reaction. Retardation factor, R_d , is used for the case of linear adsorption for comparing the effect of adsorption with that of the concentration distributions. The adsorption reaction plays a significant role in the solute transport (Figure 6.12). The transport of reactive substance was retarded by increasing the coefficient of retardation, R_d , (or increasing the linear adsorption constant, K_d). In the case of Freundlich and Langmuir isotherms, since the retardation factor depends on the solute concentration, it will not be used to represent the strength of the adsorption reaction. Details of the Freundlich and Langmuir isotherms are described in section 6.3.2.1. In the model results with Freundlich adsorption isotherm, with influent concentration of 0.5 mg/L and the fixed adsorption constant, K_f , of 0.2, the transport process is retarded by decreasing the n value. For the case of Langmuir adsorption isotherm applied in the model simulation, with the influent concentration of 0.5 mg/L and adsorption constant, K_m , of 0.2 L/Kg, increasing the maximum adsorption capacity of Q_m resulted in increasing the retardation effect during the transport process.

6.5.3.3 Decay with No Adsorption

Although the decay term commonly represents radioactive decay, it also can represent biodegradation or the chemical reaction within the solute phase, i.e., redox reaction. In most soil-water and groundwater systems, chemical reaction occurring within solution phase, e.g., redox, can arise by releasing reductive and/or oxidative substances from the dissolution of minerals or soil surfaces. The change of solute

concentration due to chemical reaction within the solution phase becomes important during the transport of chemical reactive substances.

Figure 6.15 shows the case of solute transport with a decay rate constant of $k = 0.005$ 1/sec or a half-life of 138.6 seconds. It appears that the concentration distribution is affected by the decay factor comparing with dispersion only. Figure 8.16 demonstrates the effect of different decay rate constants (0.005 1/sec to 0.03 1/sec) at 60 seconds. The shape of the concentration distribution is flattened by increasing the rate constant.

6.5.3.4 Adsorption and Decay

Figure 6.17 illustrates the influence of adsorption and decay reactions incorporated into the transport process. With a linear adsorption constant of $K_L = 0.4$ L/Kg and decay rate constant $k = 0.01$ 1/sec used in the model simulation, the concentration distribution is greatly affected by these two reactions.

6.5.3.5 Breakthrough Curve

This program can transform the output data to the breakthrough data. Figure 6.18 demonstrates the breakthrough for a nonreactive substrate transport. The breakthrough of a column with shorter length occurs earlier than that of the longer one. Comparisons of the different cases of solute transport coupled with dispersion only, adsorption with no decay, decay with no adsorption, and with both adsorption and decay are presented in Figure 6.19. It is visualized that breakthrough in the case

of dispersion only occurs earlier than in any other cases. With adsorption in the transport process, the breakthrough is retarded. Thus, with adsorption reaction during the solute transport process, it requires a longer time to reach breakthrough than the one without adsorption reaction. For the decay case, the breakthrough concentration (C/C_0) decreases from 1 to 0.6 compared with the case without decay. For a reactive substance transport in the porous media coupled with both adsorption and decay reactions, the breakthrough concentration decreases by the decay factor and retarded by the adsorption reaction.

6.5.3.6 Leaching

This is the case when influent concentration (C_f) is less than initial concentration (C_0). The leaching of a nonreactive or reactive substance from the porous media during the transport process can be simulated by this program. Comparisons of the cases of transport with dispersion only, adsorption with no decay, decay with no adsorption, and with both adsorption and decay are demonstrated in Figures 6.20 and 6.21.

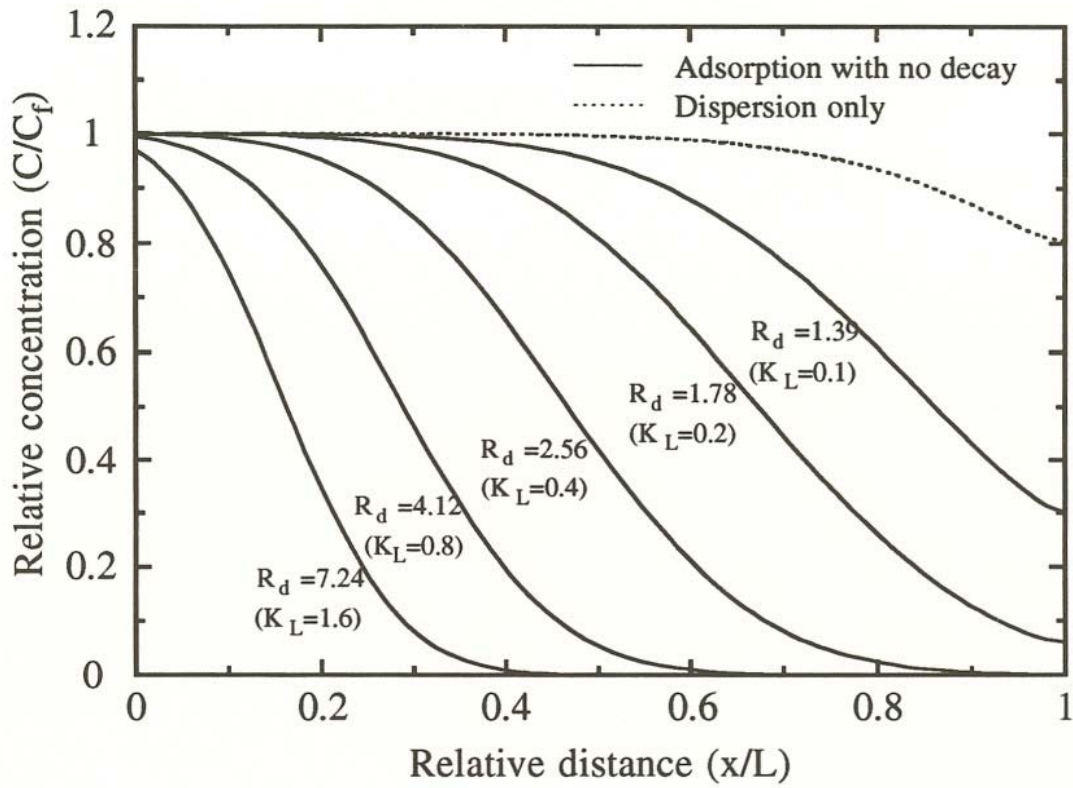


Figure 6.12 Transport with linear adsorption isotherm. The effect of adsorption constant, K_L , on the solute transport process (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 0.5$ mg/L, $C_0 = 0$ mg/L, $t = 120$ sec. and $L = 10$ cm in all cases).

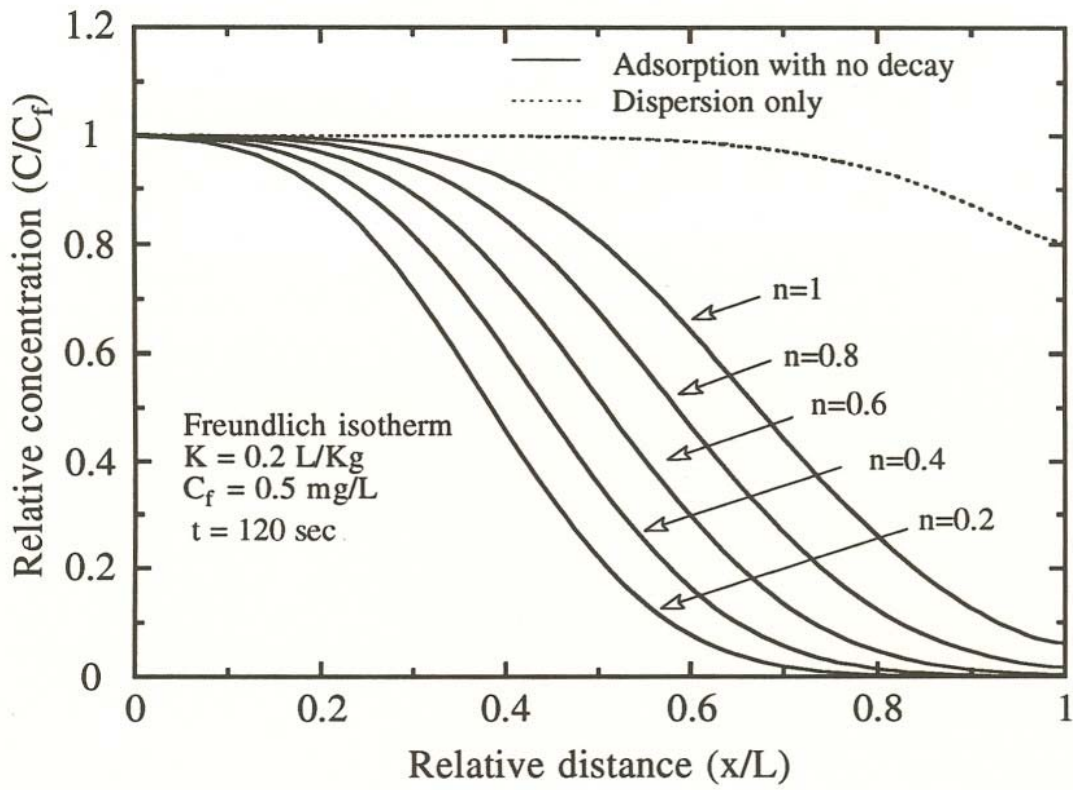


Figure 6.13 Transport with Freundlich adsorption isotherm. The effect of adsorption exponent constant, n , on the solute transport process (the third type BC, $v = 0.1 \text{ cm/sec}$, $\Delta x = 0.2 \text{ cm}$, $\Delta t = 2 \text{ sec}$, $\rho_s = 2.6 \text{ g/cm}^3$, $\phi = 0.4$, $C_f = 0.5 \text{ mg/L}$, $C_0 = 0 \text{ mg/L}$, and $L = 10 \text{ cm}$ in all cases).

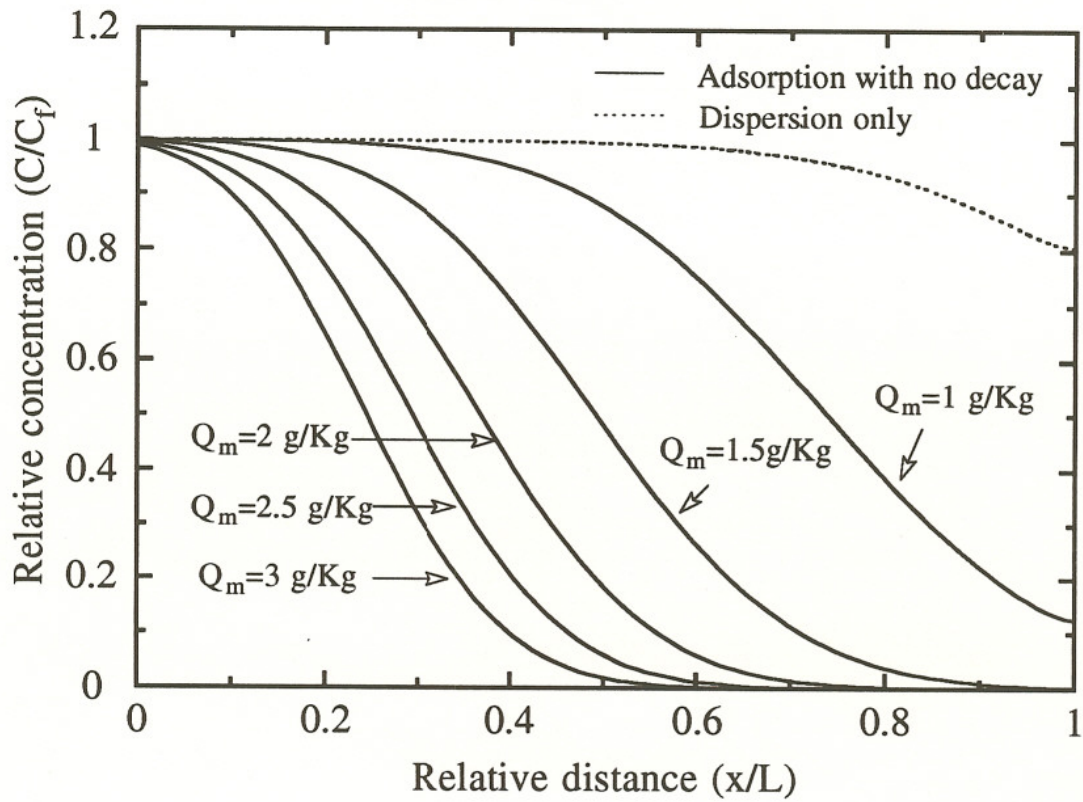


Figure 6.14 Transport with Langmuir adsorption isotherm with the third type BC. The effect of different maximum adsorption densities, Q_m , on the solute transport process ($v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 0.5$ mg/L, $C_o = 0$ mg/L, $K_m = 0.2$ L/Kg, $t = 120$ sec, and $L = 10$ cm in all cases).

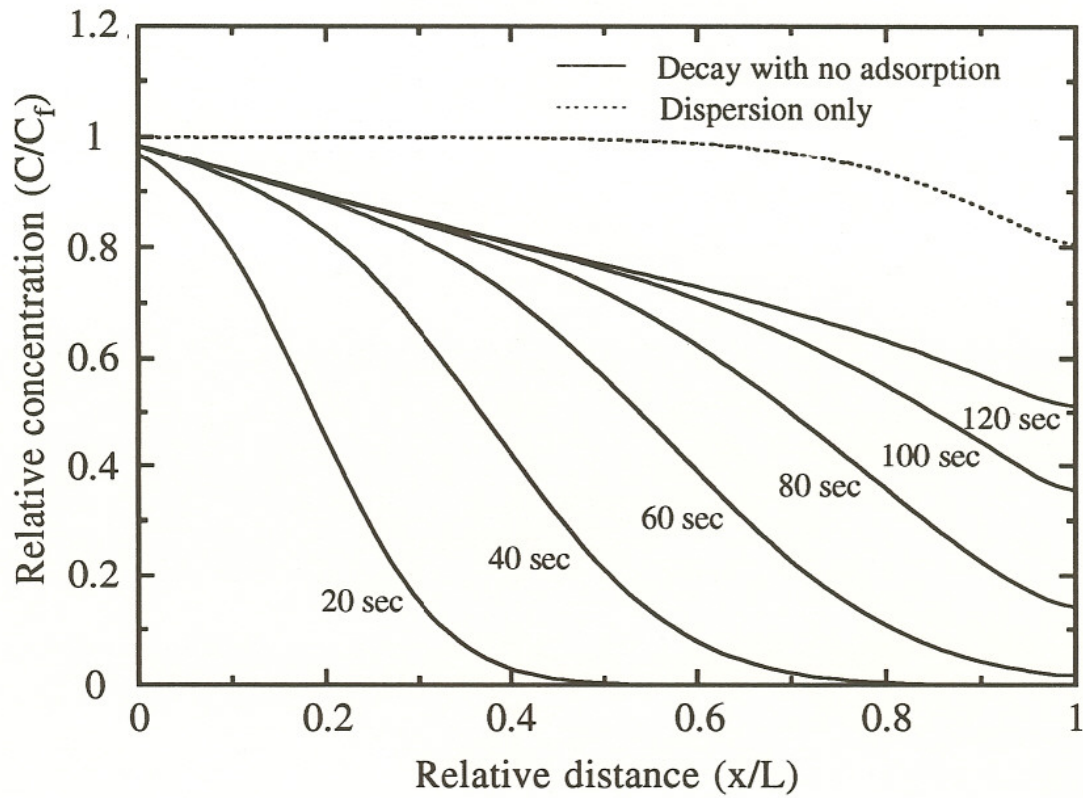


Figure 6.15 Transport with decay and the third type BC at different time scales ($v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 1$ mg/L, $C_o = 0$ mg/L, decay rate constant = 0.005 1/sec, and $L = 10$ cm in all cases).

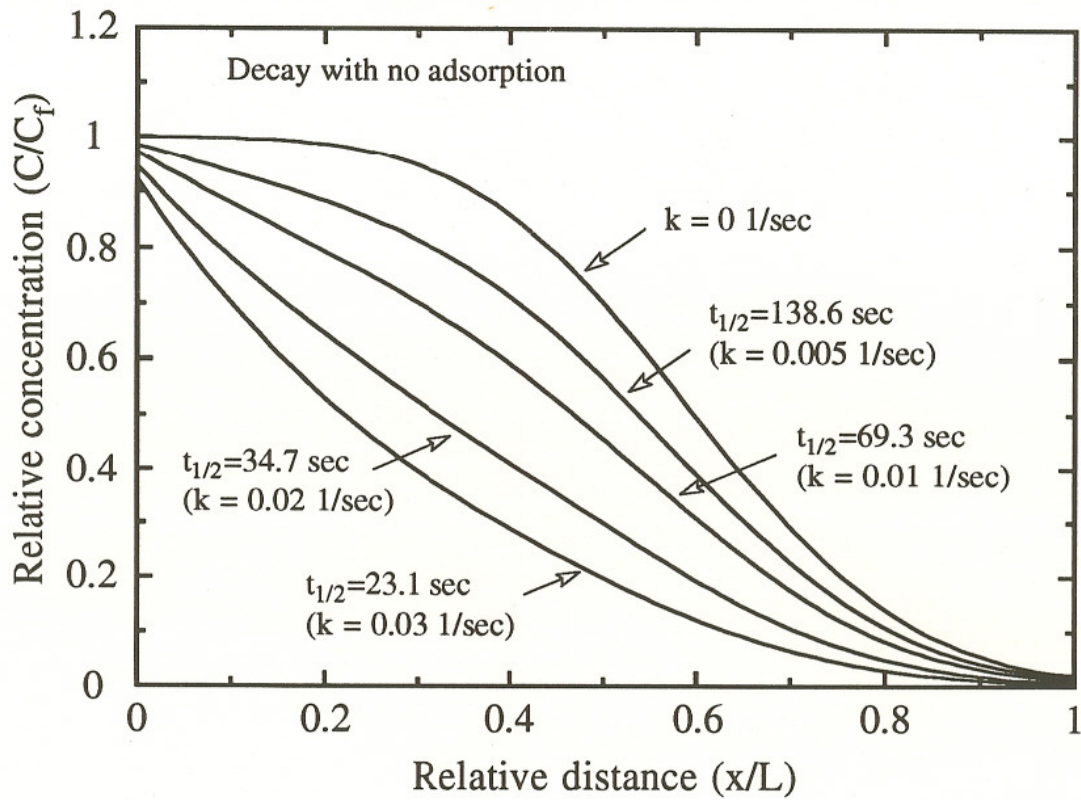


Figure 6.16 Transport with decay at different decay constants (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 1$ mg/L, $C_o = 0$ mg/L, $t = 60$ sec, and $L = 10$ cm in all cases).

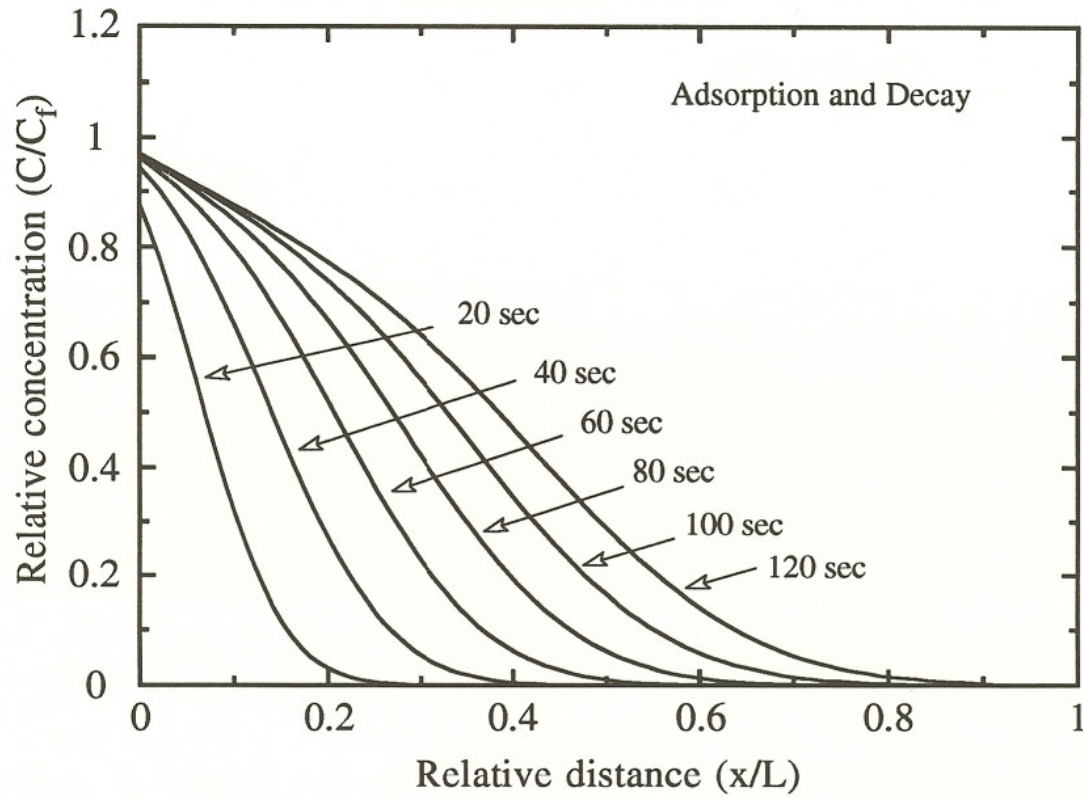


Figure 6.17 Transport with adsorption and decay at different time scales (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 1$ mg/L, $C_0 = 0$ mg/L, linear adsorption constant = 0.4 L/Kg, decay rate constant = 0.4 1/sec. and $L = 10$ cm in all cases).

