

YEAR 3

**EFFECT OF SPECIFIC CHEMICAL REACTIONS ON THE
TRANSFORMATION AND THE TRANSPORT OF
CHROMIUM IN THE SOIL-WATER SYSTEM**

Final Report

by

C. P. Huang
Hyun-Moo Shin
Herbert E. Allen
Alex. H-D. Cheng

Department of Civil Engineering
University of Delaware
Newark, Delaware 19716

Project Manager
Paul F. Sanders

New Jersey Department of Environmental Protection and Energy
Division of Science & Research
Trenton, New Jersey 08625

June 1995

TABLE OF CONTENTS

TABLE OF CONTENTS	ii
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	x
Chapter	
1 INTRODUCTION	1
2 PROJECT DESIGN AND METHODS	4
2.1 Materials	4
2.1.1 Reagents	4
2.2 Methods	5
2.2.1 Analytical Methods	5
2.2.2 Preparation of Simulated Groundwater	6
2.2.3 Isolation of Soil Humic Acid	6
2.2.4 Potentiometric Titration of Humic Acids	7
2.2.5 Cr(III) Oxidation Capacity of Soils	10
2.2.6 Batch Experiments of Cr(VI) Reduction Reactions	10
3 QUALITY CONTROL-QUALITY ASSURANCE PROCEDURES	13
3.1 Quality Assurance Procedures	13
3.2 Data Quality Requirements :	14
4 RESULTS AND DISCUSSION	16
4.1 Reduction Reactions of Chromium(VI) in Subsurface Soils	16
4.1.1 The Effect of Cr(VI) Solution Matrix	16
4.1.2 The Effect of pH on the Reduction of Cr(VI) with Soil	16
4.1.3 The Effect of Oxygen on the Reductions of Chromium	32
4.1.4 The Effect of Soil Concentration on Cr(VI) Reduction	36
4.1.5 The Effect of Temperature on Cr(VI) Reduction	45
4.1.6 Cr(VI) Reduction by Soil Organic Matter	53
4.1.6.1 Chemistry of Soil Humic Acids	53
4.1.6.2 Reduction of Cr(VI) by Soil Organic Matter	66
4.2 Oxidation Reactions of Chromium(III) in Subsurface Soils	72
4.2.1 Effect of Soil Mn Content on Cr(III) Oxidation Capacity of Soils and the Rates of Cr(III) Oxidation	72
4.2.2 Effect of Dissolved Oxygen and Temperature on Cr(III) Oxidation	81
4.2.3 Effect of pH and Cr(III) Concentration on Cr(III) Oxidation	89
4.2.4 Effect of Soil to Solution Ratio on Cr(III) Oxidation	108
4.2.5 Effect of Ionic Strength on Cr(III) Oxidation	117

4.3	Summary	120
5	CONCLUSIONS	124
5.1	Major Findings.....	124
5.2	Recommendations for Future Research	126
	REFERENCES	128
	THE REDOX REACTIONS OF CHROMIUM	136

LIST OF TABLES

Table 2.1	The Specification of Aldrich Humic Acid.	8
Table 4.1	The rate constants of Cr(VI) reduction with six kinds of soils at acidic conditions.	30
Table 4.2	Constants obtained from equation 4.7: the relation between reaction rate and concentration of hydrogen ion.	31
Table 4.3	Non-linear relationship between Cr(III) formation and soil/solution ratio at acidic conditions.	42
Table 4.4	Rate constants and activation energies for Cr(VI) reduction by Sassafras sandy loam at different temperatures.	52
Table 4.5	Average acidity constants ($p\bar{K}_a$) values of various soil humic acids. Ionic Strength = 0.1 N.	61
Table 4.6	First-order rate constants for Cr(III) oxidation by five soils.	80
Table 4.7	Rate constants of Cr(VI) formation by Washington loam at different temperatures in the aerated and deaerated Cr(III) solution.	88
Table 4.8	The rate constants for Cr(VI) formation by Washington loam at various pH values.	100
Table 4.9	The rate constants for Cr(III) depletion by Washington loam at various pH values.	101
Table 4.10	The relation of Cr(VI) produced to initial Cr(III) added.	107
Table 4.11	The first order rate constants vs. the ratio of soil to solution.	115
Table 4.12	The relation of Cr(VI) production to soil/solution ratio for various initial Cr(III) concentrations.	116

LIST OF FIGURES

Figure 2.1	Bar chart of ionic balance for the simulated groundwater (Huang et al., 1994).	9
Figure 2.2	Experimental apparatus for kinetic studies of Cr redox reactions.....	12
Figure 4.1	Cr(VI) reduction in 10^{-2} M NaNO_3 solution as a function of time. Initial pH = 2.5.	21
Figure 4.2	Cr(VI) reduction in the simulated ground water (SGW: I = 0.01 M). Initial Cr(VI) = 0.52 mg/L.	22
Figure 4.3	Effect of pH on Cr(VI) reduction with soils. Initial Cr(VI) = 10^{-4} M K_2CrO_4	23
Figure 4.4	The dissolution of Fe(III) with Cr(VI) reduction with respect to pH ranging from 2 to 12. I = 0.01 M simulated ground water.	24
Figure 4.5	The fraction of Fe(III) leached from soils with different iron content at pH ranging from 2 to 12. I = 0.01 M simulated ground water.	25
Figure 4.6	The molar ratios of Fe(II) oxidized to Cr(VI) reduced with respect to soils with different iron content. I = 0.01 M simulated ground water.	26
Figure 4.7	Rates of Cr(III) formation by Boonton Bergen county loam for four pH values in 0.01 M simulated ground water. Temperature = 25 °C.....	27
Figure 4.8	Rates of the dissolution of Fe(III) associated with the reduction reaction of Cr(VI) for four pH values. Temperature = 25 °C.	28
Figure 4.9	Relationship between rate constants of Cr(VI) reduction with soils and pH. Temperature = 25 °C.	29
Figure 4.10	The kinetics of Cr(VI) reduction by Sassafras sandy loam. Cr(VI) added = 39 mg/Kg soil	34
Figure 4.11	The kinetics of Cr(VI) reduction by soil humic acid under air and nitrogen gas conditions. I = 0.01 M simulated ground water.....	35

Figure 4.12	The concentration of Cr(III) formed as a function of soil concentration. Initial Cr(VI) concentrations are 0.52, 2.6, 3.64, 5.2, 15.6, and 26 mg/L.....	40
Figure 4.13	The amount of Cr(III) formed per unit weight of soil. The percentage of Cr(III) formed is based on the initial Cr(VI) concentration with respect to different soil concentrations. Soil = Sassafras sandy loam.	41
Figure 4.14	The concentration of iron leached, associated with reduction reaction of Cr(VI), with respect to soil/solution ratio. Soil = Sassafras sandy loam.	43
Figure 4.15	The ratio of Fe(III) oxidized to Cr(III) reduced with respect to soil/ solution ratio. pH = 2.0.	44
Figure 4.16	The rate of Cr(VI) reduction by Sassafras sandy loam at various temperatures. Initial Cr(VI) concentration = 2.6 mg/L.	48
Figure 4.17	The rate of Cr(III) formation at various temperatures. Initial Cr(VI) concentration = 2.6 mg/L.	49
Figure 4.18	The temperature dependence of rate constant, k, for Cr(VI) reduction by Sassafras sandy loam. Initial Cr(VI) concentration = 2.6 mg/L.	50
Figure 4.19	The temperature dependence of rate constants plotted by Arrhenius equation. Soil used = Sassafras sandy loam.	51
Figure 4.20a	FT-IR spectra of Aldrich humic acid.	56
Figure 4.20b	FT-IR spectra of Sassafras humic acid.	57
Figure 4.21	Titration of humic acids and HCl mixture with 0.1 N NaOH. I = 0.1 M NaNO ₃	58
Figure 4.22a	Titration analysis of Aldrich humic acid plotted $\Delta\text{pH}/\Delta\text{Volume}$ against pH.	59
Figure 4.22b	Titration analysis of Sassafras humic acid plotted $\Delta\text{pH}/\Delta\text{Volume}$ against pH.	60
Figure 4.23	The apparent solubility of Sassafras humic acid as a function of pH. Temperature = 25 °C.	64
Figure 4.24	Oxygen demand and average oxidation state of organic carbon (modified from Stumm and Morgan, 1981).	65

Figure 4.25	The reduction of Cr(VI) with soil humic acid at various pH values. Initial Cr(VI) = 1×10^{-2} M.	64
Figure 4.26	The change of Cr concentration and DOC consumption associated with the oxidation of soil humic acid as a function of pH. Temperature = 25 °C.	65
Figure 4.27	Ratio of the consumption of dissolved organic matter to Cr(III) production by Cr(VI) reduction reaction at various pH conditions. Initial Cr(VI) = 1×10^{-2} M.	70
Figure 4.28	Schematic illustration on Cr(VI) reduction with the solid form of humic acid at acidic pH. Numbers in the lump indicate apparent oxidation number of soil humic acids.	71
Figure 4.29	The relationship between Cr(III) oxidation capacity and Mn content in soils extracted by perchloric-nitric acids (acid), sodium citrate -bicarbonate - dithionite (DCB), and acid ammonium oxalate (oxalate).	71
Figure 4.30	Kinetics of Cr(III) oxidation by five soils. pH = 2.0	76
Figure 4.31	The dissolution of manganese associated with Cr(III) oxidation for five soils. pH = 2.0.	77
Figure 4.32	The ratio of soluble Mn to Cr(VI) produced in Cr solution. pH = 2.0.	78
Figure 4.33	The relationship of the rate constants of Cr(III) oxidation to manganese content in soils. pH = 2.0.	79
Figure 4.34	Effect of dissolved oxygen and temperature on the rate of Cr(VI) formation by Washington loam. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	84
Figure 4.35	The rate of Mn dissolution from Washington loam in Cr(III) solution. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	85
Figure 4.36	The rate constants of Cr(VI) formation by Washington loam at various temperatures. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	86
Figure 4.37	The temperature dependence of the rate constants of Cr(VI) formation plotted by the Arrhenius equation. Soil = Washington loam.	87

Figure 4.38	Solubility of Cr(III) as a function of pH. Cr(III) concentrations were measured in 0.22 μ m filtrates from N ₂ -equilibrated Cr(OH) ₃ (s) suspensions. pH was adjusted by 0.1 N HNO ₃ or 0.1 N NaOH. Temperature = 25 °C.....	94
Figure 4.39	The kinetics of Cr(III) oxidation by Washington loam at various pHs. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.	95
Figure 4.40	The dissolution of Mn in Cr(III) solution at various pHs. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.	96
Figure 4.41	Relation of the rate constant of Cr(III) oxidation by Washington loam to solution pH. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.	97
Figure 4.42	Change of Cr(III) concentration as a function of time at various pH values. Soil used = Washington loam.....	98
Figure 4.43	The relation of Cr(III) depletion rate to pH. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.	99
Figure 4.44	Cr(III) oxidized by a soil as a function of Cr(III) concentration added at various pH values. Temperature = 25 °C.....	104
Figure 4.45	Cr(VI) production by a soil as a function of pH at various initial Cr(III) concentrations. Temperature = 25 °C.	105
Figure 4.46	The ratio of Mn dissolved to Cr(VI) produced as a function of Cr(III) concentration and pH. Temperature = 25 °C.	106
Figure 4.47	The kinetics of Cr(VI) production as a function of time at various soil concentrations. Soil = Washington loam.	110
Figure 4.48	The dissolution of Mn associated with Cr(III) oxidation reaction as a function of time at various soil concentrations. Soil = Washington loam.....	111
Figure 4.49	The relation of the rate constant of Cr(III) oxidation to soil/solution ratio. Soil = Washington loam.	112
Figure 4.50	The relation of Cr(VI) production to soil/solution ratio for various initial Cr(III) concentrations. Soil = Washington loam.....	113
Figure 4.51	The relation of the fraction of Cr(VI) production to soil/solution ratio. Soil = Washington loam.....	114
Figure 4.52	The effect of ionic strength on Cr(III) oxidation process. Soil = Washington loam.....	118

