Environmental Fate Investigation of Chromium Contamination
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YEAR 1

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ABSTRACT

In order to establish clean-up strategies for chromium contaminated sites, chromium leaching behavior from chromium contaminated soil (Cr-soil) must be fully understood. Cr-soil samples were collected from Liberty State Park, New Jersey. Simulated rainwater (pH 4.3, typical of the Mid-Atlantic region) was used as the water source.

The Cr-soil samples had a pH_{zpc} of 6.8, which may be attributed to its high iron content (22%). Results of SEM-EDAX and wet extraction analysis indicated that the Cr-soil samples contained significant amount of Fe, Ca, Al, Mg and Cr. The soil pH ranged from 8.00 to 8.27, indicating that it was an alkaline material. The average organic matter content of the soil was ca. 9% by weight.

Equilibrium and kinetics leaching experiments were conducted. For the equilibrium studies, factors such as the solids concentration and pH (which affect the amount of Cr leached) were investigated. Results indicated that the amount of Cr(VI) leached increased with increasing Cr-soil concentration. pH played a significant role in the Cr-leaching. At low pH (< 2.5), Cr(VI) leached was not detected in the leachate. This may be attributed to the presence of ferrous ion and organic matter in the soil which tends to keep Cr in the Cr(III) form and the adsorption of chromate species onto acidic Cr-soil. It is speculated that the amount of Cr(VI) and Ca(II) leached may be governed by the solubility of $CaCrO_4$ solid. An apparent solubility product of $CaCrO_4$, $pK_{sp} = 8.5$, was obtained, suggesting that calcium chromate is the major Cr-phase in the soil. By using "treated" Cr-soil (no organic matter content) in the equilibrium study, results showed that the amount of Cr(VI) leached was much greater than for untreated Cr-soil, suggesting that the organic matter may be involved in the leaching process by drastically decreasing the Cr(VI) solution concentration. The leaching behavior of Cr(III) from the Cr-soil as a function of pH was similar to that of Fe(III), Al(III), and Mn(II). No soluble Cr(III) was detected between pH 5.0 and 11.5, which can be attributed to the presence of chromium hydroxide, $Cr(OH)_3(s)$ and other precipitates such as $(Cr_xFe_{1-x})(OH)_3(s)$, in the solution. The amount of Cr(III) leached may therefore be limited by the solubility of $(Cr_xFe_{1-x})(OH)_3(s)$. In the kinetic studies, factors such as temperature, mixing rate, and the soil-to-water ratio were investigated. Results showed that higher reaction temperatures and mixing rate, and the lower soil-to-water ratio caused larger amounts of metals to be leached. The leaching kinetics were well described by the modified Freundlich equation. The activation energy values for chromium dissolution from Cr-soil samples studied were from 11.91 to 15.46 KJ/mole. It is suggested that under the experimental conditions of this study, the leaching reaction is a diffusion-controlled process.

KEY WORDS: Chromium, Cr(VI), Cr(III), soil, leaching, pH, temperature, simulated rainwater, kinetics.

INTRODUCTION

Soil contamination by heavy metals is extremely troublesome because of the environmentally persistent characteristics of these contaminants. Unlike organic compounds, metals are refractory and can not be readily degraded or detoxified, except for a few that are volatile. Toxic metals pose a long term pollution problem to the environment. Many severe problems have been reported around chromium contaminated sites throughout the United States. In order to minimize the threat of groundwater pollution by Chromium and to establish clean-up strategies, the leaching behavior of Chromium from chromium contaminated soil (Cr-soil) must be fully understood.

Chromium (Cr) is a transition metal which exists in mainly three oxidation states, i.e. Cr(II), Cr(III), and Cr(VI). However, the predominant oxidation states are Cr(III) and Cr(VI) (Udy, 1956). Cr(III) is less toxic than Cr(VI) and is relatively immobile in the aqueous environment because of its strong adsorption onto soils (Amacher and Baker, 1982). Due to its inability to cross cell membranes, it is hence not readily bioavailable and is a relatively inactive genotoxic agent. In contrast, Cr(VI) is relatively mobile in an aqueous environment, because it is not as strongly adsorbed to soils as Cr(III). Cr(VI) compounds are corrosive and irritants because they tend to cross biological membranes easily owing to their solubility and diffusivity in tissue (Robertson, 1990; Finkel, 1983). As a result, Cr(VI) species are more readily bioavailable than are Cr(III) species. Unlike Cr(III), which is cationic and can form insoluble chromium hydroxide solid ($Cr(OH)_3$) with hydroxide ion, Cr(VI) form is anionic and soluble, existing in aqueous solution as a complex anion. Currently, the limit of soluble Cr in drinking water is 0.05 mg/l (10^{-6} M) (U.S.E.P.A., 1984), which is also the industrial effluent standard.

Adsorption/desorption reactions play a significant role in controlling the aqueous concentration of Cr species in soils and thereby their mobility. Cr(VI) can be strongly adsorbed to activated carbon (Neufeld, 1990; Huang, 1977). Chromate can be adsorbed by soil colloids including Fe, Al oxides, kaolinite, and montmorillonite (Zachara et al. 1988; Rai et al. 1988; Zachara et al. 1987; Honeyman, 1984; Griffin et al. 1977; MacNaughton, 1977). The adsorption of Cr(VI) by kaolinite and mortmorillonite decreases as pH increases and no adsorption occurs at pH > 8.5. The adsorption of chromate under acidic solution was attributed to the electromobility behavior of kaolinite and mortmorillonite. Because the pH_{zpc} of kaolinite and mortmorillonite are 4.2 and 2.5 respectively, positive charge on the clay surface increases as the pH is lowered. As a result, the extent of anionic chromate adsorption increases. Hsieh et al. (1988) have shown that the Cr(VI)

2

adsorbs onto soil at low pH and no precipitation takes place at any pH. Mayer and Schick (1981) have shown that Cr(VI) can be removed from the sediment/water interface by a two-step reaction sequence: reduction followed by adsorption on kaolinite or alumina oxide surfaces. MacNaughton (1977) has found that adsorption of Cr(VI) from aqueous solution onto alumina oxides is relatively pH-independent below pH 4.0, when the surface of Al_2O_3 is positively charged; and that a strong columbic attraction takes place for between the Al_2O_3 surface and anionic Cr(VI) species. As the pH increases above 4.0, Cr(VI) adsorption decreases, reaching approximately zero at pH 7.0 to 8.5 which is near the pH_{zpc} of alumina oxide. Zachara et al. (1987) have reported that amorphous $Fe_2O_3 \cdot H_2O$ or ferrihydrate, which is common surface coating of subsoil particles, has a particularly high Cr(VI) adsorption capacity. Adsorption of CrO_4^{2-} on $Fe_2O_3 \cdot H_2O$ decreases as the pH increases. It has been suggested that CrO_4^{2-} adsorb onto soil colloids as outer sphere complexes (Hayes et al. 1987; Zachara et al. 1988). As such, the CrO_4^{2-} ion is not held on soil particles strongly, so that it is easily leached from the soil particles under certain conditions. Zachara et al. (1988) have reported that chromate binding is reversible with respect to pH and is depressed in the presence of SO_4^{2-} and dissolved inorganic carbon, which can compete for adsorption sites.

Redox reactions are another important group of metal transformation process in soils. The oxidation of Cr(III) to Cr(VI) by manganese oxides is thermodynamically possible in soils (Amacher and Baker, 1982; Bartlett and James, 1979). 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). Neufeld et al. (1990) have reported that the reduction of Cr(VI) to Cr(III) occurs only under acidic conditions. Early and Rai (1989) have reported, in the study of dissolution of hematite and biotite, that the Fe(II) species release to solution more rapidly than Fe(III), despite the higher content of Fe(III) than Fe(II) in the solid phase. Therefore, Cr(VI) can be rapidly reduced to Cr(III) by Fe(II) and organic materials under acidic conditions (Early and Rai, 1991; Early and Rai, 1989; Amacher and Baker, 1982; Bartlett and Kimble 1976). In most surface soils, organic compounds can be expected to be the primary reductants for Cr(VI) species (Bartlett and James, 1988). In the presence of Fe(II), Cr(VI) can be reduced to Cr(III). Many researchers have reported that Cr(III) can coprecipitate with $Fe(OH)_3$ and form $(Cr_xFe_{1-x})(OH)_3(s)$ under acidic conditions (Eary and Rai, 1991; Eary and Rai, 1989; Eary and Rai, 1988; Sass and Rai, 1987; Cranston and Murray, 1978). The objective of this study was to characterize the physical and chemical properties of chromium contaminated soil (Cr-soil) and to investigate the Cr leaching

3

behavior of Cr-soil through batch equilibrium and kinetic experiments.

4
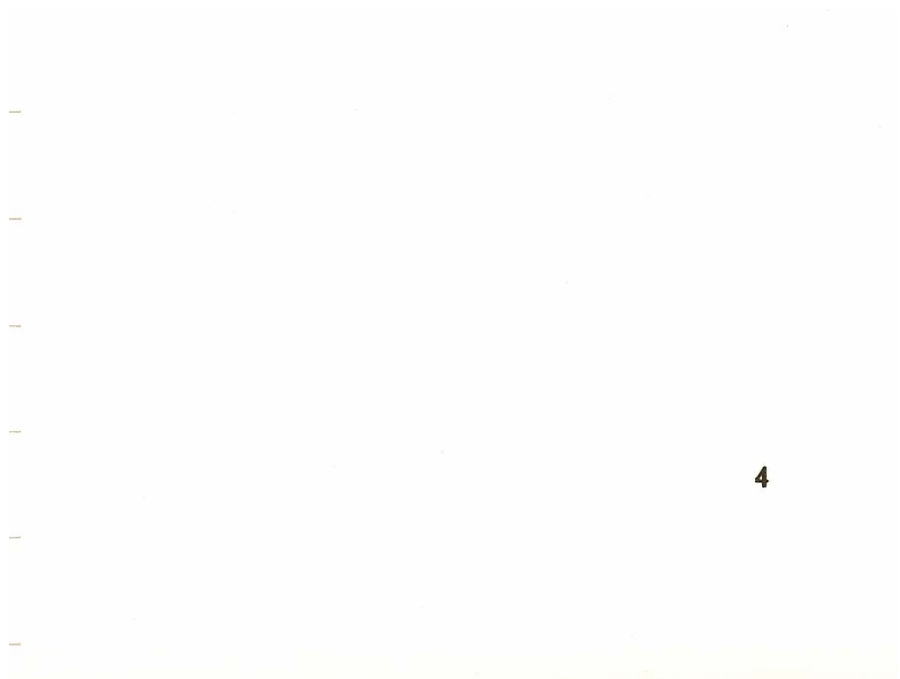
MATERIALS AND METHODS

1. Chemicals and Soil Samples

All chemicals used in this study were ACS certified grade and obtained from either the Fisher Scientific Company or the Aldrich Chemical Company. Chemicals were used as received. The chromium containing soil samples were collected from site 15, located in Liberty State Park, Hudson County, New Jersey. Composite Cr-soil samples were taken to depth of approximately 6 cm at three different locations.

2. Characterization of Cr-soil Samples

The particle size distribution of the Cr-soil samples was analyzed by sieve analysis (ASTM standard sieves). Specific surface area of the Cr-soil samples was determined by dye adsorption (Smith and Coackley, 1983). The electrophoretic mobility was determined using a zetameter (Lazer Zee Meter, Pen Kem Inc, Bedford Hills, NY, Model 500).

The soil pH was measured both in water suspensions and in 0.01M $CaCl_2$ solutions at a 1:1 soil to solution ratio with a pH meter (Model 3500 digital pH meter, Beckman, Irvine CA). This method is described as ASTM D 4972-89 (1990), a standard test method for soil pH.

The soil organic matter content was obtained from the combustion method (Nelson et al., 1982). The Cr-soil samples are placed in a furnace (400 °C) (Type 1300 furnace, Thermolyne Co. Dubuque Iowa) for 4 hours. The organic matter content was then calculated from the loss on combustion.

Metals in the soil were determinated with energy dispersion analysis by X-ray (SEM-EDAX) (Phillips 501 scanning electron microscope and Phillips EDAX 9100) and by wet extraction. Three wet extraction methods were used to determine the elements of Cr-soil samples. For method I, the soil samples were predigested with concentrated HNO_3, followed by the addition of a solution with a volume ratio of 2:5:1 = $HClO_4$:HF:H_2SO_4, using a 250 ml Teflon beaker, for 6 hours at 60-80 °C (Reisenauer, 1982). For method II, the soil samples were combusted in a furnace (400 °C) for 4 hours, then a 1:1 volume ratio of concentrated HCl-HF was added in a 250 ml Teflon beaker and 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 in a 250 ml Teflon beaker and digested for 6 more hours at 60-80 °C (Delfino and Enderson, 1978).

3. Analytical Methods

The metals extracted from soil were determined with an atomic absorption spectrophotometer (AA) (Perkin-Elmer, Model Zeeman 5000) (APHA, 1985), except for Fe(II) and Cr(VI), which were analyzed by a colorimetric method using a UV-visible spectrophotometer.

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 (510 nm, APHA, 1985). The ferrous iron and total iron reagent powder pillows were purchased from Hach Co. Fe(III) was determined from the difference of total Fe and Fe(II). Cr(VI) was analyzed by the reddish-purple (540 nm) 1.5-diphenycarbohydrazide-chromate complex in an acidic medium using a UV-visible spectrophotometer (Hitachi Perkin-Elmer 139). The procedures followed those of ASTM method D 1687-86 (1990, standard test methods for Cr in water). Total Cr was determined by oxidizing the Cr(III) to Cr(VI) with potassium permanganate, then determining the total Cr as Cr(VI). Under low concentration of total Cr(VI) (i.e. $< 10^{-4}$ M) and acidic pH, the general oxidation reaction can be written as follows:

$$5Cr^{3+} + 3MnO_4^- + 8H_2O \rightarrow 5HCrO_4^- + 3Mn^{2+} + 11H^+ \tag{1}$$
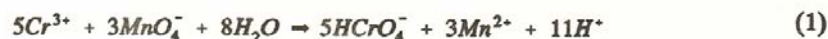
Cr(III) was determined by the difference of total Cr and Cr(VI).

4. Simulated Rainwater (Acid Rain)

Synthetic rainwater was prepared to simulate the rain in the Mid-Atlantic coastal region, following the standard reference methods of the National Bureau of Standards (Koch, 1986). Table 1 shows the chemical composition of simulated rainwater used in leaching experiments. As seen in Table 1, the average values for rainwater from Lewes, DE and Brookhaven, NY were used. Note that many of the average values are greater than the NBS certified SRM 2694 simulated rainwater. This is because in the coastal location of the Mid-Atlantic area excess sea salt (i.e. Na^+, Mg^{2+}, Ca^{2+}, and Cl^-) is commonly present in the rainwater. The high acidity of the Mid-Atlantic rainwater may be attributed to industrial activities. However, the average pH value is close to the NBS reference rainwater value.

5. Leaching Experiment

5. Leaching Experiment

5.1 Equilibrium Study

The equilibrium study on Cr-soil leaching was conducted with batch reactors. The soil samples were first air dried then ground with a ball mill (Norton, Chemical Process Products Division, Akron, OH) and sieved through a 180 μm sieve (ASTM # 80 sieve). To a series of plastic bottles, containing 100 ml of simulated rainwater, the initial pH was adjusted by 1N NaOH and/or H_2SO_4 (if needed), then a given amount of the Cr-soil was added. The samples were shaken on a shaker (Eberbach Co., Ann Arbor, MI) at a 150 excursions per minute for mixing. After shaking for 24 hours, the equilibrium pH was recorded and aliquot of the suspensions were taken and filtered (Gelman, 0.45 μm). The concentrations of Cr in the supernatant was determined. The concentrations of other metals in supernatant were also analyzed with AA except that the Fe(II) and Fe(III) ions were analyzed with the colorimetric method as described above.

5.2 Kinetic Study

In effect of temperature experiment, solution soil-to-water ratio was fixed at 1:200 and the samples were shaken on a temperature controlled water bath shaker (GCA Precision Scientific, Chicago, IL) at mixing rate 150 excursions per minute for a specific preselected time intervals.

In effect of mixing experiment, solution soil-to-water ratio was fixed at 1:200 and the same experimental procedures were used as described in equilibrium study (section 5.1), except different mixing speed and reaction time intervals were operated.

In effect of soil-to-water experiment, the same experimental procedures were used as described in equilibrium study (section 5.1), except different solution soil-to-water ratio and reaction time intervals were operated.

7

QUALITY CONTROL - QUALITY ASSURANCE PROCEDURES

1. Soil Sampling and Sample Custody Procedures

The field Cr-soil samples were collected in conjunction with NJDEP personnel from Liberty State Park (site 15). After sampling, the Cr-soil samples were immediately sealed in 10-gallon opaque black plastic buckets during the transportation and preservation stage. All sampling information and site data were labeled on a tag attached to the bucket.

2. Soil and Water Analysis

Two techniques were applied in water and soil analysis: replicate samples and spiked samples. Three or more than three replicate samples were chosen, whatever twas necessary to permit statistical evaluation of the data produced. Replicate samples were analyzed using the same procedure and instrumentation so as to provide an indication of analytical variability and error. For the spiked sample procedure, a known quantity of the standard solution of interest was added to a sample at concentrations where the analytical method was known to be accurate. For a single sample, one spiked sample was analyzed. For more than 8 samples, three spiked samples were analyzed.