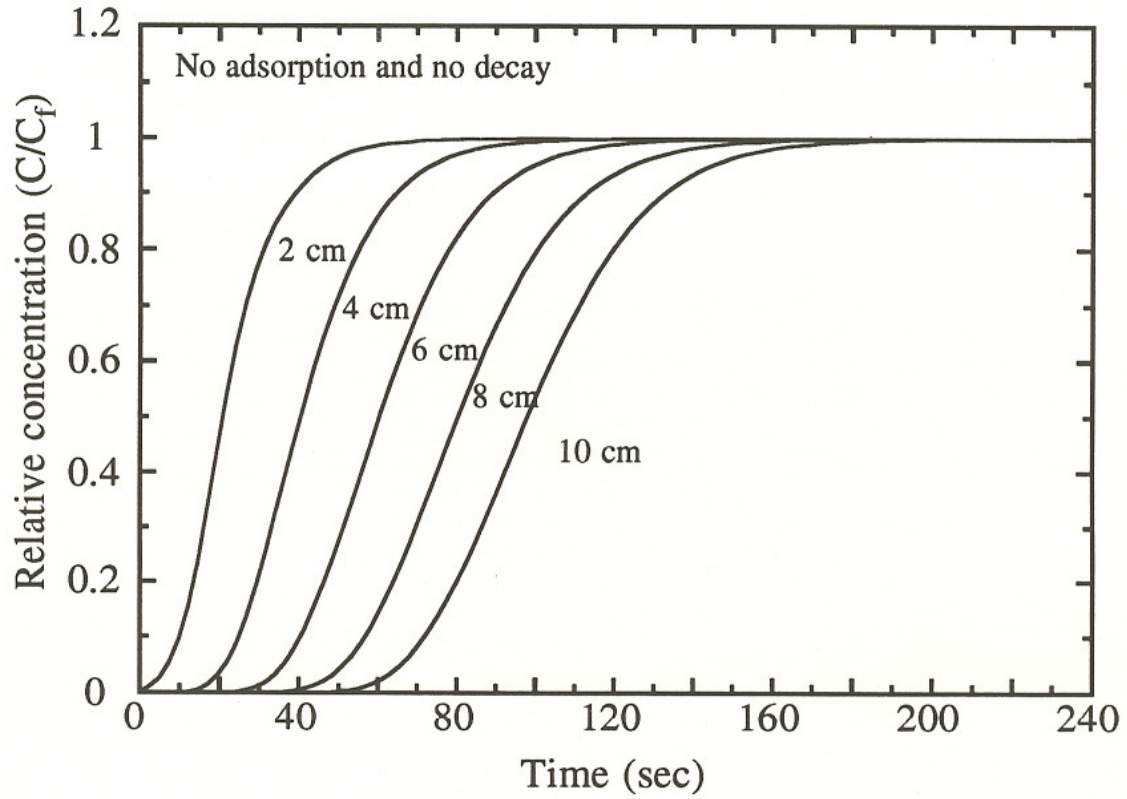


Figure 6.18 Breakthrough for solute transport with no adsorption and no decay at different length scales (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 1$ mg/L, $C_0 = 0$ mg/L, and $t = 240$ sec in all cases).

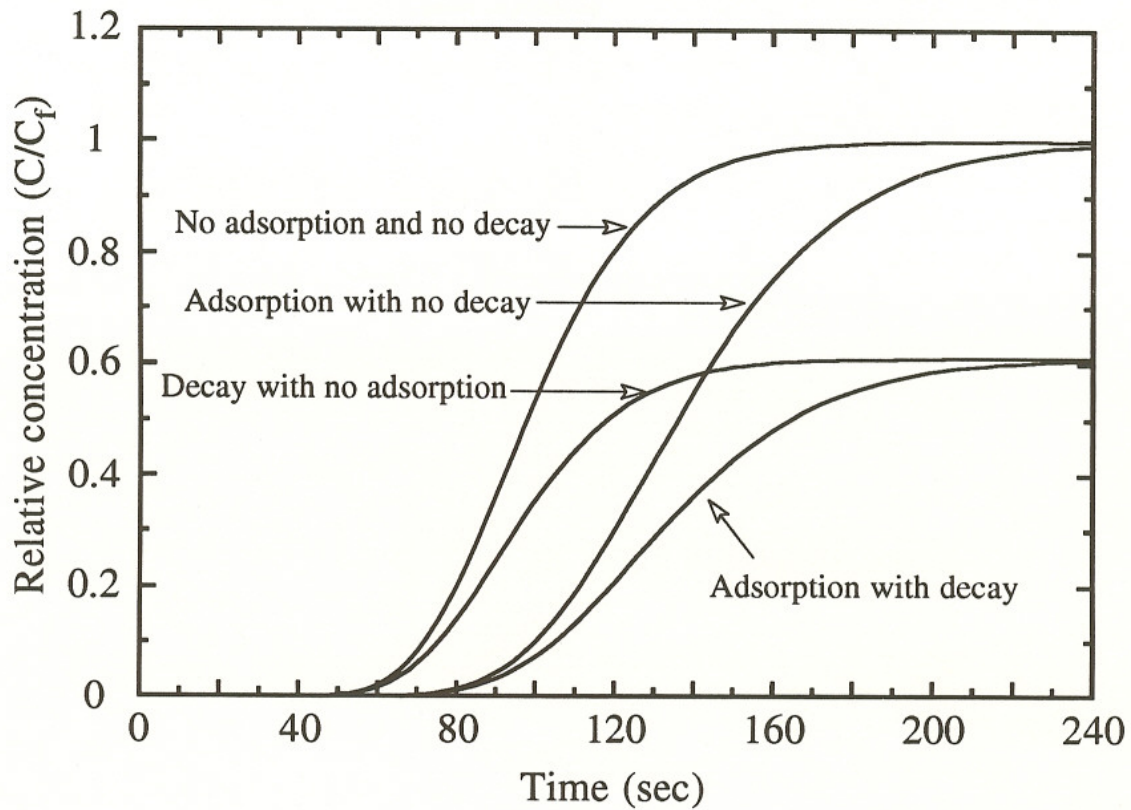


Figure 6.19 Comparison of breakthrough for solute transport with reaction (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 1$ mg/L, $C_0 = 0$ mg/L, linear adsorption constant = 0.1 L/Kg, decay rate constant = 0.001/sec, $t = 240$ sec, and $L = 10$ cm in all cases).

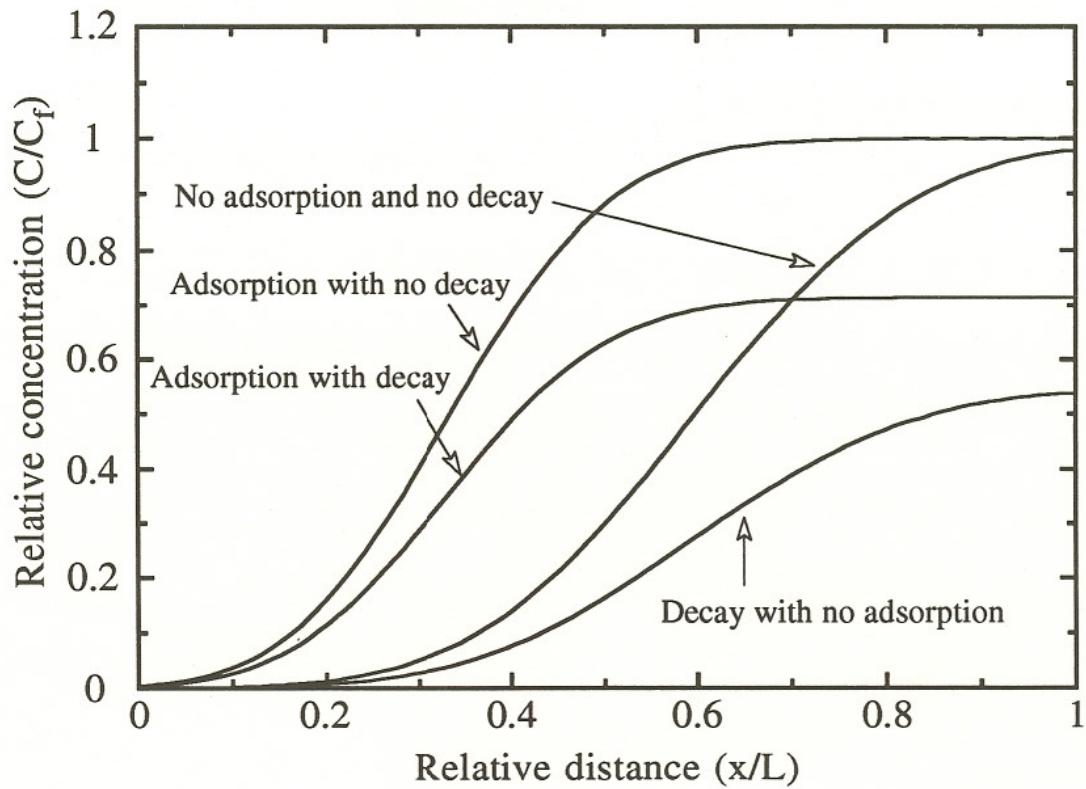


Figure 6.20 Comparison of transport with reaction (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 0$ mg/L, $C_0 = 1$ mg/L, linear adsorption constant = 0.2 L/Kg, decay rate constant = 0.01 1/sec, $t = 60$ sec, and $L = 10$ cm in all cases).

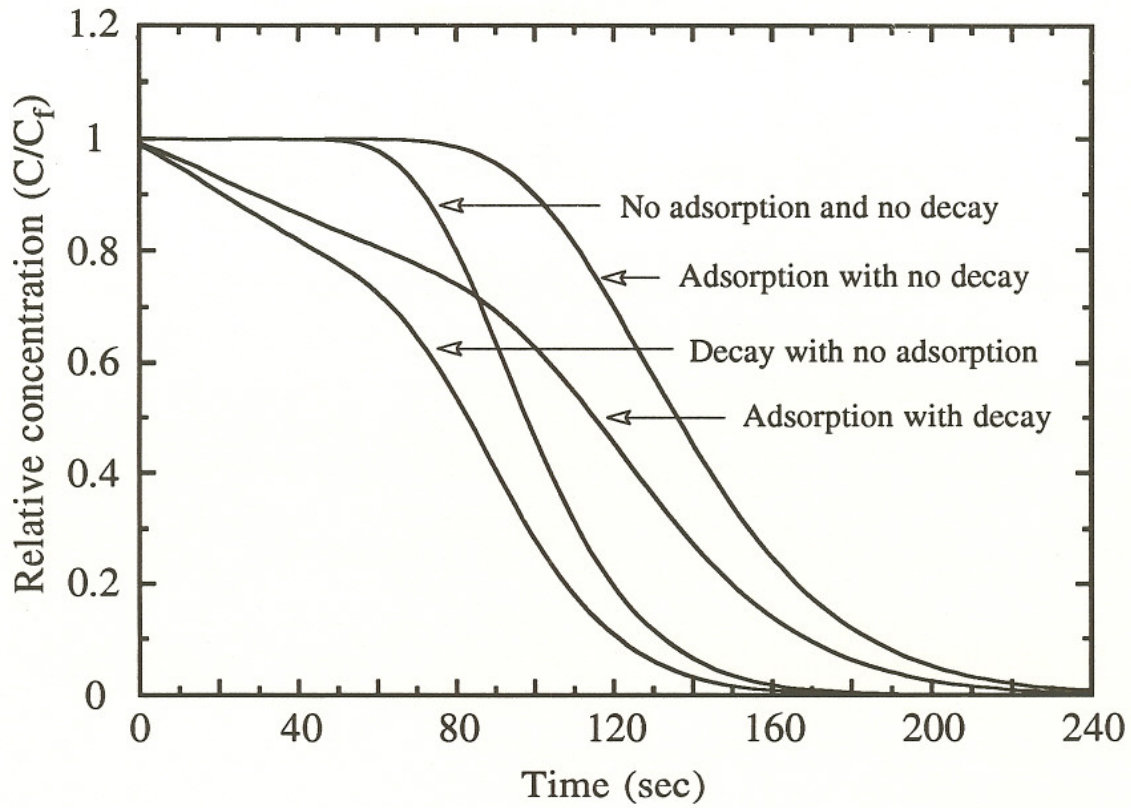


Figure 6.21 Comparison of breakthrough for solute transport with reaction (the third type BC, $v = 0.1$ cm/sec, $\Delta x = 0.2$ cm, $\Delta t = 2$ sec, $\rho_s = 2.6$ g/cm³, $\phi = 0.4$, $C_f = 1$ mg/L, $C_0 = 1$ mg/L, linear adsorption constant = 0.1 L/Kg, decay rate constant = 0.001/sec, $t = 240$ sec, and $L = 10$ cm sec in all cases).

6.6 Modeling Chromium Leaching From Chromium Contaminated Soil Derived from Chromite Ore Processing Residue

6.6.1 Experimental

After air drying, the Cr-soil sample was ground with a ball mill, and sieved to less than 1 mm in diameter. This sieved sample was then used in column experiments. ASTM standard sieve analysis was applied to determine the average particle size of this sieved sample. An average particle size of 250 μm was estimated at d_{60} as given. Simulated rainwater was used as the leaching solution. Preparation of simulated rainwater was described earlier in section 4.2.2. The Cr-Soil leaching experiments were performed with a acrylic column (1.9 cm-ID x 2.5 cm-OD), with a constant hydraulic head of 25 cm and a free board of 4 cm (Figure 6.21a). A layer of acid/base resistant polyester cloth (ASTM #400, 38 μm) from Gilson Co., Worthington, Ohio, and 2 layers of plastic crossing stitch (ASTM #40, 425 μm) was placed on the bottom of column. Simulated rainwater (pHs 2.5, 3.3, 4.3, 5.5, and 8.6) containing in 10-L buckets flowed into a series of acrylic columns. Each column contained 30 g of Cr-Soil sample. The Cr-soil sample was saturated with simulated rainwater for one day before starting the experiments. The influent flow rate was controlled with a fine adjustment clamp. Air and nitrogen gas were bubbled through the influent solution. Temperatures were controlled by a water circulation bath. The initial pH values of the leaching solution were adjusted as necessary with strong acid (1 N HNO_3) or strong base (1 N NaOH). To study the effect of temperature on Cr-Soil leaching, four different temperatures (3 $^{\circ}\text{C}$, 8 $^{\circ}\text{C}$, 23 $^{\circ}\text{C}$, and 38 $^{\circ}\text{C}$) were selected while keeping an initial rainwater pH 4.3. The experimental set-up of column leaching is given in Figure 6.21b. All the columns were wrapped by aluminum foil to minimize any

biological or photo-induced chemical reactions. For a designated time period, the effluent solution was collected and the effluent pH was recorded. The concentration of Cr(III), Cr(VI), Fe(II), Fe(III), Ca(II), Mn(II), and TOC in the effluent were determined.

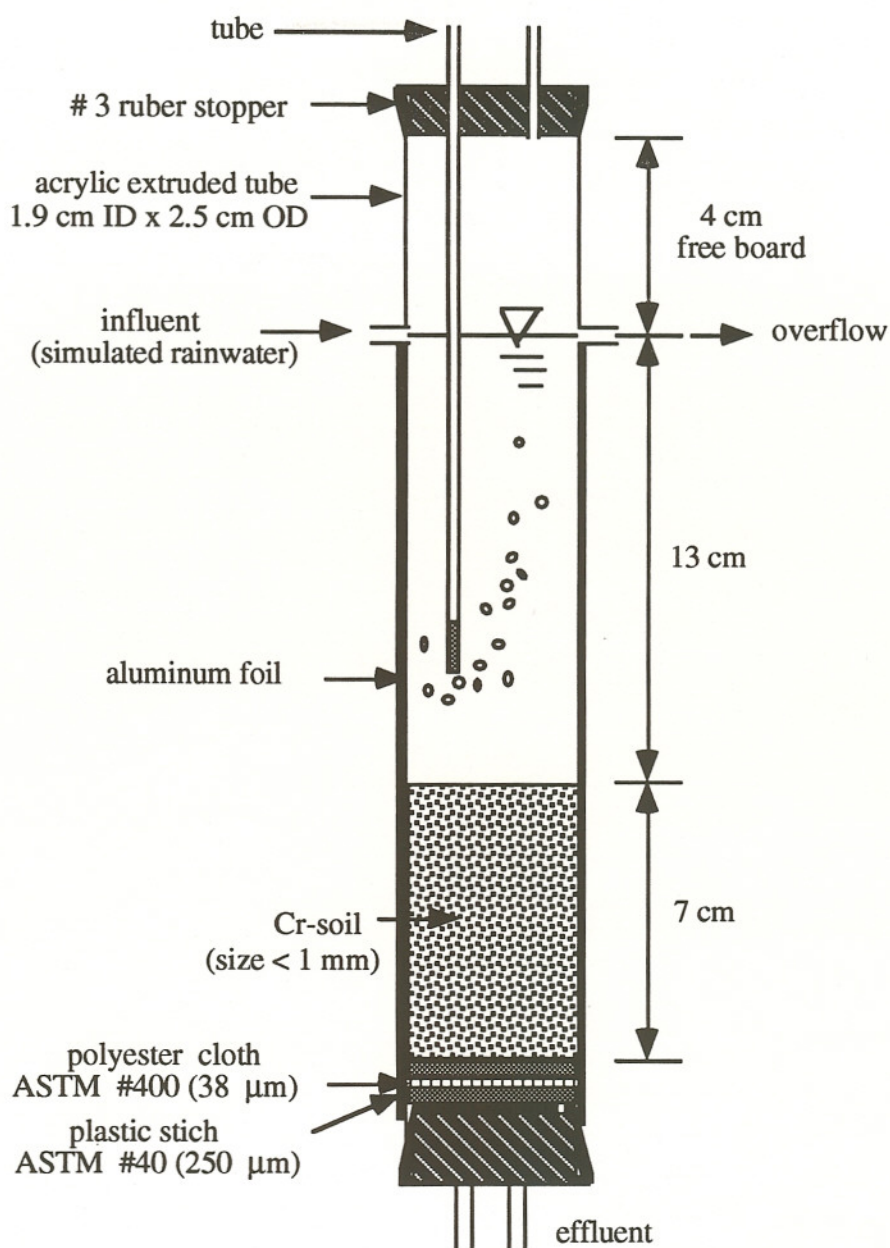


Figure 6.21a Schematic diagram of apparatus (in detail) used in the column leaching experiments.

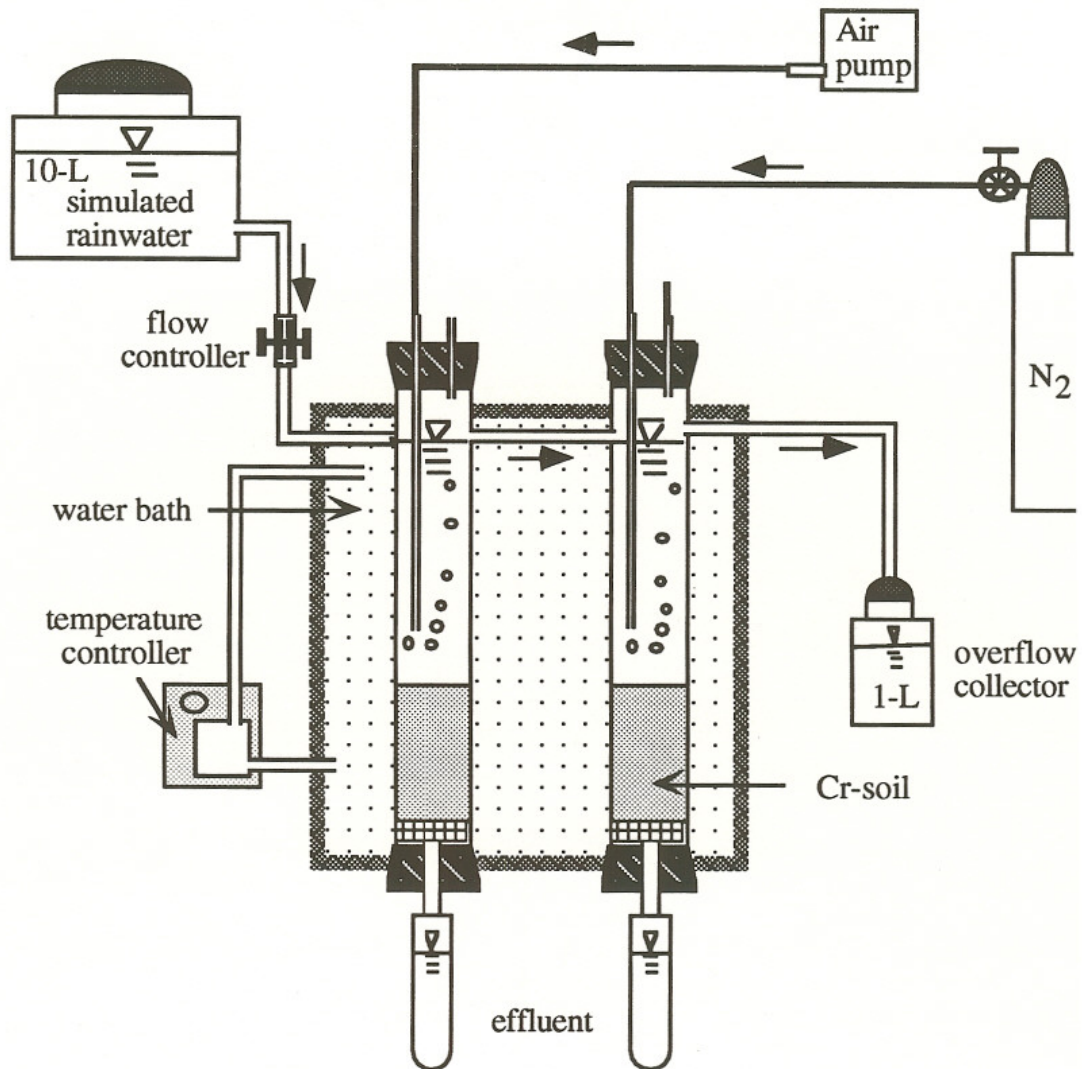


Figure 6.21b Experimental set-up for the column leaching experiments.