Figure 4.53	The effect of ionic strength on the stoichiometry of Mn dissolved to Cr(VI) produced at various Cr(III) concentrations. Soil = Washington loam.....	11
Figure A-1	Reaction rates of Cr(VI) reduction by Boonton Bergen county loam for four pH values. Temperature = 25 °C.....	13
Figure A-2	Reaction rates of Cr(VI) reduction by Sassafras sandy loam for four pH values. Temperature = 25 °C.	13
Figure A-3	Reaction rates of Cr(VI) reduction by Lakewood sandy loam for four pH values. Temperature = 25 °C.	13
Figure A-4	Reaction rates of Cr(VI) reduction by Dunellen sandy loam for four pH values. Temperature = 25 °C.	14
Figure A-5	Reaction rates of Cr(VI) reduction by Hazen gravelly sand for four pH values. Temperature = 25 °C.	14
Figure A-6	Reaction rates of Cr(VI) reduction by Freehold sandy (B horizon) for four pH values. Temperature = 25 °C.....	14
Figure A-7	The rate of Cr(VI) reduction by Sassafras sandy loam at various temperatures. Initial Cr(VI) concentration = 2.6 mg/L.	14
Figure A-8	First order kinetic plots of Cr(III) oxidation by soils. pH = 2.0.	14
Figure A-9	Concentration of dissolved oxygen in the aerated and deaerated solutions. N ₂ gas was sparged for deaeration. Data marked as diamonds were adopted from Metcalf and Eddy (1972). pH = 2.0.	14
Figure A-10	The kinetics of Cr(VI) formation by Washington loam at various temperatures. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.	14
Figure A-11	The kinetics of Cr(VI) production by Washington loam at various pH values. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.....	14
Figure A-12	The kinetics of Cr(III) depletion by Washington loam at various pHs. Initial Cr(III) = 10 ⁻³ M Cr(NO ₃) ₃ ·9H ₂ O.	14
Figure A-13	The relation of Cr(III) oxidized to Cr(III) concentration added at various pH conditions. Soil = Washington loam.....	14

ABSTRACT

It is essential to understand the chemical and physical interaction of Cr or Pb with soils, especially, the kinetics of Cr redox reactions with soil materials and sorption of organic lead to soils. Redox processes play a major role in the mobility, transport, and fate of inorganic chemicals.

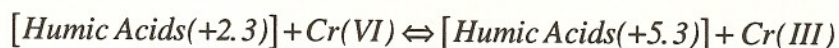
Through examination of Cr(VI) reduction in two different solution matrices, 0.01 M NaNO₃ and simulated ground water, Cr(VI) reduction could not occur in the absence of strong reductants such as Fe(II) or organic matter even under a nitrogen atmosphere, a likely reduced environment.

The formation of Cr(III) from Cr(VI) reduction reaction in soils is related to the iron content of soils and occurs only at very acidic conditions (pH < 4). Also, Cr(VI) can be reduced readily by soils with high organic matter content under acidic and more reducing conditions, such as low oxygen content.

The amount of Cr(VI) reduced increases as soil concentration increases because higher soil concentrations give more "active" sites for Cr(VI) reduction. At the same Cr(VI) loading onto soil, the amount of Cr(VI) reduced by soil (mg/Kg) decreases with increasing soil/solution ratio. This is due to a surface alteration, either by CrO₄²⁻ or Cr(III) adsorption, which would inhibit the dissolution of reductant, Fe(II), from soil surface.

Temperature was one of the most important variables in the kinetics of Cr(VI) reduction. The rate of Cr(III) formation from the reduction reaction increases exponentially, an Arrhenius-type of temperature dependence. The activation energy value of 58.7 KJ/mole for Sassafras sandy loam indicated that chemical reaction processes are rate-limiting step on Cr(VI) reduction by soil.

Cr(VI) is reduced readily at acidic condition with soil humic acids and dominant Cr(VI) reduction might occur at the surface of solid humic acid rather than with soluble humic acid at very low pH (pH 2). Soluble humic acid is the more predominant reductant for Cr(VI) reduction as pH increases up to pH 4.5. The average oxidation state of soil humic acids is about +2.3. Therefore, the reduction reaction of Cr(VI) by humic acids can be stoichiometrically expressed as:



Through the study of Cr(III) oxidation by soils at various experimental conditions, the following results were found:

The oxidation capacity and rate constant of soil is related to the manganese content in soil and sodium dithionite-citrate-bicarbonate extraction shows linear correlation. The relationship was expressed by:

$$\text{Cr(III) oxidation capacity (mg/Kg)} = 1002.3 * (\text{Mn content in soil, \%}) + 128.58$$

$$r^2 = 0.9280$$

Dissolved oxygen did not affect significantly the Cr(III) oxidation in solution, and Cr(III) oxidation occurs by direct reaction with manganese oxides in soil.

Therefore, the Cr(III) oxidation by soil is totally dependent on the amount of available Mn, which is enhanced by increasing temperature.

The activation energy for Cr(III) oxidation by Washington loam estimated by the Arrhenius equation is about 82 KJ/mol, which demonstrates that Cr(III) oxidation may be controlled by a chemical reaction.

The reaction rate constant for Cr(III) oxidation had three different values depending on the pH range. At pH less than 3.5, some inhibition effect on Cr(III) oxidation from the adsorption of anionic Cr(VI) species produced at the surface was dominant. At pH above 5, the oxidation of Cr(III) was a very slow process since the reaction was limited by the adsorption of positive chromium species and the precipitation of $\text{Cr}(\text{OH})_3$.

The production of Cr(VI) by Cr(III) oxidation increases with initial Cr(III) concentration and as the ratio of soil to solution increases. The reaction rate constant is linearly related to the soil/solution ratio.

The effect of ionic strength on Cr(III) oxidation is insignificant and the ratio of Mn to Cr(VI) in solution decreases logarithmically as Cr(III) loading increased.

Chapter 1

INTRODUCTION

The retention of heavy metals in soils brings the possibility that concentrations of soluble trace metals in natural water may increase to potentially hazardous levels. The soils act as vast reservoirs for the toxic heavy metals. The contamination of soils by heavy metals has resulted from numerous activities, such as mining, smelting, metal plating and metal finishing operations, application of industrial wastes, fly ash from incineration.

Among toxic heavy metals, Cr is the metal contaminants most commonly found in New Jersey soils. Cr(VI) species are anionic (i.e., HCrO_4^- and CrO_4^{2-}) and tend to be moderately to highly mobile in groundwater system due to high solubility and weak adsorption onto soils, which are negatively charged in most neutral to alkaline systems. On the contrary, Cr(III) is relatively immobile, because of the precipitation of low-solubility Cr(III) compounds and strong adsorption onto soils (Amacher and Baker, 1982). Chromium may be released to environment either in wastewater discharge or the soil amendment with waste sludge.

Hexavalent chromium compounds are toxic to animals and plants due to their high solubility and diffusivity through the epidermis. In contrast, the skin permeability of the Cr(III) is retarded due to strong binding with epidermal constituents, especially proteins, and its hydration, such as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ (Mali et al.,

1963). Exposure to hexavalent chromium has been associated with respiratory cancer, dermatitis, perforation of nasal septum, renal and hepatic lesions (Davies, 1984; Lindberg and Hedensteirna, 1983; IARC, 1980). Casarett and Doull (1980) reported that 0.5 g to 1.5 g of $K_2Cr_2O_7$ was fatal to human. The threshold limit values established by American Conference of Government Industrial Hygienist (ACGIH) for Cr(III) and Cr(VI) compounds are 0.5 mg/m^3 and 0.05 mg/m^3 , respectively (ACGIH, 1980). The current drinking water limit for soluble Cr is 0.05 mg/L (U.S.EPA, 1984).

The disposal of chromium wastes produced from a number of industrial activities in landfills can cause the release of either Cr(VI) or Cr(III) species to surface and ground waters depending upon environmental conditions. It has been reported the cases of human poisoning with chromium in Japan (Forstner and Wittman, 1981). Building blocks manufactured from Cr(VI)-containing wastes were used in fortifying reclaimed lands, recreational and school areas. Contact with this material was responsible for 30 deaths and over 200 incurable conditions. Along with this, chromium concentration in Tokyo drinking water, which was obtained from groundwater beneath the chromium waster heaps was exceeded 2,000 times the allowable chromium concentration limit. Chromate (CrO_4^{2-}) production and manufacturing activities in Hudson County, New Jersey, created approximately 2 million tons of chromite ore processing residue (COPR) from 1905 to 1975 (ESE, 1988). Until 1960, COPR were used as fill material for the creation of residential, industrial, and commercial area in Hudson County. In recent years, public concern has been raised about the possible health hazards associated with contact or inhalation of Cr(VI) compounds from soil, water, or airborne dust. Cr crystals were found in the walls of basements in the residential area and crusts containing chromate appeared on

the surface of poorly drained soils after a drying period. Moreover, in the summer of 1990, chromium was discovered in the carpet dust, vacuum cleaners of an elementary school, and in the children's blood (Stricharchuk, 1990). ESE (1988) reported that contaminated soils sampled at residential areas of Hudson County contained total chromium levels as high as 4,600 mg/Kg on subsurface soil and as high as 3,580 mg/Kg on the surface soil and as much as 30 % of this chromium was hexavalent which is potential toxin to human and animals.

Remediation of these sites is necessary to reduce the public health hazard from those toxic heavy metals. To achieve this goal, it is essential to understand the chemical and physical interaction of Cr with soils, especially, the kinetics of Cr redox reactions with soil materials. Redox processes play a major role in the mobility, transport, and fate of inorganic chemicals (Barcelona and Holm, 1991). Even though many studies have been conducted on Cr behavior with soil or soil materials, some information may not be useful for the specific sites due to the diversity of soil materials and other environmental conditions. The leachate from COPR has a higher pH (ca. 8.0) than usual pH of most groundwater (5-7) due to high levels of carbonates (Weng, 1994).

The major goal of this research was to evaluate the kinetic parameters of chromium redox reactions in soils with respect to various environmental conditions similar conditions to those at the contaminated site.

Chapter 2

PROJECT DESIGN AND METHODS

2.1 Materials

2.1.1 Reagents

Reagent grade sodium chromate, $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ (CAS Reg. 10034-82-9), was used as a source of Cr(VI). The Cr(III) stock solution (1×10^{-2} M in 0.1M HNO_3) was prepared with reagent grade chromium nitrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (CAS Reg. 7789-02-8). Deionized water was deaerated by purging with inert gas (99.99 % N_2) before using it for all purposes. Distilled and deionized water was used to make Cr(VI) stock solution. Either sodium nitrate, NaNO_3 , or simulated ground water ($I = 0.01$ M) was used as electrolyte to keep an ionic strength. Cr(VI) solutions ranging from 10 μM to 500 μM (0.52 mg/L~26 mg/L) were prepared with the simulated groundwater, acidified with 1N HNO_3 and then kept in 20 gal of polyethylene containers (NALGENETM) till use. Phosphoric acid (H_3PO_4 ; 1+1), 5×10^{-3} M potassium permanganate (KMnO_4), 2×10^{-2} M sodium azide (NaN_3), and 1×10^{-2} M 1,5 diphenylcarbazide (dissolved in acetone) were prepared and preserved in the refrigerator for chromium analysis. The Ferro Ver iron reagent and Ferrous powder pillows were purchased from Hach Co. (Ames, IA) and used as received.

The humic acids (HA) were either obtained from the Aldrich Chemical Company (Milwaukee, WI) or extracted directly from the Sassafras sandy loam which

is the most representative soil in New Jersey. The specification of Aldrich HA is listed in Table 2.1.