3. Data Quality Requirements

Parameter	Sample Matrix	Detection Limit	Quantitation Limit	Precision	Accuracy
pH	Wastewater	±0.01	1.00 - 14.00	±1%	99%
Metals	Wastewater (Details in EPA 303)				
Cr(VI)	Wastewater	0.01 mg/l	0.5 mg/l	±5%	99%
Cr(III)	Wastewater	0.01 mg/l	0.5 mg/l	±10%	95%
Total Cr	Soil-Wastewater	0.01 mg/l	0.5 mg/l	±5%	95%
Soil pH	Soil-Wastewater	± 0.01	1.00 -14.00	±1%	99%
Organic Matter	Soil	0.1%	100%	±10%	95%
pH_{zpc}	Soil	0.1 mv	± 100 mv	±5%	95%
Surface Area	Soil	0.05 m^2/g	---	±5%	99%
EDAX	Soil	---	---	±5%	95%
Particle Size Distribution	Soil	38 μm	25 mm	±5%	95%

NOTE: Method of detection limit, quantitation limit, precision, and accuracy was calculated according to ASTM D1687-86 p. 366, 1990. The detection concentration range, 0.01-0.5 mg/l, was based on the practical detection level. The range can be extended by appropriate sample dilution. The ±5% precision means that any data within ±5% bias was acceptable.

4. Data Quality Assessments

Only data which fell in the stated precision region were selected to represent the characteristics of a population. The data precision value was controlled within a ±5% range with respect to a standard calibration curve or by comparing the results to other values available from the literature.

5. Calibration

For each analysis, a calibration curve was prepared which covered the entire working range of the method. The curve was constructed using at least four points, including one near the upper limit (quantitation limit) of the concentration range and one near the lower limit (quantitation limit) with a reasonably equitable distribution of the remaining points. A recalibration was carried out if new reagents are prepared or different operators were involved. At least one blank and four chromium standard solutions were analyzed to verify the original test calibration each time that the test was performed. A chart was prepared showing the calibration curve slope on the various dates when samples are analyzed. This chart aided in establishing errors in reagent or standard preparation.

6. Quality Control Checks

One each of four types of quality control samples (spiked, replicate, reagent check, and blank samples) were used in one group of samples for this project. However, if more than 8 samples were analyzed, an appropriately larger number of quality control samples was used.

7. Documentation, Data Reduction, Systems Audit and Reporting

The data were recorded daily in a laboratory notebook and permanently preserved. For data reduction, the data were tabulated and/or graphed after statistical analysis. The QA/QC officers (principal investigators) checked the data and quality control sample data through the quality control chart.

RESULTS AND DISCUSSIONS

1. Characterization of Cr-soil Samples

The grain size distribution of Cr-soil samples was determined by ASTM standard sieve analysis. The results showed that these Cr-soil samples consist predominately of sand-sized particles with a small percentage of silt-sized particles. The results of SEM-EDAX analysis of Cr-soil samples indicated that the major elements of Cr-soil were Ca, Fe, Cr, Al and Si, and the minor elements were Mg, K, and Ti (Table 2). The appreciable amount of calcium in Cr-soil suggested that the majority of chromium ore exists in the Cr-soil as calcium chromate ($CaCrO_4$). Two methods were used to determine the total Fe and Cr in the extraction solution: atomic absorption spectrophotometry and visible spectrophotometry, in which total Fe is determined by using Hach ferroVer iron reagent and total Cr is determined by oxidizing the Cr with permanganate followed by analysis of Cr(VI). Table 3 shows the major elements extracted from the Cr-soil samples by three wet extraction methods. It can be seen in Table 3 that extraction method 1 and 2 extracted more metals than did method 3. Obviously, hydrofluoric acid (HF) plays a significant role on metal extraction from Cr-soil, especially for extraction of total Cr, Fe, Mg, and Al, in this study. The use of HF insured the complete release of metals from Cr-soil mineral matrices, however great care must be taken during the extraction. The total Cr and Fe obtained from AA yielded similar values to those from the colorimetric method. A 5% difference was estimated between those two analytical methods. In general, about 2.5% by weight of total Cr, and 22% by weight of total Fe were leached from the Cr-soil. From Table 3, one can visualize that Fe, Cr, Mg, Ca, and Al are the major extractable elements in the Cr-soil. There are no major differences of chemical composition among these three Cr-soil samples, except that the Ca content in these three Cr-soil samples follows the order: sample III (63 g/kg) > sample II (53 g/kg) > sample I (46 g/kg). The content of these major ions agree with the results of surface spectroscopic analysis (SEM-EDAX) (Table 2). Trace metals such as Na, K, Mn, Zn, Ni, Pb, Cu, and Cd were also detected by surface spectroscopic analysis.

The major physical-chemical properties of these three Cr-soil samples are shown in Table 4. The organic matter was directly estimated from loss on ignition. The high organic matter content (about 9%) may contribute toward to the reduction of Cr(VI) to Cr(III) under acidic conditions (Bartlett and Kimble, 1976). The surface area of Cr-soil samples was determined by dye adsorption. The surface area among these three Cr-soil samples was identical (Table 4): sample III (39.0 m^2/kg), sample II (37.2 m^2/g), and sample III (36.6 m^2/g). The high soil pH value indicated that the Cr-soil

11

is a highly alkaline material (the major chromium ore existing in the Cr-soil is probably $CaCrO_4$) and has strongly acid buffering capacity.

The zeta potential determined from the electrophoretic mobility measurements of these three Cr-soil samples as a function of solution pH is shown in Figure 1. It should be noted that, at a given pH, the zeta potential varied with the ionic strength in the solution. The higher the ionic strength is, the less the zeta potential is. This is caused by electrical double layer compression. The point of 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 positive charge nature of the soil was indicative of a multicomponent solid mixture (Elliott and Sparks 1981). In this study, an iron content of about 22% by weight (Table 3) in the Cr-soil samples was observed. 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 (i.e. γ-Fe_2O_3 [6.7], Fe_3O_4 [6.5], amorphous $Fe(OH)_3$ [8.5-8.8], and α-FeOOH [5.9-6.7], Stumm and Morgan 1970, Park 1965), it is speculated that the neutral pH_{zpc} value of Cr-soil particles is attributed to high iron content in the Cr-soil.

2. Leaching experiments

Leaching experiments were conducted by equilibrium and kinetic studies. In the equilibrium study, factors such as solid concentration and pH, which may affect the amount of Cr leached, were investigated. In the kinetic study, factors such as temperature, mixing rate, and the soil-to-water weight ratio were investigated.

2.1 Equilibrium Study
2.1.1 Effect of Solid Concentration

Figure 2 shows the amount of Cr(VI) leached from these three Cr-soil samples as a function of Cr-soil concentration in simulated rainwater with an initial pH of 4.30. After 24-hours reaction, the solution had an average final pH of 8.30, 8.1, and 7.9 for samples I, II, and III, respectively. From Figure 2, it is seen that the amount of Cr(VI) leached linearly increased with increasing Cr-soil concentration and follows the order of sample I > sample II > sample III. The relationship between Cr(VI) leached (C, mg) and Cr-soil amount (S, g) is: $C = 0.163 S$ for sample I, $C = 0.093 S$ for sample II, and $C = 0.032 S$ for sample III. It must be mentioned that the Cr(VI) leached equation

12

is only valid for dilute aqueous solution i.e. soil-to-water weight ratio < 0.01.

2.1.2 Effect of pH

The amount of Cr(VI) leached under different pH values are shown in Figure 3. Results show that pH plays a significant role in the Cr dissolution from Cr-soil. At low pH value (pH < 2.5), no Cr(VI) was detected. At a pH of between 2.5 and 6.0, the amount of Cr(VI) leached sharply increased, reaching a maximum value at pH about 6.0. At pH > 6.0, the Cr(VI) leached slowly decreased to pH 11.0 then increased until pH 12.5. The major Cr(VI) species leached from Cr-soil will be $HCrO_4^-$ at acidic pH and CrO_4^{2-} at alkaline pH. The absence of Cr(VI) at pH < 2.5 was in excellent agreement with others. Zachara et al. (1989) have found that chromate adsorption occurs on acidic soil enriched in kaolinite and crystalline Fe oxides. Hsieh et al. (1988) have shown that the Cr(VI) adsorbed on the soil at low pH did not precipitate at any pH. Neufeld et al. (1990) have reported that the reduction of Cr(VI) to Cr(III) occurred only under acidic conditions. Huang and Bowers (1976) have revealed that the maximum Cr(VI) adsorptive capacity of activated carbon occurred at pH 2.5 and decreased rapidly between 2.5 and 7.1. They also reported that the chromium was recovered only in the Cr(III) form under strong acid carbon regeneration, which indicated that the Cr(VI) was reduced under acidic conditions.

Figure 3 also shows the effect of soil organic on Cr(VI) leached from the Cr-soil. The experiment was conducted by heating the Cr-soil samples in the furnace (400 °C) for 4 hours in order to remove the organic matter from the soil. The soil sample was designated as "treated" Cr-soil. It is assumed that the "treated" soil contains no organic matter. Results showed that the amount of Cr(VI) leached from the "treated" soil was much greater than from the "untreated" soil (having about 9 % organic matter). The organic matter can reduce the Cr(VI) species to the Cr(III) species, and dramatically decrease the solution concentration of Cr(VI) over a wide range pH, i.e. 2 - 11. It is speculated that the different amount of Cr(VI) leached from these three "untreated" Cr-soil samples may be attributed to different soil characteristics, specifically the soil organic matter. Apparently, the organic matter plays a significant role on Cr(VI) leached from the Cr-soil. On the contrary, no major difference in the amount of Cr(VI) leached among all "treated" Cr-soil samples was observed. This indicates that these Cr-soil samples may have similar chemical composition. The results of wet extraction analysis (Table 3) and physical properties analysis (Table 4) showed that these soil samples were almost identical in their chemical composition. It must be noted that all three Cr-soil samples were collected from the same site.

13

The pH effect on Cr(III) leached from the Cr-soil samples is shown in Figure 4. From Figure 4, it can be seen that the leaching behavior of Cr(III) from Cr-soil is similar to that of Al, Fe, and Mn (Figure 7-10), in that the amount of metals leached increased sharply with decreasing pH. Apparently, pH has a significant effect on the leaching behavior of Cr(III) in Cr-soil. At pH < 4.0, the amount of Cr(III) leached increased sharply. No soluble Cr(III) was detected at pH > 5.0 (except that a small amount of Cr(III) was present at 10 < pH < 12.0) which can be attributed to the formation of chromium hydroxide, $Cr(OH)_3$ and/or other precipitates such as $(Cr_xFe_{1-x})(OH)_3$ (Eary and Rai, 1991; Eary and Rai, 1989; Eary and Rai, 1988; Sass and Rai, 1987; Cranston and Murray, 1978). The results of Cr(VI) and Cr(III) dissolution agree with that 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 depend on solution pH. They have found that as pH increases from 4 to 9, the removal of Cr(III) increases, but the reverse is found for Cr(VI). Under their experimental conditions, they have concluded that the adsorption is the main mechanism responsible for both the Cr(III) and Cr(VI) removal.

From Figure 3, little Cr(VI) was found at pH < 3 which may be attributed to the adsorption of Cr(VI) onto the soil and the reduction of Cr(VI) to Cr(III) by Fe(II) and organic matter. The anionic chromate ion can adsorb on acidic soil, which is related to the electromobility behavior of Cr-soil (pH_{zpc} = 6.80, Figure 1). When the solution pH is less than pH_{zpc}, the soil surface is characterized by positive charge. In acidic systems, the anionic chromate species can be adsorbed on positively charged sites of soil particles. Decreasing solution pH will increase positive surface sites, causing increases in Cr(VI) adsorption. It is speculated that the Fe (22 % in Cr-soil) and other oxides (Table 3) may play a significant role in chromate adsorption on Cr-soil. Clearly, chromate adsorption was drastically influenced by pH. No chromate adsorption can occur in high solution pH, resulting appreciable amount of chromate leached from Cr-soil at high pH region. Another possible reason for the small amount of Cr(VI) leached at pH < 3.0 is that the Cr(VI) ion may be reduced to Cr(III) by Fe(II) and/or organic matter in the Cr-soil. The Cr(III) then coprecipitate with noncrystalline Fe oxyhydroxide (Rai et al., 1988).

Results of Ca(II) and Mg(II) leached from Cr-soil samples as a function of pH are shown in Figures 5 and 6. The appreciable amount of exchangeable bases, i.e. Ca(II) and Mg(II), leached from Cr-soil at pH < 9 indicates that the Cr-soil is a high alkalinity soil with a high acid buffering capacity. The large amount of Ca(II) found in the Cr-soil may come from two sources: (a) the origin

14

of chromium ore wastes, e.g. calcium chromate, and (b) the exchangeable cation complexes in the uncontaminated soils. It is interesting to note that the amount of Ca(II) leached follows the order of sample I > sample II > sample III. The amount of Ca(II) leached under low pH (pH < 5.5) was directly related to the soil constituent of Ca(II) found from wet extraction analysis (Table 3). The amount of Ca(II) leached was small compared with the total Ca(II) content of the Cr-soil (46, 53, and 63, mg/g for sample I, II and III, respectively) from wet extraction. This may be attributed to the precipitation of $CaCrO_4$ during leaching experiments. It is speculated that the solution concentration of Cr(VI) and Ca(II) may be governed by the solubility of $CaCrO_4$ solid. The solubility of $CaCrO_4$ from the leaching experiment is shown in Figure 11. The concentration of CrO_4^{2-} is calculated from

$$[CrO_4^{2-}] = [Cr(VI)] \left(\frac{K_a}{K_a + [H^+]}\right) \tag{2}$$

where [Cr(VI)] is the measured Cr(VI) concentration, K_a is the equilibrium acidity constant of $HCrO_4^-$. A K_a value of $10^{-6.58}$ and an ionic strength 0.025 M was used (Table 5). By comparing the theoretical solubility of $CaCrO_4$ ($pK_{sp} = 3.15$, Dean, 1985) and experimental data from this study, using the log $[CrO_4^{2-}]$ versus pH diagram, it is found that, for all three Cr-soil samples, although the trend is similar, the observed CrO_4^{2-} concentration ($log[CrO_4^{2-}]$) is far lower than the theoretical values ($pK_{sp} = 3.15$). This can be attributed to the heterogeneity of Cr-soil samples, the aging time (24 hours) of $CaCrO_4$ precipitates, and the presence of other reactions (such as adsorption, redox reaction, ion exchange, and other precipitations). It is interesting to note that the concentration of Ca leached from leaching experiments ($log[Ca^{2+}] = -2.3$) is limited by the bulk concentration of Cr-soil from wet extraction analysis (log [total Ca] equal to -2.25, -2.18, -2.10 for sample I, II, and III, respectively) under acidic conditions. The solubility product of $CaCrO_4$ from experimental data is shown in Figure 12. The apparent K_{sp} is about $10^{-8.5}$ for all three Cr-soil samples. A nonlinear relationship existed between pK_{sp} and pH for pH < 7.0 region. This may be attributed to the reduction of Cr(VI) to Cr(III) by Fe(II) and organic matter and the adsorption of Cr(VI) onto solid surfaces under acidic condition. Therefore, the apparent solubility product ($pK_{sp} = 8.5$) is valid for the alkaline region.

Figures 8 and 9 show the Fe(III) and Fe(II), respectively leached from the Cr-soil. At pH < 3.5, the amount of Fe(III) leached was appreciable, probably in the form of Fe^{3+}, $Fe(OH)_2^+$, and

15

$Fe(OH)^{2+}$. 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 was less than that of Fe(III) leached. The small amount of Fe(II) observed can be attributed to redox reactions that may take place in the system. It is speculated that a portion of solution Cr(VI) species are reduced to Cr(III) at pH < 6.5 by Fe^{2+} ion. The source of Fe^{2+} may come from hydrolysis of ferruginous silicate materials in acidic solution (Eary and Rai, 1989). The reduction of Fe(III) silicates or Fe(III) oxides by organic acid may also bring Fe(II) into the solution (Hering and Stumm, 1990). The high content of organic matter (about 9%) and total Fe (about 22%) in Cr-soil samples makes it difficult to determine the predominant substance contributing to the reduction of Cr(VI) to Cr(III). However, in acidic aqueous solution, the overall reduction reaction of Cr(VI) by Fe(II) can be described as:

$$Cr(VI) + Fe(II) \rightarrow Cr(III) + Fe(III) \tag{3}$$

where $[Cr(VI)] = [HCrO_4^-] + [CrO_4^{2-}] + [Cr_2O_7^{2-}]$, $[Fe(II)] = [Fe^{2+}] + [Fe(OH)^+]$, $[Cr(III)] = [Cr^{3+}] + [Cr(OH)_2^+] + [(CrOH)^{2+}]$, $[Fe(III)] = [Fe^{3+}] + [Fe(OH)_2^+] + [Fe(OH)^{2+}]$. Depending on solution pH, total Cr and Fe, the composition of the solution, and experimental conditions, the Cr and Fe species will vary. Since Fe^{3+} and Cr^{3+} have the same charge and similar ionic radii (0.64 and 0.63 A, respectively, Lide, 1991), they are exchangeable between the solid phase formed by these ions. Sass and Rai (1987) have reported when both Cr(III) and Fe(III) are present in acidic solutions, the resulting hydroxide precipitate, $(Cr_xFe_{1-x})(OH)_3(s)$ will occur under slightly acidic to alkaline solution conditions depending on their concentration. They have proposed the following reaction mechanism:

$$xCr(III) + (1-x)Fe(III) + 3H_2O = (Cr_xFe_{1-x})(OH)_3(s) + 3H^+ \tag{4}$$
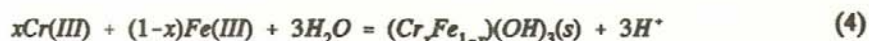
where x can vary between 0 to 1. The Cr hydroxide solids, $Cr(OH)_3(s)$ and $(Cr_xFe_{1-x})(OH)_3(s)$ can precipitate rapidly under slightly acidic to slightly alkaline solution and a general relationship:

$$log(CrOH^{2+})] = -2pH + 4.18 + 0.28(1-x)^2 - 1.79(1-x)^3 + logx. \tag{5}$$

The equation was generated from a series of solubility data and can be used to predict the aqueous Cr(III) concentration between solution pH 2-6. Sass and Rai, (1987) have reported a value of < 0.69 for x.