6.6.2 Column Leaching Experimental Results

Figures 6.22-6.29 show the results of column Cr-soil leaching experiments. Effluent pH versus cumulative flow are shown in Figures 6.22 and 6.23 for different influent pHs and temperatures, respectively. The effluent pH initially increased rapidly from any of the influent values 2.8, 3.3, 4.3, 6.0, and 8.0 to 8.3 ± 0.3 either air or N_2 atmosphere. The effluent pH is close to the Cr-soil pH of 8.5 (chapter 3) in the first 500 mL (or about 5 days) leachate collected. As the leachate reaches to about 4000 mL, the pH values decrease to about 7.2 ± 0.3 . In the cases of acidic influent pH of 2.8, 3.3, and 4.3, the effluent pH did not reach the inflow pH even after 51 days leaching, when the experiments were stopped. The acidic inflow was apparently buffered by the Cr-soil. Figure 6.23 also demonstrated that the effluent pH was not significantly affected by temperature or air/ N_2 atmosphere.

Results of column experiments on Cr-soil leaching show a significant amount of Cr(VI), Ca, and TOC in the effluent; however, Cr(III), Fe(III), Fe(II), and Mn were not detected in the leachate. Concentrations of Ca leached greatly decreased from about 25 mg/l to 10 mg/l in the first 5 days leaching period. It then remained relatively constant at a concentration of about 5 mg/l and a linear relationship between the mass of Ca leached ($\sum C_i V_i$), and cumulative flow ($\sum V_i$) was observed (Figures 6.24 and 6.25). The mass of Ca leached depends on the temperature. The higher the temperature, the greater amount of Ca leached (Figure 6.25). There is almost no difference in the amount of Ca leached under air or N_2 atmosphere, indicating that Ca leaching is unaffected by oxygen levels. When an acidic influent solution was introduced into the Cr-soil column, the mass of Ca leached increased drastically (Figure 6.24). Based on the results shown in Figures 6.22-6.25, it is concluded that

the mass of Ca leached is governed by the dissolution of a Ca-mineral. In chapter 4 it was shown that the dominant Ca-mineral is calcite based on the XRD analysis.

The amount of TOC leached decreases from about 70 mg/l to about 25 mg/l in the first 500 mL leaching solution collected. It then remained relatively constant at a concentration of about 22 mg/l. A similar leaching pattern was observed for both air or N₂ atmosphere (Figure 6.26). A linear relationship between the total mass of TOC leached ($\sum C_i V_i$), and cumulative flow ($\sum V_i$) is shown in Figures 6.26 and 6.27 for experimental conditions at different influent pHs and various temperatures, respectively. The results show that TOC leaching is not dependent on the inflow pH and temperatures. The mass of TOC leached is not affected by the air or N₂ atmosphere. The leaching pattern for TOC was the same as for calcium. Increasing the flow results in an increased the mass of TOC leached, indicating that the mass of TOC leached is governed by a dissolution process.

It is interesting to note that during the first day period, the leachates were light yellow and contained Cr(VI) concentrations as high as 70 mg/l. More than 60 mg/l of Cr(VI) was detected at the beginning in most of the cases; it then greatly decreased to less than 5 mg/l at the fifth day leaching. Less than 0.5 mg/l of Cr(VI) was observed in about 1500 mL of leachate collected. When the effluent solution contained less than 0.05 mg/L of Cr(VI), the experiment was stopped. Figures 6.28 and 6.29 show the total mass of Cr(VI) collected in the effluent as a function of cumulative flow. The total mass Cr(VI) leached ($\sum C_i V_i$) under different inflow solution pHs and different temperatures is listed in Table 6.1. Increasing temperature results in increasing the mass of Cr(VI) leached. The mass of Cr(VI) leaching increases with inflow pH, indicating that adsorption and desorption reactions are active during the leaching

process. For the leaching conditions of influent pH 4.3, air atmosphere, and 23 °C, the total mass of Cr(VI) leached is about 0.235 mg/g which has the same magnitude observed in the 24-hour batch equilibrium experiments (chapter 4) under similar conditions. Thus, the 24-hour batch equilibrium experiment can be used to determine the total mass Cr(VI) leached from Cr-soil. The total mass of Cr(VI) leached accounted for about 1% of the total Cr (25 mg/g) in the Cr-soil sample. From the results of XRD study (Figure 3.2), the Cr form in the Cr-soil is predominantly chromite ore which is known to be acid resistant. Apparently, majority of total Cr in the COPR sample can be accounted as nonleachable Cr species which are in the trivalent state. Based on the batch and column leaching studies, chromium leaches rapidly during column studies suggests that Cr(VI) would be rapidly washed away from a waste site. The fact that we are still seeing it after 50 years leads one suspect that there is continuous slow oxidation onsite of trivalent chromium, and that the environments are at a steady-state between chromium oxidation and chromium leaching via rainfall. Redox reactions of chromium in Cr-soil need to extensively investigate.

The leaching pattern is not varied by changing conditions under air or N₂ atmosphere. There are no significant differences for the mass of Cr(VI) leached between conditions under air or N₂ atmosphere. It is concluded that the mass of Cr(VI) leached from Cr-soil leaching is not affected by these conditions. However, the possibility of redox reactions occurring during the leaching process can not be ruled out. It is most likely to occur that the organic matters in the Cr-soil provide a source of electrons for the reduction of Cr(VI). As reported in chapter 3, Cr-soil consists of about 9% organic matters. An appreciate amount of TOC was also

detected in the effluent (Figures 6.26 and 6.27), suggesting that a possible reduction occurs during the leaching process. Under an anaerobic condition, it would be expected that Fe(II) would be oxidized to Fe(III) and be therefore unable to reduce Cr(VI). Consequently, less amount of Cr(VI) leached under anaerobic condition (reductive environment) than under aerobic condition (oxidative environment) during the leaching process.

The Cr(VI) leaching behavior is different from those of Ca and TOC. A linear relationship with cumulative volume was observed for the mass of Ca and TOC leached, but not for mass of Cr(VI) leached. If the leaching sources of Cr(VI) and Ca are derived from the same mineral, the leaching of these two species should exhibit a similar leaching behavior. However, no similarity between leaching of Ca and Cr was found in this study. Moreover, based on XRD analysis, chromate salts such as CaCrO_4 were not found in the Cr-soil. Obviously, the leaching of Ca and Cr are not derived from the same minerals.

Table 6.1 The mass of Cr(VI) leached, $\sum C_i V_i$, (mg/g) from Cr-soil. Data was obtained from Figures 6.28 and 6.29.

	Influent solution pH ^a					Temperature ^b			
Conditions	2.8	3.3	4.3	6.0	8.0	3 °C	8 °C	23 °C	38 °C
Air atmosphere (mg/g)	0.200	0.227	0.235	0.233	0.233	0.206	0.209	0.235	0.260
N ₂ atmosphere (mg/g)	0.209	0.230	0.234	0.236	0.244	0.205	0.212	0.234	0.260

^a50.1 days leaching period at 23 °C.

^b37.8 days leaching period at influent solution pH 4.3.

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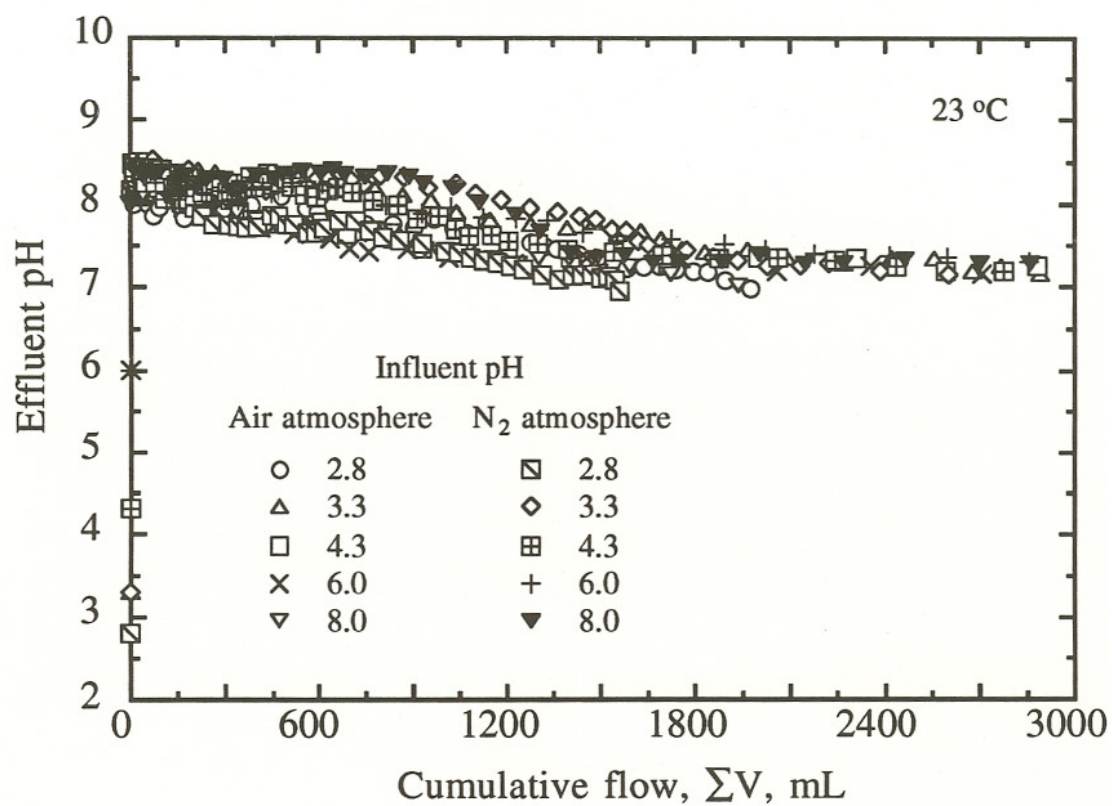


Figure 6.22 Plot of effluent pH as a function of cumulative flow at different influent pHs.

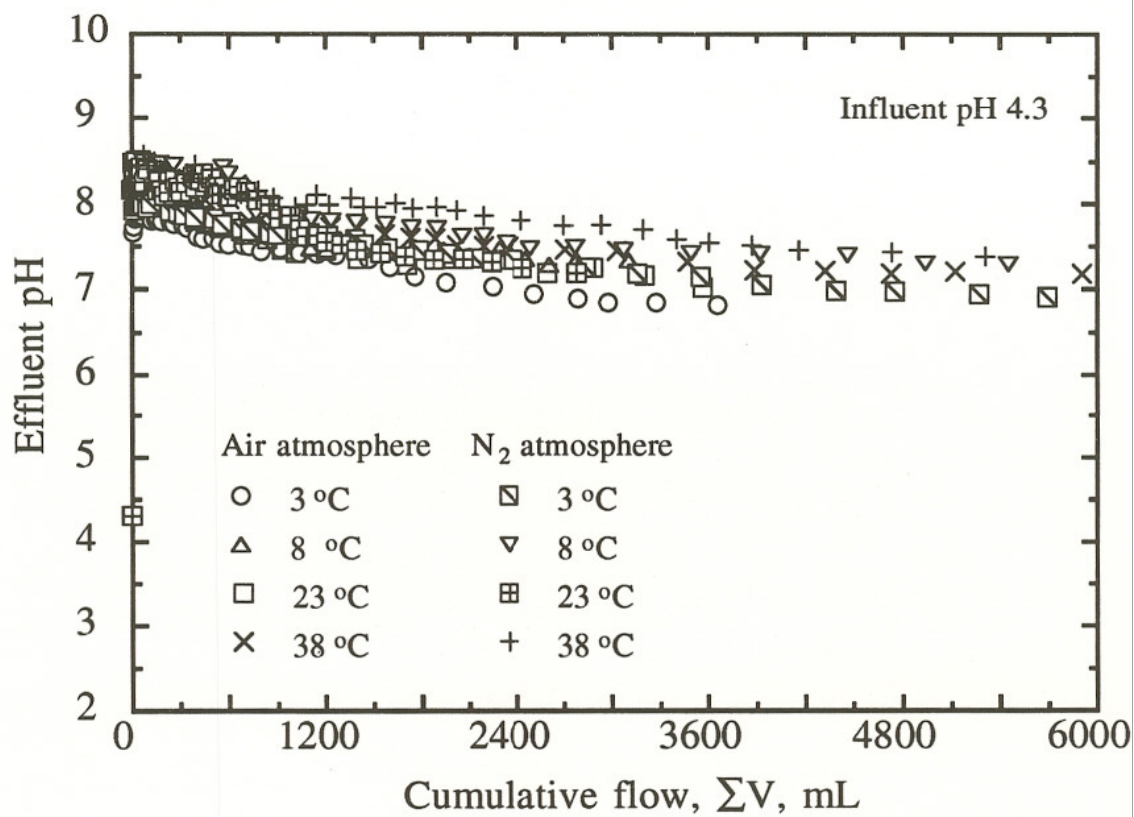


Figure 6.23 Plot of effluent pH as a function of cumulative flow at different controlling temperatures.

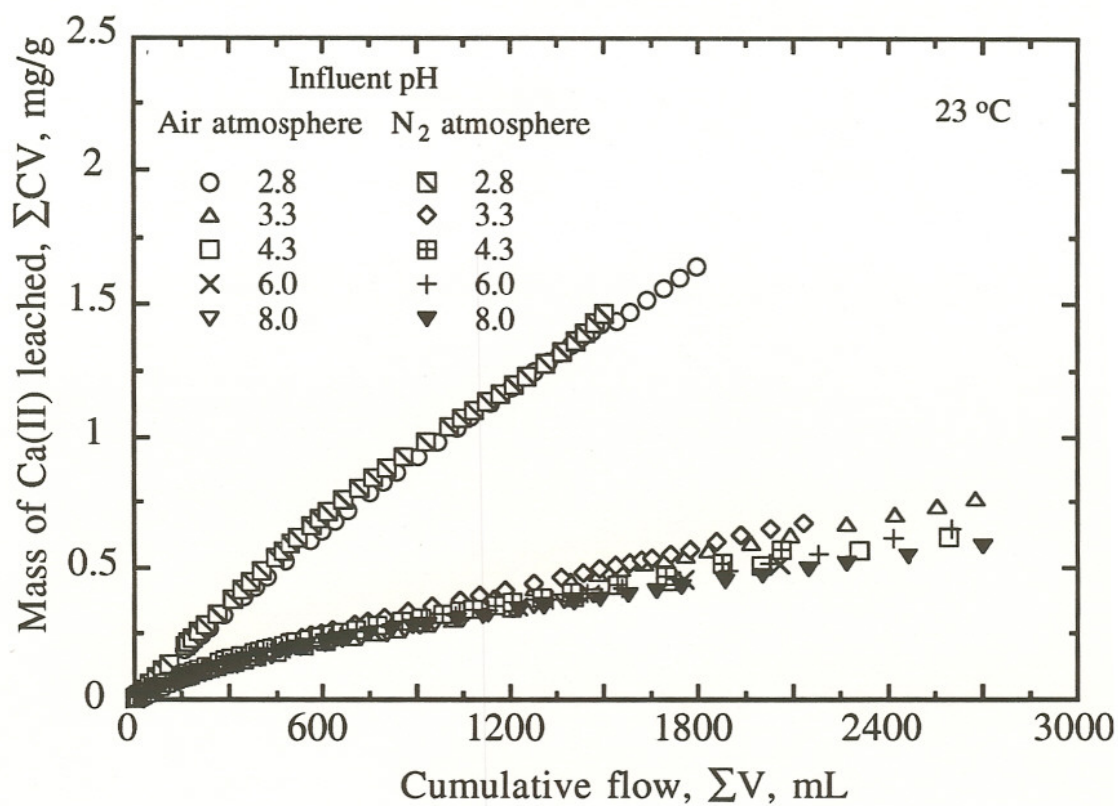


Figure 6.24 Mass of Ca leached as a function of cumulative flow at various influent pHs.

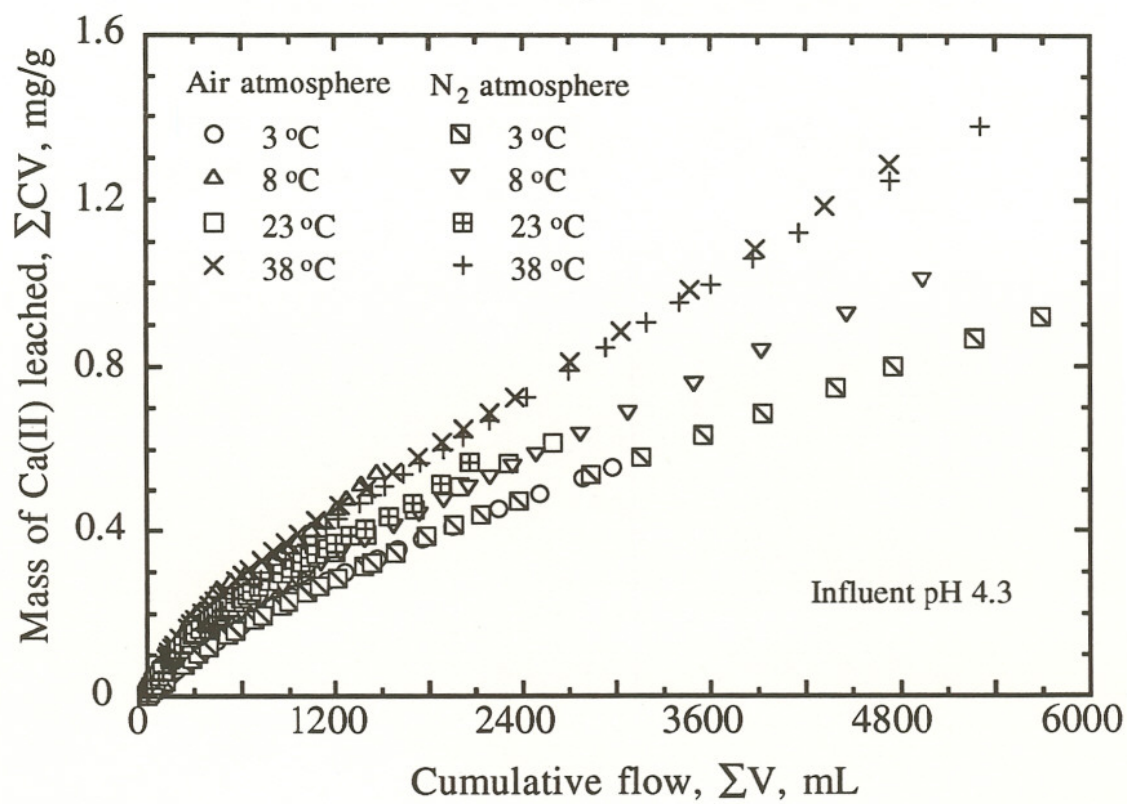


Figure 6.25 Mass of Ca leached as a function of cumulative flow at various controlling temperatures.

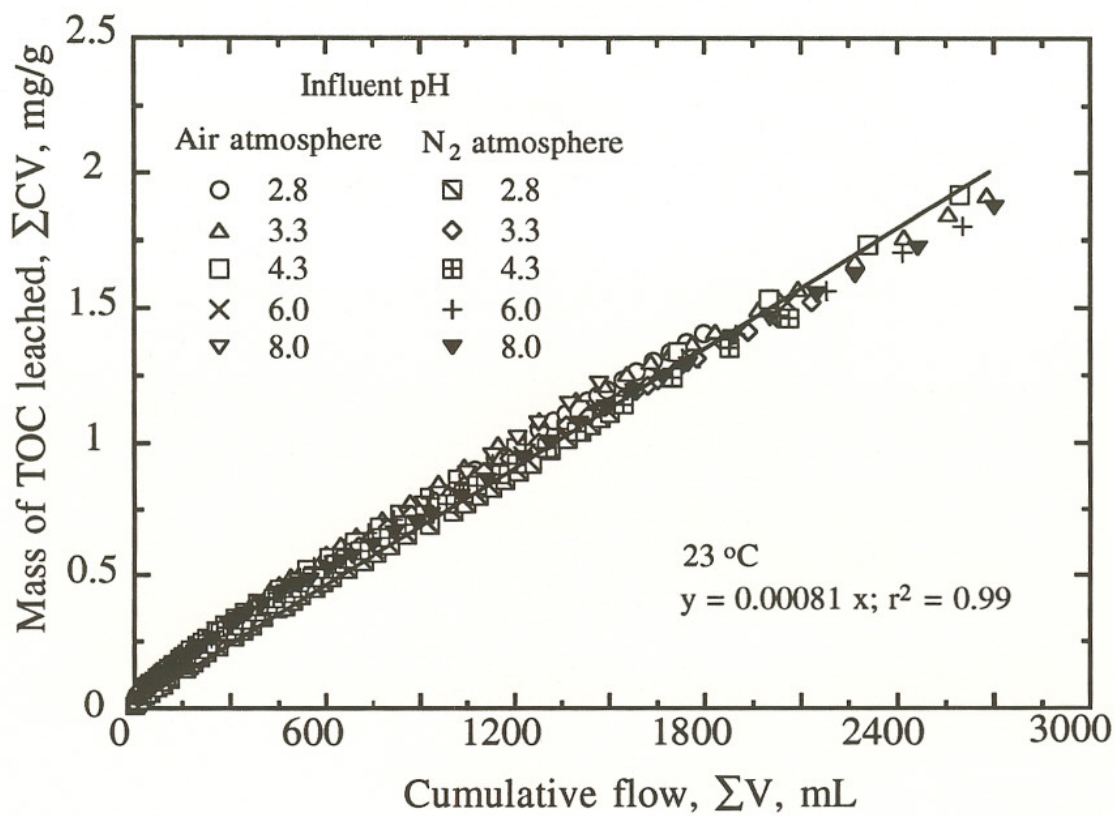


Figure 6.26 Mass of TOC leached as a function of cumulative flow at various influent pHs.