2.2 Methods

2.2.1 Analytical Methods

The concentrations of Cr(VI), total Cr, total Fe, and Fe(II) were analyzed by colorimetric methods and other metals were determined with an atomic absorption spectrophotometer (Perkin-Elmer, Model Zeeman 5000, Norwalk, CT). Procedures followed that described in standard methods (APHA, 1985). Cr(VI) was determined by modified 1,5 diphenylcarbohydrazide method using a UV-visible spectrophotometer at 540 nm (Huang et al., 1991). Five ml of extract was acidified with 1 drop of H_3PO_4 (1+1) and mixed completely. Then 1~2 drops of 1,5 diphenylcarbohydrazide reagent were added, mixed and let stand for ca. 15 minutes until a magenta color was developed. Total Cr was determined by oxidizing the Cr(III) to Cr(VI) with potassium permanganate then measuring the Cr(VI) as total Cr (Huang and Bower, 1978). Therefore, Cr(III) can be obtained from the difference of concentration between total Cr and Cr(VI). In analysis of total Cr, 5 mL of extract was acidified with 1 drop of H_3PO_4 (1+1) and add 1~2 drops of KMnO_4 solution, and then thoroughly mixed. The mixture of sample was digested in boiling water for 15 minutes, 1 drop of sodium azide solution was added, and then the sample was heated for 1 to 2 minutes until the purple color disappeared. The digested sample was cooled to room temperature and then the same procedures were followed as were used for Cr(VI) analysis. Total Fe and Fe(II) were determined by the 1,10 phenanthroline method using HachTM Ferro Ver iron reagent and Ferrous powder pillow at wavelength

of 510 nm. Fe(III) was determined from the difference of concentration between total Fe and Fe(II). The amount of organic matter leached from soil was determined by total organic carbon analysis (Beckman Model 915-B, Rosemount Inc.).

2.2.2 Preparation of Simulated Groundwater

It is hypothesized that rainwater dissolves ions from soil during penetrating Cr contaminated surface soil and become groundwater. Groundwater containing Cr may react with uncontaminated subsurface soil. Therefore, it may be reasonable to use simulated ground for the experiments of Cr with subsurface soils. Huang et al. (1994) determined the composition of groundwater by extracting ions from Cr-soil (COPR) using simulated rainwater (pH 4.3). The major ions found were Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , NO_3^{-} , and Cl^{-} . The recipe of the simulated groundwater which has an ionic strength of ca. 10^{-2} M is shown in Figure 2.1.

2.2.3 Isolation of Soil Humic Acid

Humic acid was isolated from the air dried Sassafras sandy loam by a method similar to that used by Tipping et al. (1988). Extraction was done with 250 g of soil and 1L of 0.1 N NaOH under N_2 . The solution was filtered through G-4 glass filter and centrifuged to remove suspended materials. The filtrate was acidified to pH lower than 2 with HCl to precipitate humic acid and then the precipitant was collected. The precipitant was washed three times with 0.1 N HCl and with water until dissolution was no longer observed. Collected humic acid was preserved in the refrigerator for future use.

2.2.4 Potentiometric Titration of Humic Acids

The procedures of titration was a same as that used by Takamatsu and Yoshida (1978). One gram of humic acid was dissolved in 100 mL of 0.05 N NaOH at an ionic strength of 10^{-1} M NaNO_3 . A 50 mL of aliquot was taken into a titration beaker and the pH of the solution was adjusted to about 2 by adding 0.1 N HCl. Titration was undertaken by adding 0.1 N NaOH at 25 °C under a N_2 gas atmosphere. The pH measurement was carried out with a pH meter (Cole/Parmer Chemcadet pH meter: model 5984-50) fitted with sealed combination electrode with a silver/silver chloride reference.

Table 2.1 The Specification of Aldrich Humic Acid.

	Items	Relative values
General & Physical Characteristics	Lot No.	121137W
	Source	Open pit mining in Oberhessen, Germany
	Color	Dark brown
Chemical Characteristics	Insoluble in hot HNO ₃	10-30 %
	Oxide content	9.4 % Fe oxides
	Carbon	50.5 %
	Hydrogen	3.83 %
	Nitrogen	0.5 %

Data source: Schulthess (1985)

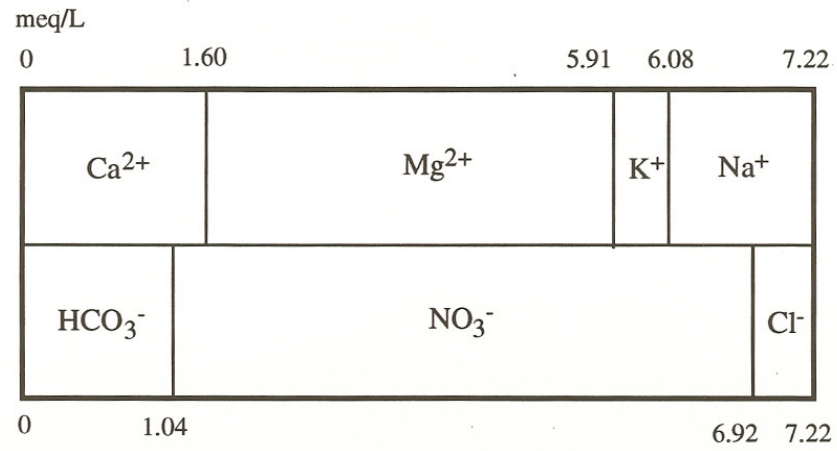


Figure 2.1 Bar chart of ionic balance for the simulated groundwater (Huang et al., 1994).

2.2.5 Cr(III) Oxidation Capacity of Soils

Cr(III) oxidation capacity of soil was estimated by the procedure used by Bartlett and James (1979). 5 g (dry weight basis) samples of 15 New Jersey soils were shaken with 50 mL 1×10^{-3} M Cr(III) for 2 hours and 10 mL 0.1 M KH_2PO_4 was then added. The solution pH was maintained at 2.5 with 0.1 M HNO_3 during the reaction. After adding 0.1 M KH_2PO_4 , the samples were shaken an additional 10 minutes. Supernatants were filtered through 0.22 μm membrane filters and analyzed for Cr(VI) by the colorimetric method. The oxidation capacity of soil was then calculated by the amount of Cr(III) oxidized (mg) per kg of soil.

2.2.6 Batch Experiments of Cr(VI) Reduction Reactions

In order to study kinetics of chromium reactions with soil, a batch reactor was used. The reactor has a volume of 1.5 L, an inlet for either air or nitrogen gas purging, and a sampling port as shown in Figure 2.2. Samples were taken at each pre-selected time using a syringe and filtered with 0.45 μm membrane filter (25 mm, Gelman Sciences Co., Ann Arbor, MI). Filtrate was analyzed for Cr(VI), Fe(II), and TOC immediately and the remainder was kept in the refrigerator for future use. The reaction pH was kept constant with 1N NaOH and HNO_3 as necessary. During experiments, simulated ground water was used as solution media.

Equilibrium experiments were conducted using 125 mL polyethylene bottles. Various amounts of soil and 100 mL of chromium solution were added into a

series of polyethylene bottles. Controls have same amounts of soil and same volume of simulated groundwater but lack chromium. The pH values were initially adjusted with strong acid (1N HNO₃) and base (1N NaOH). The samples were shaken on a reciprocating shaker (Eberbach Co., Ann Arbor, MI) at excursion rate of 150 per minute for at least 24 hours, which is based on kinetic experimental results. The equilibrium pH's were recorded. Aliquots of the suspensions were taken and filtered the same as for kinetic experiments. The concentrations of metals in the filtrate were analyzed by methods described in Section 2.2.

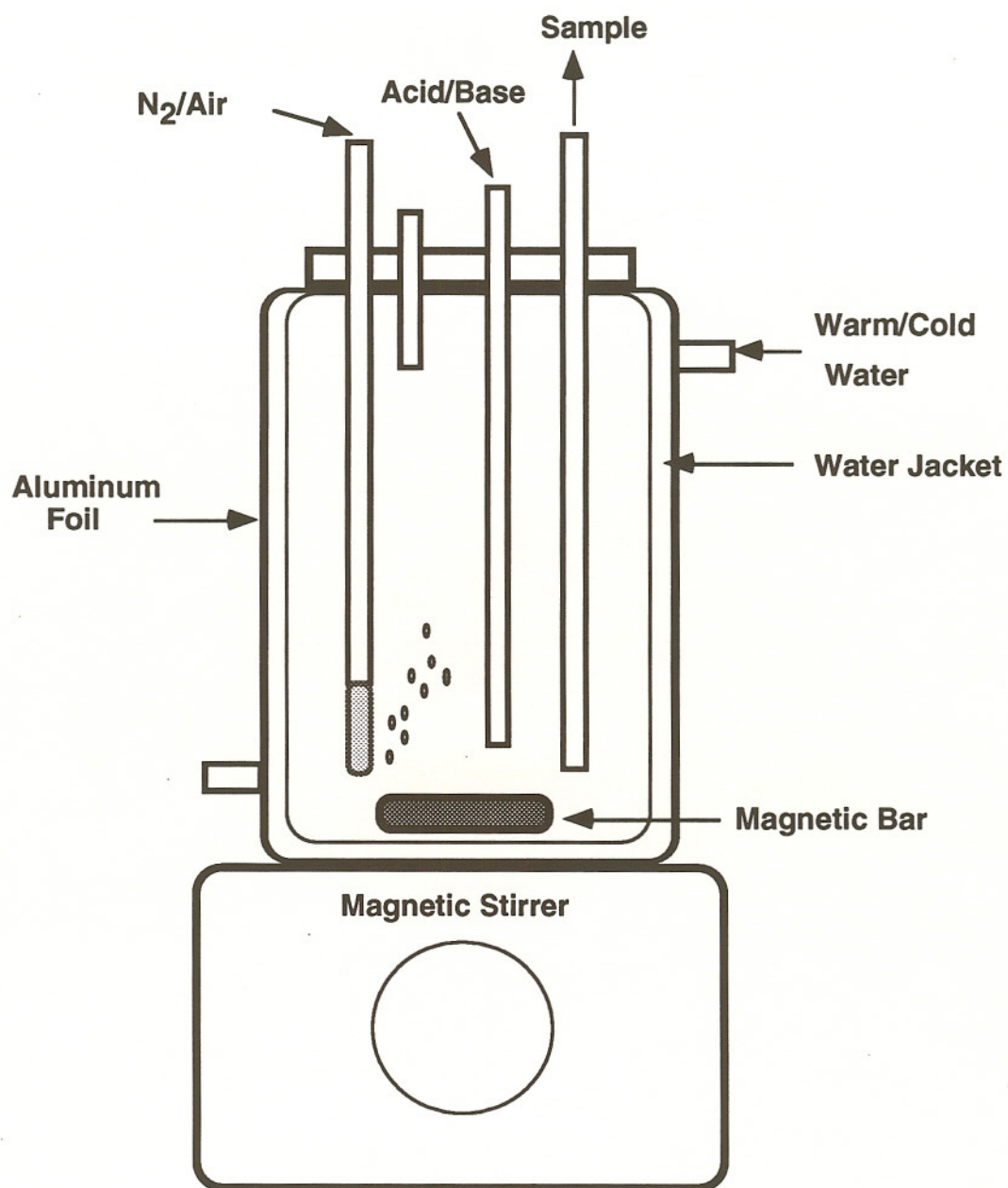


Figure 2.2 Experimental apparatus for kinetic studies of Cr redox reactions.

Chapter 3

QUALITY CONTROL-QUALITY ASSURANCE PROCEDURES

3.1 Quality Assurance Procedures

Procedures in Standard Methods (17th Edition) will be followed in analyzing Cr(VI) and Cr(III). EPA trace metal reference samples are routinely analyzed for method calibration. All laboratory analyses conducted at least triplicate. Samples are preserved and stored in accordance with Standard Methods guideline. Other measurements of the properties of soils followed procedures of ASTM. All test protocols used in our laboratory are documented. Instruments are daily calibrated, and the results of all these analyses, as well as experimental results and procedures, are kept in permanent notebook.

The following procedures are to be exercised in order to assure analytical quality:

- a. Calibration curves are based on the analysis of a blank and four more standards.
- b. Instrument baseline are established at approximately 5 chart divisions. A baseline drift of more than 5 chart divisions (full scale equals 100 divisions) per 10 samples are acceptable.
- c. Calibration curves are analyzed at the beginning and the end of each series of samples. The slope of each calibration curve are calculated by the method of at least squares. The difference between the slopes of initial and final calibration

curves may not be greater than 10 % for acceptance of results. The mean values of two slopes are used to calculate the metal concentration of samples.

d. Following the analyses of no more than five samples, a single mid-concentration standard are analyzed. If the peak height differs by more than 10 % from that calibrated mean slope of calibration curve, samples are regarded as questionable ones and re-analyzed.

e. Triplicate sample cups are prepared and analyzed for 10 % of samples in each group of analyses.

f. The recorder chart are labeled to indicate the analysis, date, analyst and page of the laboratory notebook onto which peak heights are transcribed. Each peak on the recorder chart are identified by sample number and type of standard concentration.

g. The data and quality control are regularly checked by the project quality assurance personnel who are principal and co-principal investigator.