The solubility diagram of Cr(III)-solids, $Cr(OH)_3$ and $(Cr_xFe_{1-x})(OH)_3$, is shown in Figure

16

13. In this study, a brown precipitate was found under acidic condition. Precipitates of the same color were also found by Eary and Rai (1988) in their study of chromate reduction with ferrous ion. It is not possible to identify the brown precipitate as $Cr(OH)_3$ or $(Cr_xFe_{1-x})(OH)_3$. However, based on results from Figure 13, the concentration of Cr(III) is controlled by a solubility process rather than an adsorption reaction. The mole fraction of $Cr(OH)_3(am)$ in the precipitate, x, can be identified in the rage of 0.01 to 0.69 according to Equation (5) (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 to 0.69 because of the heterogeneous solution and short aging time (24 hours reaction time). In a similar study, Eary and Rai (1988) have shown a Fe/Cr ratio near 3.0 and concluded that the x value was 0.25, giving the Cr-Fe precipitate a solution composition of $(Cr_{0.25}Fe_{0.75})(OH)_3$; Eary and Rai (1991) have shown that the x value was significantly less than 0.25 in studying chromate reduction by subsurface soils under acidic conditions.

Figure 10 shows the leaching of Mn(II) from Cr-soil. No Mn(II) was detected at pH > 6.5. The amount of Mn(II) leached out was small comparing with the other metals. However, the oxidation of Cr(III) to Cr(VI) by manganese oxides should not be ignored. This reaction occurs despite the present of organic matter that would tend to keep Cr in its trivalent state (Amacher and Baker, 1982). Manganese oxides usually can be found more abundant in bottom soils (e.g. B-horizon) than top soils (e.g. A-horizon). Cr contamination of groundwater is highly probable at Cr waste sites, because of the possibility of oxidation of Cr(III) to Cr(VI) by manganese oxides, poor adsorption of Cr(VI) on clay minerals, and a rather small organic content in deeper soils.

2.2 Kinetic Study

2.2.1 Kinetic model

A kinetic study on Cr(VI) leaching from Cr-soil samples was conducted to establish important factors such as temperature, mixing rate, and the soil-to-water weight ratio on Cr-soil leaching. The kinetics of chromium dissolution was analyzed by a modified Freundlich equation. The Modified Freundlich equation, developed by Kuo and Lotse (1973), has the form:

$$C = k_d \, t^b \tag{6}$$

17

where

       C = concentration of Cr(VI) leached at any given time (mg Cr(VI)/g Cr-soil).

       t = time (hour).

       k_d = dissolution rate constant (hour^{-1}).

       b = constant.

By plotting [ln C] versus [ln t], the linear relationship yields an intercept, b and a slope, ln k_d. The modified Freundlich equation has been successfully used to describe phosphate desorption from soil (Chien and Clayton, 1980; Chien et al., 1980), K-Ca exchange on soils (Sparks et al., 1980), arsenite sorption and desorption on soils (Elkhatib, et al., 1984a; Elkhatib, et al., 1984b), and copper desorption from soil and clay mineral (Jopony and Young, 1987).

2.2.2 Effect of Temperature

The effect of temperature on the kinetics of dissolution of Cr(VI), Ca(II), and Mg(II) from three Cr-soil samples was studied over a temperature range of 0°C to 46°C. The results indicated that the dissolution reaction was greatly affected by temperature. The higher the temperature, the larger the amounts of these metals that were leached. In general, the initial reaction rate of Cr(VI) leached from Cr-soil was very rapid and more than 50% of the Cr(VI) leached during the first hour at all temperatures. The large amount of Cr(VI) leached at high temperature indicated that temperature plays a significant role on Cr(VI) leaching behavior. Increasing temperature usually causes a marked increase in reaction rate. The amount of Cr(VI) released remained relatively constant over a 48 hour period. All three Cr-soil samples had the same kinetic profiles in terms of Cr(VI) leaching behavior, an initial rapid dissolution followed by a relatively constant rate. At a given temperature and reaction time, the amount of Cr(VI) leached from these Cr-soil samples followed the order: Sample I > Sample II > Sample III.

The kinetics of Cr(VI) dissolution from the three Cr-soils samples were analyzed using the modified Freundlich equation (Eq. 6). Figure 14 shows the plot of [ln Cr(VI) leached (mg/g)] versus [ln t (hr)]. A linear relationship exists between [ln Cr(VI)] and [ln t] for all different temperatures over the reaction time interval studied. The linear correlation coefficient (R^2) and the standard error of estimate (SE) are listed in Table 6. The high R^2 (greater than 0.93 in all three soil samples at different temperatures) and the low SE values observed, indicates that the data can be well described by the modified Freundlich equation.

18

The apparent rate constants, k_d, for dissolution of Cr(VI) from the three Cr-soil samples at four reaction temperatures are listed in Table 6. The reaction rate constants increased as temperature increased. Leaching of Cr(VI) was more favorable at high temperatures. The rate constant, k_d, followed the order: Sample I > Sample II > Sample III.

Increasing temperature markedly increased the Cr(VI) leaching rate. The relationship between k_d and temperature can be described by the Arrhenius equation:

$$k_d = A \, e^{-\frac{E}{RT}} \tag{7}$$

or

$$\ln k_d = \ln A - \frac{E}{RT} \tag{8}$$

where

k_d = the apparent rate constant ($hour^{-1}$),

A = a frequency factor,

E = the energy of activation (KJ/mole),

R = the universal gas constant (8.3145 J/mole-$^{\circ}$K), and

T = absolute temperature ($^{\circ}$K).

Thus, the activation energy, E, can be obtained from the slope of the plot of [$\ln k_d$] vs. 1/T. The results of rate constant from modified Freundlich equation fit the Arrhenius equation well, with R^2 = 0.9642, 0.9889, and 0.9867, respectively for these three Cr-soil samples (Fig. 15). The activation energy of Cr(VI) leached from Cr-soil sample I, II, and III are 15.46, 13.56, and 11.91 KJ/mole, respectively. The low E value (< 42 KJ/mole) usually indicates diffusion-controlled processes whereas higher E values indicate that chemical reaction processes control the rate (Sparks, 1986; Sparks, 1989a). These low E values may indicate that the leaching processes is governed by a diffusion-controlled reaction, rather than a surface-controlled reaction, the latter of which usually has a high E value. We suggest that the reaction is not a chemical kinetics phenomena, because if the reaction is governed by the chemical-controlled processes, the rate will not be affected by mixing and/or flow rate (Skopp, 1986). Results of effect of mixing on Cr(VI) leaching (section 2.2.2) show that the reaction rate was affected by various mixing rates. We will discuss more about the mixing rate effect on the dissolution rate. Another factor which affects the transport rate is the

19

heterogeneity of Cr-soil. This heterogeneity results from different particle sizes, different types of surface sites, different sorption/desorption mechanisms on the various sites, and different soil constituents. From above discussion, the leaching processes is primary governed by a diffusion-controlled reaction. However, these transport-controlled phenomena do not exclude surface reactions occurring simultaneously with the dissolution processes. From Eq. 7, it is seen that, the smaller the E values, the greater the reaction rate will be.

The transport process of dissolved species from Cr-soil particle may take place in four steps (Fig. 16):

(1)   Desorption or dissolution (surface chemical reaction) occurring on the particle surfaces.

(2)   Particle diffusion (PD) occurring in the macropore of the soil particle.

(3)   Film diffusion (FD) occurring in the hydration sphere.

(4)   Bulk diffusion (BD) occurring in the solution medium, and transport of the dissolved ion species toward the bulk phase.

In general, the surface chemical reaction and particle diffusion steps are slow while film diffusion is fast (Weber, 1984). In the soil system, because of the tortuous paths, film diffusion and particle diffusion will tend to be slow. In the Cr(VI) dissolution process, the reaction mechanism is rather complicated due to the heterogeneity of Cr-soil. Several major reactions can occur simultaneously through chemical reaction, particle diffusion, and film diffusion steps, including redox, adsorption, desorption, and precipitation reactions. For example, organic substances can act as reducing agents, converting the Cr(VI) to Cr(III). The Cr(III) may precipitate as $Cr(OH)_3$. In the presence of MnO_2, Cr(III) may be oxidized to Cr(VI) bringing Cr(VI) into solution. No attempt will be made to differentiate these reaction steps in this study.

We have suggested that Cr(VI) dissolution from Cr-soil is governed by a diffusion-controlled process. The following evidence suggests film diffusion as the rate limiting step:

(1)   Low E values (11.91 - 15.46 KJ/mole) which are less than 42 KJ/mole for Cr(VI) dissolution. This indicates that film diffusion is a predominant step (Boyd et al., 1947; Reichenberg, 1957).

(2)   Film diffusion usually can not be reduced or eliminated by traditional batch reactor techniques, unless vigorous mixing is provided (Sparks, 1989b). If static or miscible displacement techniques are employed in the experiment, the mass transfer (particle

20

diffusion and film diffusion) will be pronounced in the reaction process. In this study, the mixing rate of 150 rpm used in dissolution kinetic experiments should provide an adequately dynamic condition as to reduce the significance of the particle diffusion step, making film diffusion the rate-limiting step.

(3)   Film diffusion usually predominates with small particles and particle diffusion is usually rate-limiting for large particles (Sparks, 1989b). Since the particle size used in the experiments is less than 180 μm, which can be considered small, film diffusion will be rate-limiting.

(4)   Low solids concentration usually favors film diffusion-controlled processes, while high solids concentration favors the particle diffusion control step (Sparks, 1989b). The soil-to-water ratio used in this experiment was 1:200 for Sample I and II, 1:100 for Sample III. This is considered a low solid solution concentration which will favor film diffusion as the controlling step.

The rates of Cr(VI) dissolution increased with increasing temperature in the order: Sample I > Sample II > Sample III. In general the E values of Cr(VI) leaching ranged from 11.91 to 15.46 KJ/mole. The low E values can be treated as an energy barrier for the Cr(VI) leaching from Cr-soil.

2.2.2 Effect of Mixing

The experimental conditions for the mixing effect experiment, were the same as for the temperature effect experiment, except that the temperature was controlled at 25 °C and three different mixing rates were used: 50, 150, and 250 rpm. In general, the dissolution rate curves for Cr(VI) leached were similar to those for the temperature effect studies. The dissolution rate increased with increasing mixing rate. Plots for the amount of Cr(VI) leached are shown in Figure 17 using the modified Freundlich equation. A linear logarithmic relationship between the rate constant and the mixing rate was observed for all three soil samples. Table 7 shows the correlation coefficients (R^2) and standard errors of estimate (SE) for fitting the kinetic equation. Relatively high values of R^2 and low value of SE indicate that the leaching of Cr(VI) from Cr-soil can be described by the modified Freundlich equation. A linear relationship between log k_d versus mixing rate with high value of R^2 and low value of SE is shown in Figure 18. Apparently, the mixing rate does play an important role in Cr-soil dissolution. Since the leaching rate varied with changes in mixing rate, we suggest that the leaching reaction is controlled by the mass transport step rather than the surface

21

chemical reaction.

2.2.4 Effect of Soil-to-Water Ratio

The study of the effect of soil-to-water ratio on Cr(VI) dissolution was conducted under the same experimental conditions as the temperature effect experiment except that the soil-to-water ratio was varied from 1:200 to 1:10. A similar trend was found. In general, the amount of Cr(VI) leached decreased with increasing solid concentration (soil-to-water ratio). The modified Freundlich equation was applied to describe the rates of dissolution of Cr(VI) from these three Cr-soil samples (Fig. 19). A linear log-log relationship was obtained by the modified Freundlich equation plot with a high value of R^2 and a low value of SE (Table 8). A linear relationship between log k_d vs. soil-to-water ratio with a high value of R^2 and a low value of SE is shown in Figure 20. Apparently, the solid concentration can alter the Cr(VI) dissolution rate. A large solids concentration impedes the rate of mass transfer, thereby decreasing the extent of Cr-soil dissolution. It is interesting to note that even in the high solid concentration (1:10 soil-to-water ratio), the dissolution of Cr(VI) can be described by the modified Freundlich equation.

The kinetic study of Cr(VI) showed that leaching was affected by temperature, mixing effect, and soil-to-water ratio. The results are summarized in Table 9.

22

SUMMARY AND CONCLUSIONS

Batch equilibrium and kinetic experiments were conducted to study the leaching behavior of Cr contaminated soil collected from Liberty State Park, New Jersey. Simulated rainwater (pH 4.3) typical of the Mid-Atlantic region was used. For equilibrium experiments, factors such as Cr-soil concentration, pH, and temperature were investigated. For kinetic experiments, factors such as temperature, mixing rate, and the soil-to-water ratio were investigated. The results are summarized as follows:

1. Soil characterization analyses indicated that the Cr-soil was a high pH buffering material. Ca (about 5.5% by weight), Fe (about 22% by weight), Cr (about 2.5 % by weight), and organic substances (about 9% by weight) were the major elements in the Cr-soil that affect Cr(VI) leaching behavior. Due to the high content of organic matter and Fe in the Cr-soil, the solution concentration of Cr(VI) species leached can be decreased by reduction reaction. The Cr-soil has a pH_{zpc} of 6.8 (for all three Cr-soil samples) which may be attributed to the high iron content. The neutral pH_{zpc} value may inhibit the adsorption of anionic chromate on the Cr-soil under alkaline conditions. The specific surface area of the Cr-soil ranged from 36.6 - 39.0 m^2/g.

2. In the equilibrium study, the behavior of Cr leached from the Cr-soil was affected by the Cr-soil concentration and pH. The amount of Cr(VI) leached increases linearly with the Cr-soil concentration, at least under a soil-to-water ratio of 1:100. The solution pH played a significant role in the leaching behavior of Cr-soil. At a low pH value (pH < 2.5), no Cr(VI) was leached. This may be attributed to the reduction of Cr(VI) to Cr(III) by Fe(II) and organic matter in the soil and the adsorption of anionic chromate species onto the Cr-soil. Between pH 2.5 and 6.0, the amount of Cr(VI) leached sharply increased to a maximum value at pH 6.0. At pH > 6.0, the Cr(VI) leached decreased up to pH 11.0, then sharply increased up to pH 12.5. It is speculated that the amount of Cr(VI) and Ca(II) leached may be governed by the solubility of $CaCrO_4$ solid. An apparent solubility product, $pK_{sp} = 8.5$ was obtained for $CaCrO_4$, suggesting that calcium chromate ($CaCrO_4$) is the major Cr(VI) species in the Cr-soil. The leaching behavior of Cr(III) from Cr-soil as a function of pH was similar to that of Fe(III), Al(III), Mn(II). The amount of metal leached increased sharply with decreasing pH. No soluble Cr(III) was detected at pH > 5.0 which may be attributed to the formation of precipitates such as $Cr(OH)_3(s)$ or $(Cr_xFe_{1-x})(OH)_3(s)$ and/or the adsorption

23

of Cr(III) on to Cr-soil.

3. In the kinetic study, the leaching rate was greatly affected by reaction temperature, mixing rate, and the solid-to-water ratio. The higher the reaction temperature, the higher the mixing rate, and the lower the solid to water ratio, the larger the amount of Cr(VI) that was leached. In general, the leaching of Cr(VI) from Cr-soil had similar kinetics in that the initial reaction rate was rapid during the first hour, then remained relatively constant over next the 48 hours. The leaching kinetics was well described by the modified Freundlich equation. The activation energy, E, values ranged from (11.91 to 15.46 KJ/mole, indicating that the leaching reaction was a diffusion-controlled process.

RECOMMENDATIONS AND SUGGESTIONS FOR FUTURE WORK

1. The data generated from this study will be useful for the design of chromium contaminated site remediation processes. Physical-chemical properties such as, pH_{zpc}, specific surface area, organic matter content and chemical content are variables that affect the amount of Cr leached and its leaching behavior. Based on the equilibrium studies, it is possible to characterize Cr leaching tendencies in soil. Kinetically, the time-dependence of the amount of Cr leached can be estimated from the modified Freundlich equation. The Cr leaching rate as a function of temperature, mixing rate, and soil-to-water ratio provides quantitative prediction of the amount of Cr leached.

(2). Adsorption and redox reactions play a significant role in determining the mobility of chromium in the soil system. The toxicity of chromium is governed by its oxidation state and its concentration in aquatic systems. Cr(VI) species are mobile and more toxic than the Cr(III) species. Major active redox materials, such as pyrite, Fe-oxides, Mn-oxides, and organic matter, occur in the soil system, and directly or indirectly affect the transformation of chromium in soil system, and thereby its mobility. The mechanism of chromium reaction with these active redox materials in heterogeneous systems needs to be investigated.

(3). In order to understand the behavior of chromium in concrete-water systems and to determine the mechanism controlling the movement of chromium through porous concrete materials, a set of laboratory experiments for chromium reaction with concrete materials needs to be conducted.

(4). The remediation technology needs to be developed experimentally, suitable for existing chromium waste sites in New Jersey.

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Table 1.   Chemical composition of simulated rainwater.

		Lewes, DE[1] 8/1978 - 919/87	Brookhaven, NY[1] 1973 - 1983	Average[2]	NBS[3] SRM 2694
Avg. Precip. (cm/yr)		104.8	116.3	110.5	----
H^+	($\mu eq/l$)	47.9	42.7	45.3	----
pH		4.32	4.37	4.34	4.30
NH_4^+	($\mu eq/l$)	14.0	10.3	12.1	6.2
Ca^{2+}	($\mu eq/l$)	6.0	4.6	5.3	0.5
Na^+	($\mu eq/l$)	54.2	31.3	42.7	8.7
Mg^{2+} [4]	($\mu eq/l$)	12.3	---	12.3	1.0
K^+ [4]	($\mu eq/l$)	1.8	---	1.8	1.3
SO_4^{2-}	($\mu eq/l$)	51.0	43.4	48.4 [5]	56.2
Cl^-	($\mu eq/l$)	64.5	35.9	50.2	13.2
NO_3^-	($\mu eq/l$)	23.1	18.6	20.9	8.1

Note: (1). Unpublished data -- personal contacts with Dr. Tom Church, College of Marine
Studies, University of Delaware.