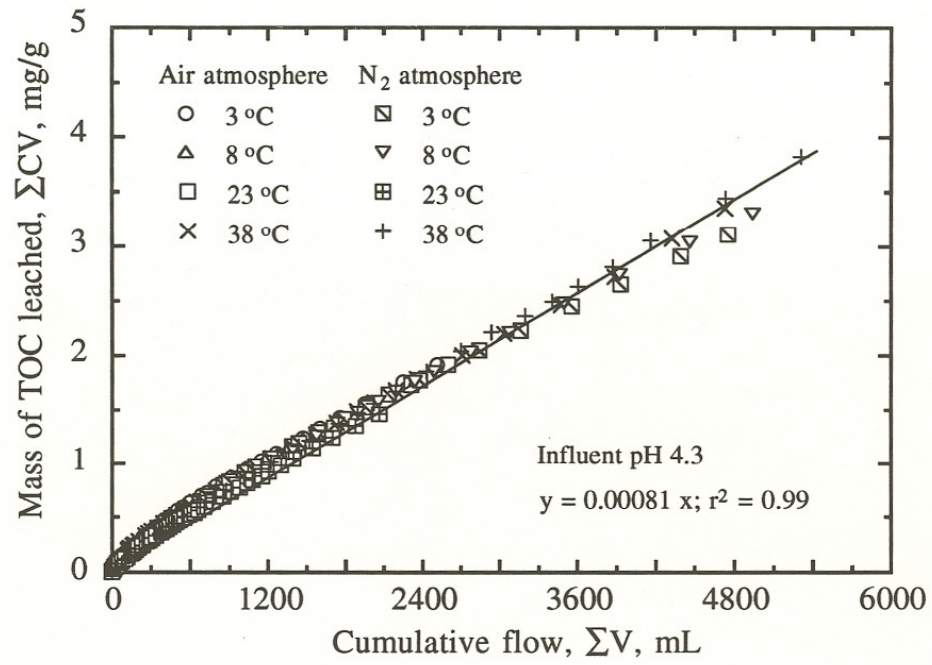


Figure 6.27 Mass of TOC leached as a function of cumulative flow at various controlling temperatures.

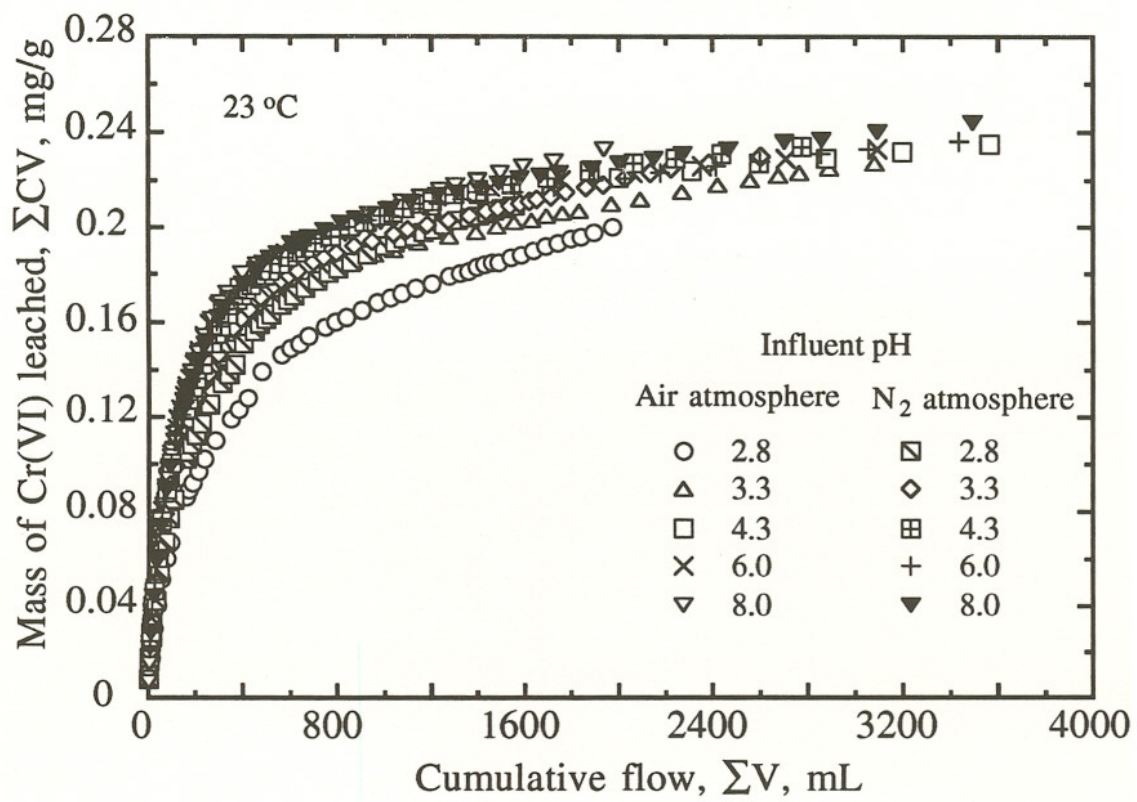


Figure 6.28 Mass of Cr(VI) leached as a function of cumulative flow at various influent pHs.

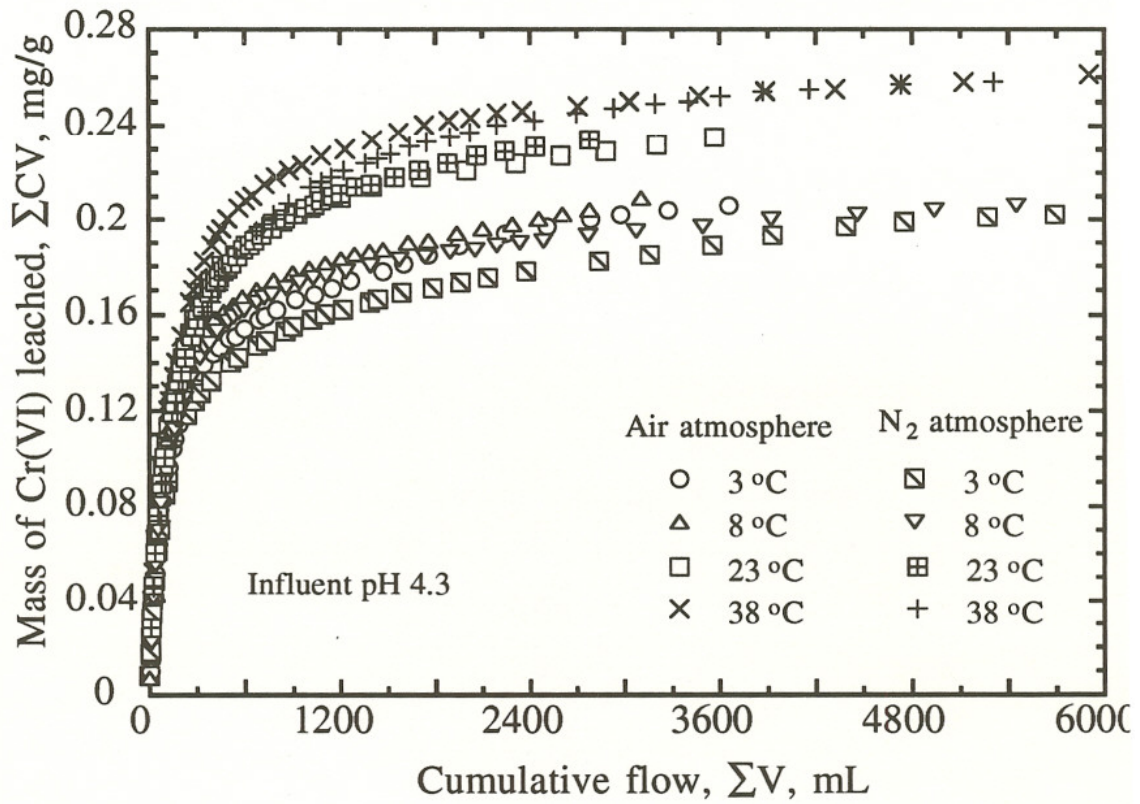


Figure 6.29 Mass of Cr(VI) leached as a function of cumulative flow at various controlling temperatures.

6.6.3 Determination of the Coefficient of Hydrodynamic Dispersion

The equation representing the transport of unreactive substances in a soil column under steady state and saturated flow is expressed as:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial X^2} - v \frac{\partial C}{\partial X} \quad (6.31)$$

For an infinite column with the input concentration, C_f , and the background concentration of the solute in the column, C_o , the solution for above governing equation is (Bear 1979):

$$\frac{C(x,t) - C_o}{C_f - C_o} = 0.5 \operatorname{erfc} \left(\frac{x - vt}{\sqrt{4D_h t}} \right) \quad (6.55)$$

For a column of length L , with $\varepsilon = C/C_o$ denoting relative concentration, and assuming $C_o = 0$, equation (6.55) becomes:

$$\varepsilon = \frac{C}{C_f} = 0.5 \operatorname{erfc} \left(\frac{L - vt}{\sqrt{4D_h t}} \right) \quad (6.56)$$

At $\varepsilon = 0.5$, the substance travels with the mean flow and the variance of the concentration distribution is proportional to the total path (L) traveled. Thus, let $t_0 = L/v$ = the break through time of $\varepsilon = 0.5$ and $t^* = t/t_0$, equation (6.56) yields:

$$\varepsilon = 0.5 \operatorname{erfc} \left[\frac{1 - t^*}{\sqrt{\frac{4D_h t^*}{Lv}}} \right] \quad (6.57)$$

It can be shown that:

$$t_{0.841}^* - t_{0.159}^* = 2\sigma = 2\sqrt{\frac{2D_h}{Lv}} \quad (6.58)$$

where σ , $t_{0.841}^*$, and $t_{0.159}^*$ are the standard deviation, t^* at $\varepsilon = 0.841$ and t^* at 0.159, respectively. Substituting equation (6.58) into equation (6.57), D_h can be determined by equation (6.59):

$$D_h = 0.125 vL (t_{0.841}^* - t_{0.159}^*)^2 \quad (6.59)$$

Experimentally, the determination of D_h was conducted by introducing a nonreactive solution of NaCl (5×10^{-2} M) into the soil column that was packed with the porous media. For a designated period, the Cl^- concentration in the effluent was measured. Cl^- concentration was determined by potentiometric method.

With a known column length and velocity, it is possible to calculate the coefficient of dynamic dispersion from the Cl^- breakthrough curve,. The experimental determination of D_h is exemplified in the Figure 6.30 for $L = 7$ cm and $v = 0.833$ cm/hr. From the Cl^- breakthrough curve shown in Figure 6.30a, a t_0 of 5 hours is obtained. By plotting t^* versus ε , values of $t_{0.841}^*$ and $t_{0.159}^*$ can be determined (Figure 6.30b). Results of the calculated D_h are summarized in Table 6.2. A linear relationship with a good correlation between D_h and v is observed (Figure 6.31). Increasing the flow velocity results in increasing the dispersion coefficient. It is assumed that the molecular diffusion can be neglected; therefore the coefficient of hydrodynamic dispersion can be formulated as:

$$D_h = \alpha_L \cdot v \quad (9.6)$$

where α_L is the longitudinal dispersivity of the isotropic porous medium (characteristic length). The dispersivity is generally related to the physical characteristics of the porous media such as tortuosity, incomplete channel connectivity, recirculation, velocity eddies, and dead end pores (Bear 1979). The dispersivity for a porous media of Cr-soil was determined to be 0.281 cm (Figure 6.31). Grove and Stollenwerk (1985) have determined the dispersivity of 0.43 cm for size fraction < 2-mm of alluvial material collected near Telluride, Colorado.

Determination of the hydrodynamic dispersion coefficient of concrete was followed the procedure describes. A value of 0.0005 m²/day was determined.

Assuming Cr⁻ does not react with Cr-soil, thus dispersion and advection are responsible for the transport process. Figure 6.32 shows the comparsion of experimental data and model simulation of Cl⁻ transport through Cr-soil. A good fit is observed which imply the model can also be served as a tool for determination of the dispersion coefficient

Table 6.2 The velocity, v , (m/day) and coefficients dispersion, D_h ($\times 10^{-4}$ m²/day) used in the column leaching study.

		Influent solution pH ^a					Temperature ^b		
Conditions	Parameter	2.8	3.3	4.3	6.0	8.0	3 °C	8 °C	38 °C
Air atmosphere	v	0.502	0.457	0.2	0.159	0.174	0.402	0.251	0.495
	D_h	13.0	10.5	8.2	5.3	5.7	10.0	6.5	12.0
N ₂ atmosphere	v	0.453	0.542	0.402	0.366	0.477	0.850	0.578	1.142
	D_h	13.0	14.8	13.6	12.4	12.1	24.0	18.0	32.5

^acontrolled at 23 °C for all pHs.

^binfluent solution pH 4.3 for all temperatures.

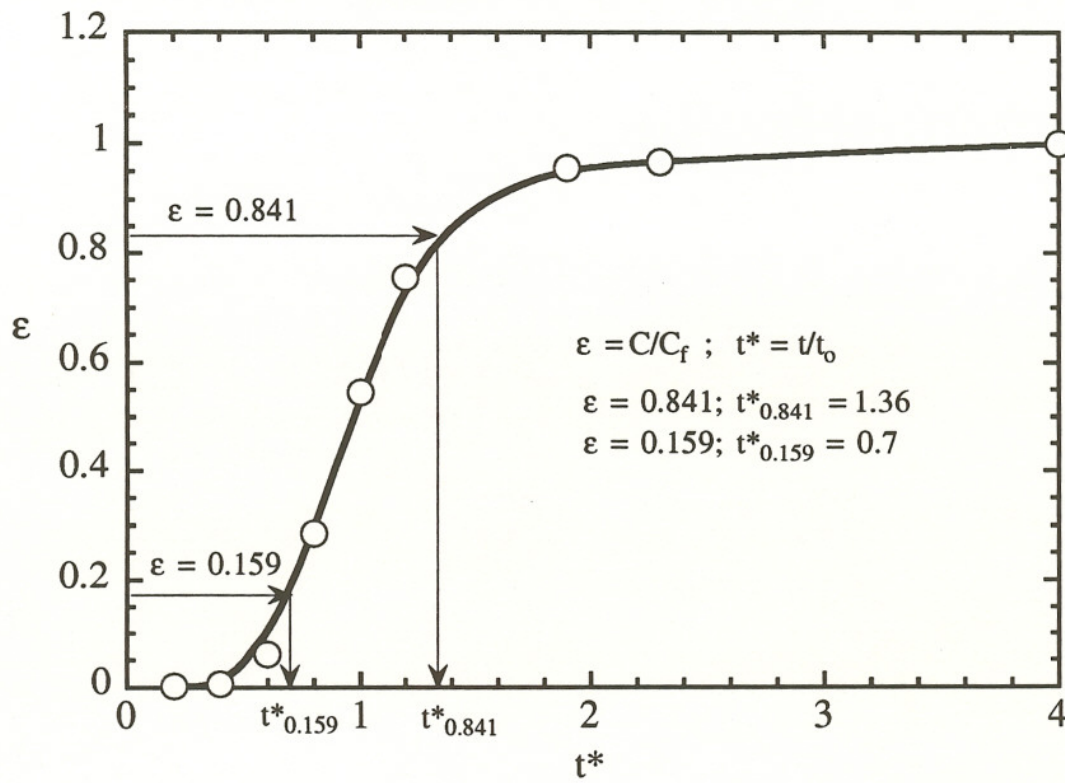


Figure 6.30 Normalized plot for computing D_h ($t_0 = C/C_f = 5$ hours, 5×10^{-2} M NaCl, 23 °C, and air atmosphere).

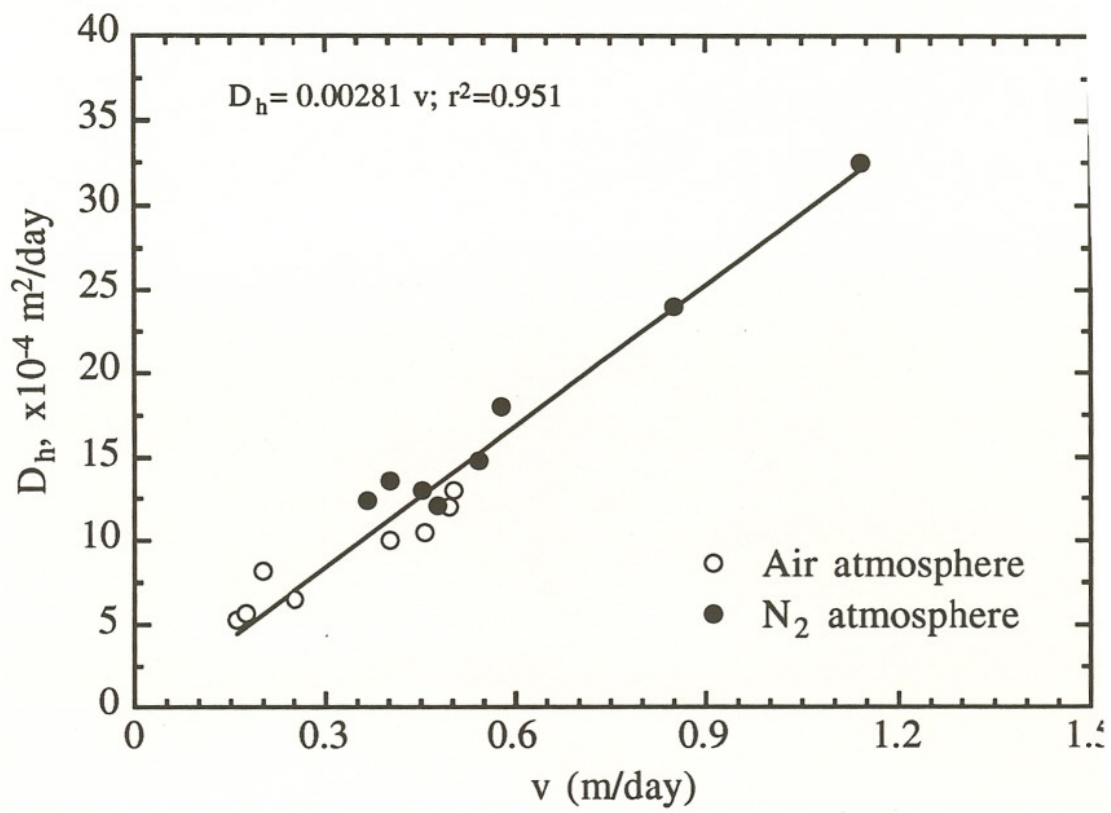


Figure 6.31 Coefficient of hydrodynamic dispersion D_h is a function of velocity v . Data obtained from Table 6.2.

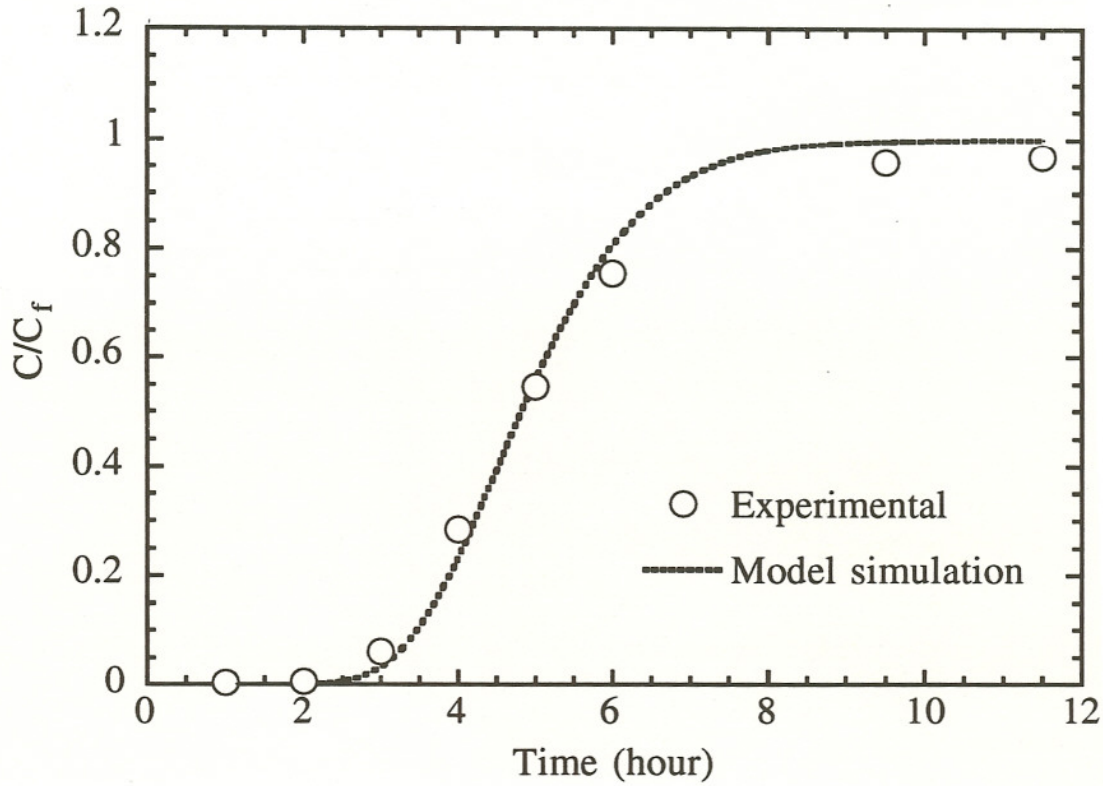


Figure 6.32 Comparison of experimental and model simulation breakthrough curves for the Cl^- transport in Cr-soil column. ($D_h = 0.00082 \text{ m}^2/\text{day}$, $v = 0.34 \text{ m/day}$, $\Delta x = 0.0014 \text{ m}$, $\Delta t = 0.004 \text{ day}$, $\rho_s = 2.64 \text{ g/cm}^3$, $\phi = 0.3$, $C_f = 1 \text{ mg/L}$, and $C_o = 0 \text{ mg/L}$). Experimental conditions were $5 \times 10^{-2} \text{ M NaCl}$, 23°C , and air atmosphere.