3.2 Data Quality Requirements :

Parameter	Sample Matrix	Detection Limit	Quantitation Limit	Precision	Accuracy
pH	wastewater	± 0.01	1.00 - 14.00	$\pm 1 \%$	99 %
Cr(III)	wastewater	0.01 mg/L	0.5 mg/L	$\pm 5 \%$	99 %
Cr(VI)	wastewater	0.01 mg/L	0.5 mg/L	$\pm 5 \%$	99 %
Fe(II)	wastewater	0.5 mg/L	10 mg/L	$\pm 5 \%$	99 %
Fe _{Total}	wastewater	0.5 mg/L	10 mg/L	$\pm 5 \%$	99 %
Mn _{Total}	wastewater	0.5 mg/L	10 mg/L	$\pm 5 \%$	99 %
TOC	wastewater	1 mg/L	1000 mg/L	$\pm 10 \%$	99 %

This table lists the most pertinent items to be considered in data analysis.

Chapter 4

RESULTS AND DISCUSSION

4.1 Reduction Reactions of Chromium(VI) in Subsurface Soils

4.1.1 The Effect of Cr(VI) Solution Matrix

Cr(VI) reduction experiments in the simulated ground water (SGW: I = 0.01 M) and in 0.01 M NaNO₃ were carried out to determine the solution matrix effect on Cr redox reactions. Figures 4.1 and 4.2 indicated that no Cr(VI) reduction occurred in either solution in acidic condition (pH = 2.5). In these figures, concentrations of Cr(VI) were constant over reaction time (24 hours) and there were no difference between SGW and 0.01 M NaNO₃ under air and nitrogen gas atmospheres. This indicated that there was no solution matrix effect and that Cr(VI) reduction might not occur by itself even under a deoxygenated atmosphere without other strong reductants such as Fe(II) or organic matter.

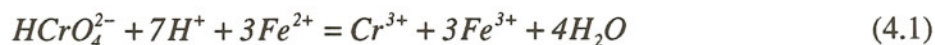
4.1.2 The Effect of pH on the Reduction of Cr(VI) with Soil

Cr(III) formed with soils are shown in Figure 4.3 for a range of pH. The reductions of Cr(VI) occurred only at very acidic conditions (< pH 4) which is lower than typical groundwater pH (ca. 8) and even rain water (pH 4.3) for six different soils. Cr(VI) reduction decreased as the pH increased. The content of amorphous Fe oxides in soils extracted by sodium dithionite-citrate-bicarbonate (DCB) are in the

order (Lee, 1994): Boonton Bergen County (2.080 %) $\approx$ Sassafras sandy loam (1.973 %) > Freehold sandy loam (B horizon; 1.813 %) > Lakewood sand (1.600 %) > Hazen gravelly loam (1.494 %) > Dunellen sandy loam (1.281 %). The amounts of Cr(III) formed at a pH of 2.0 with respect to six soils decrease in the order: Boonton Bergen county loam > Sassafras sandy loam > Lakewood sand > Dunellen sandy loam > Hazen gravelly loam > Freehold sandy loam (B horizon).

Results indicated that the reduction of Cr(VI) was strongly dependent on the solution pH and iron content in soils. Figures 4.4 and 4.5 showed the concentration of ferric iron and the fraction of ferric iron in solution relative to the initial content of amorphous Fe oxides extracted by DCB for a range of pH with respect to six soils, respectively. In both figures Lakewood sand showed the highest Fe dissolution even though the iron content was lower than that of Sassafras sandy loam. Because in highly organic soils organic matter may complex with heavy metals such as iron and manganese and fixate to the solid phase strongly, the dissolution of metals by water can be restrained (Jenne, 1968). In other words, iron may be dissolved readily from the soil with low organic matter content. The organic matter content of soil is as the following order (Lee, 1994) : Boonton Bergen county loam (5.3 %) > Hazen gravelly loam (3.1 %) > Freehold sandy loam (B horizon; 2.4 %) > Dunellen sandy loam (1.9 %) > Sassafras sandy loam (0.6 %) > Lakewood sand (0.5 %). However, some soils used in the experiment are out of order because the dissolution mechanisms of soil materials are too complicate to simplify. In spite of the complexity of the inter-relationship, it is clear thing is that the reduction of Cr(VI) depends on pH.

Figure 4.6 shows the molar ratios of Fe(II) oxidized to Cr(VI) reduced by soils at a pH 2.0. Reduction of chromate by the ferrous ions produced by dissolution of iron oxides from soils in acidic conditions is described by the reaction:



The molar ratio of ferrous iron to chromate is 3:1 based on the stoichiometric equation. The ratios shown in Figure 4.8 range from 0.3 (Boonton Bergen county) to 6.5 (Lakewood sand). Chromium reduction reactions with a Fe(III)/Cr(III) ratio less than 3 would indicate that Cr(VI) was reduced to Cr(III) by gaining electrons from other electron donors besides Fe(II) species (Eary and Rai, 1991). Ratios greater than 3 suggest that Fe(III) was dissolved from soil minerals in addition to Fe(II) and that Fe(II) was dominant electron donor for the chromium reduction reaction. This is supported by the high ratio of 6.5 for Lakewood sand, from which Fe (III) is most readily leached. Eary and Rai (1989) reported that at very acidic conditions chromate reacted dominantly with ferrous iron rather than with dissolved oxygen.

The kinetics of Cr(III) formation by Boonton Bergen county loam with respect to different hydrogen ion concentrations are shown in Figure 4.7. Results indicate that at any selected pH the rate of Cr(III) formation as a function of time is fast up to about 12 hours and then decreases. The rate of Cr(III) formation reaches a plateau, indicating apparent equilibrium, and is faster as pH lowered. Figure 4.8 shows the dissolution of ferric iron from a soil during the chromium reduction reaction shown in Figure 4.7. In aqueous solution iron exists as ferrous or ferric iron at low pH (Bruland, 1983). However, during the Cr(VI) reduction reactions ferrous ion was not detected at four pH conditions studied. It is speculated that ferrous iron can be

oxidized by Cr(VI) and the ferric iron form is prevalent. There are two mechanisms that possibly explain the presence of ferric ion in solution: (1) ferrous iron was released and subsequently oxidized to more stable ferric iron either by chromium reduction or by dissolved oxygen, (2) the ferrous iron component at the soil surface was oxidized first and dissolved as ferric iron.

Figures A-1 to A-6 in Appendix A show the plots of Cr(VI) reduction calculated based on a first-order kinetic reaction. The form of first-order relations has been used in environmental fate modeling for transport and transformation processes in which only the concentration of the pollutant is a variable (Burns et al., 1981; Saleh et al., 1989). The change of Cr(VI) concentration due to the reaction given by equation (4.1) can be expressed as:

$$-\frac{dC}{dt} = kC \quad (4.2)$$

With boundary conditions, $C = C_0$ at $t = 0$ and $C = C_t$ at $t = t$, equation (4.2) can be integrated to:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (4.3)$$

and the half-life is:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k} \quad (4.4)$$

where C_t is the concentration of Cr(VI) at time t and C_0 is the initial concentration of Cr(VI). It is impossible to differentiate quantitatively the amount of Cr(VI) adsorbed, reduced, and precipitated by analytical methods used in this study (Huang et al., 1994). Therefore, the changes of Cr(VI) were evaluated in terms of the reduction of

Cr(VI). The rate constants and half-lives with respect to six soils at four pH conditions are summarized in Table 4.1 and plotted in Figure 4.9. Results demonstrate that rates of Cr(VI) depletion are clearly dependent on pH, i.e., they decrease with increasing pH for all soils. The pH dependence for the Cr(VI) reduction can be expressed by:

$$k = A[H^+]^n \quad (4.5)$$

where k is a rate constant, A and n are constants. This equation in logarithmic form becomes

$$\log k = \log A + n \log [H^+] \quad (4.6)$$

or

$$\log k = \log A - npH \quad (4.7)$$

Table 4.2 lists constants estimated by equation (4.7) which express the dependence of Cr(VI) reduction on hydrogen ion activity at low pH. The values of slope, n , range from 0.214 to 0.570. Eary and Rai (1989) have reported that the rate of chromate reduction is dependent on the dissolution rate of ferrous iron from hematite and biotite. They found that chromate was completely reduced by oxidation of ferrous iron within the first one or two minutes. The decrease of the rate of chromate reduction with the increase of pH may be explained by the dissolution of ferrous iron followed by rapid oxidation to ferric iron. Figure 4.10 demonstrates clearly that the dissolution of ferric iron is dependent on the pH, i.e., the lower the pH, the more the Fe(III) in solution.

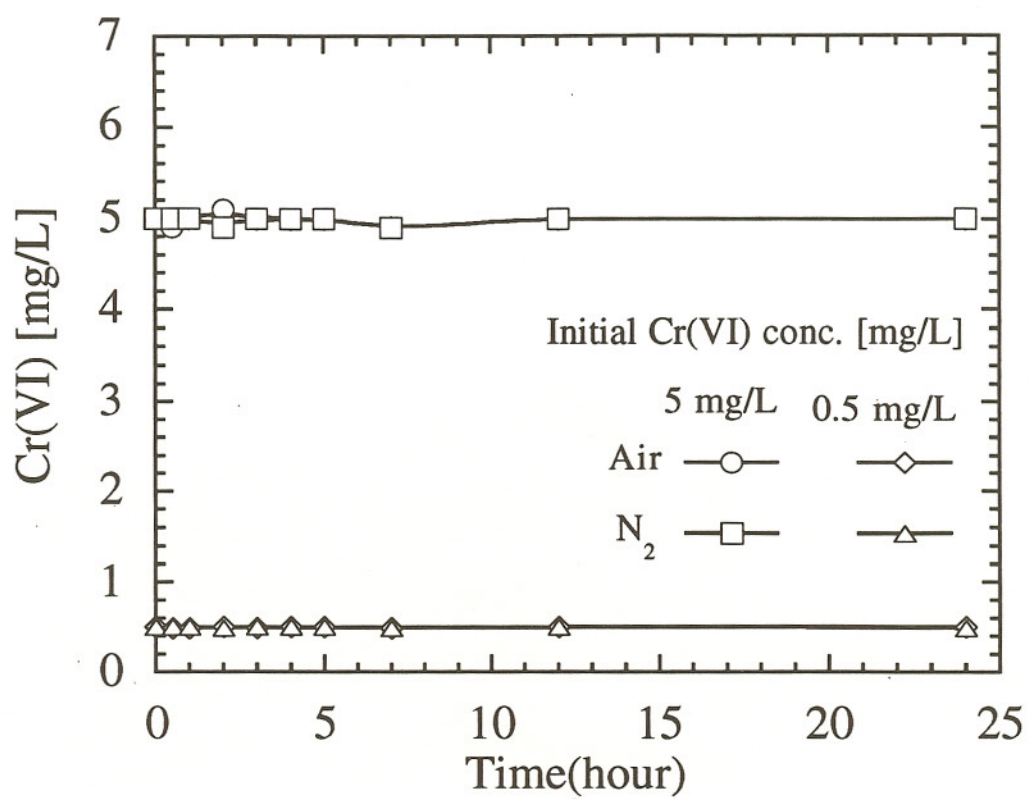


Figure 4.1 Cr(VI) reduction in 10^{-2} M NaNO_3 solution as a function of time. Initial pH = 2.5; Temperature = 23 °C.