(2). Composition for the preparation of simulated rainwater.

(3). Koch, W. F., "Standard reference materials: methods and procedures used at the
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(5). We added 1.2 $\mu eq/l$ SO_4^{2-} in order to satisfy the electroneutrality relationship.

Table 2. Analysis of Cr-soil chemical elements by EDAX analysis.

Soil sample No.	Constituent (Atom % Element)							
	Mg	Al	Si	K	Ca	Ti	Cr	Fe
I (T)	4.42	3.76	1.32	---	54.37	---	4.36	35.34
I (M)	2.69	5.56	2.11	---	51.75	0.90	4.42	32.58
I (B)	1.43	5.42	26.93	1.54	25.38	1.41	4.09	33.79
II (T)	1.25	18.13	52.30	7.71	5.28	2.89	2.28	10.17
II (M)	0.83	3.51	4.27	0.93	38.66	1.24	6.65	43.92
II (B)	1.63	8.80	18.30	2.68	22.47	1.64	5.48	39.00
III (T)	2.70	3.40	1.57	0.50	61.96	0.71	3.53	25.63
III(M)	1.86	4.03	4.57	0.79	44.56	1.07	5.64	37.47
III (B)	1.27	4.23	5.39	0.80	41.89	1.24	5.62	39.56

Note: T = Particle size > 4.75 mm.

M = Particle size < 4.75 mm and > 0.6 mm.

B = Particle size < 0.18 mm.

Table 3.   Comparison of various wet extraction methods for analyzing Cr-soil elements.

Soil sample No.	I			II			III		
Extraction Methods	1	2	3	1	2	3	1	2	3
(g/kg)									
Cr	25.54	23.38	5.45	24.22	21.22	6.23	33.29	27.42	6.62
Cr [¶]	26.90	22.99	5.82	27.37	21.74	6.37	33.47	28.39	6.00
Fe	222.22	240.48	103.28	182.65	188.74	111.87	210.05	232.88	117.02
Fe [‡]	232.00	253.54	127.16	171.12	185.46	127.16	216.00	241.51	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	53.1	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

Note: All metals were detected by atomic absorption spectrophotometry except as noted.

¶ by oxidizing with K_2MnO_4 and visible spectrophotometry.

‡ by Hach ferroVer iron regent and visible spectrophotometry.

Method 1. The samples were predigested with concentrate HNO_3, then a 1:2:5 volume ratio of concentrated H_2SO_4-$HClO_4$-HF was added in a 250 ml Teflon beaker continuously heating at 60-80 °C until the dark color, due to organic matter disappeared (Reisenauer, 1982).

Method 2. The samples were combusted in a furnace (400 °C) for 4 hours, then a 1:1 volume ratio of concentrated HCl-HF was added in a 250 ml Teflon beaker for 2 hours at 60-80 °C (Perkin-Elmer, 1982).

Method 3. The samples were combusted in a furnace (400 °C) for 4 hours, then a 1:3 volume ratio of concentrated HNO_3-HCl was added in a 250 ml Teflon beaker for 6 hours at 60-80 °C (Delfino and Enderson, 1978).

Table 4.   Some physical-chemical properties of the Cr-soil samples.

Soil Sample No.	I	II	III
Organic Matter (% by weight)	8.56	9.26	8.92
pH_{zpc}	6.80	6.80	6.80
Surface Area (m^2/g)	36.6	37.2	39.0
Soil pH in Distilled water	8.51	8.52	8.11
Soil pH in 0.01 M $CaCl_2$	8.27	8.25	8.00

Table 5.   The equilibrium constants [log K] for Cr(VI) and Cr(III) hydrolysis reaction.

Equilibria	I = 0.025 M log K	I = 0 M log K	Sources for log K at I= 0 M
$H_2CrO_4(aq) = HCrO_4^- + H^+$	0.33	0.20	Smith & Martell, 1981
$HCrO_4^- = CrO_4^{2-} + H^+$	-6.58	-6.51	
$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$	1.59	1.53	

Equilibria	I = 0.025 M log K	I = 0.01 M log K	Sources for log K at I= 0.01 M
$Cr(OH)_3(s) + 3H^+ = Cr^{3+} + 3H_2O$	<9.89	<9.76	Rai, et al., 1987
$Cr(OH)_3(s) + 2H^+ = Cr(OH)^{2+} + 2H_2O$	6.00	5.96	
$Cr(OH)_3(s) + H^+ = Cr(OH)_2^+ + H_2O$	<-0.44	<-0.44	
$Cr(OH)_3(s) = Cr(OH)_3^0$	<-6.84	<-6.84	
$Cr(OH)_3(s) + H_2O = Cr(OH)_4^- + H^+$	-18.20	-18.25	

Note: Activity coefficients γ for (I = 0.025 M) are calculated from Davies equation (Stumm & Morgan, 1981).

$$\log \gamma = -A Z^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 I \right), \quad \text{For } I < 0.5 \text{ M},$$

where A = constant = 0.5, Z = charge of ion, I = ionic strength = $(1/2) \Sigma(C \times Z_i^2)$.

Table 6.   Regression data from modified Freundlich equation plot and apparent rate constants. Effect of temperature on Cr(VI) leached from Cr-soil   samples.

| Soil sample | Temp. | Regression data [§] | | | | Apparent rate constant |
		a	b	R^{2} [¶]	SE [♣]	k_d [‡] (hour^{-1})
I	0 °C	-2.9637	0.2445	0.9329	0.0232	0.0516
	25 °C	-2.5351	0.2487	0.9350	0.0219	0.0795
	35 °C	-2.2740	0.1951	0.9667	0.0128	0.1029
	46 °C	-1.9442	0.1561	0.9687	0.0099	0.1431
II	0 °C	-3.3892	0.2000	0.9771	0.0108	0.0337
	25 °C	-2.9398	0.2102	0.9513	0.0159	0.0529
	35 °C	-2.7650	0.1921	0.9528	0.0151	0.0630
	46 °C	-2.5028	0.1533	0.9912	0.0051	0.0819
III	0 °C	-4.5396	0.1820	0.9548	0.0140	0.0107
	25 °C	-4.1504	0.1993	0.9435	0.0163	0.0158
	35 °C	-3.9945	0.1730	0.9366	0.0159	0.0184
	46 °C	-3.7586	0.1359	0.9755	0.0076	0.0233

§ For $\ln C = a + b \ln t$, where C is Cr(VI) leached from Cr-soil (mg Cr(VI)/g soil) and t is time (h).

¶ Correlation coefficients.

♣ Standard errors of estimate.

‡ $k_d = \exp(a)$.

Table 7.   Regression data from modified Freundlich equation plot and apparent rate constants.

Effect of mixing rate on Cr(VI) leached from Cr-soil samples.

| Soil sample | Mixing rate | Regression data [§] | | | | Apparent rate constant |
		a	b	R^2 [¶]	SE [♣]	k_d [‡] (hour^{-1})
I	50 rpm	-2.5910	0.2382	0.9894	0.0082	0.0750
	150 rpm	-2.5351	0.2487	0.9350	0.0219	0.0795
	250 rpm	-2.2584	0.1777	0.9666	0.0110	0.1045
II	50 rpm	-3.0637	0.2351	0.9787	0.0116	0.0467
	150 rpm	-2.9398	0.2102	0.9513	0.0159	0.0529
	250 rpm	-2.7731	0.1813	0.9750	0.0092	0.0625
III	50 rpm	-4.3107	0.2077	0.9482	0.0182	0.0134
	150 rpm	-4.1504	0.1993	0.9435	0.0163	0.0158
	250 rpm	-3.8661	0.1308	0.9737	0.0072	0.0209

§   For $\ln C = a + b \ln t$, where C is Cr(VI) leached from Cr-soil (mg Cr(VI)/g soil) and t is time (hour).

¶   Correlation coefficients.

♣   Standard errors of estimate.

‡ $k_d = \exp(a)$.

37

Table 8.   Regression data from modified Freundlich equation plot and apparent rate constants. Effect of soil-to-water ratio on Cr(VI) leached from Cr-soil samples.

Soil sample	Solid to water ratio	Regression data [§]				Apparent rate constant
		a	b	R^2 [¶]	SE [♣]	k_d [‡] (hour^{-1})
I	1:200	-2.5351	0.2487	0.9350	0.0219	0.0795
	1:33.3	-2.5891	0.1983	0.9178	0.0198	0.0751
	1:10	-3.1133	0.1990	0.9709	0.0115	0.0445
II	1:200	-2.9398	0.2102	0.9513	0.0159	0.0529
	1:33.3	-2.9990	0.1781	0.9850	0.0073	0.0498
	1:10	-3.6299	0.2479	0.9734	0.0137	0.0265
III	1:200	-3.8259	0.1308	0.9111	0.0154	0.0218
	1:100	-4.1504	0.1993	0.9435	0.0163	0.0158
	1:33.3	-4.1566	0.1129	0.9911	0.0036	0.0157
	1:10	-4.7973	0.1531	0.9764	0.0079	0.0083

§ For ln C = a + b ln t, where C is Cr(VI) leached from Cr-soil (mg Cr(VI)/g soil) and t is time (hour).

¶ Correlation coefficients.

♣ Standard errors of estimate.

‡ k_d = exp(a).

Table 9.   Summary of temperature effect, mixing effect, and soil-to-water ratio effect on apparent rate constants of Cr(VI) leaching from Cr-soil samples.

Soil Samples No.		Apparent rate Constants, k_d (1/h)		
		I	II	III
Temperature [1]	0 °C	0.0516	0.0337	0.0107
	25 °C	0.0795	0.0529	0.0158
	35 °C	0.1029	0.0529	0.0184
	46 °C	0.1431	0.0819	0.0233
Mixing Rate [2]	50 rpm	0.0750	0.0467	0.0134
	150 rpm	0.0795	0.0529	0.0158
	250 rpm	0.1045	0.0625	0.0209
Soil-to-water Ratio [3]	1:200	0.0795	0.0529	0.0218
	1:100	0.0158	-------	-------
	1:33.3	0.0751	0.0498	0.0157
	1:10	0.0445	0.0265	0.0083

Note: 1. Experimental Conditions: mixing rate 150 rpm, soil-to-water ratio 1:200.
2. Experimental Conditions: temperature 25 °C, soil-to-water ratio 1:200.
3. 1. Experimental Conditions: mixing rate 150 rpm, temperature 25 °C.
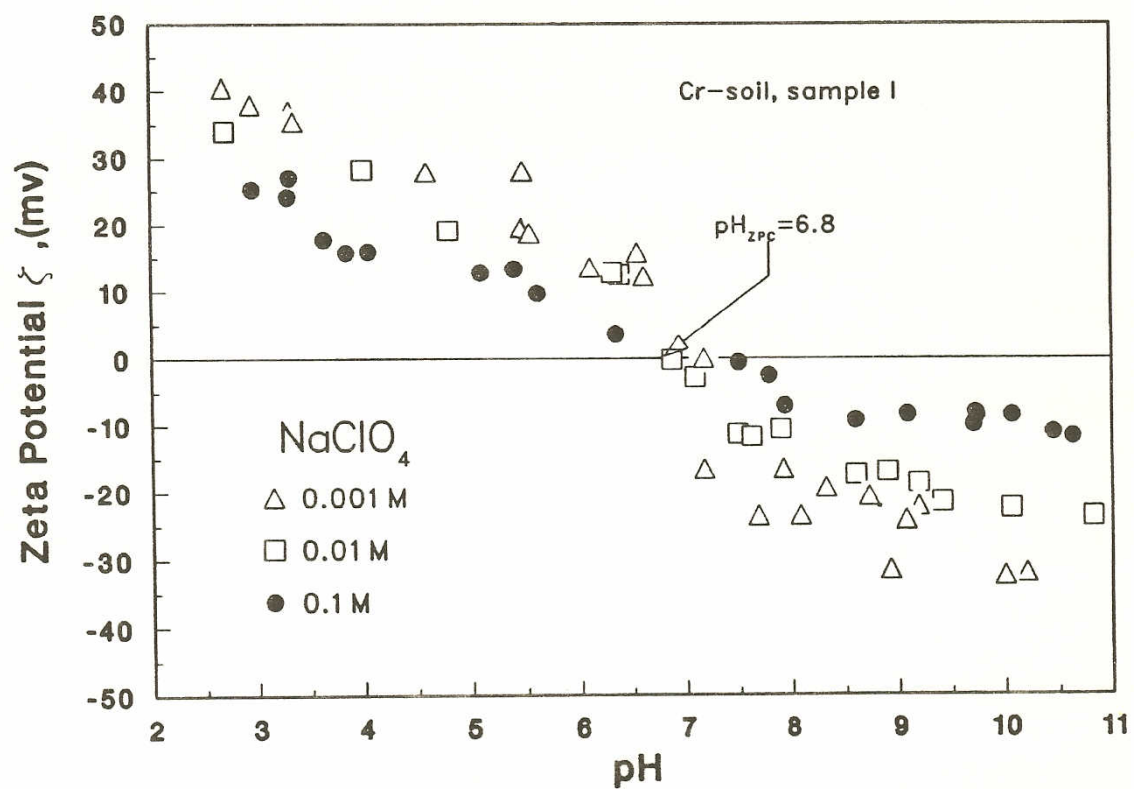
(a): sample I

Figure 1.   Electromobility measurement of Cr-soil as a function of pH at various ionic strength (electrolyte NaClO$_4$). (a): sample I, (b): sample II, and (c): sample III.   Experimental conditions: soil-to-water concentration 0.5 g/l, 25 °C.
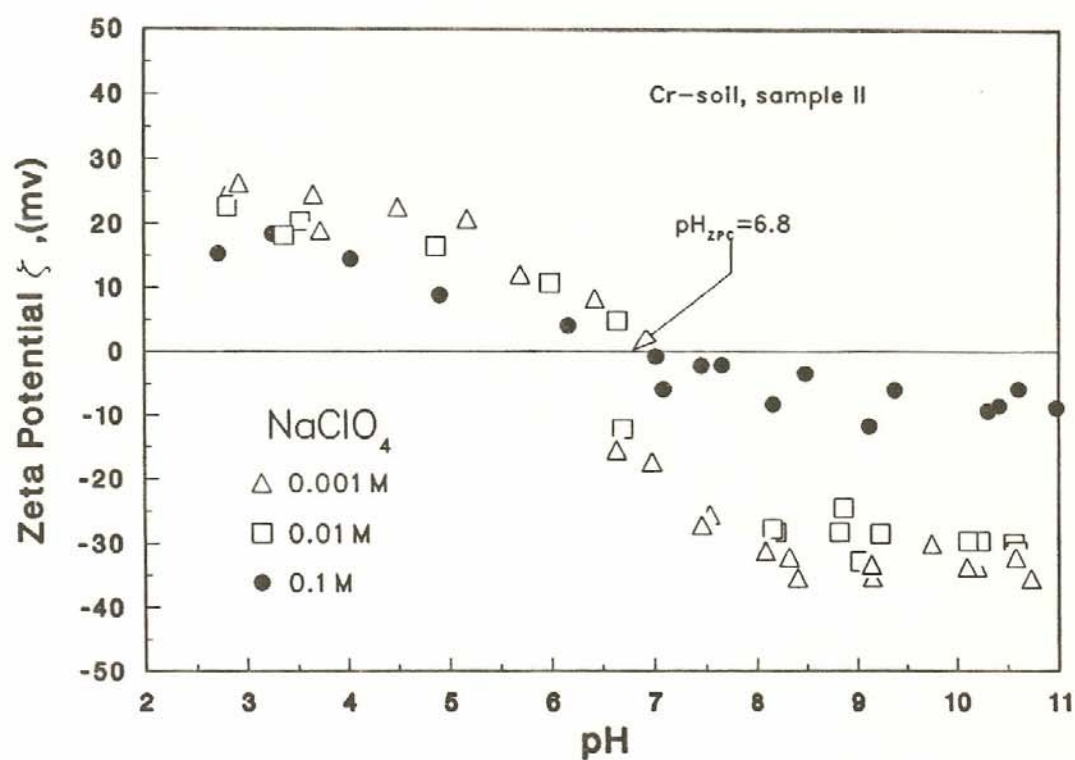
(b): sample II

Figure 1.   Electromobility measurement of Cr-soil as a function of pH at various ionic strength
(electrolyte $NaClO_4$). (a): sample I, (b): sample II, and (c): sample III. Experimental
conditions: soil-to-water concentration 0.5 g/l, 25 °C.