6.6.4 Simulation of Chromium Leaching from Cr-soil

Figure 6.33 shows the comparison between the model simulation and experimental results for influent solution pH 4.3 at 23 °C under air atmosphere. It is noted that during the first 4 day leaching period, most of Cr(VI) released from Cr-soil by introducing Cr-free simulated rainwater, then it was followed by a slow releasing phenomena. The Freundlich adsorption constants of K_f (44) and n (0.566) for a Boonton loam (Union County, NJ) (Allen et al. 1994) was used in the model simulation. The choice of adsorption constant of Boonton loam in the modeling is because it consists a high amount of organic matter (8.6%) and the sample was located near Hudson County. The Cr-soil contains 9% of organic matter. Hence, the decay constant (Cr(VI) reduces to Cr(III)) k of 20 1/day was adjusted for a good fit. The model can adequately simulate the leaching process when adsorption and decay reactions involve in the transport process, but not in the cases with adsorption only or dispersion only. The discrepancy between the experimental data and the model simulation (Figure 6.33, solid line) is due to the inadequacy of the assumption inherent in the development of the transport model. For example, the water flow variations occur in the column over time that violate the assumption of steady state condition. Based on the results of model simulation, it is concluded that the Cr(VI) leaching process is involved in adsorption and reduction reactions. Changing the adsorption constant K_f and the magnitude of the decay constant k is also affecting the model simulation (Figures 6.34 and 6.35). The higher the K_f is, the greater the leaching will be retarded. The leaching process is accelerated by increasing the decay rate. Figures 6.36-6.39 show the good-fit to the experimental data for different influent pHs and temperatures under air and N_2 atmospheres. Parameters used in the simulation

process are listed in Table 6.3. Based on the results of model fitting (Figures 6.36 and 6.37), k value increases with decreasing influent pH which could result from the dissolution of reductants, such as Fe-minerals from Cr-soil, under acidic condition. Temperature is another factor affecting the leaching process. Based on the results of model simulation (Figures 6.38 and 6.39), k value increases with decreasing temperature. It is concluded that the leaching process is accelerated under acidic condition and/or low temperature conditions.

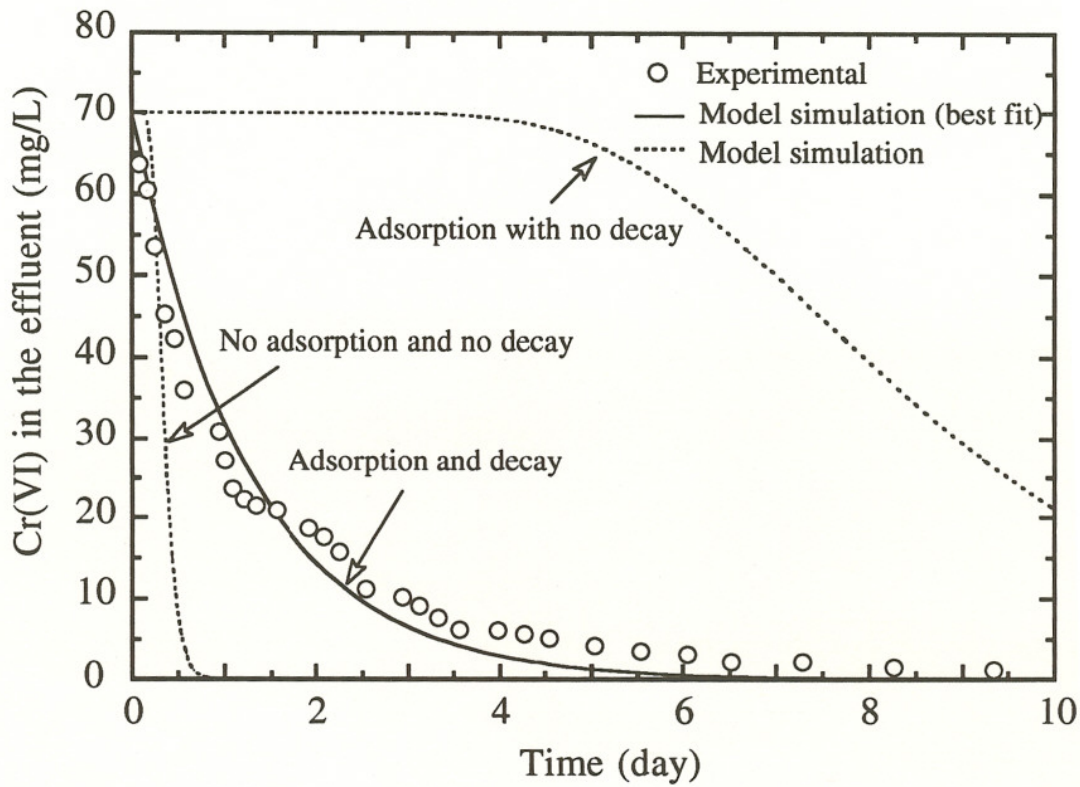


Figure 6.33 Comparison of experimental (influent pH 4.3, 23 °C, air atmosphere) and model simulation for Cr(VI) leaching from Cr-soil ($D_h = 0.00082 \text{ m}^2/\text{day}$, $v = 0.2 \text{ m/day}$, $\Delta x = 0.0014 \text{ m}$, $\Delta t = 0.008 \text{ day}$, $\rho_s = 2.64 \text{ g/cm}^3$, $\phi = 0.3$, $C_f = 0 \text{ mg/L}$, $C_o = 70 \text{ mg/L}$, and $L = 0.07 \text{ m}$ in all cases. Freundlich adsorption constants $K_f = 44$ and $n = 0.566$ (values from Allen et al. 1994), decay rate constant $k = 20 \text{ 1/day}$ (best fit value) are applied for the case of adsorption and/or decay). Solid line is the best fit of model simulation.

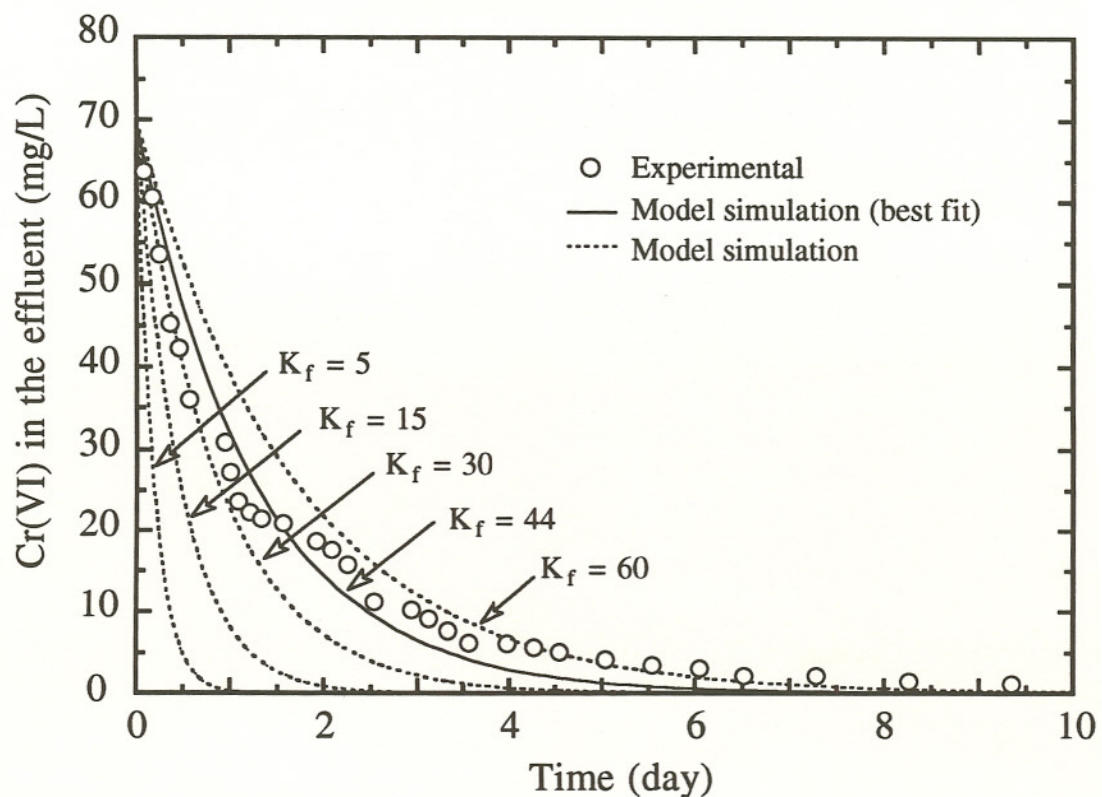


Figure 6.34 Comparison of experimental (influent pH 4.3, 23 °C, air atmosphere) and model simulation for Cr(VI) leaching from Cr-soil at different Freundlich adsorption constant K_f ($D_h = 0.00082 \text{ m}^2/\text{day}$, $v = 0.2 \text{ m/day}$, $\Delta x = 0.0014 \text{ m}$, $\Delta t = 0.008 \text{ day}$, $\rho_s = 2.64 \text{ g/cm}^3$, $\phi = 0.3$, $C_f = 0 \text{ mg/L}$, $C_o = 70 \text{ mg/L}$, and $L = 0.07 \text{ m}$, decay rate constants $k = 20 \text{ 1/day}$, and Freundlich adsorption constant $n = 0.566$ in all cases). Solid line is the best fit of model simulation

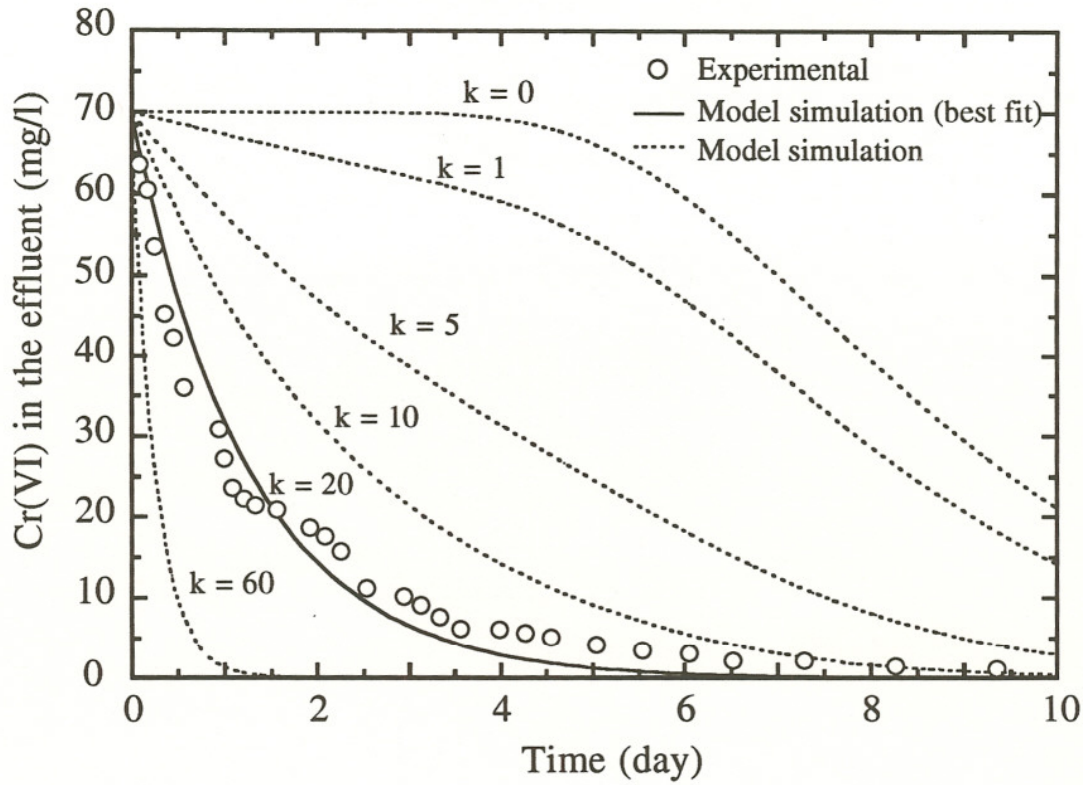


Figure 6.35 Comparison of experimental (influent pH 4.3, 23 °C, air atmosphere) and model simulation for Cr(VI) leaching from Cr-soil at different decay rate constant k ($D_h = 0.00082 \text{ m}^2/\text{day}$, $v = 0.2 \text{ m/day}$, $\Delta x = 0.0014 \text{ m}$, $\Delta t = 0.008 \text{ day}$, $\rho_s = 2.64 \text{ g/cm}^3$, $\phi = 0.3$, $C_f = 0 \text{ mg/L}$, $C_0 = 70 \text{ mg/L}$, and $L = 0.07 \text{ m}$, and Freundlich adsorption constants $K_f = 44$ and $n = 0.566$ (values from Allen et al. 1994) in all cases). Solid line is the best fit of model simulation.

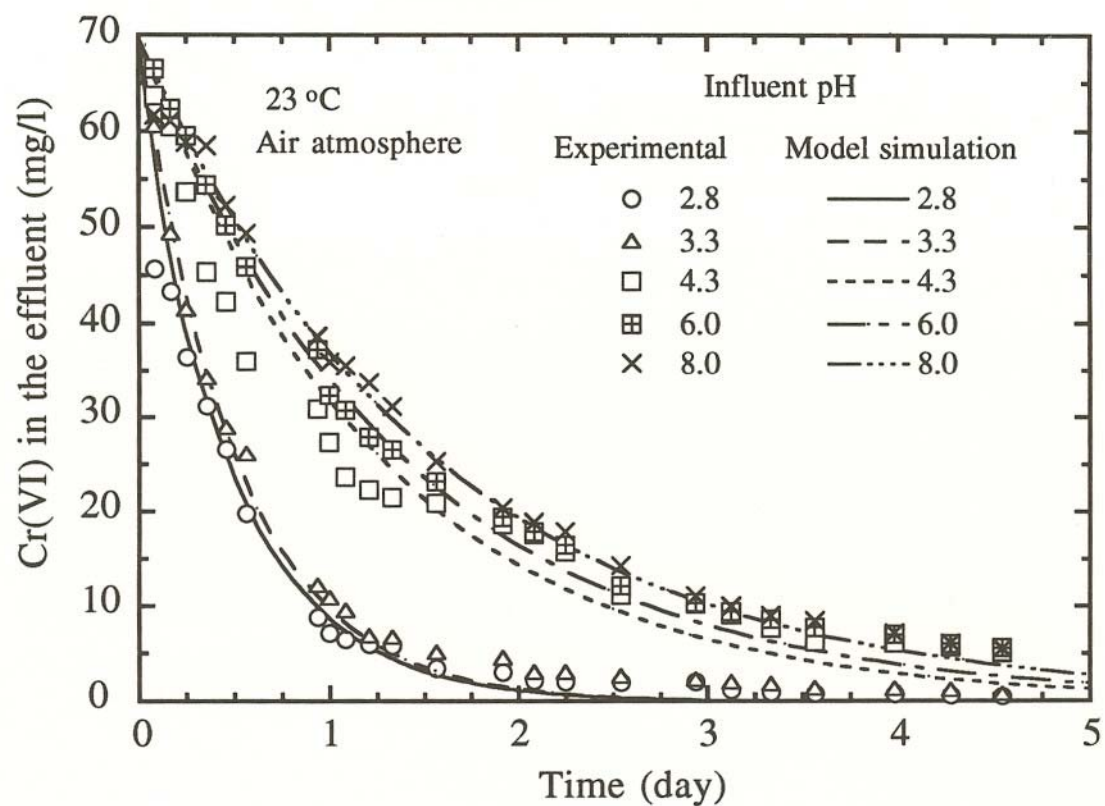


Figure 6.36 Comparison of experimental data (different influent pHs, air atmosphere, and model simulations for Cr(VI) leaching from Cr-soil. Lines are the best fit of model simulation.

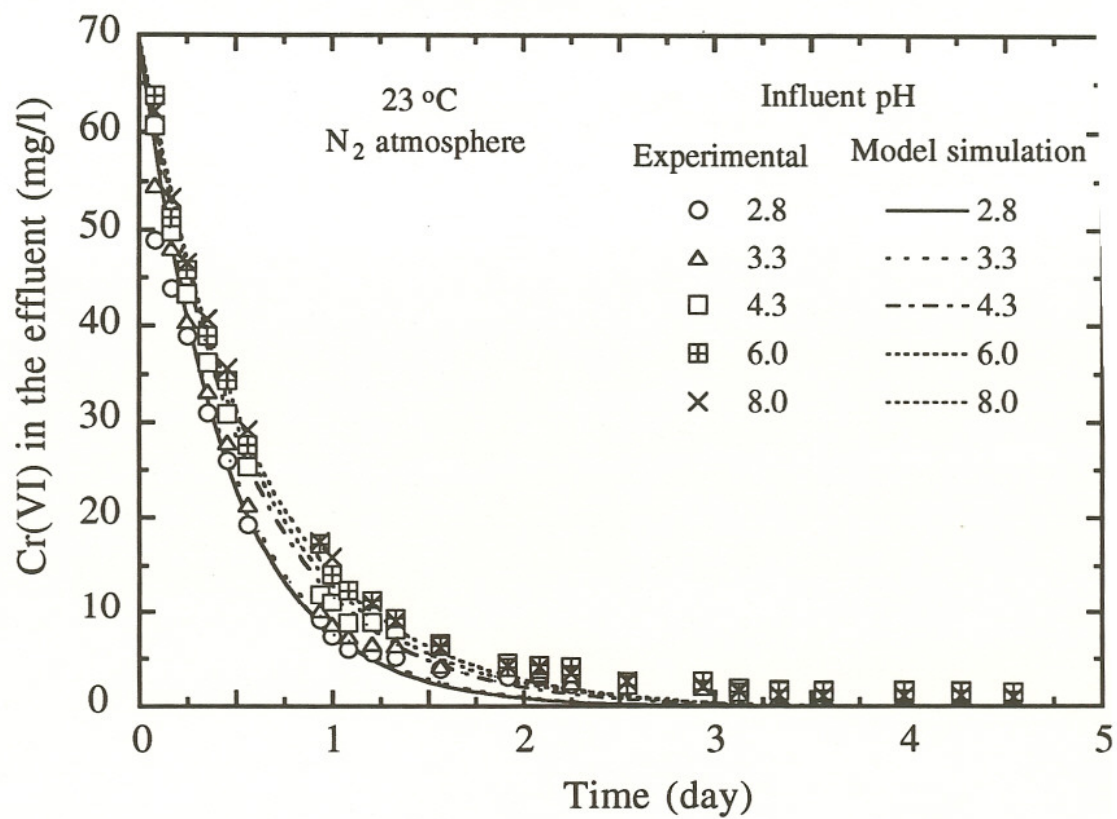


Figure 6.37 Comparison of experimental (different influent pHs, N₂ atmosphere) and model simulation for Cr(VI) leaching from Cr-soil. Lines are the best fit of model simulation.