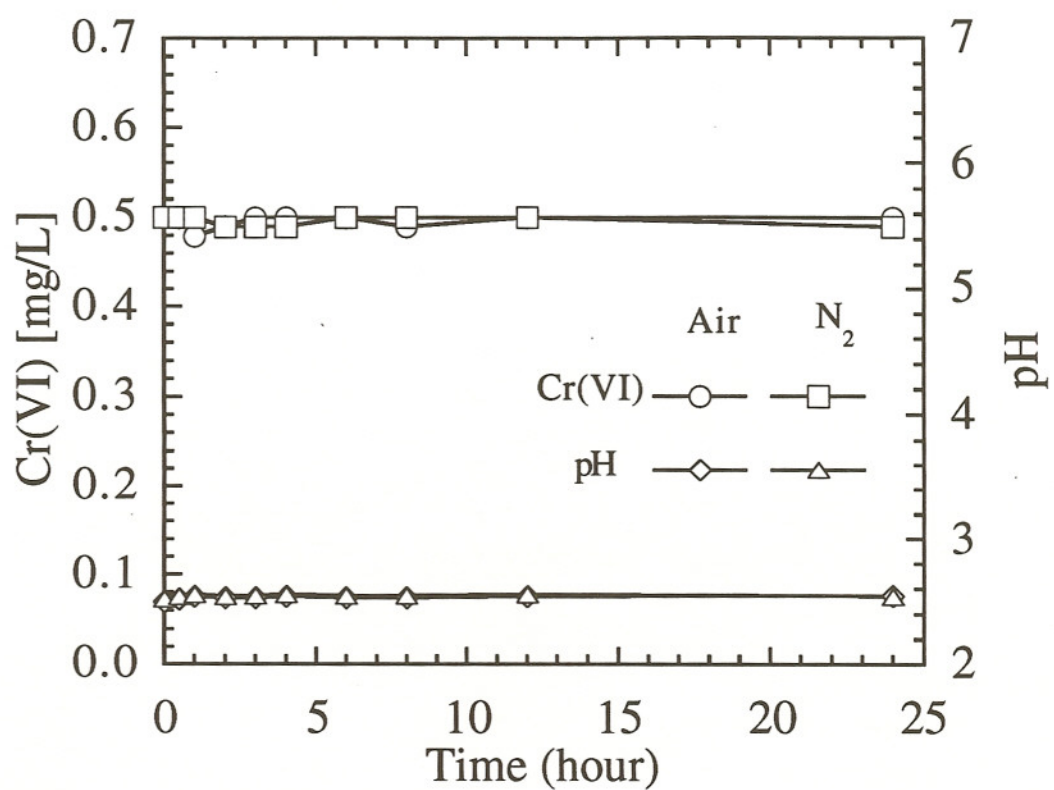


Figure 4.2 Cr(VI) reduction in the simulated ground water (SGW: I = 0.01 M). Initial Cr(VI) = 0.52 mg/L; pH = 2.5. Temperature = 23 °C.

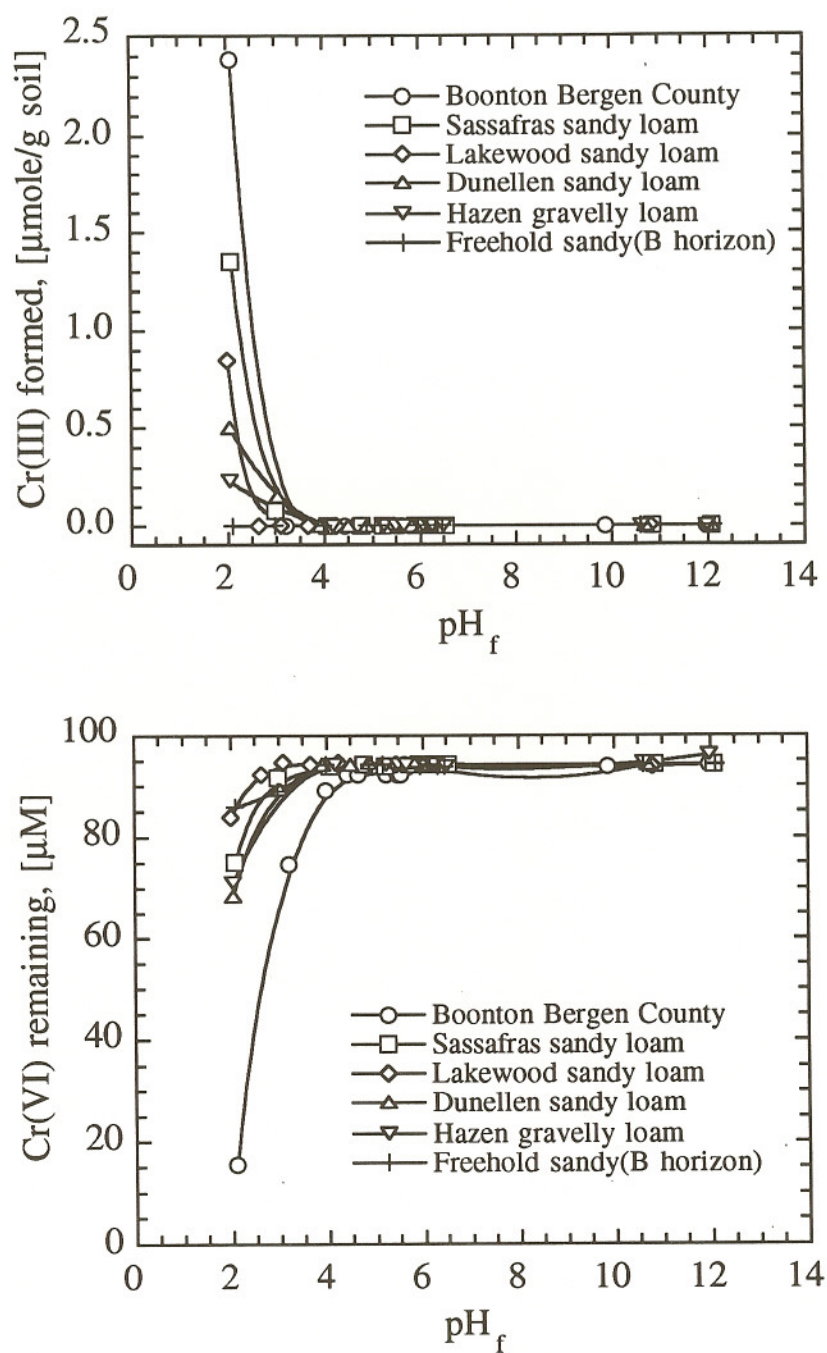


Figure 4.3 Effect of pH on Cr(VI) reduction with soils. Initial Cr(VI) = 10^{-4} M K_2CrO_4 ; I = 0.01 M simulated ground water; Temperature = 25 °C; Soil/solution = 0.5 g/50 mL; Reaction time = 48 hours.

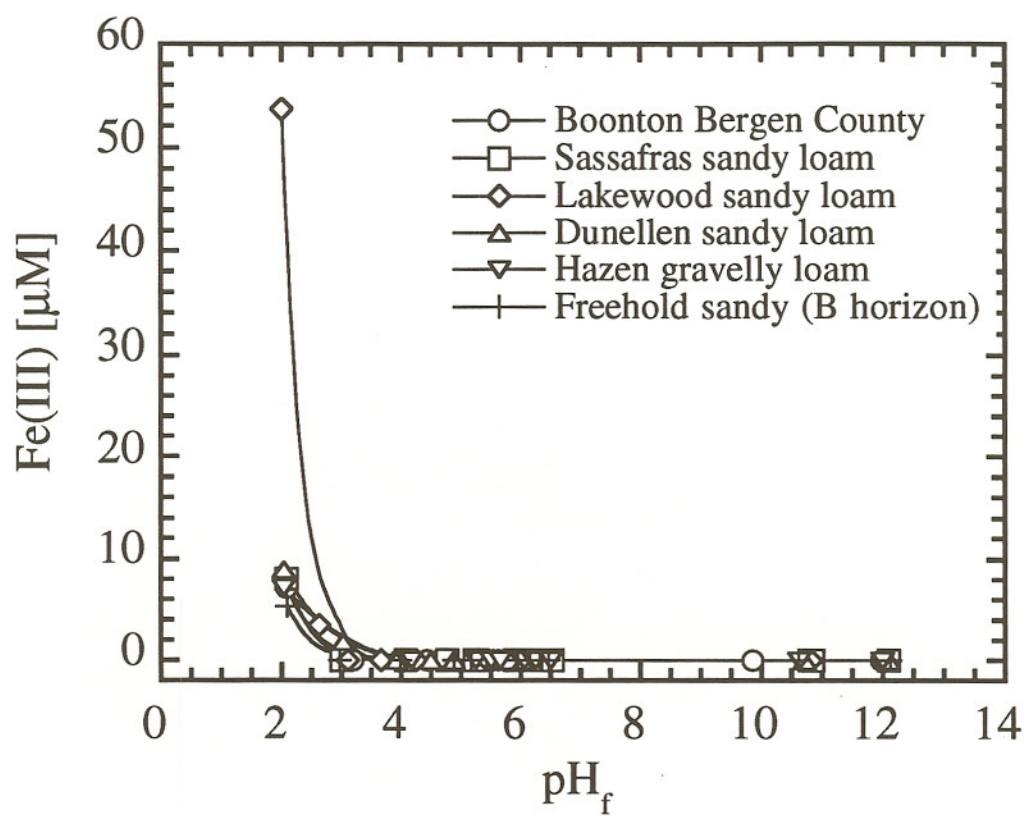


Figure 4.4 The dissolution of Fe(III) with Cr(VI) reduction with respect to pH ranging from 2 to 12. $I = 0.01 \text{ M}$ simulated ground water; Temperature = 25°C ; Soil/solution = $0.5 \text{ g}/50 \text{ mL}$; Reaction time = 48 hours.

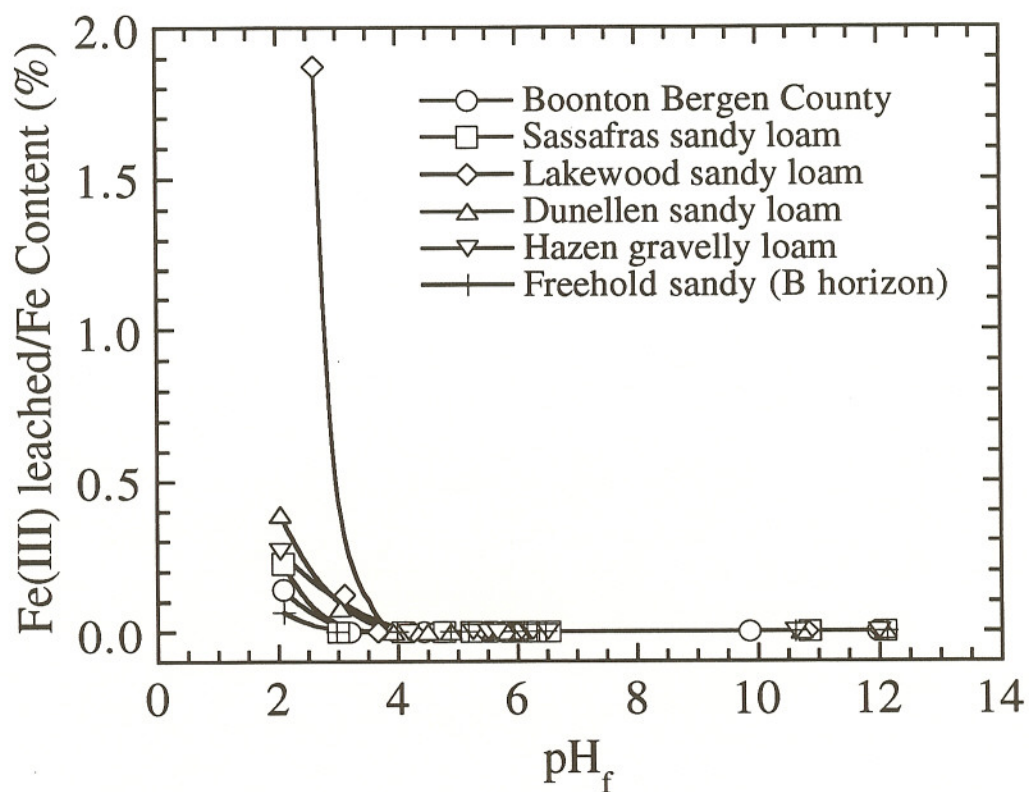


Figure 4.5 The fraction of Fe(III) leached from soils with different iron content at pH ranging from 2 to 12. $I = 0.01$ M simulated ground water; Temperature = 25 °C; Soil/solution = 0.5 g/50 mL; Reaction time = 48 hours.