41
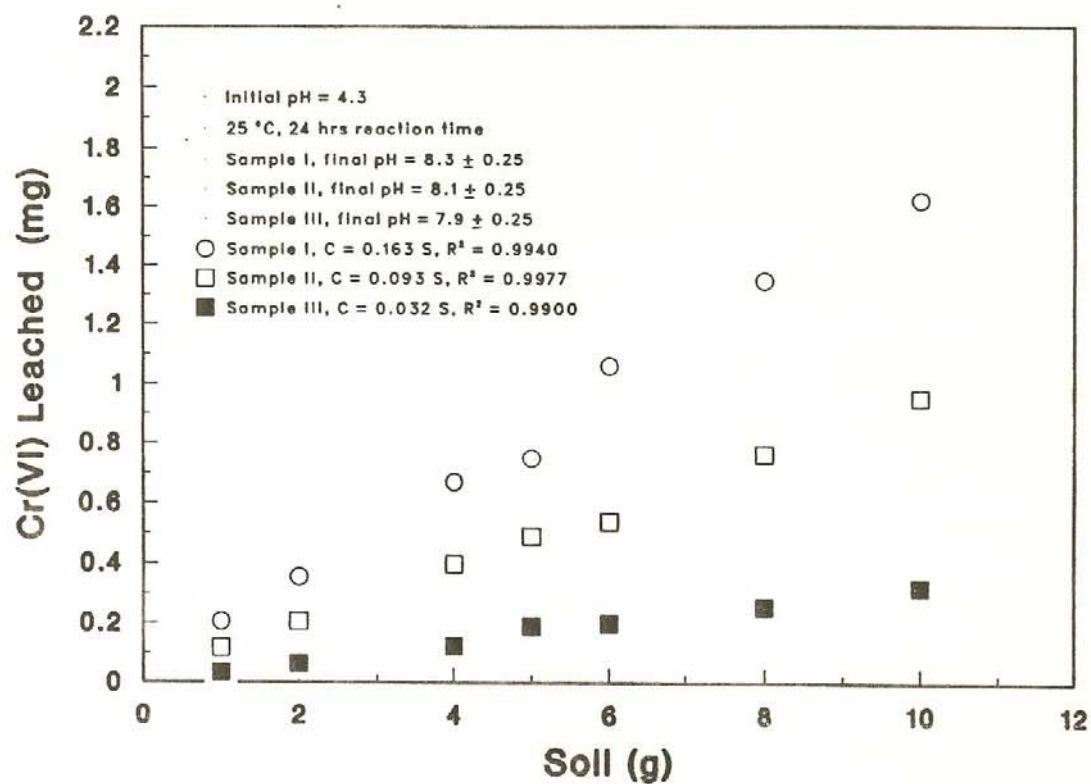
Figure 2.   Cr(VI) leached as a function of soil concentrations. Experimental conditions: 24 hours reaction time in 100 ml of simulated rain water, initial pH 4.3, 25 °C.

43
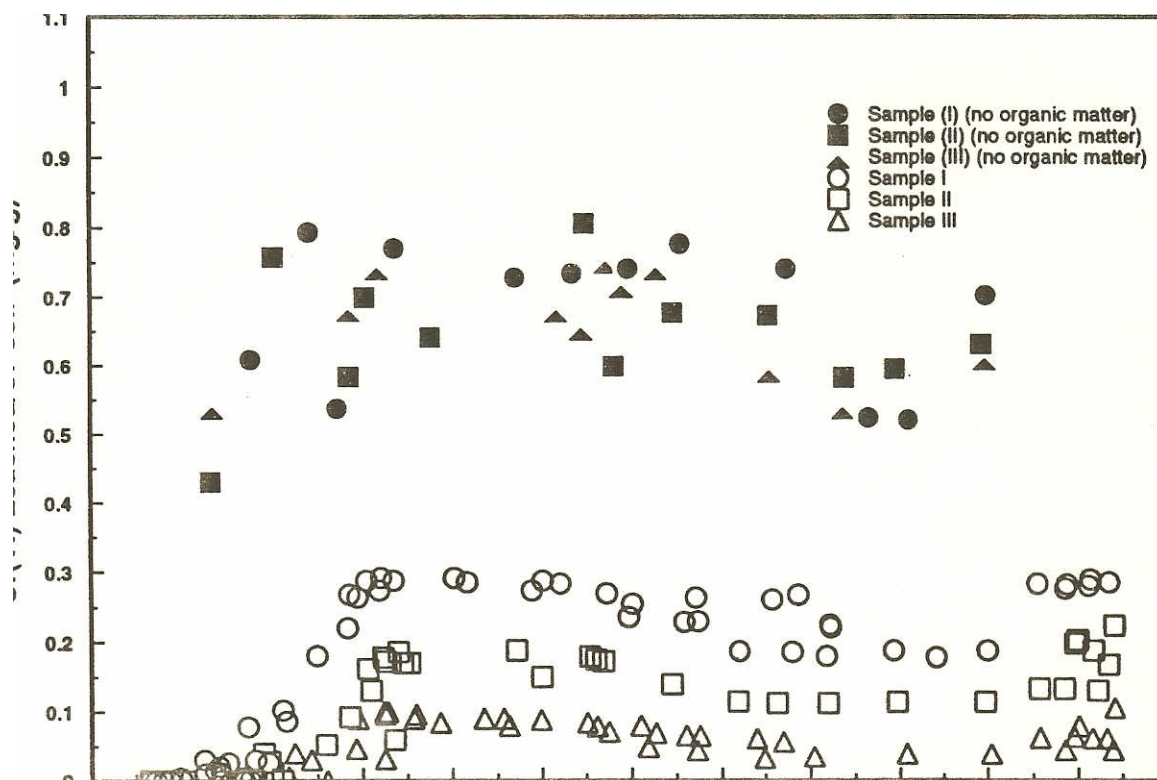
Figure 3. Cr (VI) leached as a function of pH.   Experimental conditions: 24 hours reaction time, soil-to-water ratio 5 g/l, 25 °C.
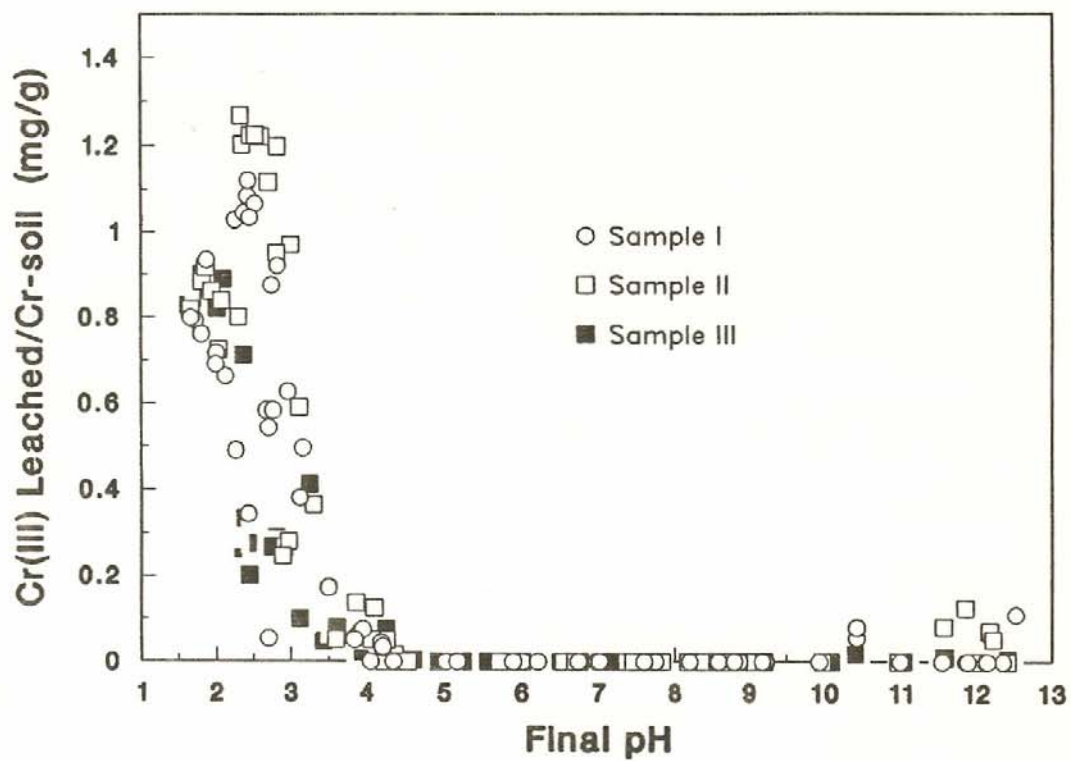
Figure 4.   Cr(III) leached as a function of pH. Experimental conditions: 24 hours reaction
time, soil-to-water ratio 5 g/l, 25 °C.

45
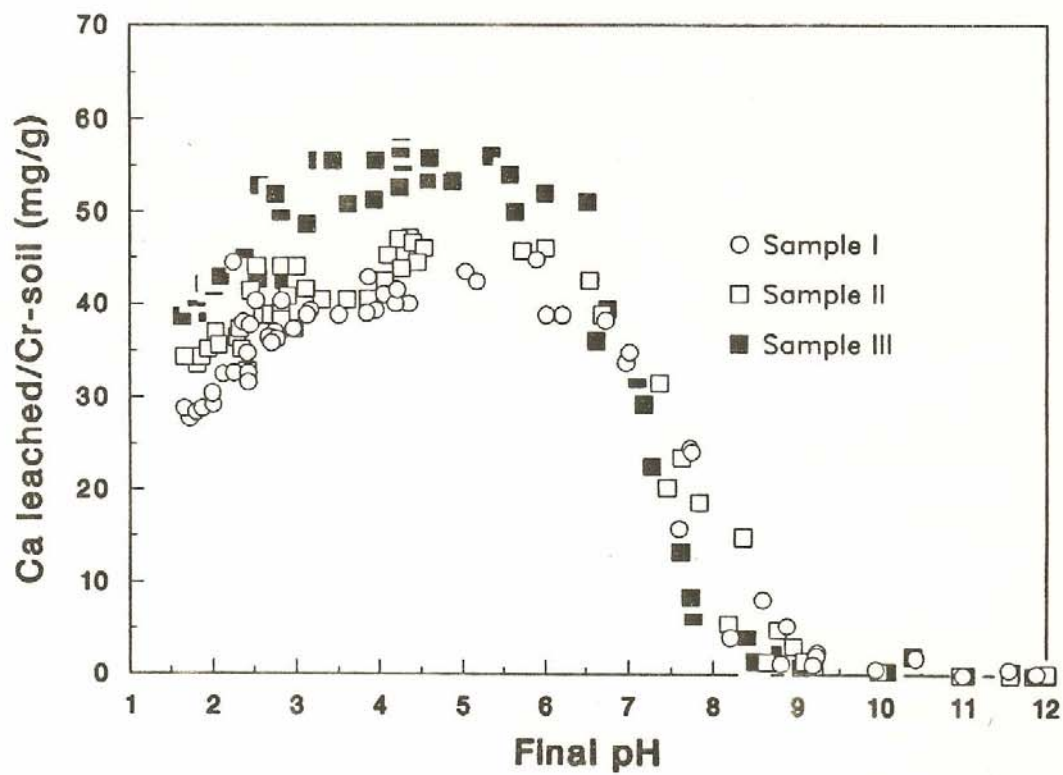
Figure 5.   Ca(II) leached as a function of pH. Experimental conditions: 24 hours reaction time, soil-to-water ratio 5 g/l, 25 °C.
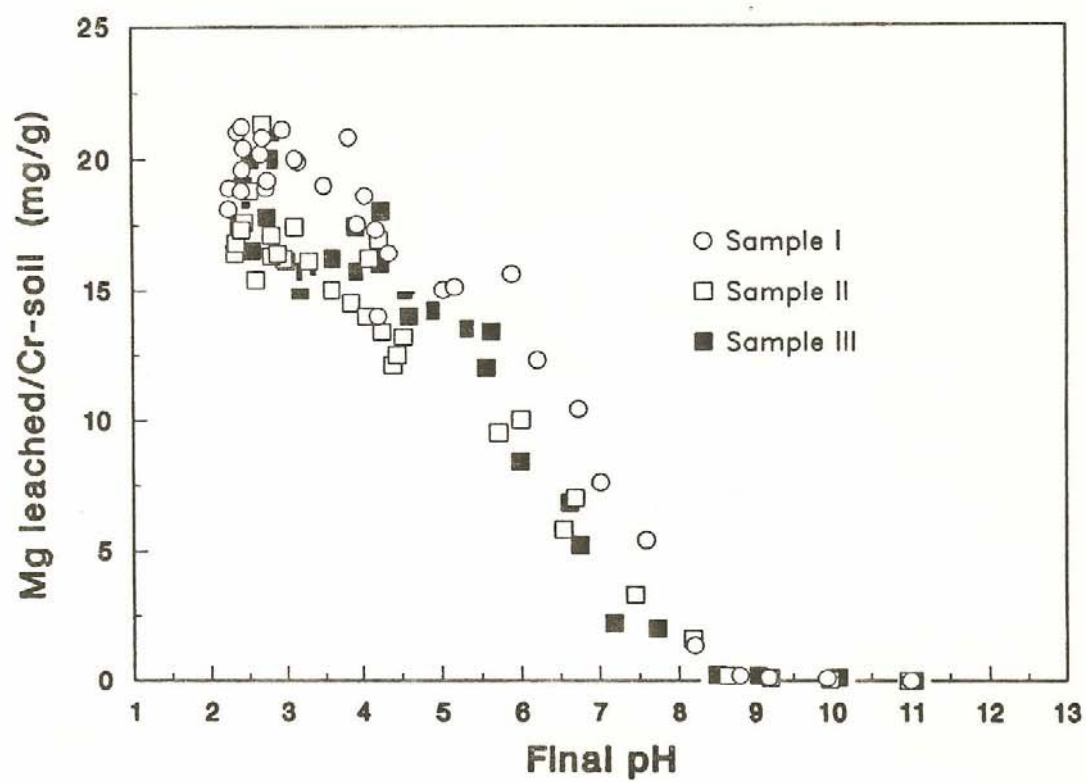
Figure 6.   Mg(II) leached as a function of pH.   Experimental conditions: 24 hours reaction
time, soil-to-water ratio 5 g/l, 25 °C.

47
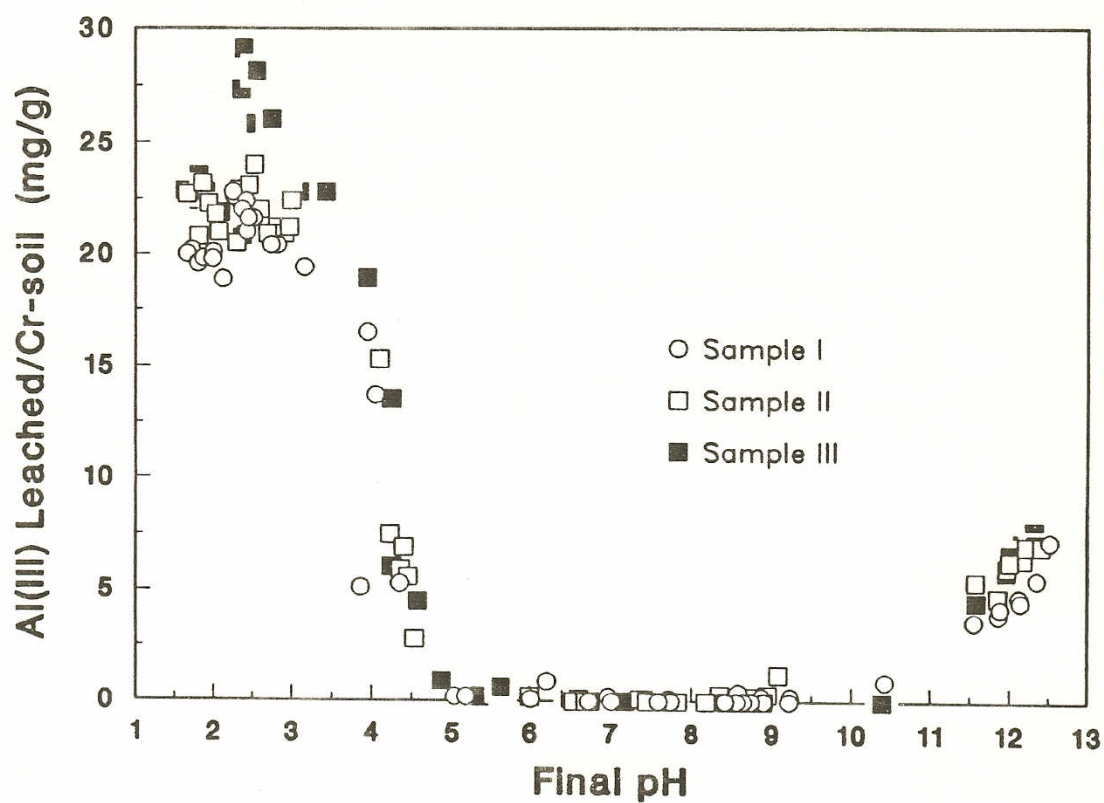
Figure 7.   Al(III) leached as a function of pH. Experimental conditions: 24 hours reaction
time, soil-to-water ratio 5 g/l, 25 °C.