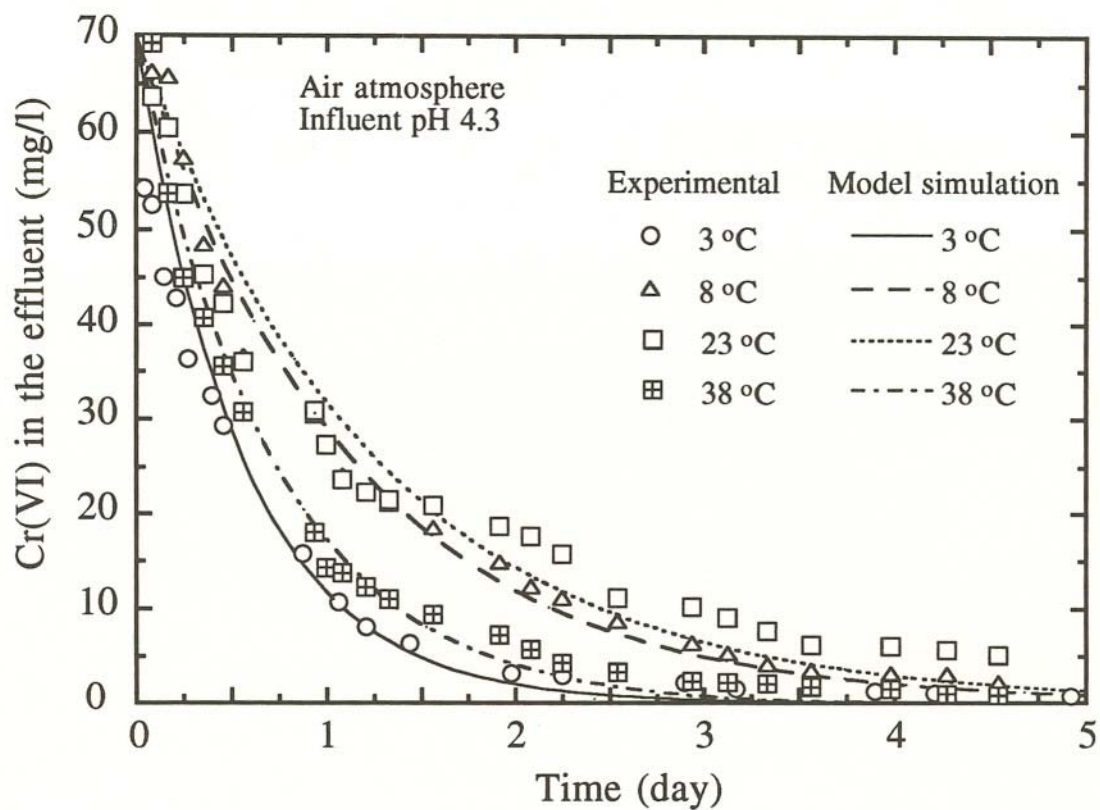


Figure 6.38 Comparison of experimental (different temperatures, air atmosphere) and model simulation for Cr(VI) leaching from Cr-soil. Lines are the best fit of model simulation.

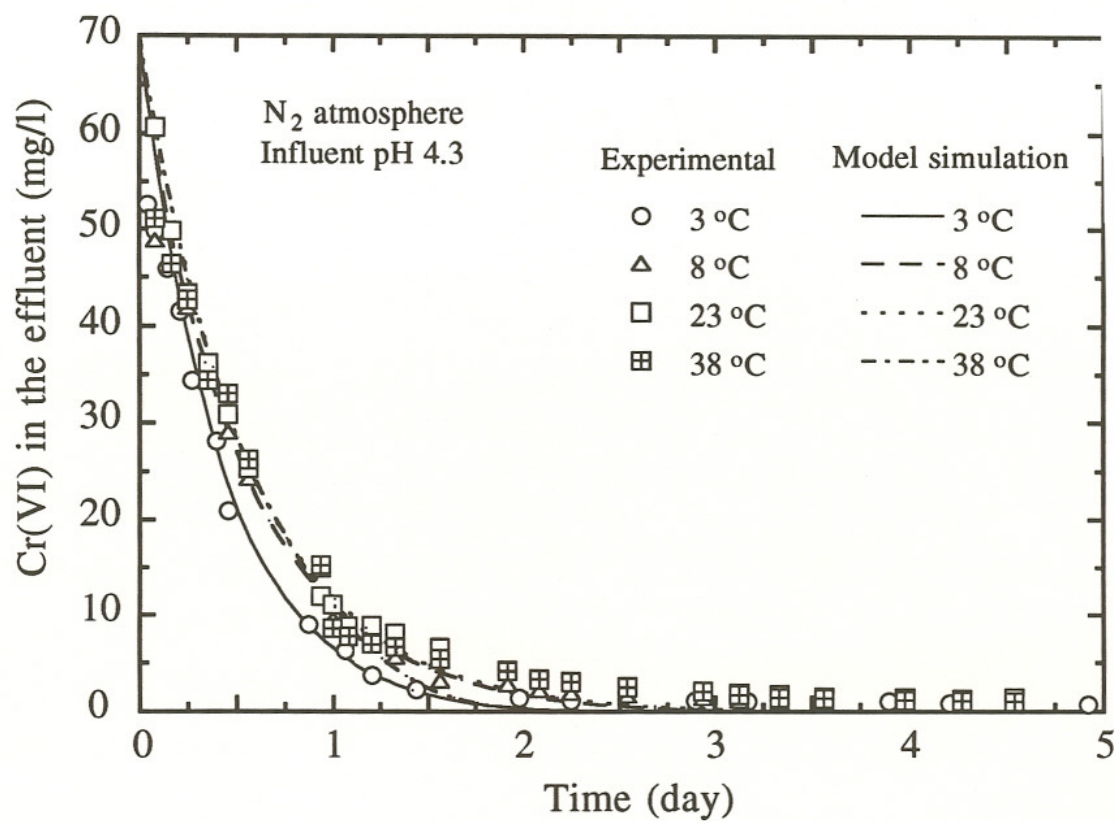


Figure 6.39 Comparison of experimental (different temperatures, N_2 atmosphere) and model simulation for Cr(VI) leaching from Cr-soil. Lines are the best fit of model simulation.

Table 6.3 Parameters used in the model simulation for Cr(VI) leaching from Cr-soil

		Influent solution pH ^a					Temperature ^b		
Conditions	Parameter	2.8	3.3	4.3	6.0	8.0	3 °C	8 °C	38 °C
Air atmosphere	v^c	0.502	0.457	0.2	0.159	0.174	0.402	0.251	0.495
	D_h^c	13.0	10.5	8.2	5.3	5.7	10.0	6.5	12.0
	Δt	0.003	0.003	0.01	0.01	0.01	0.003	0.006	0.003
	k^d	55	50	20	18	16	45	20	20
N ₂ atmosphere	v^c	0.453	0.542	0.402	0.366	0.477	0.850	0.578	1.142
	D_h^c	13.0	14.8	13.6	12.4	12.1	24.0	18.0	32.5
	Δt	0.004	0.003	0.004	0.004	0.003	0.002	0.002	0.001
	k^c	55	53	45	42	40	60	45	45

Note: $\rho_s = 2.64 \text{ g/cm}^3$, $\phi = 0.3$, $\Delta x = 0.0014 \text{ m}$, $C_f = 0 \text{ mg/L}$, $C_o = 70 \text{ mg/L}$, $L = 0.07 \text{ m}$, and $K_f = 44$ and $n = 0.566$ for a Boonton loam (Allen et al. 1994) are used in all cases.

Units: v (m/day); D_h ($\times 10^{-4} \text{ m}^2/\text{day}$); Δt (day); Δx (m); k (1/day).

^aControlled at 23 °C for all pHs.

^bInfluent solution pH 4.3 for all temperatures.

^cExperimental value.

^dBest fitting value.

6.7 Modeling Chromium Transport in Concrete

6.7.1 Experimental

Column study was performed using an acrylic column (1.9 cm-ID x 2.5 cm OD), fixing a hydraulic head of 60 cm and a free board of 7 cm (Figure 6.40). The concrete block was cut to a rectangular shape 2.5 cm thick, 2.5 cm wide, and ranging from 5 to 25 cm long with a diamond saw at the Delaware Brick Co., Wilmington DE. These concrete sticks were immersed for more than 1 day before using in the column experiments. The moisture saturated concrete stick was then placed on the bottom of acrylic column and was wrapped by rubber to avoid the growth of algae, photocatalytic reaction, and the leaking problems. Synthetic groundwater with initial pH of 8.0 containing 0.5 mg/l of Cr(VI) was pumped into a series of acrylic column that consisting different lengths (5, 10, 15, 20, and 25 cm) of concrete stick. This experiment was operated at room temperature. The effluent pH was recorded and the concentrations of Cr(III), Cr(VI), Fe(II), and Fe(III) in the effluent were measured

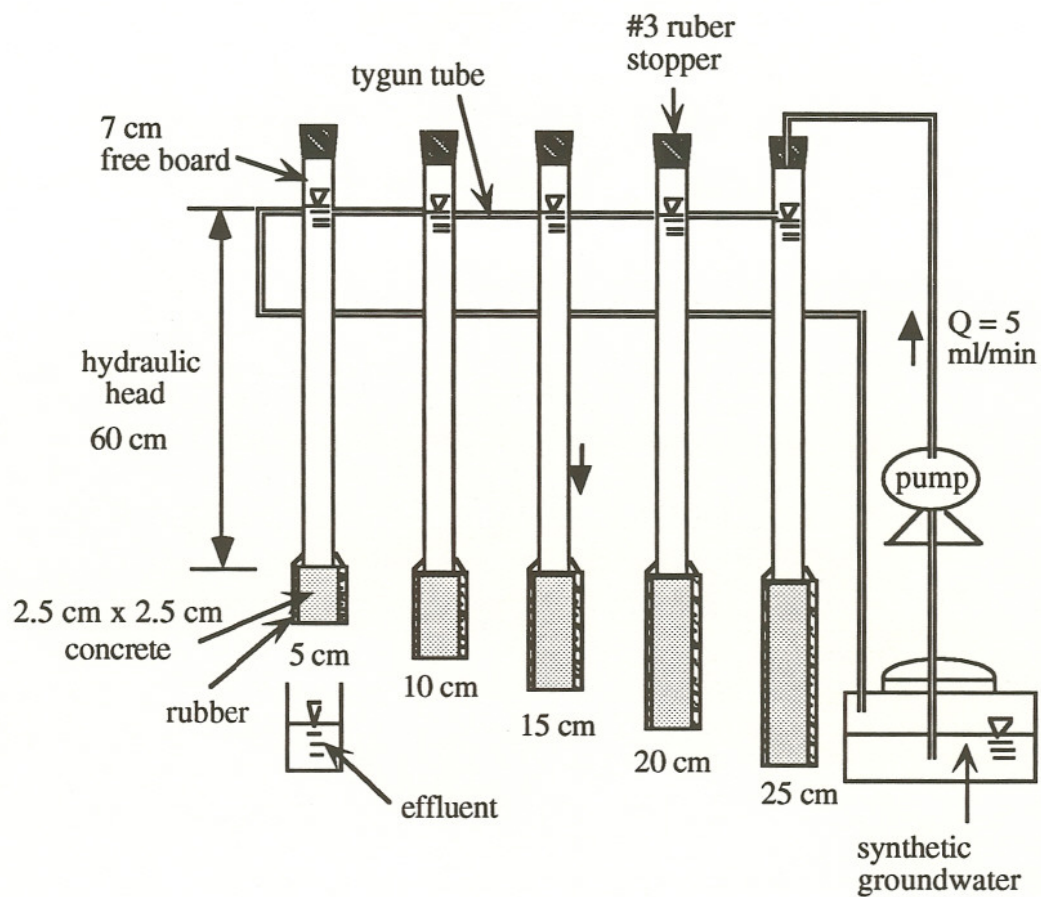


Figure 6.40 Schematic diagram of apparatus used in the column Cr(VI) transport through concrete experiments.

6.7.2 Experimental Results and Simulation of Chromium Transport in Concrete

Simulated groundwater spiked with 0.5 mg/L of Cr(VI) was passed through the concrete column until the concentration of Cr(VI) in the effluent was equal to that in the influent. An average effluent pH 11.2 was observed for all columns. The high effluent pH is expected because concrete consists of a high amount of alkaline materials such as CaO. It is assumed that the transport of Cr(VI) in concrete included an adsorption reaction. Batch experiments did not provide the adsorption isotherms for the Cr(VI) adsorption onto concrete at high pH (about 11). For the sake of simplicity, a linear adsorption constant was used in the model simulation. Results of model fitting show a good fit to the experimental data for all different lengths of concrete sticks from 5 to 25 cm (Figure 6.41) with a dispersion coefficient $0.0005 \text{ m}^2/\text{day}$, velocity 0.015 m/day , and assuming a linear adsorption constant of K_L 0.0025 L/Kg for best model fitting. The adsorption coefficient K_L was adjusted for a good fit. With the assumed value of linear adsorption constant, the model adequately describes the transport of Cr(VI) in the concrete. In fact, the magnitude of linear adsorption constant is small, implying that the contribution of adsorption to transport process is small. Figure 6.42 shows a comparison of the simulation for the transport process coupled with adsorption and without adsorption to the experimental data. It is visualized that the retardation effect of the transport process is small. The transport of Cr(VI) in the concrete at high pH may neglect the effect of adsorption reactions.

6.7.3 Prediction of Chromium Distribution in the Concrete

It is hypothesized that Cr-soil is next to the concrete block. Assume an amount of 70 mg/L of Cr(VI) is continuously leached from Cr-soil, i.e., the initial effluent concentration, C_f , is 70 mg/L. Based on the column and batch leaching study, about 0.25 mg/g leachable Cr(VI) in Cr-soil was found. This concentration (70 mg/L) is equivalent to a v/v ratio 1:6.6 of total leachable Cr(VI) in the Cr-soil. Basically, the transport model can simulate any lengths of concrete. For a concrete block with dimension in 14.6 cm x 19.2 cm x 40 cm. To simulate the Cr(VI) concentration profile in a 0.4 m long concrete block, input parameters D_h of 0.0005 m²/day, v of 0.015 m/day, Δx of 0.008 m, Δt of 0.5 day, and Freundlich adsorption constants K_f of 0.806 and n of 0.263 (appendix A) were used in the model computation. After 50 days, about 95% of the Cr(VI) has migrated towards the other side of the concrete block. It is expected that in about 2 months, the 70 mg/L Cr(VI) zone will move through 0.4 m of concrete. If the transport processes include adsorption and decay, the migration of Cr(VI) towards to the other side of concrete block is greatly affected by these two reactions. As seen in Figure 6.44, for a 20-day travel period through a 0.4 m long concrete block, the transport of Cr(VI) is retarded by adsorption and slowed down by the decay reaction, i.e., Cr(VI) reduction to Cr(III).

Simulation of Cr(III) transport through a 15 cm long concrete block is shown in Figures 6.45 and 6.46 with parameters D_h of 0.0005 m²/day, v of 0.015 m/day, Δx of 0.003 m, Δt of 0.5 day, the influent Cr(III) concentration of 0.5 mg/L, Freundlich adsorption constants K_f of 2.8 and n of 0.7. It is seen that the migration of Cr(III) is drastically retarded by the adsorption reaction. Only about 60% of Cr(III) migrates through a 15 cm long concrete block after 800 days period. With only dispersion

governing the transport process, 95% of 0.5 mg/L Cr(III) will pass through the concrete block in 20 days. However, for the transport process including adsorption and decay (i.e., Cr(III) oxidizes to Cr(VI)) reactions, the migration of Cr(III) is largely retarded by these reactions. Only about 60% of Cr(III) migrated through the other side of concrete in 800 days.

Based on the results of modeling simulation, it appears that the transport of Cr(VI) through concrete block indeed is much faster than that of Cr(III). A Cr(III) concentration of 0.5 mg/L, does not pose a hazard to the environment. Moreover, Cr(III) is not likely to be oxidized to Cr(VI) under the circumstances of the transport process. The transport of Cr species in the concrete is apparently in the form of Cr(VI) (CrO_4^{2-}). Since the concrete is a high alkaline material, the solution pH is expected to remain high during the transport process. Adsorption reactions are not significant in the transport Cr(VI) through concrete at high pH. Therefore, the migration of Cr(VI) in the concrete is mainly controlled by the advection and dispersion at high pH. In a case of concrete long term exposed to acidic chromate solution for long times, adsorption and redox reactions in the Cr(VI) transport process become important when the concrete loses its buffering capacity.

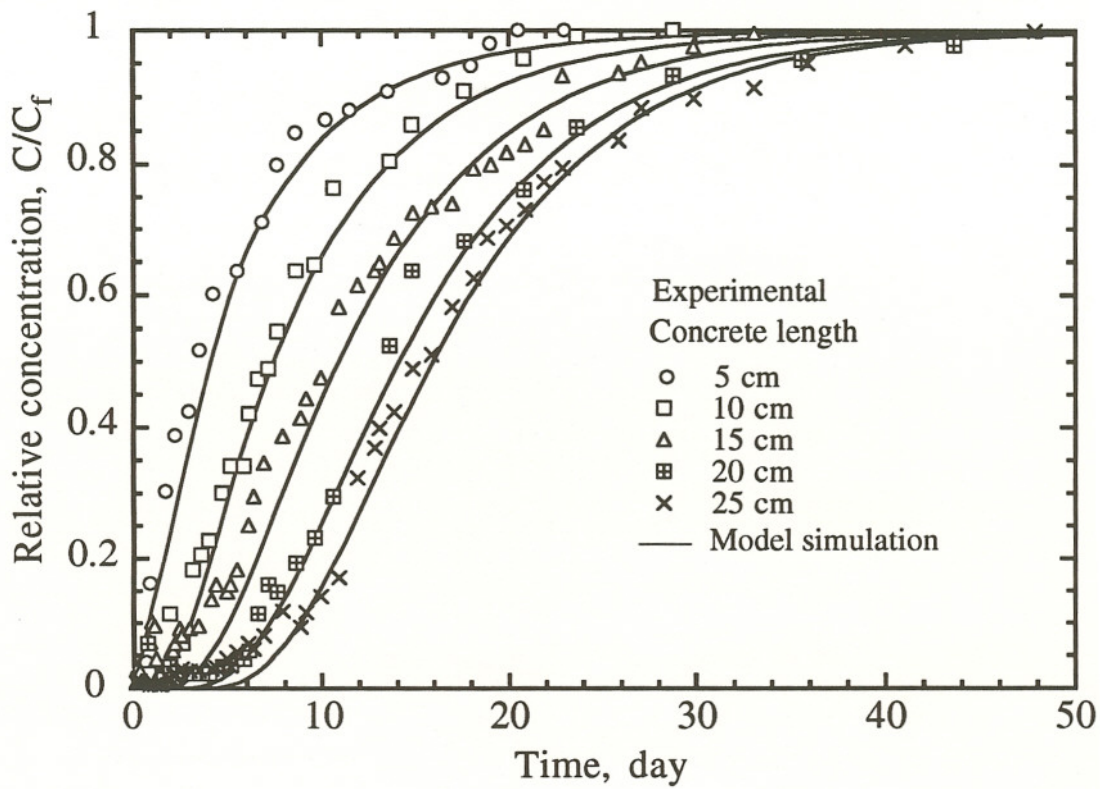


Figure 6.41 Comparison of experimental and model simulation for Cr(VI) transport through concrete material. ($D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\Delta x = 0.03 \text{ m}$, $\Delta t = 2 \text{ day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 0.5 \text{ mg/L}$, $C_o = 0 \text{ mg/L}$, and linear adsorption constant $K_L = 0.0025 \text{ L/Kg}$ (assumed for best fit) in all cases).

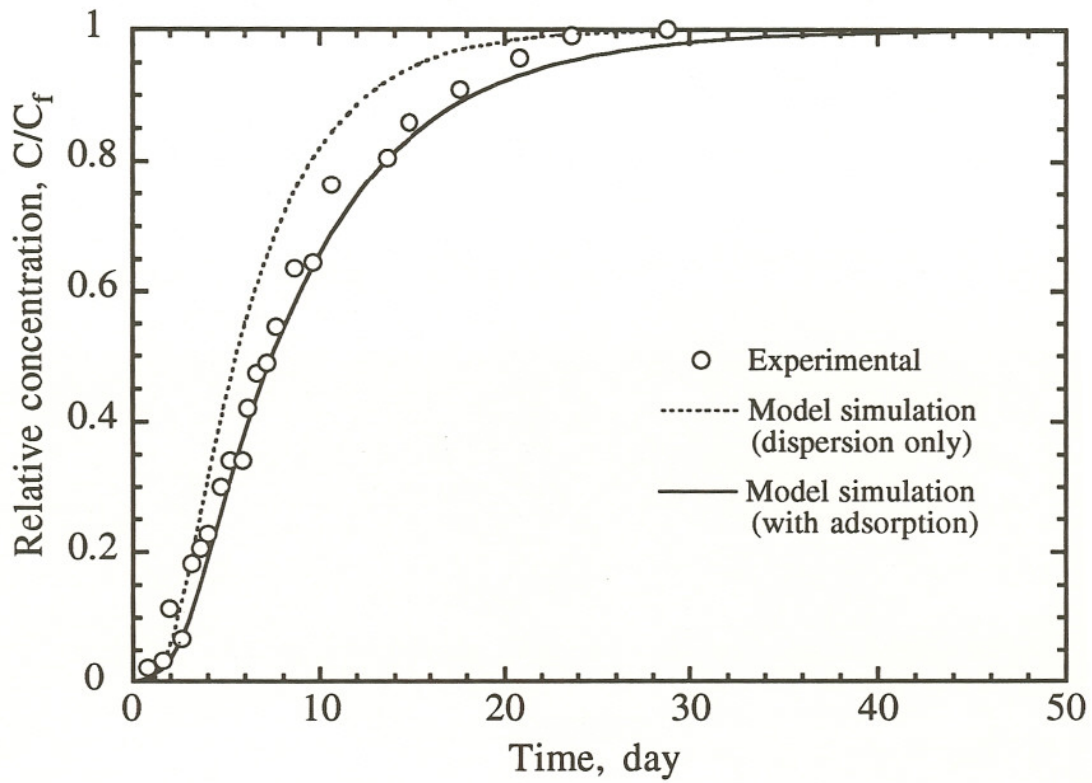


Figure 6.42 Comparison of experimental (concrete length 10 cm) and mode simulation (without adsorption and with adsorption) for Cr(VI) transport through concrete material ($D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\Delta x = 0.02 \text{ m}$, $\Delta t = 0.1 \text{ day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 0.5 \text{ mg/L}$, and $C_0 = 0 \text{ mg/L}$ for all cases; linear adsorption constant $K_L = 0.0025 \text{ L/Kg}$ (assumed for best fit) for adsorption case).