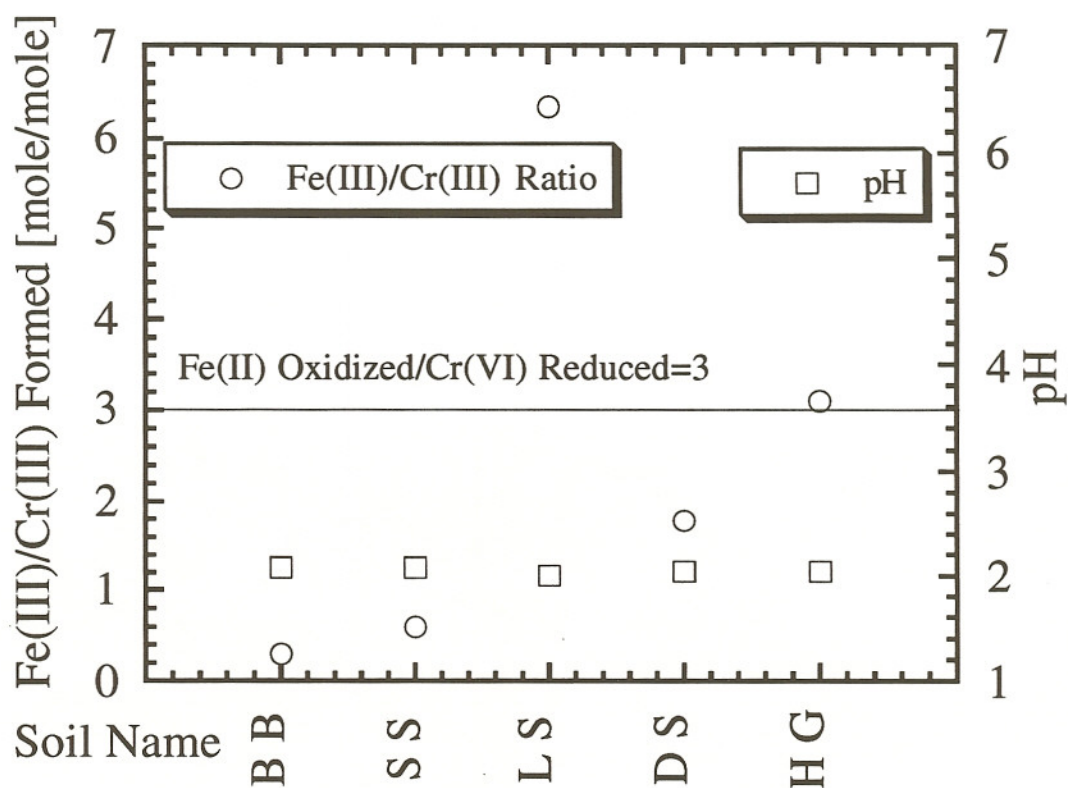


Figure 4.6 The molar ratios of Fe(II) oxidized to Cr(VI) reduced with respect to soils with different iron content. $I = 0.01$ M simulated ground water; Temperature = 25°C ; Soil/solution = $0.5\text{ g}/50\text{ mL}$; Reaction time = 48 hours. The horizontal line in the box indicates the stoichiometric ratio of Fe(III) and Cr(III) predicted for the redox reaction. BB: Boonton Bergen county loam; SS: Sassafras sandy loam; LS: Lakewood sand; DS: Dunellen sandy loam; HG: Hazen gravelly soil.

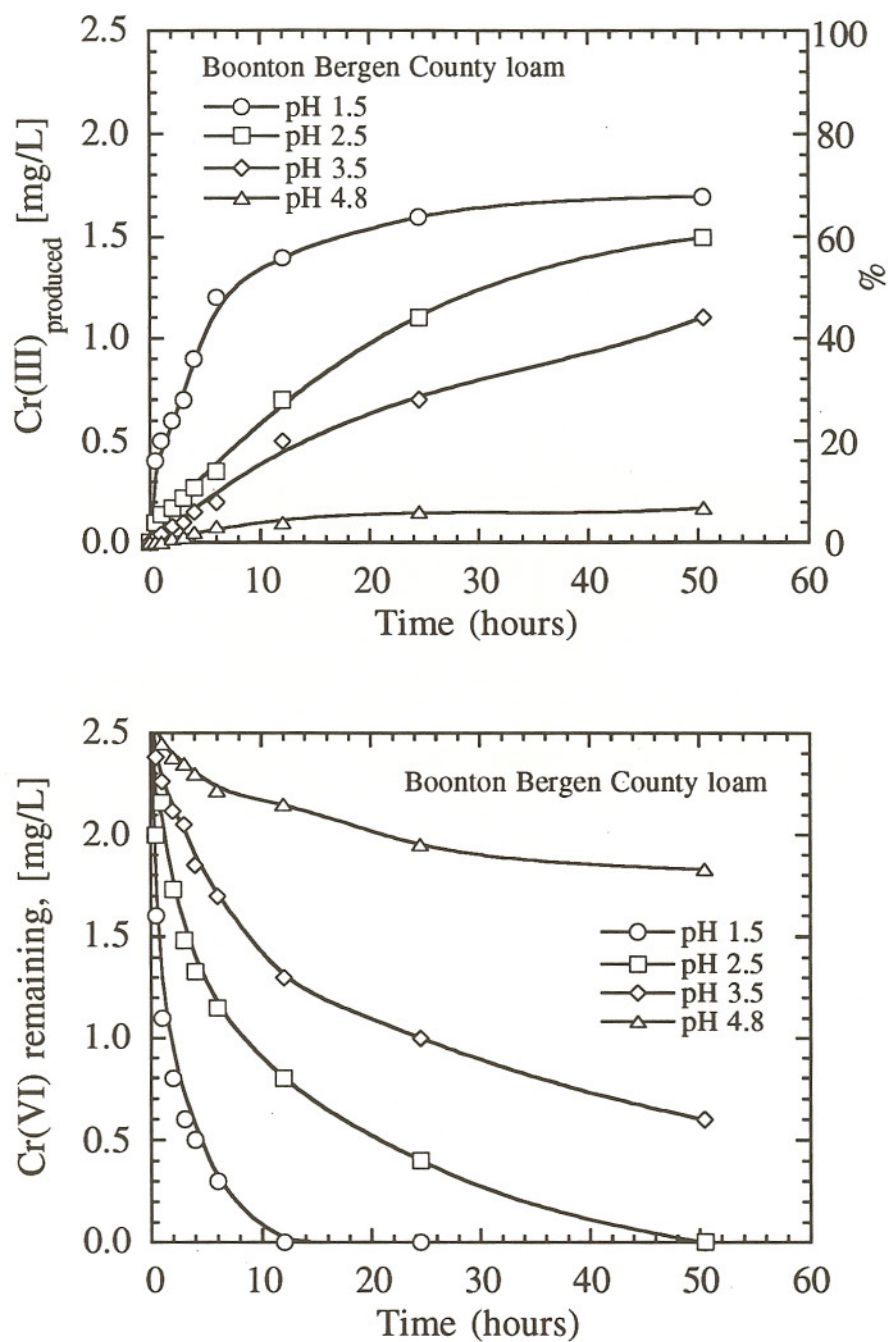


Figure 4.7 Rates of Cr(III) formation by Boonton Bergen county loam for four pH values in 0.01 M simulated ground water. Temperature = 25 °C; Initial Cr(VI) = 2.6 mg/L; Soil/solution = 3.3 g/0.1 L.

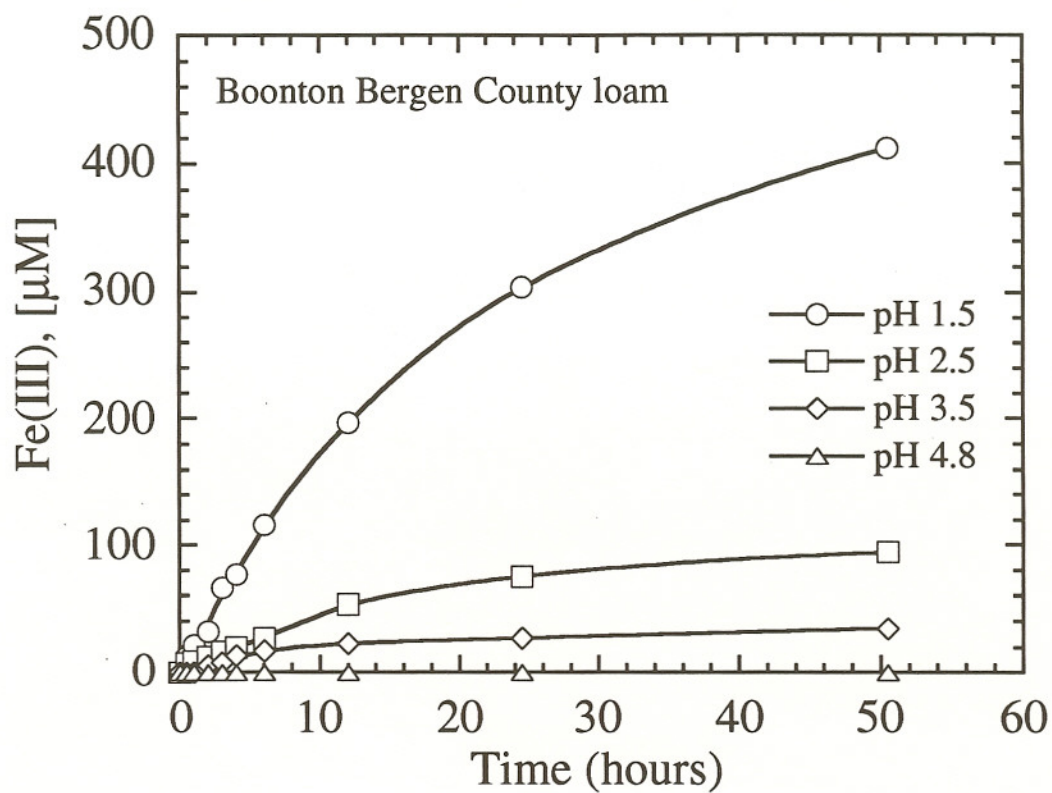


Figure 4.8 Rates of the dissolution of Fe(III) associated with the reduction reaction of Cr(VI) for four pH values. Temperature = 25 °C; I = 0.01 M simulated ground water; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L; Soil used is Boonton Bergen county loam.

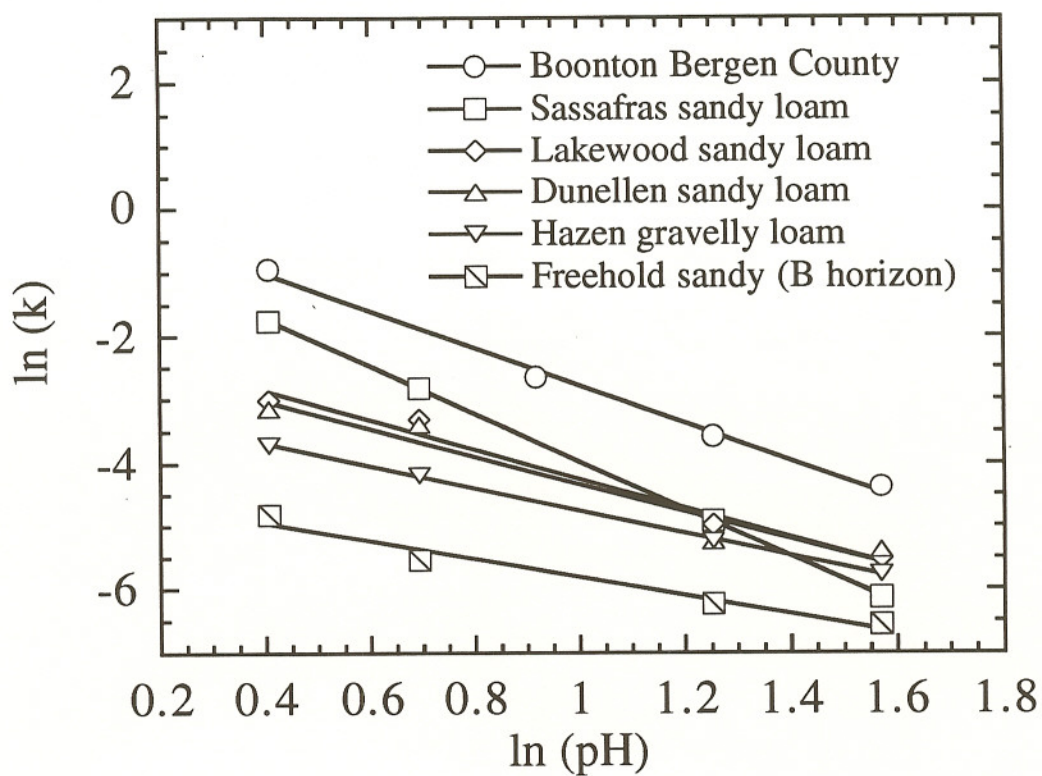


Figure 4.9 Relationship between rate constants of Cr(VI) reduction with soils and pH. Temperature = 25 °C; I = 0.01 M simulated ground water; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

Table 4.1 The rate constants of Cr(VI) reduction with six kinds of soils at acidic conditions.