48
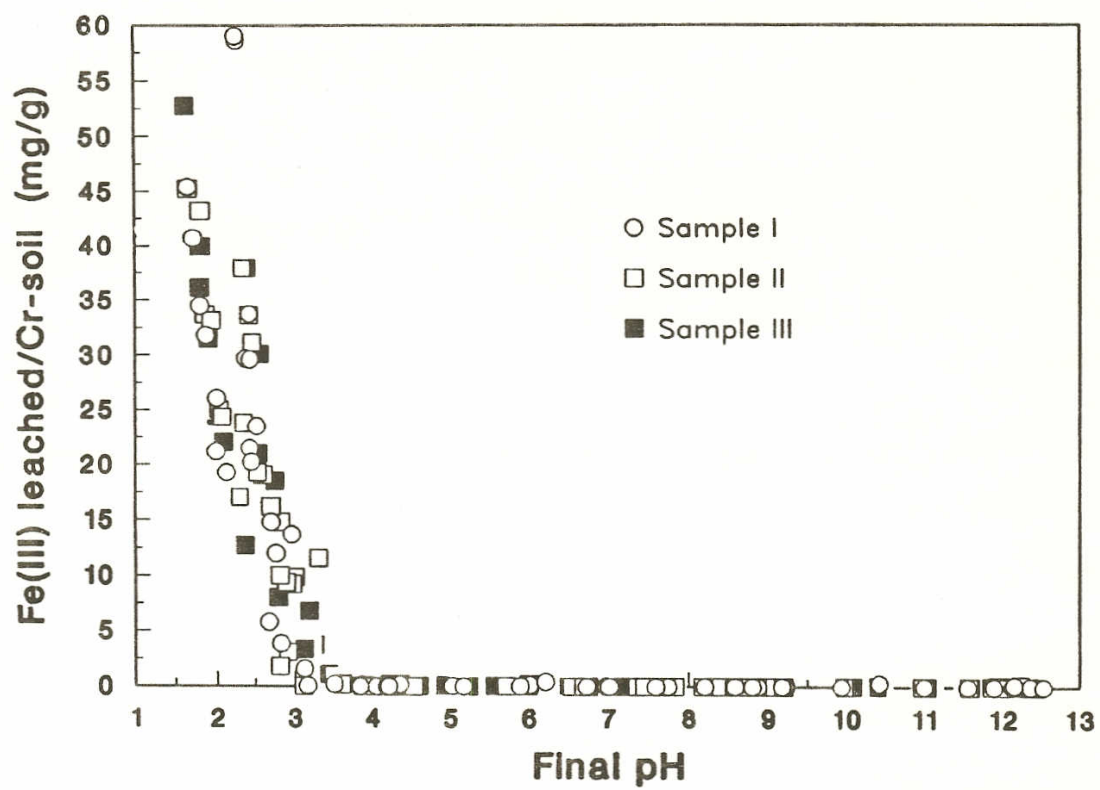
Figure 8.   Fe(III) leached as a function of pH. Experimental conditions: 24 hours reaction time, soil-to-water ratio 5 g/l, 25 °C.
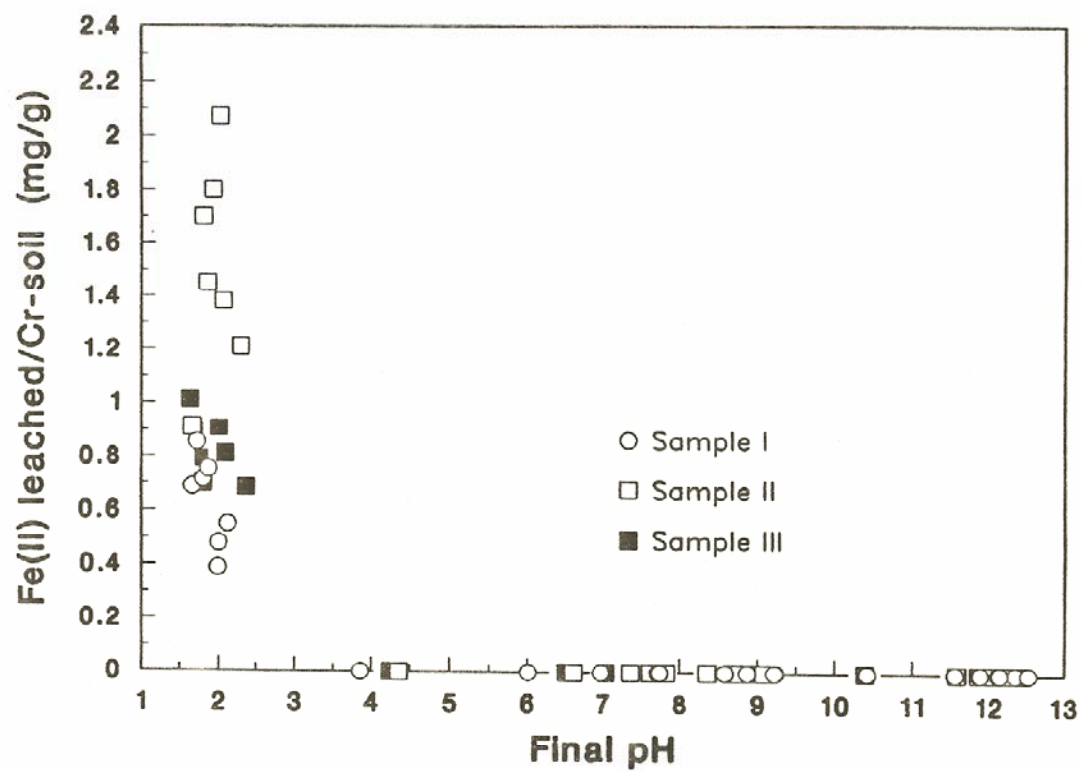
Figure 9.   Fe(II) leached as a function of pH. Experimental conditions: 24 hours reaction
              time, soil-to-water ratio 5 g/l, 25 °C.

50
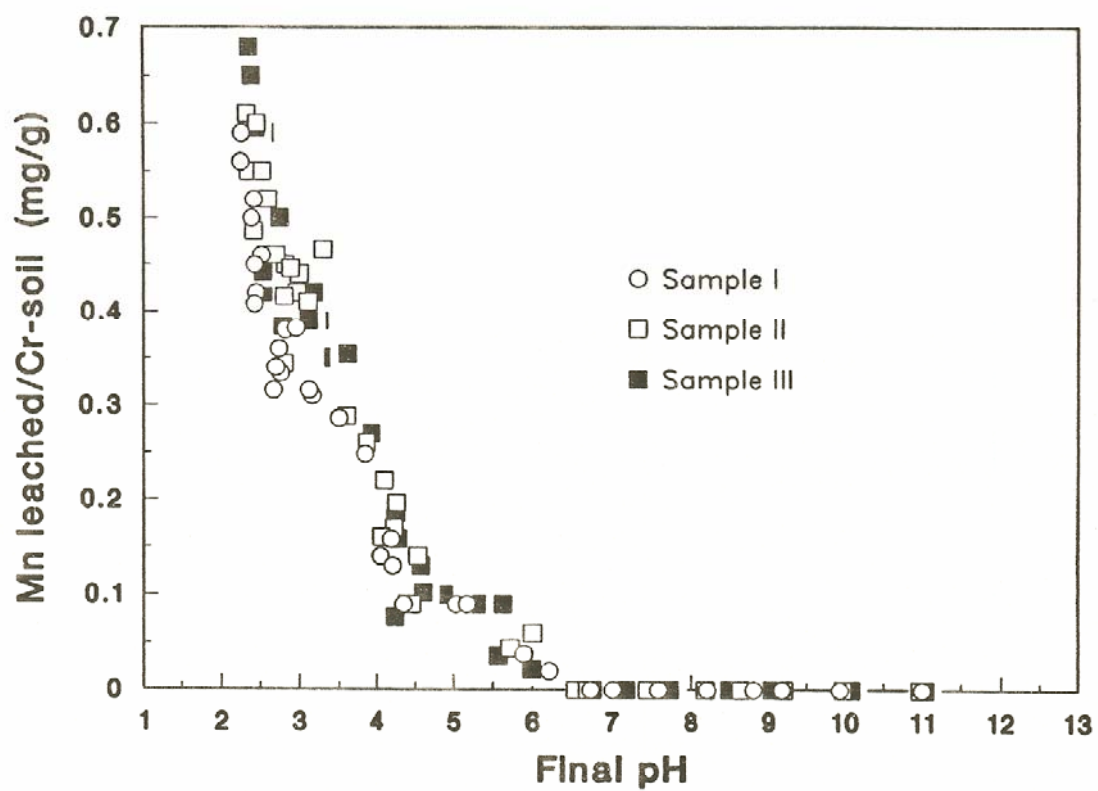
Figure 10   Mn(II) leached as a function of pH. Experimental conditions: 24 hours reaction time, soil-to-water ratio 5 g/l, 25 °C.
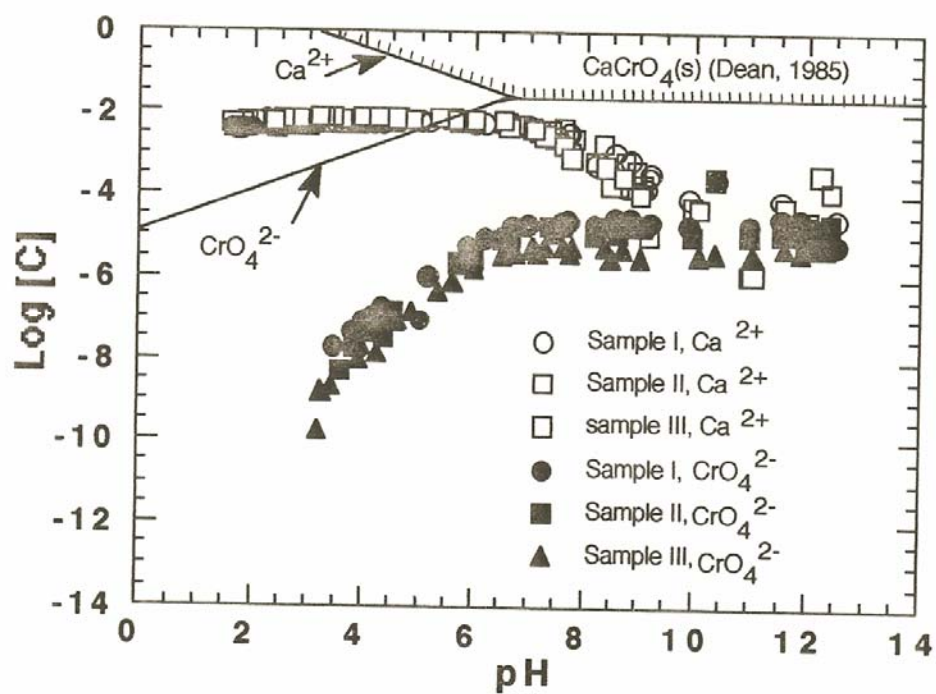
Figure 11   Logarithematic plot of soluble CrO_4^{2-} as a function of pH. Solid lines represent
theoretical solubility of $CaCrO_4$ (Dean, 1985).

52
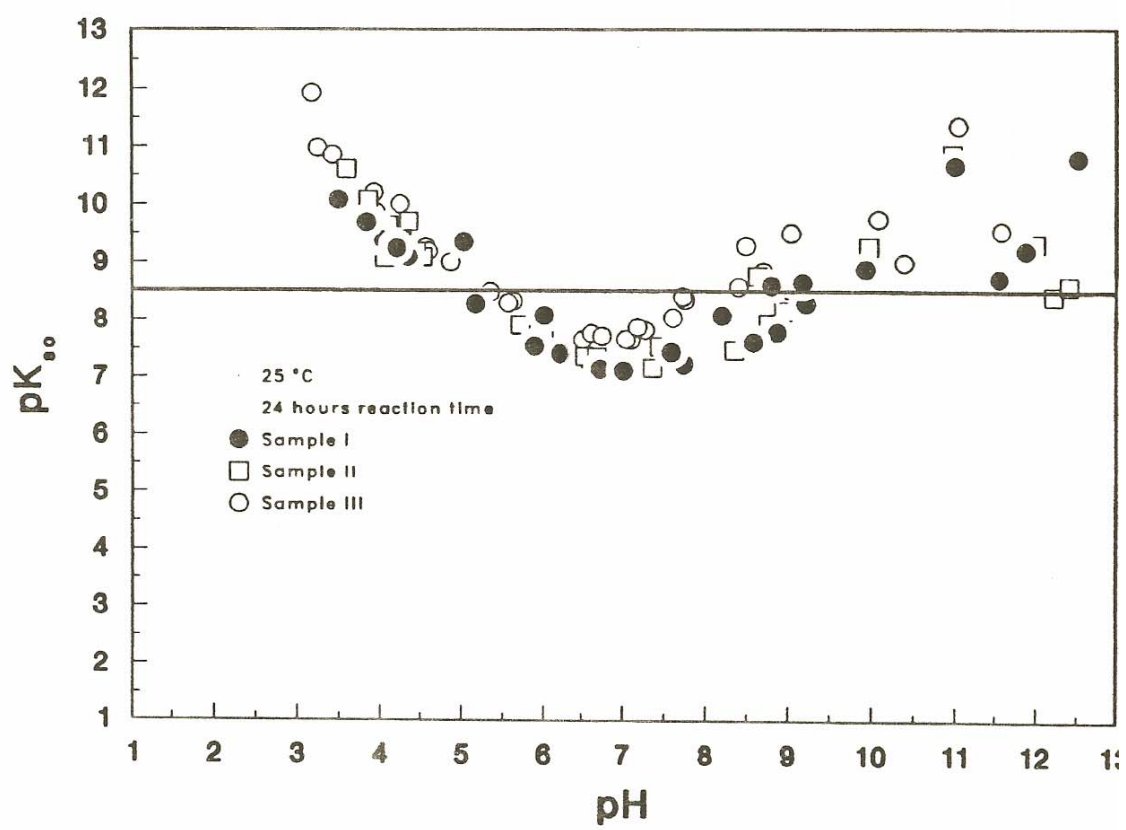
Figure 12   Solubility product of CaCrO$_4$ calculated from equilibrium leaching experiment.
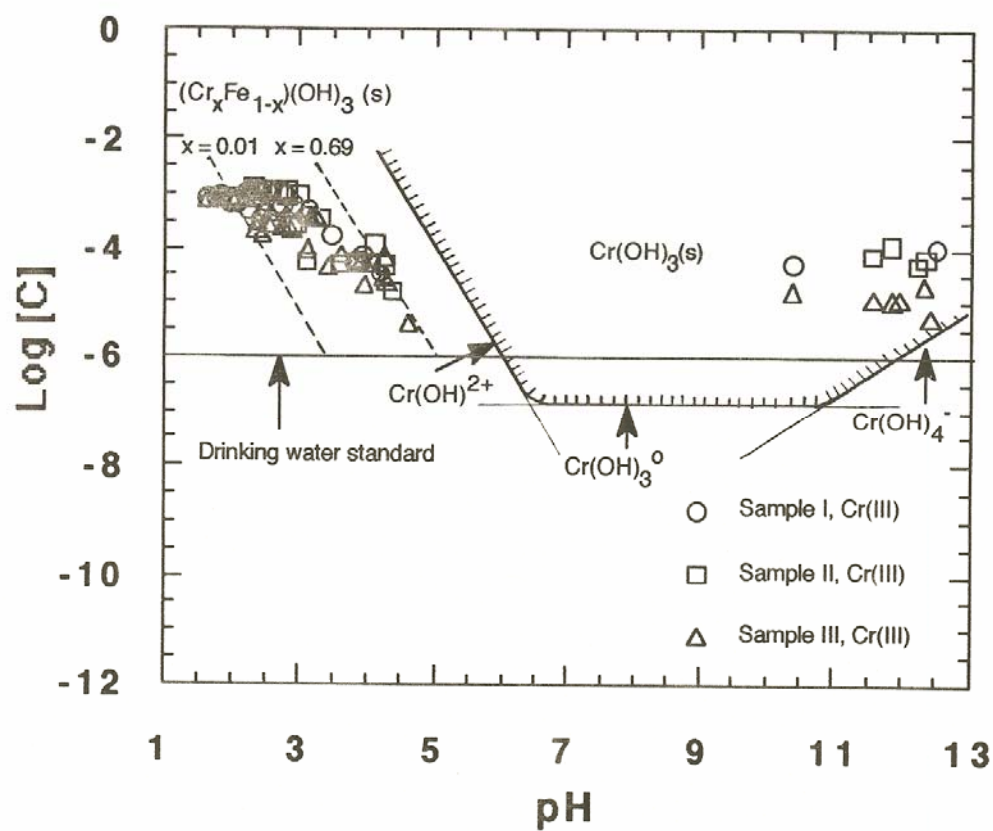
Figure 13   Comparison of solubility of $Cr(OH)_3(s)$ and $Cr_xFe_{1-x}(OH)_3(s)$. Dashed lines represent $Cr_xFe_{1-x}(OH)_3(s)$ at different values of x ($Cr(OH)_3$ mole fraction). Solid lines represent $Cr(OH)_3(s)$.