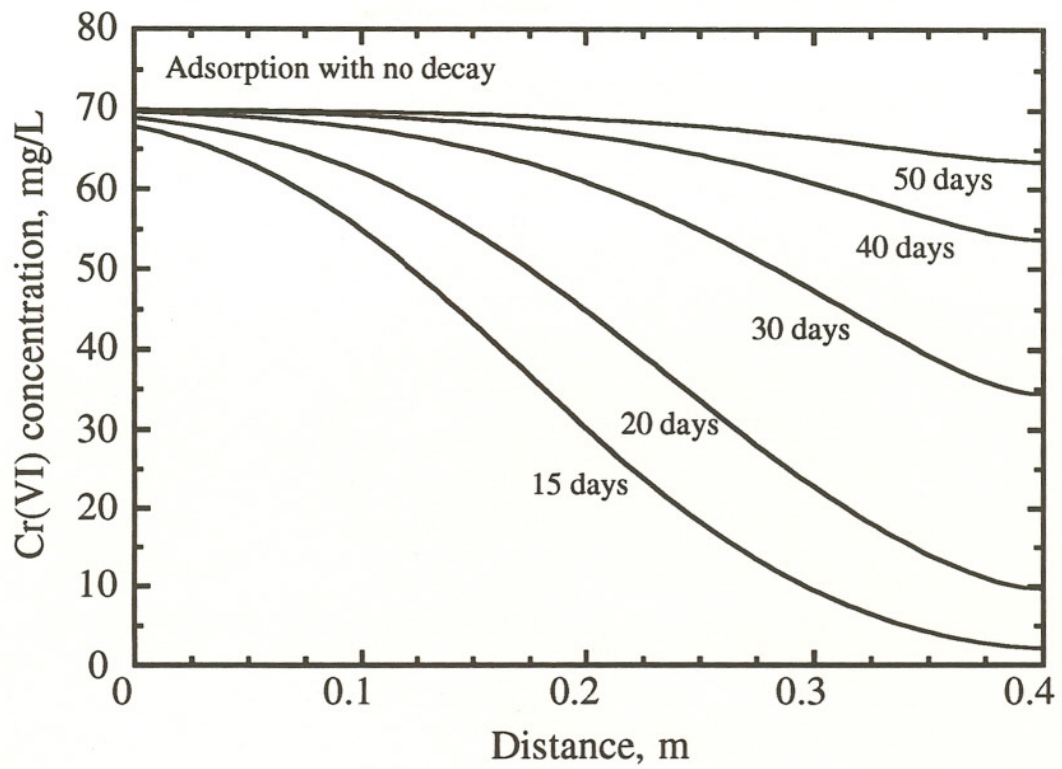


Figure 6.43 Prediction of Cr(VI) transport through concrete material ($D_h = 0.0005$ m²/day, $v = 0.015$ m/day, $\Delta x = 0.008$ m, $\Delta t = 0.5$ day, $\rho_s = 2.12$ g/cm³, $\phi = 0.084$, $C_i = 70$ mg/L, $C_o = 0$ mg/L, Freundlich adsorption constants $K_f = 0.806$, $n = 0.263$ (appendix A), and $L = 0.4$ m in all cases).

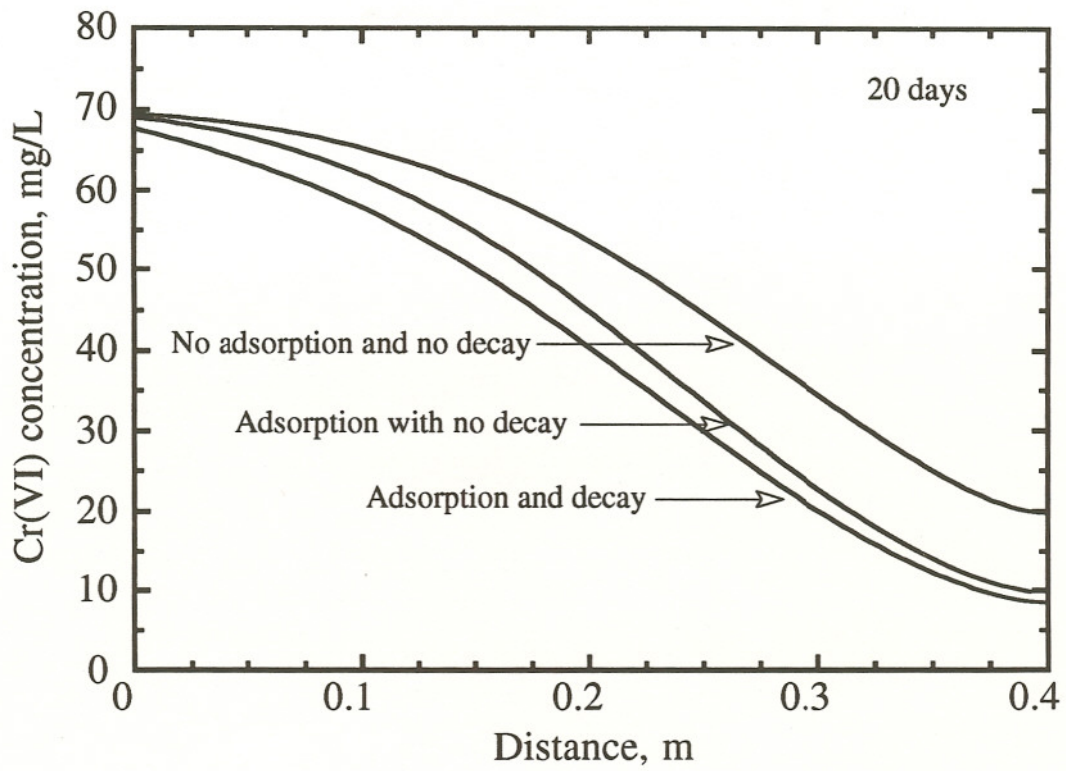


Figure 6.44 Comparison model simulation of Cr(VI) transport through concrete material coupled with different reactions ($D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\Delta x = 0.008 \text{ m}$, $\Delta t = 0.5 \text{ day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 70 \text{ mg/L}$, $C_o = 0 \text{ mg/L}$ Freundlich adsorption constant $K_f = 0.806$, $n = 0.263$ (appendix A), decay rate constant 0.01 1/day , and $L = 0.4 \text{ m}$ in all cases).

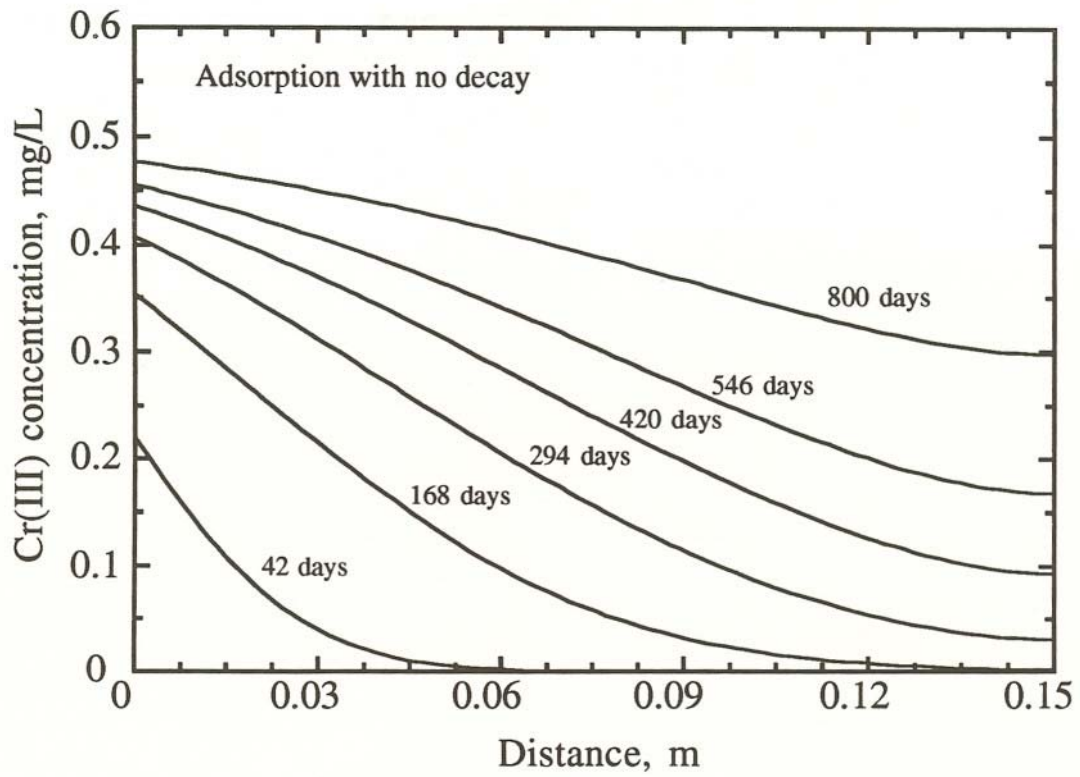


Figure 6.45 Simulation of Cr(III) transport through concrete coupled with adsorption reaction ($D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\Delta x = 0.003 \text{ m}$, $\Delta t = 0.5 \text{ day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 0.5 \text{ mg/L}$, $C_0 = 0 \text{ mg/L}$, Freundlich adsorption constant $K_f = 2.8$, $n = 0.7$ (appendix A), and $L = 0.4 \text{ m}$ in all cases).

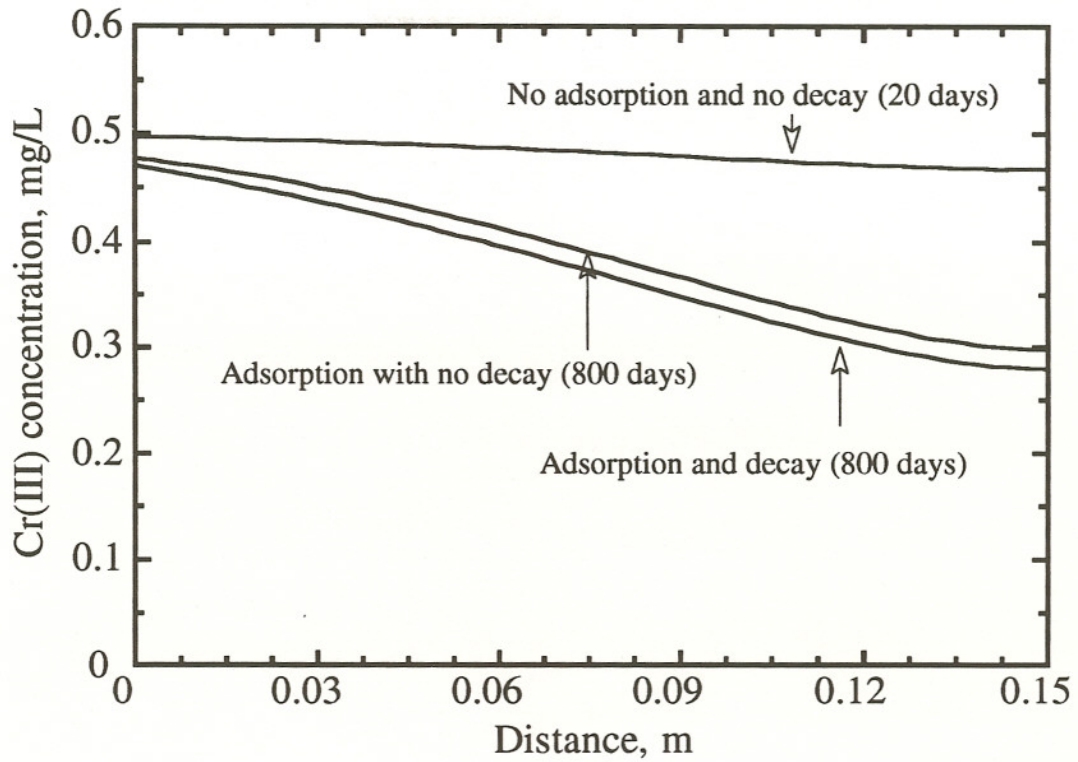


Figure 6.46 Comparison model simulation of Cr(III) transport through concrete coupled with different reactions ($D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\Delta x = 0.003 \text{ m}$, $\Delta t = 0.5 \text{ day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 0.5 \text{ mg/L}$, $C_0 = 0 \text{ mg/L}$, Freundlich adsorption constant $K_f = 2.8$, $n = 0.7$ (appendix A), decay rate constant 0.01 1/day , and $L = 0.4 \text{ m}$ in all cases).

6.7.4 Transport of Cr(VI) in Concrete: Effect of Wet-Dry Cycle

It is hypothesized that during the wet season, rainfall percolates through the Cr-soil and brings Cr (mostly hexavalent chromium) into solution. Anionic Cr(VI) species will travel to the groundwater systems, forming a Cr(VI) contaminated plume. A high groundwater table brings lateral plume movement that carries concentrated soluble Cr(VI) ions towards the external surface of the concrete block wall then through its pores towards the inside of concrete wall. When wetting proceeds, Cr(VI) moves into the other side of the concrete wall. During the dry season, water recedes from the concrete block wall leaving behind the entrapped Cr(VI). This wet-dry cycle repeats itself over time. Eventually, accumulated concentrated Cr(VI) ions appear on the other side of concrete wall. When the concrete wall is near by or adjacent to waste site, the soluble Cr(VI) can directly move to concrete wall by wetting the external surface during the rainfall season.

Under wet-dry cycle conditions, transport of Cr(VI) in concrete can be simulated using the computer spreadsheet program developed in this study. To do so, the concrete length is divided into number of sections. Transport in each section is simulated with different parameters. The precision of this simulation for a concrete depends on the number of sections. For simplicity, five sections are considered for the transport of Cr(VI) in a 0.4-m concrete wall with adsorption reaction. A wet period of 10 days and a dry period of 5 days are assumed for the wet-dry cycle. A total of three wet-dry cycles of Cr(VI) transport in concrete is simulated. Freundlich adsorption constants of pH 5.0 (appendix A) are used in the model simulation. Parameters used in the model simulation is listed in Table 6.4. Results of wet-dry cycle simulation are shown in Figure 6.47. Figure 6.48 shows the transport of Cr(VI) in concrete under all

wet condition. Based on the comparison of Figures 6.47 and 6.48, it appears that the transport process is diminished by the wet-dry cycle.

Table 6.4 Parameters used in the model simulation of Cr(VI) transport in concret under wet-dry cycle condition.

Section	I	II	III	IV	V
x/L	0 - 0.2	0.2 - 0.4	0.4 - 0.6	0.6 - 0.8	0.8 - 1.0
Δx (m)	0.0016	0.0032	0.0048	0.0064	0.008
Δt (day)	0.1	0.2	0.25	0.4	0.5
C_0 (mg/L)	58.2	47.4	34.5	22.1	12.3
(Cycle II)	($x/L=0.1$)	($x/L=0.3$)	($x/L=0.5$)	($x/L=0.7$)	($x/L=0.9$)
C_0 (mg/L)	66.0	60.5	56.0	43.6	39.0
(Cycle III)	($x/L=0.1$)	($x/L=0.3$)	($x/L=0.5$)	($x/L=0.7$)	($x/L=0.9$)

Note: $D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 70 \text{ mg/L}$, Freundlich adsorption constants $K_f = 0.806$, $n = 0.263$ (appendix A, at pH 5.0), $L = 0.4 \text{ m}$, wet period 10 days, and the third type of BC for all cases.

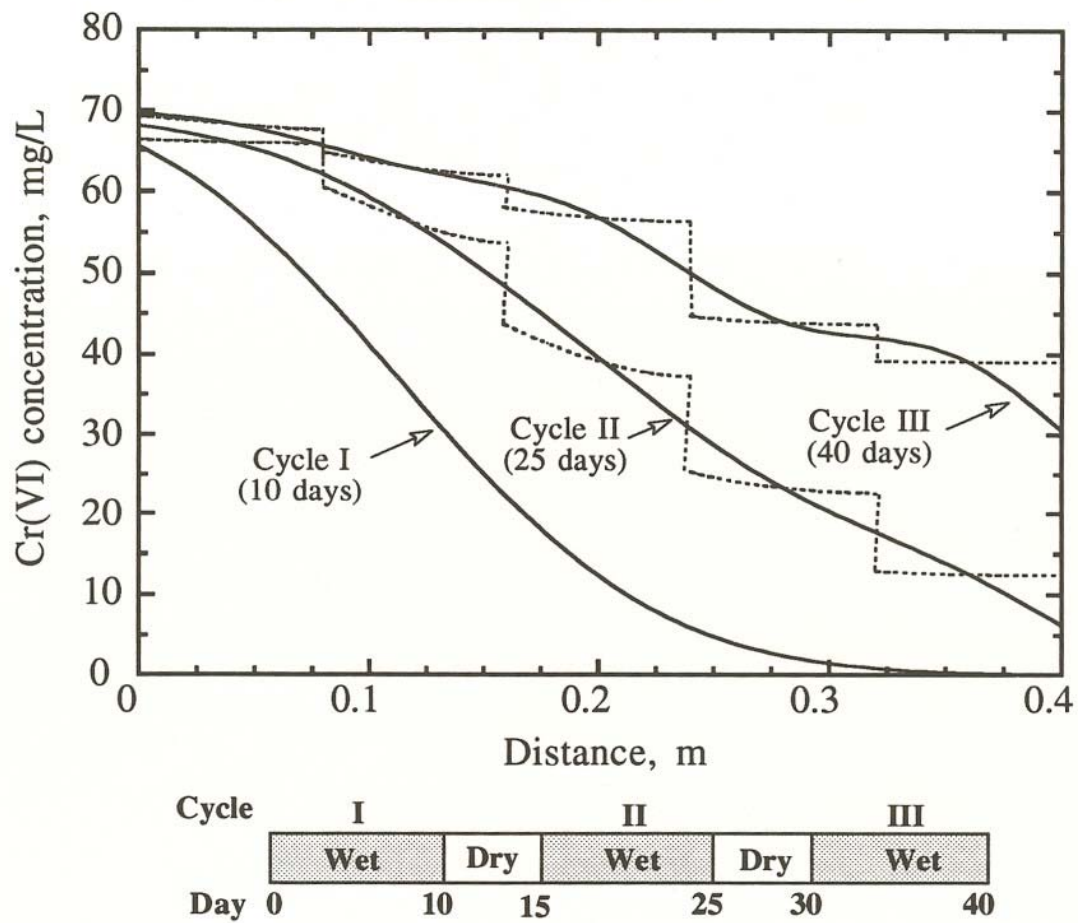


Figure 6.47 Simulation Cr(VI) transport through concrete coupled with adsorption reaction at pH 5.0 under wet-dry cycle conditions. Dashed and solid lines in cycle I and III are the simulation results and smoothed curves of these simulation results respectively. Parameters used in the model simulation are listed in Table 6.4.

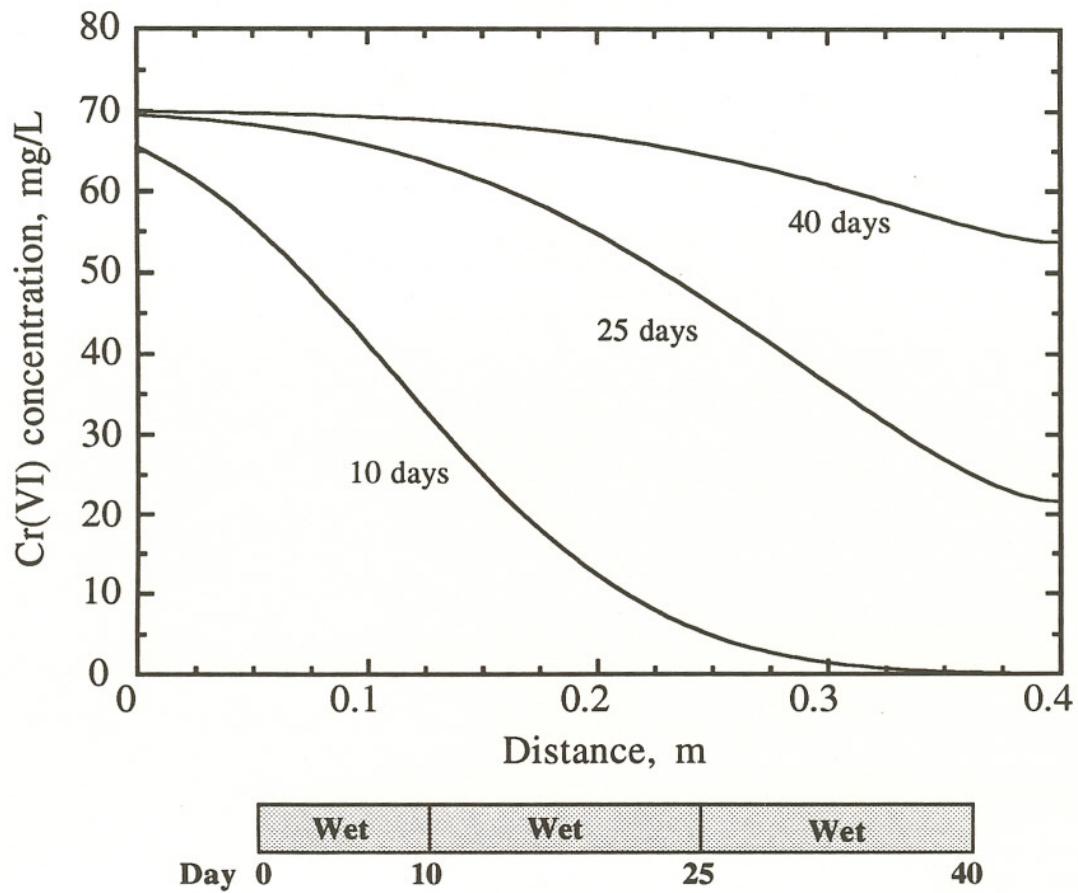


Figure 6.48 Simulation Cr(VI) transport through concrete coupled with adsorption reaction at pH 5.0. ($D_h = 0.0005 \text{ m}^2/\text{day}$, $v = 0.015 \text{ m/day}$, $\rho_s = 2.12 \text{ g/cm}^3$, $\phi = 0.084$, $C_f = 70 \text{ mg/L}$, $C_o = 0 \text{ mg/L}$, Freundlich adsorption constants $K_f = 0.806$, $n = 0.263$ (appendix A, at pH 5.0), $L = 0.4 \text{ m}$, and the third type of BC for all cases.)