Soil Name	pH	k (1/hr)	$t_{1/2}$ (hr)	r^2
Boonton Bergen county loam	1.5	3.9×10^{-1}	1.78	0.9882
	2.5	7.1×10^{-2}	9.78	0.9715
	3.5	2.8×10^{-2}	24.84	0.9701
	4.8	1.3×10^{-2}	54.53	0.9447
Sassafras sandy loam	1.5	1.7×10^{-1}	4.00	0.9915
	2.0	6.0×10^{-2}	11.58	0.9918
	3.5	7.3×10^{-3}	94.43	0.9497
	4.8	2.2×10^{-3}	319.40	0.8506
Lakewood sandy loam	1.5	4.9×10^{-2}	14.02	0.9804
	2.0	3.7×10^{-2}	18.84	0.9758
	3.5	6.9×10^{-3}	100.04	0.9550
	4.8	4.0×10^{-3}	172.54	0.9706
Dunellen sandy loam	1.5	4.3×10^{-2}	15.96	0.9686
	2.0	3.4×10^{-2}	20.99	0.9618
	3.5	5.3×10^{-3}	131.64	0.9310
	4.8	4.6×10^{-3}	151.23	0.9387
Hazen gravelly loam	1.5	2.5×10^{-2}	27.95	0.9735
	2.0	1.5×10^{-2}	45.42	0.9671
	3.5	5.3×10^{-3}	130.16	0.9426
	4.8	3.1×10^{-3}	221.23	0.8552
Freehold sandy loam (B horizon)	1.5	8.1×10^{-3}	85.11	0.9721
	2.0	3.9×10^{-3}	176.04	0.9866
	3.5	2.0×10^{-3}	352.53	0.9597
	4.8	1.4×10^{-3}	487.55	0.9634

Table 4.2 Constants obtained from equation 4.7 : the relation between reaction rate and concentration of hydrogen ion.

Soil Name	A	n	r ²
Boonton Bergen county loam	1.2609	0.440	0.9704
Sassafras sandy loam	0.9668	0.570	0.9910
Lakewood sandy loam	0.1631	0.351	0.9827
Dunellen sandy loam	0.1270	0.328	0.9493
Hazen gravelly loam	0.0565	0.272	0.9891
Freehold sandy loam (B horizon)	0.0132	0.214	0.9527

A and n: constants

r²: correlation coefficient

4.1.3 The Effect of Oxygen on the Reductions of Chromium

Figure 4.10 shows the kinetics of Cr(VI) reduction by Sassafras sandy loam under the air and nitrogen gas environments. These results demonstrate that Cr(VI) reduction occurred both under aerated and deaerated condition. The reduction of Cr(VI) seemed to have occurred in two steps. Fast reactions would occur in minutes to hours, and slower reactions would occur in several days. Generally, the reduction rates of Cr(VI) have been faster under anaerobic conditions than under aerobic conditions (Saleh et al., 1989; Bloomfield and Pruden, 1980). As would be expected, Cr(VI) with soil was reduced more under anaerobic conditions than under aerobic conditions but the differences are small. Soils have a potential reducing capacity that could be related to the amount of reducing agents present, such as iron and organic matter.

Figure 4.11 shows the rate of reduction of Cr(VI) by organic carbon under aerobic and anaerobic conditions. The source of organic carbon used was the soil humic acid extracted from Sassafras sandy loam. Bartlett and James (1988) reported that organic compounds could be expected to be the primary reductants for Cr(VI) species in most surface soils. Although the reduction of Cr(VI) by soil under aerobic and anaerobic conditions was not extensively different, under anaerobic condition the effect was quite large when the soil humic acid was used as reducing agent. In Figure 4.11 Cr(VI) under the anaerobic condition was completely reduced after 24 hours, but under aerobic conditions reduction was accomplished after 48 hours. The results indicate that soils with high organic matter content could reduce Cr(VI) readily under

acidic and anaerobic conditions. However, subsurface soils which may contact with waste leachate generally have much lower organic matter contents than surface soils, and hence may be less likely to reduce Cr(VI) with organic matter. In soils with low organic matter, reduction with Fe(II)-containing minerals is probably involved (Eary and Rai, 1991). This result implies that for contaminated soil such as COPR, Cr(VI) itself could be dissolved in groundwater without further reduction when soil adsorption capacity is exceeded. Then, that Cr(VI) could threaten human health through the contaminated groundwater system.

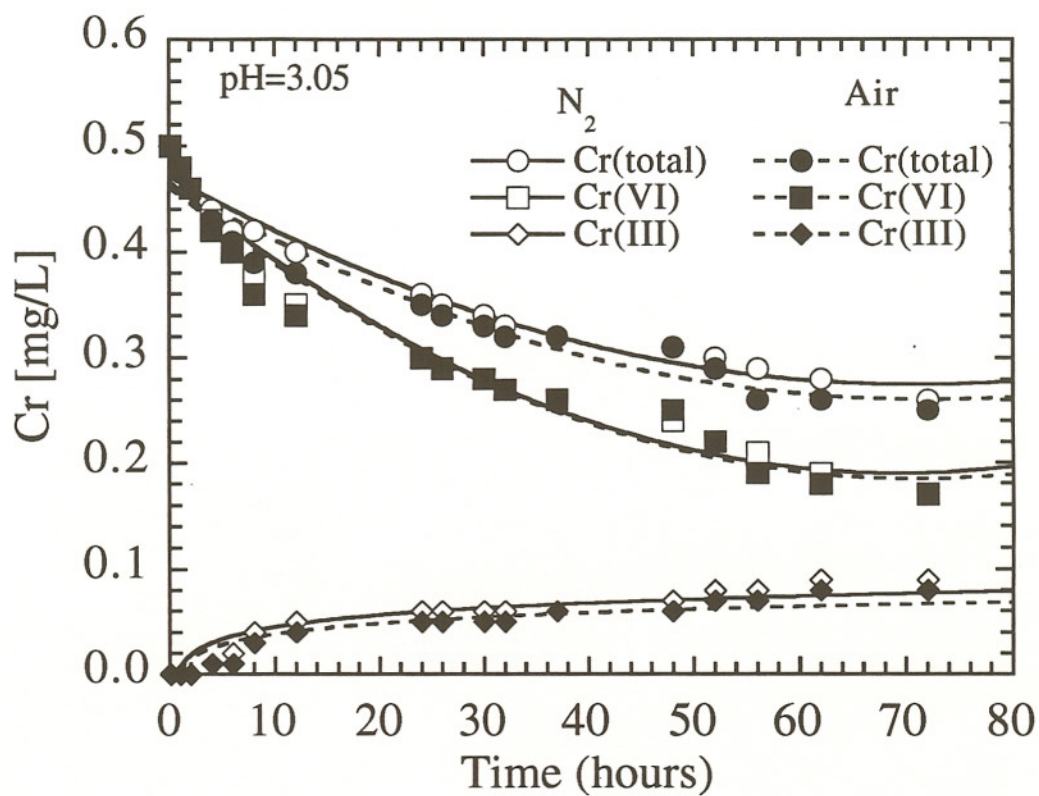


Figure 4.10 The kinetics of Cr(VI) reduction by Sassafras sandy loam. Cr(VI) added = 39 mg/Kg soil; Temperature = 25 °C; Soil/solution = 20 g/1.5 L.

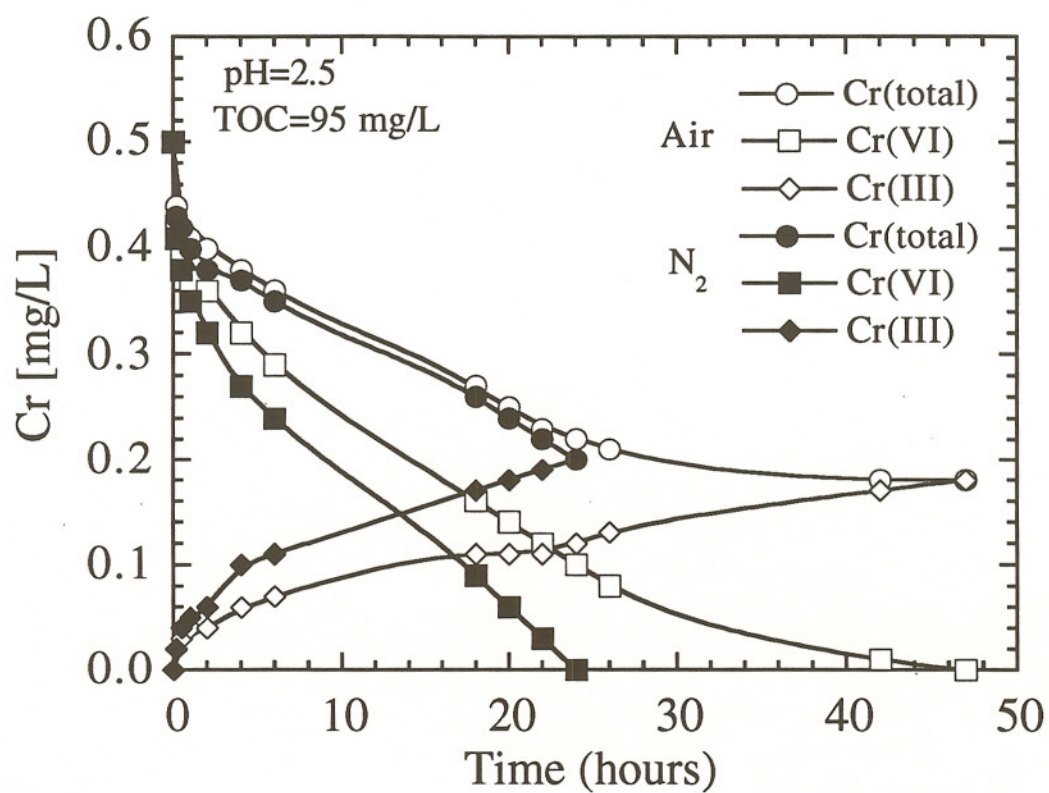


Figure 4.11 The kinetics of Cr(VI) reduction by soil humic acid under air and nitrogen gas conditions. I = 0.01 M simulated ground water; Temperature = 25 °C.

4.1.4 The Effect of Soil Concentration on Cr(VI) Reduction

The amount of reaction sites is one of the important variables in Cr(VI) reduction with soils because the amount of reactant is related to the concentration of "active" sites of solids. Changing the amount of soil per given volume of solution (soil/solution ratio) can change the amount of reaction sites (Amacher, 1991). In this experiment, different initial concentrations of Cr(VI) ranging from 0.52 to 26 mg/L were used to obtain a constant Cr(VI) loading of 37.5 mg Cr(VI)/Kg soil. Figure 4.12 indicates that the amount of Cr(VI) reduced increases with increasing soil concentration and is strongly related to the $[H^+]$ of the soil solution. The reduction of Cr(VI) occurred only at acidic conditions ($pH < 5.6$).