54
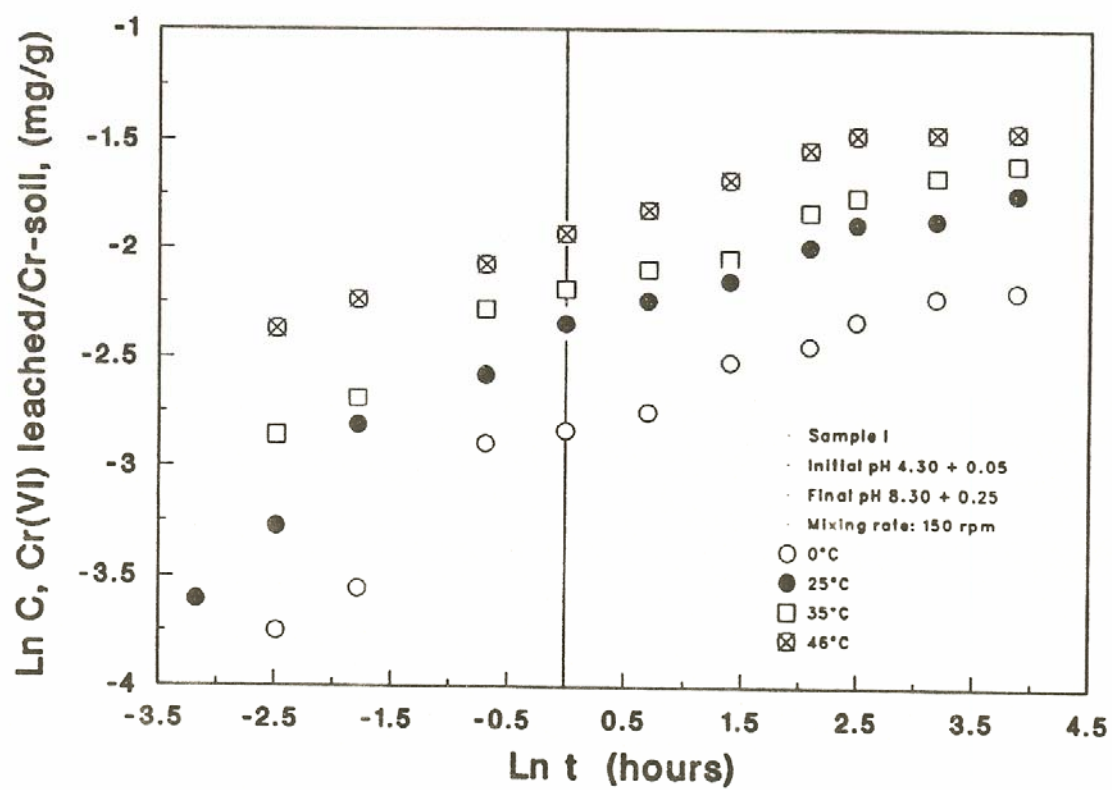
(a): sample I

Figure 14   Plot of modified Freundlich equation. Effect of temperature on Cr(VI) leaching from Cr-soil. (a): sample I, (b): sample II, and (c): sample III. Experimental conditions: simulated rainwater initial pH = 4.3, mixing rate 150 rpm, soil-to-water ratio 1:200.
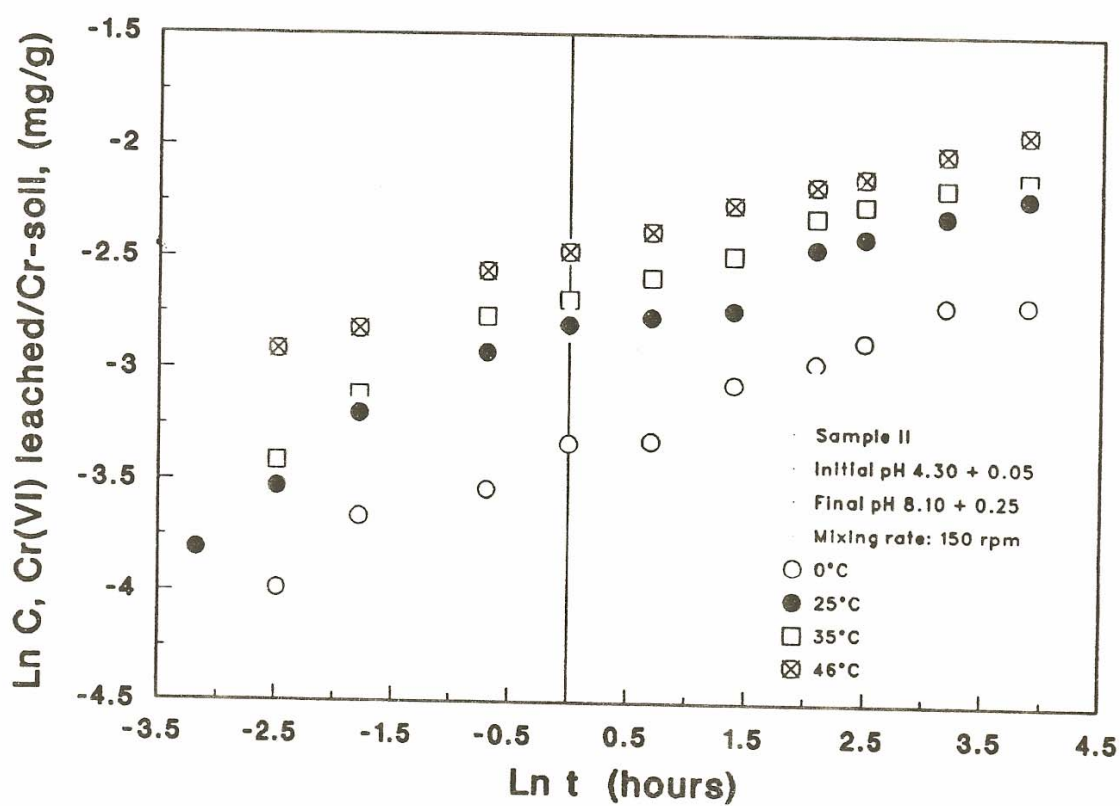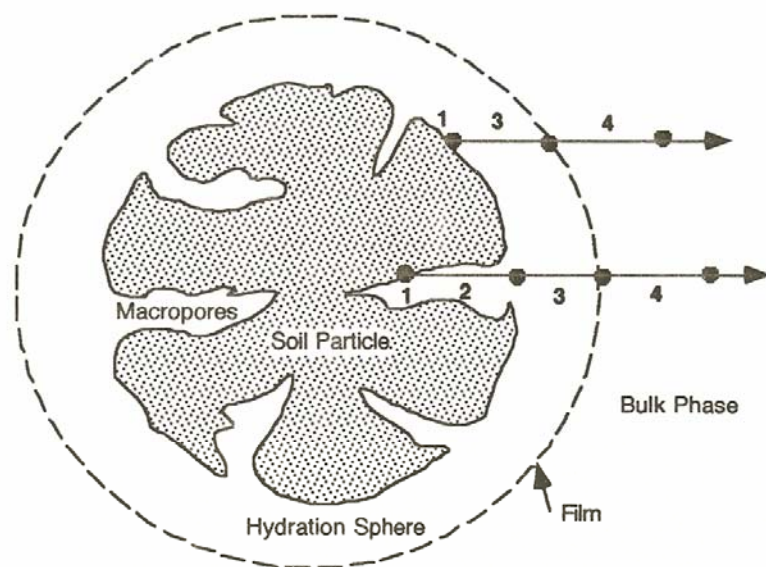
(b): sample II

Figure 14   Plot of modified Freundlich equation. Effect of temperature on Cr(VI) leaching
          from Cr-soil.   (a): sample I, (b): sample II, and (c): sample III.   Experimental
          conditions: simulated rainwater initial pH = 4.3, mixing rate 150 rpm, soil-to-water
          ratio 1:200.
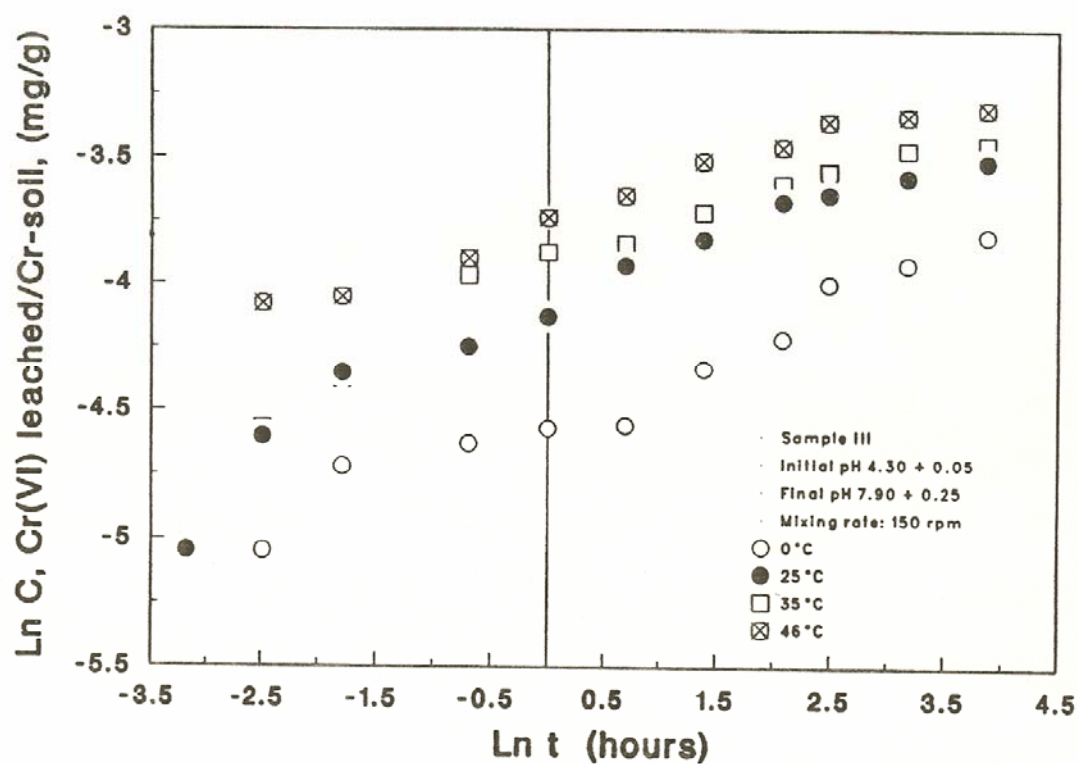
(c): sample III

Figure 14   Plot of modified Freundlich equation. Effect of temperature on Cr(VI) leaching from Cr-soil. (a): sample I, (b): sample II, and (c): sample III. Experimental conditions: simulated rainwater initial pH = 4.3, mixing rate 150 rpm, soil-to-water ratio 1:200.
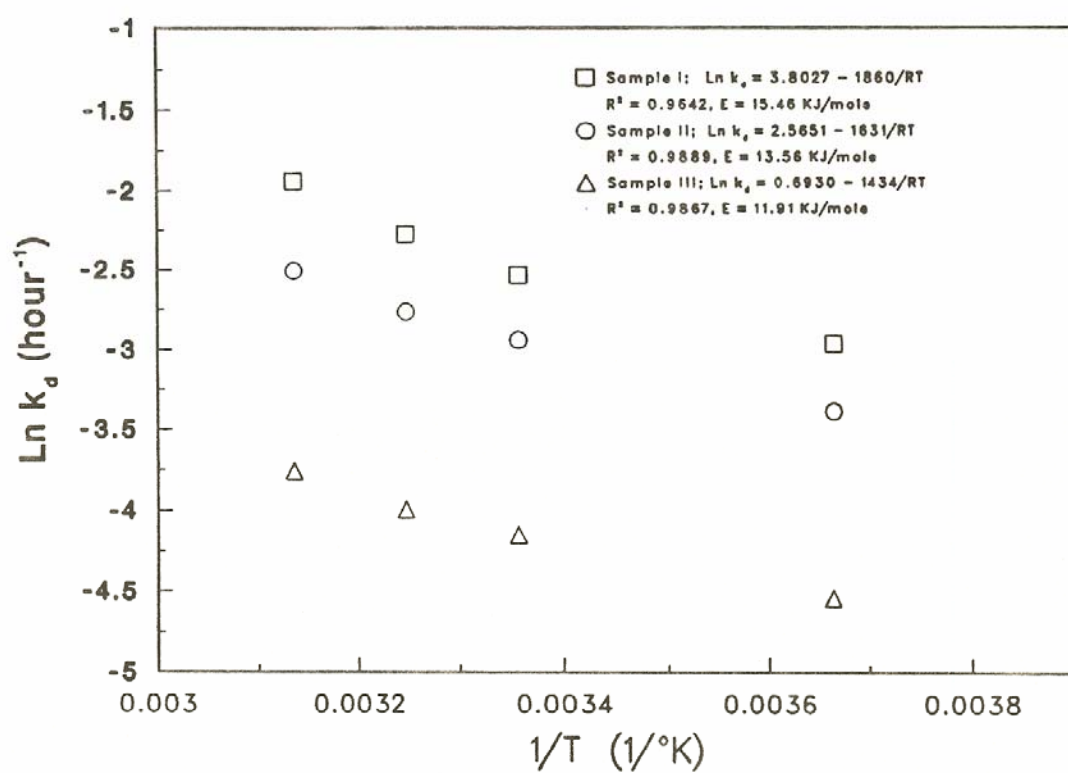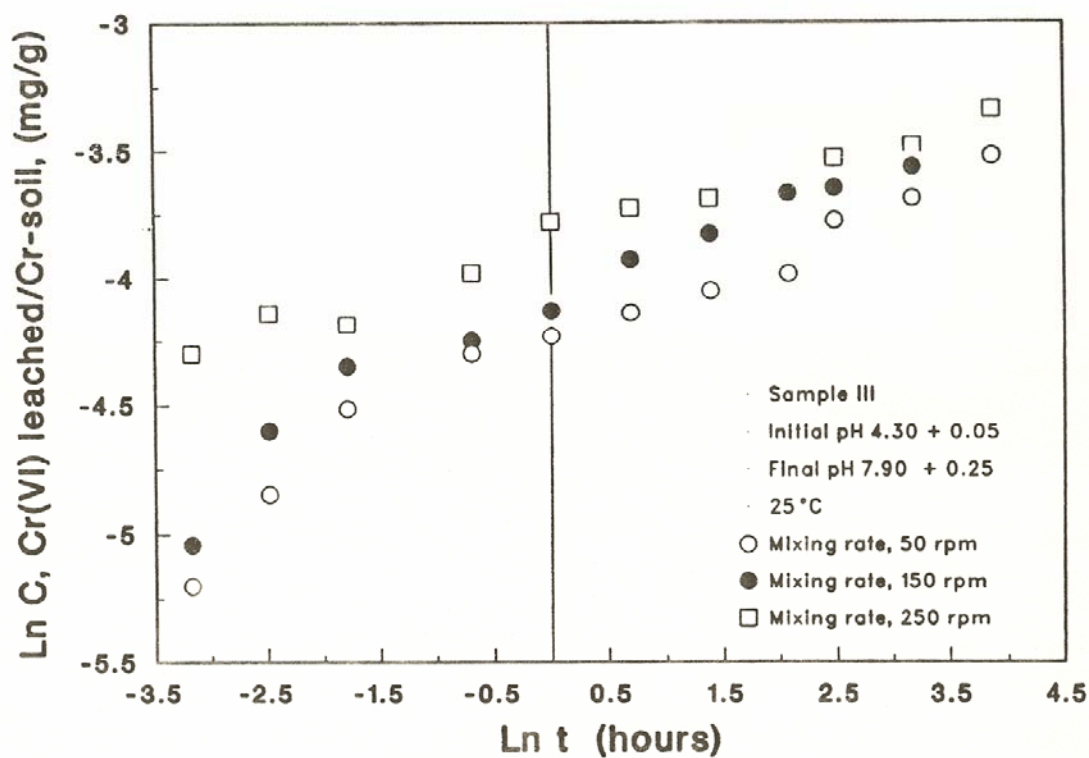
Figure 15   Arrhenius plot of rate constants from the modified Freundlich equation for Cr(VI) dissolution from Cr-soil samples. Experimental conditions: simulated rainwater initial pH = 4.3, mixing rate 150 rpm, soil-to-water ratio 1:200 for sample I and II, 1:100 for sample III.

Transport process of dissolved species from the Cr-soil particle:

Step 1: Desorption or dissolution (surface chemical reaction) occurring on the soil particle surfaces.

Step 2: Particle diffusion occurring in the macropore of the soil particle.

Step 3: Film diffusion occurring in the hydration sphere.

Step 4: Bulk diffusion occurring in the solution medium, and transport of the dissolved ion species toward the bulk phase.

Figure 16   Transport process   steps of dissolved species from Cr-soil particles.
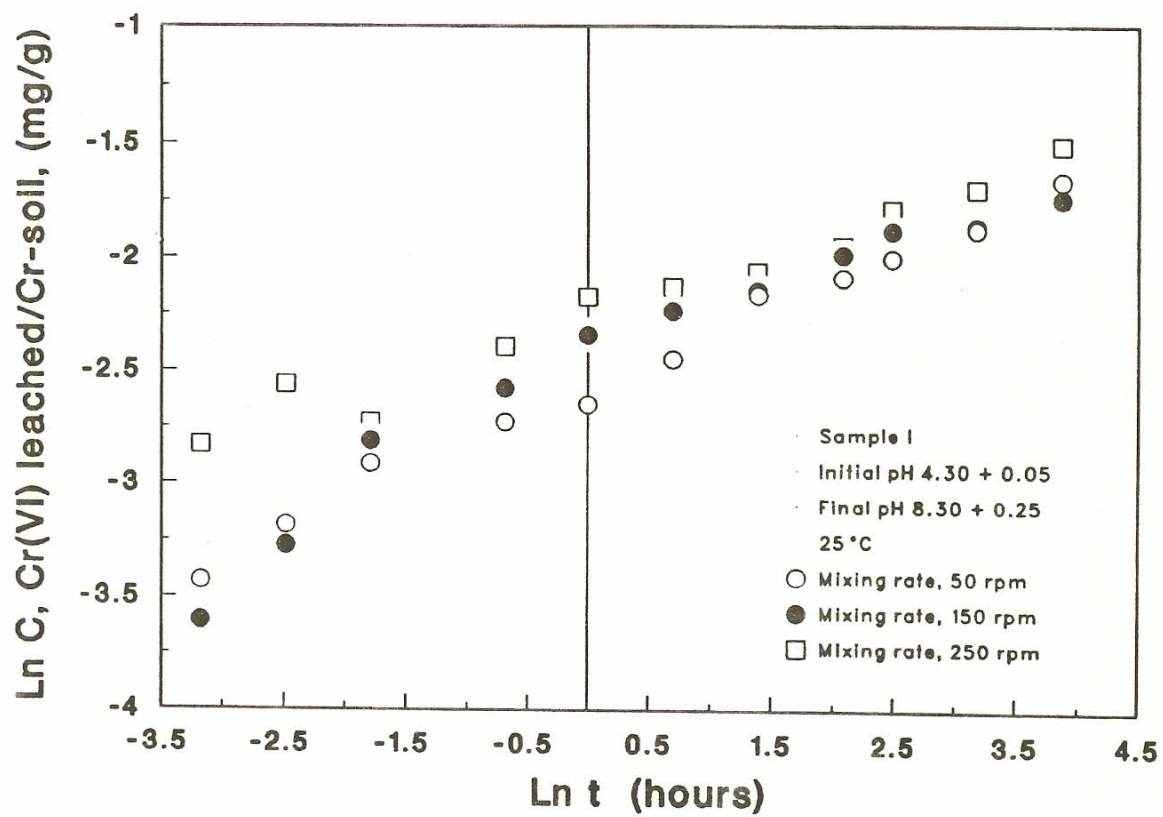
(a): sample I