6.8 Summary

The governing equations of the numerical model for transport of chromium in porous media are solved using the finite difference method. An interactive spreadsheet computer program was developed to simulate reactive substance transport in porous media coupled with adsorption and decay. The numerical model is confirmed by the exact analytical solution. Chromium leaching from Cr-soil and transport in concrete can be simulated using this model. Column leaching study shows that the mass of Cr(VI) leached is independent of air or N₂ atmosphere, but it is dependent on the influent pH and temperature. The model simulation results support the suggestion that the Cr(VI) leaching process is mainly governed by the adsorption/desorption, precipitation, and redox reactions. Cr(VI) is mobile in the concrete because Cr(VI) is not favorably adsorbed by concrete at high pH. Thus the transport of Cr(VI) in the alkaline concrete block is mainly caused by dispersion and advection only. However, the transport of Cr(III) in the concrete is drastically retarded by the adsorption process. It is possible that when acidic chromate solutions are in prolonged contact with the concrete, the concrete will gradually lose its buffering capacity. As a result, the transport of Cr(VI) under such conditions should include adsorption and decay (hence redox) reactions. Dissolution of the Ca or other alkaline material in the concrete by H⁺ or by exchanging with ions in the leachate results in loss of their buffering capacities, and thereby more Cr(VI) will be adsorbed on the concrete and weaken the concrete strength.

Chapter 7

CONCLUSIONS

7.1 Major Findings

Physico-chemical properties of Cr-soil have been characterized. Soil derived from chromite ore processing residue (COPR) is a highly alkaline material containing a large amount of calcium, presumably in the form of CaCO_3 . By XRD analysis, the major Cr form was identified as chromite. Although, calcium chromate salts were not identified, the presence of these salts in the Cr-soil should not be ruled out. The amount of Cr leached depends on the extraction process. Using the combination of HNO_3 , H_2SO_4 , and HClO_4 in the extraction process, as much as four times total Cr was extracted compared with using HNO_3 and HCl . HF appears to be the most effective extractant of Cr from Cr-soil derived from COPR. Based on the batch and column experiments, total chromium estimated in the material is about 2.5% (25 mg/g) by weight, and about 1% (0.25 mg/g) of this is in the form of hexavalent chromium that is readily leachable at pH between 4 and 12. The bulk of the remaining chromium mainly consists of trivalent chromium which is nonleachable between pH 4 and 12.

Leaching of chromium and all the other metals with synthetic rainwater is highly pH sensitive. Low pH (< 4.5) promotes Cr(VI) reduction to Cr(III), and thereby decreases the mass of Cr(VI) leached. Temperature plays a significant role in

affecting the mass of Cr(VI) leached. High temperature enhances Cr(VI) leaching. Thus, the amount of Cr(VI) leached can vary depending on the seasonal conditions at the chromium contaminated sites. It is expected that more Cr(VI) will be leached during the hot than the cold season. Organic matter is another parameter affecting the amount of Cr(VI) leached. Organic matter in the Cr-soil primarily acts as an electron donor to reduce Cr(VI) to Cr(III). Accordingly, the amount of Cr(VI) leached from a high organic matter containing Cr-soil will be less than that of a low organic matter one.

The mass of Cr(VI) leached is not substantially different under air or N₂ atmosphere. Model simulation indicates that the Cr(VI) leaching process is mainly governed by the adsorption/desorption, precipitation, and redox reactions. Possible dissolution of COPR might occur during the leaching process, but no direct evidence was found from this work.

A hazardous condition arising from COPR is deterioration of concrete structures. Because the Cr-soil is in contact with concrete block walls, knowledge of the chemical interaction between Cr and concrete is important for establishing the clean-up strategy. This study shows that adsorption, redox, and precipitation reactions are the major processes affecting the concentration and speciation of chromium in the chromium-concrete interface, and that solution pH is the crucial parameter affecting these chemical interactions. Below pH 3.5, the removal of Cr(VI) is controlled by reduction reactions. Cr(VI) is reduced to Cr(III) by reaction with aqueous Fe(II) derived from Fe(II)-containing concrete materials. The concentration of Cr(III) is governed by the $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})$ and/or $\text{Cr}(\text{OH})_3(\text{s})$ precipitates. At pH 4 to 9, adsorption is mainly responsible for Cr(VI) removal. Prediction of the Cr(VI)

adsorption density for different sizes of concrete particles can be extrapolated by knowing the specific surface area of the concrete particles. Among all parameters studied, pH appears to be the most important governing the fate of chromium in concrete. The adsorption of Cr(VI) onto concrete particles can be described by surface complex formation model. Because the magnitude of favorable electrostatic energy and the adverse solvation and lateral interaction energy which contribute to the total adsorption are relatively small in comparison with the favorable specific chemical energy, I conclude that the specific chemical interaction is the major mechanism responsible for the adsorption process.

Transport of Cr in the concrete is highly dependent on the solution pH. Since the pH of the Cr-soil and concrete are both high, Cr(VI) is only minimally adsorbed and will transport readily up to and through the concrete wall. Cr(III), however, can be adsorbed strongly by concrete at high solution pH. As a result, the transport of Cr(III) in the concrete is drastically retarded by the adsorption process. It is possible that when acidic chromate solutions are in prolonged contact with the concrete, the concrete will gradually lose its buffering capacity. As a results, the transport of Cr(VI) under such condition should include adsorption and decay (hence redox) reactions. Dissolution of the Ca or other alkaline material in the concrete by H^+ or by exchange with ions in the leachate results in loss in buffering capacity, and thereby more Cr(VI) will be adsorbed on the concrete and weaken the concrete strength.

7.2 Recommendation for Future Research

The extension of this study would be to examine the toxicity of Cr-soil and the redox reaction in the subsurface. Although the content of readily leachable Cr(VI) in Cr-soil is low, it is potentially hazardous to the environment. The results of a toxicity test would give us more in depth information to determine the remediation requirements. The fact that chromium leaches rapidly during column studies suggests that Cr(VI) would be rapidly washed away from a waste site. The fact that we are still seeing it after 50 years leads one to suspect that there is continuous slow oxidation onsite of trivalent chromium, and that environments are at a steady-state between chromium oxidation and chromium leaching via rainfall. The oxidation of hydroxyl Cr(III) species and Cr(III) precipitates by Mn-oxide such as MnO_2 , Mn_2O_3 , and MnOOH is thermodynamically possible. This reaction will further bring more Cr(VI) into solution. Thus, the redox reactions of Cr in the Cr-soil, natural soil and groundwater are important with respect to the concentration level leached from Cr-soil. Major active redox materials such as pyrite, Fe-oxides, Mn-oxides, and organic matter, occur in the soil-water system, and directly or indirectly affect the transformation of chromium in the system.

pH apparently is a crucial parameter affecting the amount of Cr(VI) leached from Cr-soil as well as the transport of Cr(VI) in the concrete. Chemical treatment may be applied to some selected sites to minimize the leaching of Cr(VI) by adding some reducing chemicals under acidic condition. Based on this study, it is possible to prevent or minimize the migration of Cr through concrete wall by adjusting the pH below 6. Remediation efforts may be selected only for those chromium contaminated sites which have persistent high levels of Cr(VI) leached and which exceed the state clean-up standard or exhibit concentration levels that are toxic to environment.

Additional future experimentation should be concentrated on the development of in-situ remediation technologies suitable for chromium waste sites in New Jersey. Weng et al. (1994b) have conducted a feasibility study of in-situ treatment of Cr-soil using electro-osmosis (EO) process. According to the preliminary results of their study, more than 95% of soluble Cr(VI) can be removed by controlling the pH of the processing fluid at 9.0 during the EO process while applying a 1.2 Volt per meter of electrical strength to the Cr-soil. They suggested that the EO process can be an effectively in-situ treatment of Cr-soil. This in-situ treatment technique (EO) should be priority listed for future study.

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APPENDIX A

FREUNDLICH ADSORPTION PLOT FOR CR(VI) ADSORPTION ONTO CONCRETE

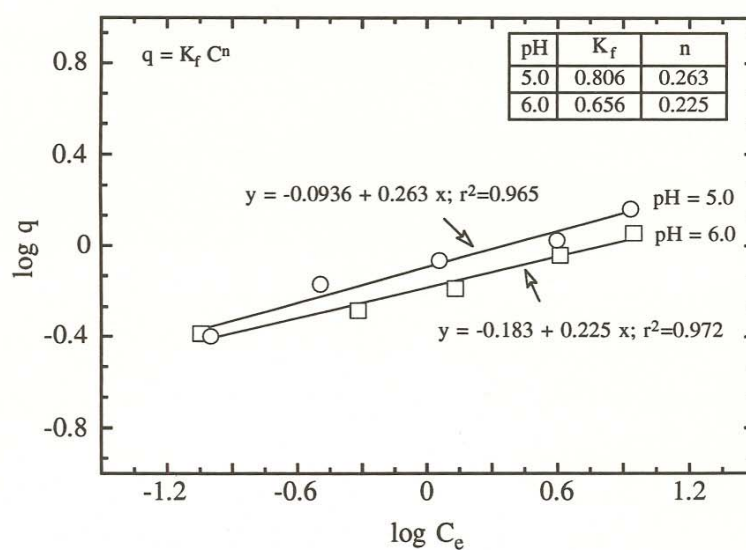


Figure A1 Freundlich plot for Cr(VI) adsorption onto concrete at pH 5.0 and 6.0. Adsorption density, q (mg/g) and equilibrium concentration, C_e (mg/L) are obtained from Figure 5.8.

APPENDIX B

MANUAL FOR THE INTERACTIVE SPREADSHEET PROGRAM FOR CONTAMINANT TRANSPORT IN POROUS MEDIA COUPLED WITH ADSORPTION AND DECAY

B.1 Requirements

An IBM-PC or compatible installed with Lotus 1-2-3 Release 4 for Windows is required to run this program. A PC of 486DX2-50MHz with 8MB Ram is recommended. Depending upon the configuration of the PC, the speed of running this program will be different. For a PC with 486DX2 66MHz and 8MB Ram, the running time of 2000 time steps is about 20 minutes. If the computer is installed with Intel-Pentium chip processor, the speed of running this program is even faster.

In order to get maximum benefit from using this program, the user needs to know the flow transport behavior. Because this program was written with Lotus 1-2-3 macros and it was therefore set up in the Lotus 1-2-3 spreadsheet, basic knowledge of Lotus 1-2-3 may be necessary. Since finite difference method (FDM) is used to solve the governing transport equations, basic knowledge of FDM may be required in order to get maximum benefit of this program.

B.2 How to Install the program

To install the program on your IBM-PC hard drive

1. Place your disk into your disk drive.

2. Copy the program file into your hard drive.
3. Install Lotus 1-2-3 Release 4 for Windows in your hard disk.
4. Double-click on the program file.

B.3 Limitation

This program is limited to one-dimensional transport, one-contaminant per simulation, equilibrium adsorption (only for linear, Freundlich, and Langmuir adsorption isotherms), and first order decay.

B.4 How to Run This Program

1. Prepare the data set. The data set should include: coefficient of hydrodynamic dispersion, pore velocity, solid density, porosity of the porous media, adsorption (linear, Freundlich or Langmuir adsorption constants), first order decay rate constant (or kinetic rate constant), influent solute concentration, initial solute concentration in the column, column diameter, and column length.
2. Select values for distance step (Δx) and time step (Δt). The maximum length simulation is 50 times Δx . The total time simulated will be Δt times the number input steps.
3. Open the program file. Two boxes will promptly show on the screen. The control box consists of a series of buttons for performing programming tasks (e.g., data inputting and program executing) by clicking the buttons using mouse action. The data recording box consists of a number of cells which record the input data through the practice of program.

3. To start the program, click the **“Start”** button in the controlling box, then follow the directions of the popup dialog to input the data. After the data is input, the results will show in the data recording box.

4. You can also bypass the data inputting button and directly run the program by clicking the **“Run”** button.

5. To see the results, click **“Output-Last Step”** button.

6. To quit the program while the program is running: press **“Ctrl+Break”**.

7. To print the results, use mouse to highlight the printing range, then click the printer smart icon at the left top corner of or press **“Ctrl+P”**.

B.5 Output Editing

The output graph generated in the Lotus-123 can be directly copy-edited. One can save and customize the graph, such as modifying the axis scales, size, title, and color the graph, using Lotus-123 chart tools from the menu bars to make the output graph more presentable.

B.6 Unlimited Time Steps Simulating.

This operation may require that the user turn off the **“Undo”**. To disable **“Undo”**, using Tools-User Setup from the menu bar in the LOTUS-123 program, then choose Edit Undo or press **“CTRL+Z”**. When one works with the Microsoft Windows and Lotus-123 Release 4 in a PC with 8 MB Ram, the program can be run up to 2300 steps without turning off the **“Edit-Undo”**.

B.7 Help

One can click the **"Help"** button in the control box to obtain more information about this program. The help section includes: "About this program", "How to run this program", "Governing equations", "About adsorption isotherm", "Finite difference method", and "Initial and boundary conditions".

B.8 Running Program in Macintosh

Although the program is designed to be used in the IBM-PC, it is possible to run this program in Macintosh using a software called "SoftPC with Windows" which emulates an Intel processor and runs the Windows program directly in 68040 Macintosh. With a software called "SoftWindows" installed in Apple Power Macintosh, one can run this program at speed up to a 486SX-PC.

B.9 Transfer output data to Macintosh

1. Copy the output data to a separate Lotus 1-2-3 file, then save it as ".wk1" to a IBM-formatted disk.
2. In Macintosh, use the software called "Apple File Exchange" to transfer data from IBM to Macintosh from the ".wk1" file stored in the IBM-formatted disk.
3. In Macintosh, use the software called "MacLink Plus/PC" to transfer Lotus 1-2-3 ".wk1" file to Macintosh spreadsheet software, e.g. Microsoft Excel.

B.10 Warning

If the user inputs some unreasonable data values, the program will automatically prompt a warning sign and ask the user to reinput a data value.

B.11 Example:

An example to simulate contaminants transport through soil-water system coupled with adsorption is demonstrated as follow:

Key in those data as order:

1. Click "**Start**" button.
2. Input soil density of **2.6** (g/cm³), press enter.
3. Input soil porosity (ϕ) of **0.3**, press enter.
4. Select one set of units for dispersion coefficient (D_h), porosity (ϕ), and decay constant (k) from the popup menu. Select **D_h -m/day, v-m/day, k-1/day** using allow key or mouse action, then click "OK".
5. Input dispersion coefficient (D_h) of **0.03** m/day, press enter
6. Input Pore velocity (v) of **0.1** m/day, press enter.
7. Input distance step (Δx) of **0.2** m (for a 10-m long column).
8. Input time step (Δt) of **1** day. If the Peclet number Pe and Courant number Cr exceed the criteria of $Pe < 2$ and $Cr < 1$, this program will prompt for the selection of an adjustment of input parameters, Δx and Δt , or skip the advice. To skip the advice, click "Cancel".
9. Select a transport condition from the popup menu. Click "**With adsorption w/o Decay**" for this case, then click "OK".
10. Select one a adsorption isotherm, then click "OK". Click the "**Linear adsorption isotherm**", press enter.
11. Input linear adsorption constant of **0.2** L/Kg, press enter.

12. Input influent concentration (C_f) of **10** mg/L, press enter.
13. Input initial concentration (C_0) of **0** mg/L, press enter.
14. Select the type of boundary condition. Click **Cauchy (Third Type)**, then click "OK".
15. Input pass word.
16. Input the simulation time step of **80**, press enter.
17. Select one type of output and plot Click "**The last step only**", click "OK".
18. Print the result of output. Highlight the printing area, then click the printer smart icon at the left top corner or press "**Ctrl+P**".
19. Click "**Quit**" to return to the control box and data recording box (Figure B1)
You can click "**Output-Last Step**" to check the results generated from this example (Figure B2).

Dispersion Coeff., Dh	0.03	m ² /day	Influent Conc., Cf	10.00	mg/L
Pore Velocity, v	0.1	m/day	Initial Conc., Co	0.00	mg/L
Distance Step, Delta x	0.2	m	Boundary Condition	Cauchy	
Time Step, Delta t	1	day	Linear Ads. Const.		
Peclet Number, Pe	0.6667		K	0.200	L/Kg
Courant Number, Cr	0.5		Freundlich Ads. Const.		
Solid Density	2.6	g/cm ³	K	0.000	
Bulk Density	1.82	g/cm ³	n	0.000	
ϕ	0.3		Langmuir Ads. Const.		
Column Diameter		m	K	0.000	L/Kg
Column Length		m	Max Ads. Capacity, Qm	0.000	g/Kg
Solid Weight		g	Retardation Factor, Rd	2.21	
Pore Volume		mL	Decay Constant, k	0.0000	1/day
Length Simulated	10	m			
Time Simulated	80	day			

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Start	Help
↓	
Physical Parameters Dh, v, Delta x, Delta t Adsorption Isotherms	
↓	
IC. ? BC. ? Run	
↓	
Output-Last Step Output-C-t, C-PV	

Figure B1 The control box (right hand side) and data recording box (left hand side) for operating the interactive spreadsheet program.

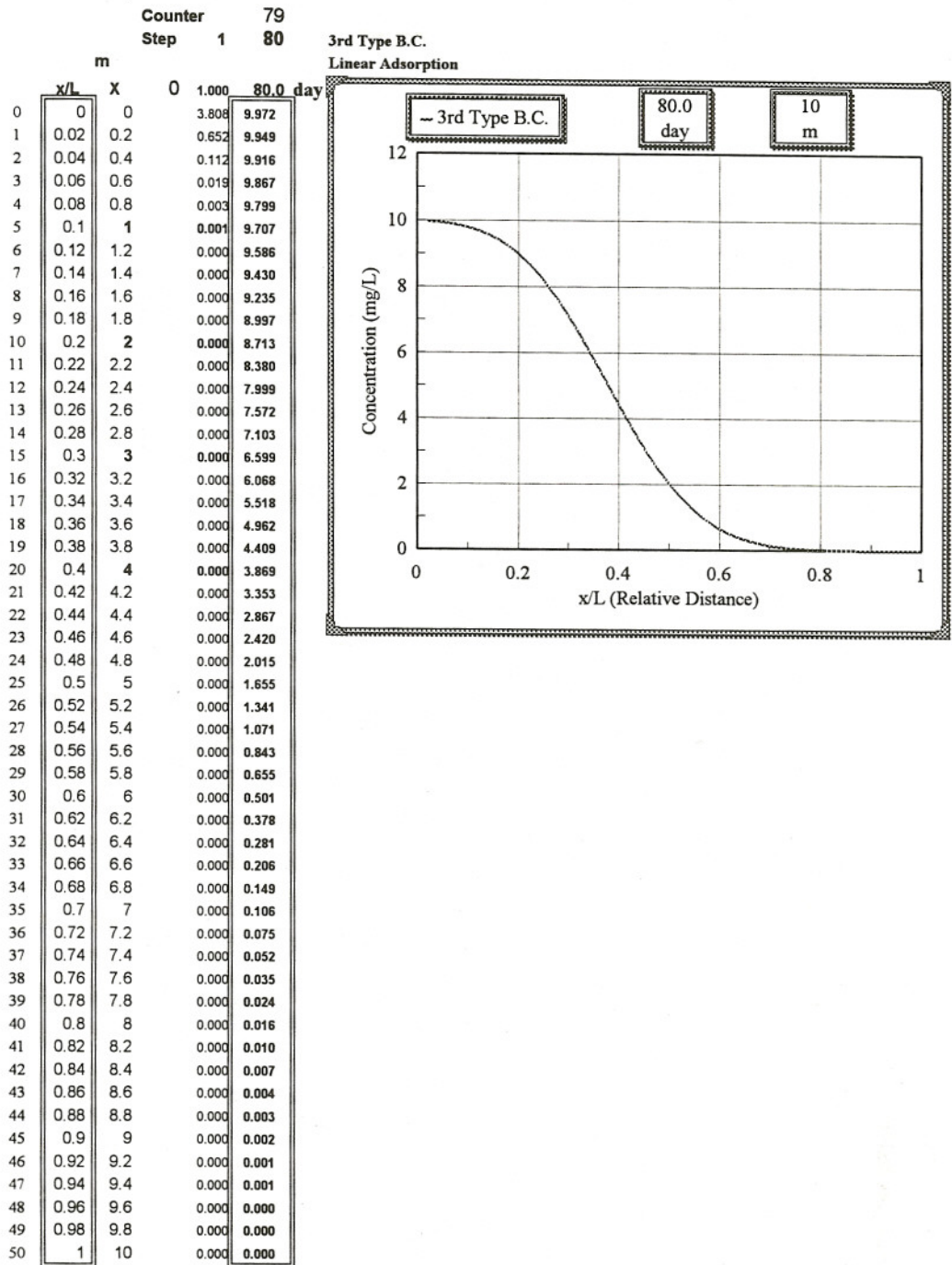


Figure B2 An example of program output for a contaminant transport in porous media.