Figure 17   Plot of modified Freundlich equation. Effect of mixing rate on Cr(VI) dissolution from Cr-soil.   (a): sample I, (b): sample II, and (c): sample III. Experimental conditions: simulated rainwater initial pH = 4.3, 25 °C, soil-to-water ratio 1:200.
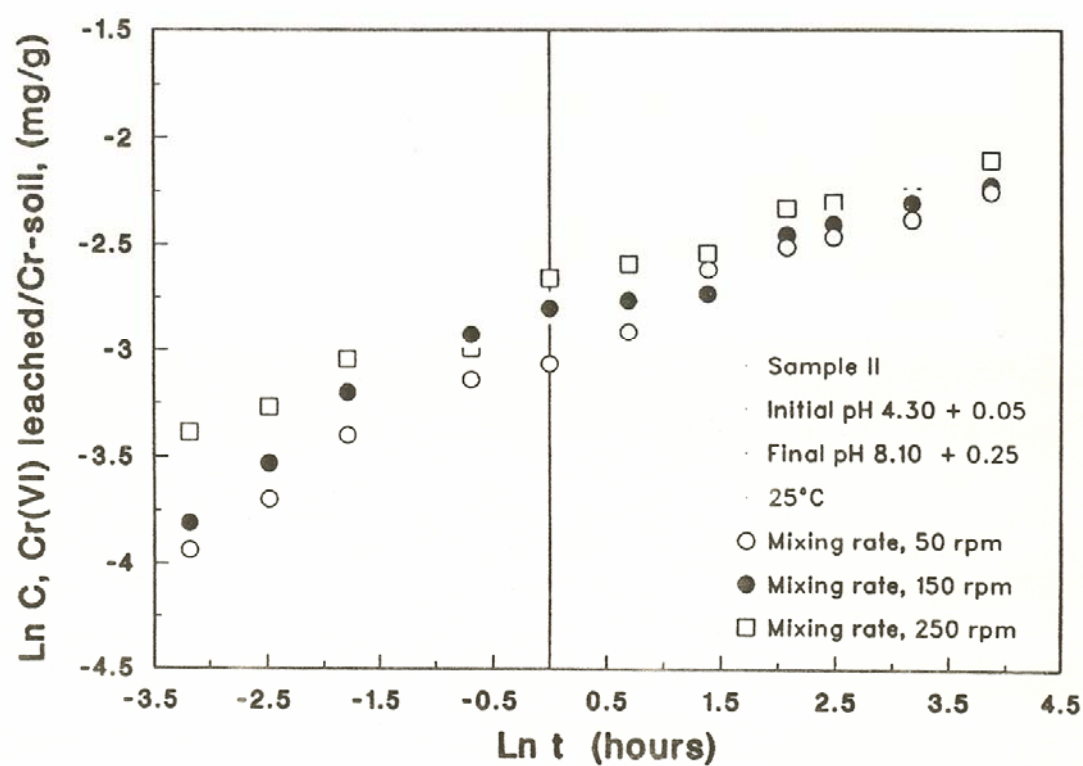
(b): sample II

Figure 17   Plot of modified Freundlich equation. Effect of mixing rate on Cr(VI) dissolution
from Cr-soil.   (a): sample I, (b): sample II, and (c): sample III. Experimental
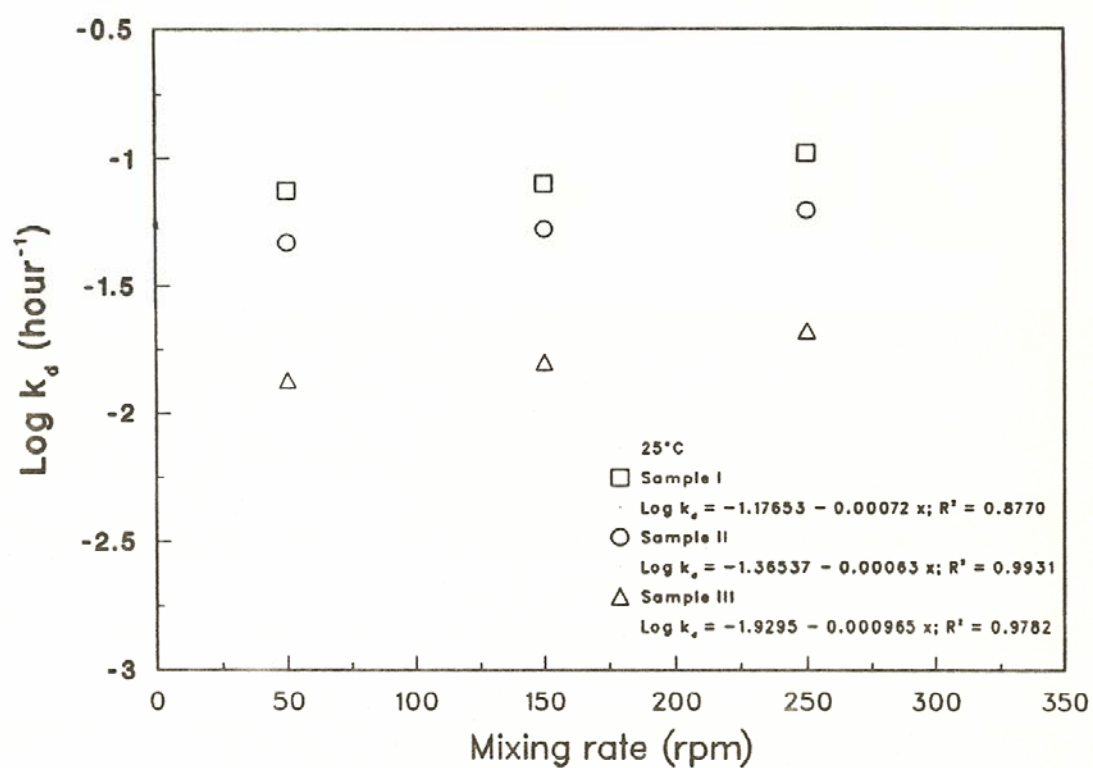conditions: simulated rainwater initial pH = 4.3, 25 °C, soil-to-water ratio 1:200.

(c): sample III

Figure 17   Plot of modified Freundlich equation. Effect of mixing rate on Cr(VI) dissolution from Cr-soil. (a): sample I, (b): sample II, and (c): sample III. Experimental conditions: simulated rainwater initial pH = 4.3, 25 °C, soil-to-water ratio 1:200.
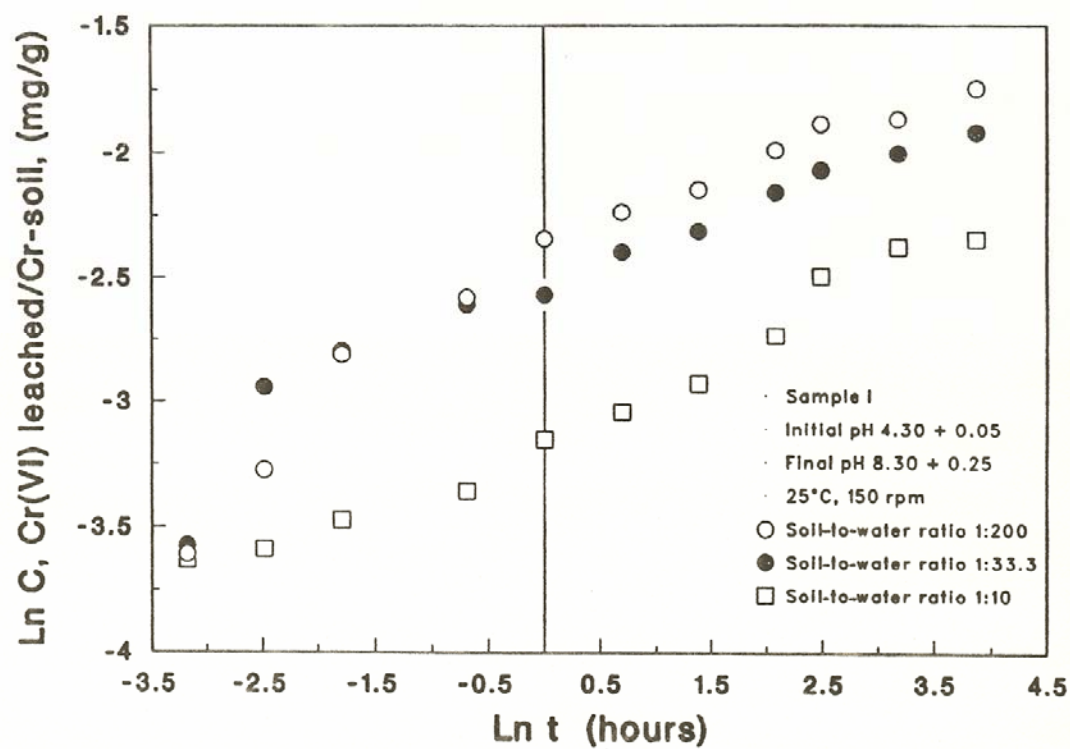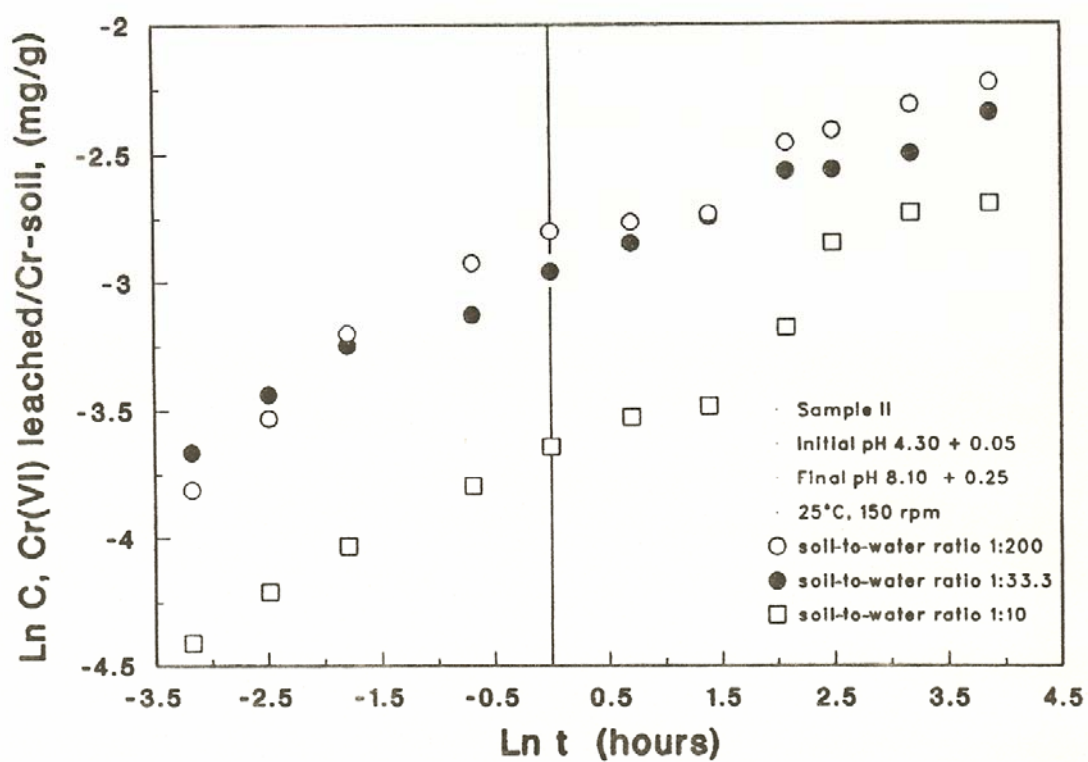
Figure 18   Logarithematic plot of rate constant, K_d, as a function of mixing rate. Experimental conditions: simulated rainwater initial pH = 4.3, 25 °C, soil-to-water ratio 1:200 for sample I and II, 1:100 for sample III.
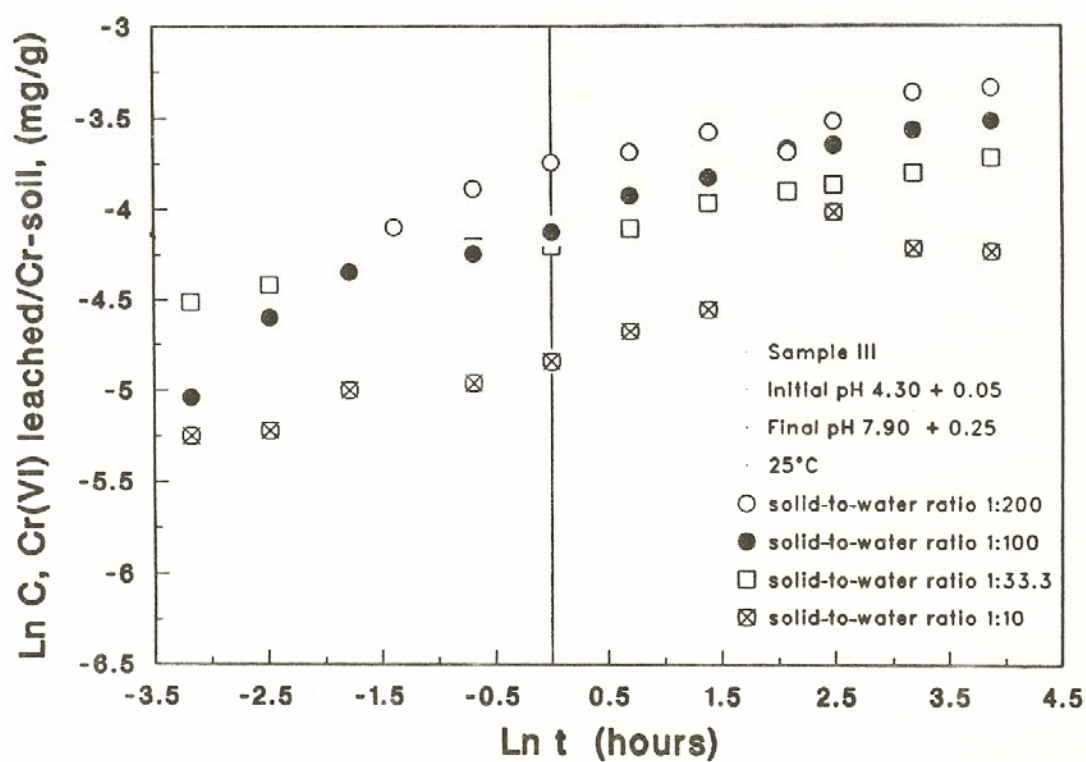
(a) sample I

Figure 19   Plot of modified Freundlich equation. Effect of soil-to-water ratio on Cr(VI)
             leaching from Cr-soil sample I. Experimental conditions: simulated rainwater initial
             pH = 4.3, 25 °C, mixing rate 150 rpm.

(b): sample II

Figure 19   Plot of modified Freundlich equation. Effect of soil-to-water ratio on Cr(VI) leaching from Cr-soil sample I. Experimental conditions: simulated rainwater initial pH = 4.3, 25 °C, mixing rate 150 rpm.

(c): sample III

Figure 19   Plot of modified Freundlich equation. Effect of soil-to-water ratio on Cr(VI) leaching from Cr-soil sample I. Experimental conditions: simulated rainwater initial pH = 4.3, 25 °C, mixing rate 150 rpm.
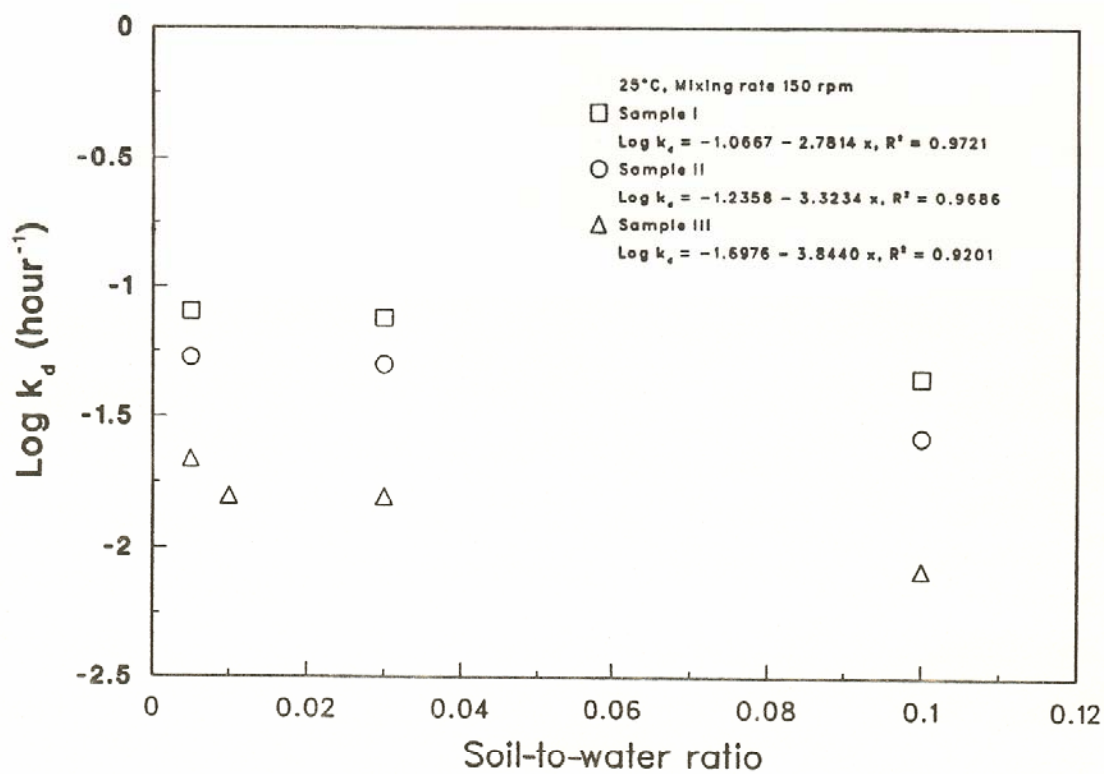
25°C, Mixing rate 150 rpm

□ Sample I

Log k_d = -1.0667 - 2.7814 x, R^2 = 0.9721

○ Sample II

Log k_d = -1.2358 - 3.3234 x, R^2 = 0.9686

△ Sample III

Log k_d = -1.6976 - 3.8440 x, R^2 = 0.9201

Figure 20   Logarithematic plot of rate constant, K_d, as a function of soil-to-water ratio. Experimental conditions: simulated rainwater initial pH = 4.3, 25 °C, mixing rate 150 rpm.

67