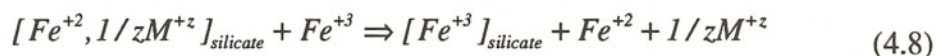
Figure 4.13 shows the Cr(III) formed by Sassafras sandy loam with constant initial Cr(VI) loading, expressed as Cr(III) formed to Kg of soil used and percentage with respect to initial Cr(VI) concentration used. It was expected that the amount of Cr(III) formed would be either constant or increase with increasing soil/solution ratio due to the increase of the quantity of reductants present in soil. The result, however, demonstrated that the amounts of Cr(III) decrease as the soil/solution ratio increase from 0.01 to 0.66. In addition, Cr(VI) reduction was also observed to increase as the pH decreased from 5.2 to 2.0, suggesting that dissolution is an important process that controls the Fe(II) release. Under very acidic conditions, however, the parallel reduction of Cr(VI) by soil organic material is possible, which also increases as the pH is decreases (Eary and Rai, 1991). Table 4.3 gives the relationships between the amount of Cr(III) formed and soil/solution ratio at different

values of pH. Eary and Rai (1991) proposed that the rate of Cr(VI) reduction by organic matter is similar in magnitude to reduction by Fe(II)-containing materials under acidic conditions, making it difficult to determine which reaction is predominant in the soil experiments.

Figure 4.14 shows the concentrations of Fe dissolved from soil associated with Cr(VI) reduction at pH 2.0. The results demonstrate that both Fe(II) and Fe(III) concentrations increase up to the soil/solution ratio of 0.15, and decreasing as soil/solution ratio was further increased. In this figure, the observation of a bell shape rather than a linear or logarithmic increase with soil/solution ratio increase may be explained by the inhibition of Fe(II) dissolution from the soil surface due to a surface alteration. Stumm (1992) explained the inhibition of mineral dissolution well. He suggested that CrO_4^{2-} tends to inhibit the dissolution because CrO_4^{2-} maintains a high redox potential at the oxide-water interface and thus revealing inertia and preventing the dissolution of Fe(II). The Cr(III) reduced can be adsorbed to the oxide surfaces and then the adsorbed Cr^{3+} or CrOH^{2+} surface complex inhibits the dissolution of Fe(II). However, at an experimental pH of 2.0, the Cr(III) adsorption onto Sassafras sandy loam may be negligible because the pH_{zpc} of that soil is 3.40 which is higher than pH 2.0 and soil surface could be positively charged. At lower soil/solution ratio (<0.15), however, it was observed that the inhibition of Fe dissolution was not significant due to low surface "blockage" (Figure 4.14).

The reduction of Cr(VI) with soil may occur by the following steps, assuming that Fe(II) is the only reductant involved in Cr(VI) reduction: (1) Fe(II) dissolution at acidic condition, (2) Cr(VI) reduction reaction by Fe(II), which is described as $\{\text{Cr(VI)} + \text{Fe(II)} \Rightarrow \text{Cr(III)} + \text{Fe(III)}\}$, and then (3) adsorption of Cr(III)

onto surface or co-precipitation of Cr(III) and Fe(III) as a form of $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(\text{s})(\text{am})$, where X represents the mole fraction of $\text{Cr}(\text{OH})_3(\text{s})$ in solid solution (Sass and Rai, 1987; Eary and Rai, 1991; Weng, 1994). In step (1), adsorption of Cr(VI) onto the soil possibly occurs. In either step (2) or (3), coupled electron-cation transfer (CECT) can be involved, which is described as (White and Yee, 1985; White et al., 1985; Weng, 1994):



where brackets represents the solid surface and M is a cation of charge +z. It is speculated that at lower soil/solution ratio (<0.15) CECT reaction may be the predominant mechanism in the increase of Fe(II) dissolution. In the beginning of the reaction, a sufficient amount of Fe(II) to reduce all Cr(VI) may be dissolved. Then, some portion of Fe(II) can be used for Cr(VI) reduction and the rest of Fe(II) may be remain in solution. In this reaction, the oxidation of Fe(II) to Fe(III) by dissolved oxygen is insignificant because this reaction rate is very slow. Eary and Schramke (1990) reported that the half-life of Fe(II) oxidation by dissolved oxygen at pH 1 to 3 is in the range of month to year. Subsequently, Fe(III) produced by Cr(VI) reduction may reduce Fe(II) at soil surface and promote more Fe(II) dissolution by CECT reaction. However, at higher soil/solution ratio (>0.15) Fe(II) dissolution may be retarded either by more Cr(VI) adsorption or by the surface "blockage" associated with Fe-Cr co-precipitation. Dissolution of Fe(II)-oxide, Fe(II)-silicate, 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., 1985; White and Yee, 1985).

Stoichiometric information provided by the Fe concentrations may provide additional information for the upper limit on the amount of Cr(VI) reduced by Fe(II), assuming that the predominant form of Fe dissolved from soils was Fe(II) (Eary and Rai, 1991). Figure 4.15 shows the ratio of Fe(III) to Cr(III) produced from Cr(VI) reduction reaction. It is observed that Fe(III)/Cr(III) ratio decreases logarithmically as soil/solution ratio is increasing and the relationship is described as:

$$\left[\frac{Fe(III)}{Cr(III)} \right] = -1.4893 - 5.1155 \log(Soil / Solution) : R^2 = 0.9853 \quad (4.9)$$

In the figure, the stoichiometric ratio of Fe(III)/Cr(III) that is 3 is observed only at soil/solution ratio of 0.15 where the dissolution of Fe is highest (Figure 4.14).

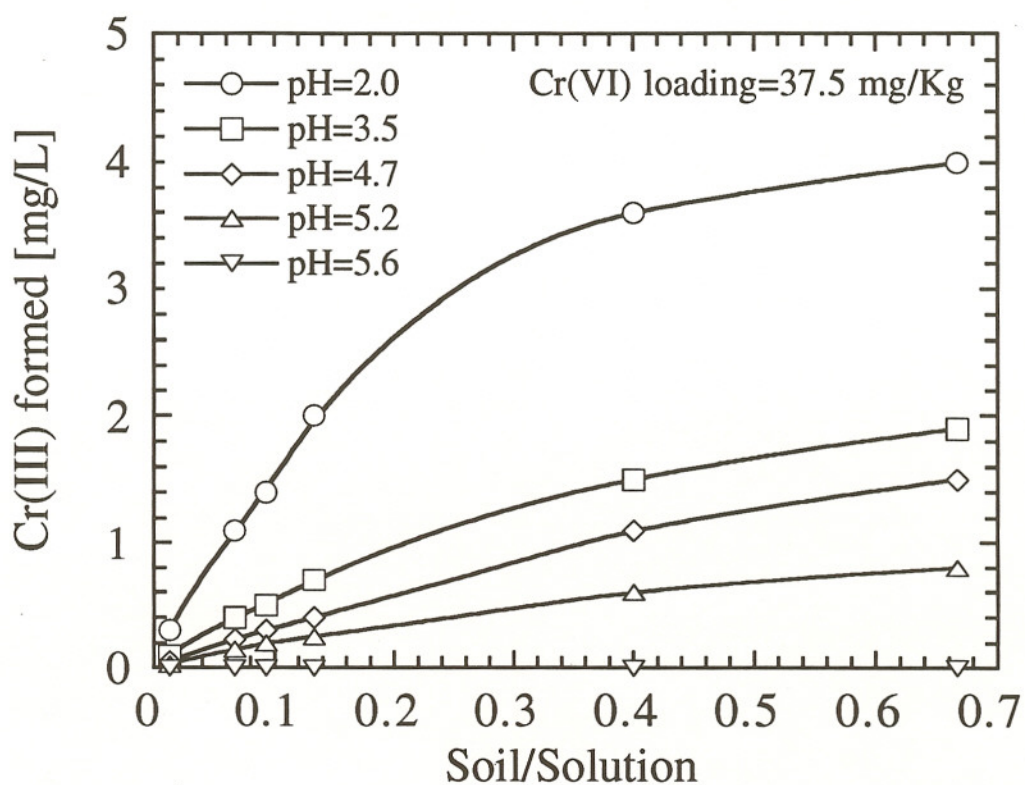


Figure 4.12 The concentration of Cr(III) formed as a function of soil concentration. Initial Cr(VI) concentrations are 0.52, 2.6, 3.64, 5.2, 15.6, and 26 mg/L; Volume of solution = 0.1 L; I = 0.01 M simulated ground water; Temperature = 25 °C; Reaction time = 48 hours.

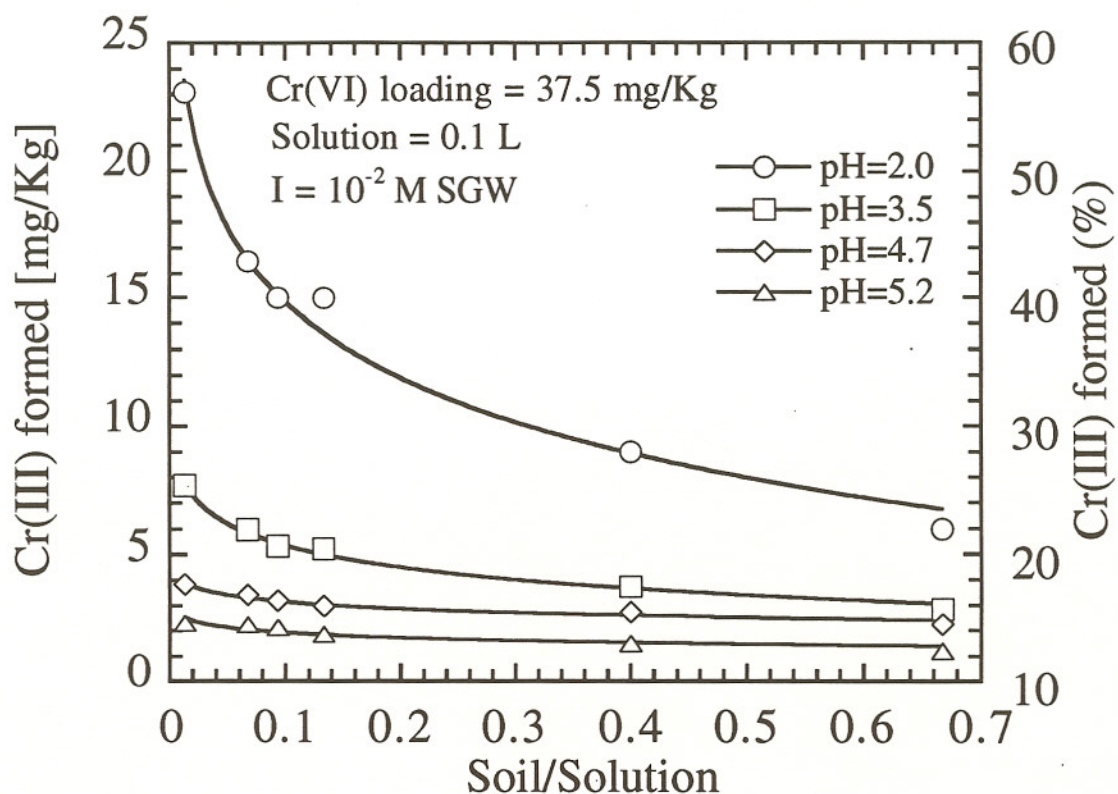


Figure 4.13 The amount of Cr(III) formed per unit weight of soil. The percentage of Cr(III) formed is based on the initial Cr(VI) concentration with respect to different soil concentrations. Soil = Sassafras sandy loam; Volume of solution = 0.1 L; I = 0.01 M simulated ground water; Temperature = 25 °C; Reaction time = 48 hours.

Table 4.3 Non-linear relationship between Cr(III) formation and soil/solution ratio at acidic conditions.

pH	Regression for Cr(III) formed *	R ²
2.0	$y = 5.036 - 9.808 \log (X)$	0.99246
3.5	$y = 2.571 - 2.792 \log(X)$	0.99461
4.7	$y = 2.260 - 0.893 \log(X)$	0.97437
5.2	$y = 1.256 - 0.675 \log (X)$	0.91746

* : $y = \text{Cr(III) formed, [mg Cr(III)/Kg soil]}$

$X = \text{Soil/Solution ratio}$

Experimental conditions :

- Soil used : Sassafras sandy loam
- Cr(VI) loading = 37.5 mg/Kg
- Volume of solution = 0.1 L
- Temperature = 25 °C
- $I = 10^{-2}$ M Simulated ground water

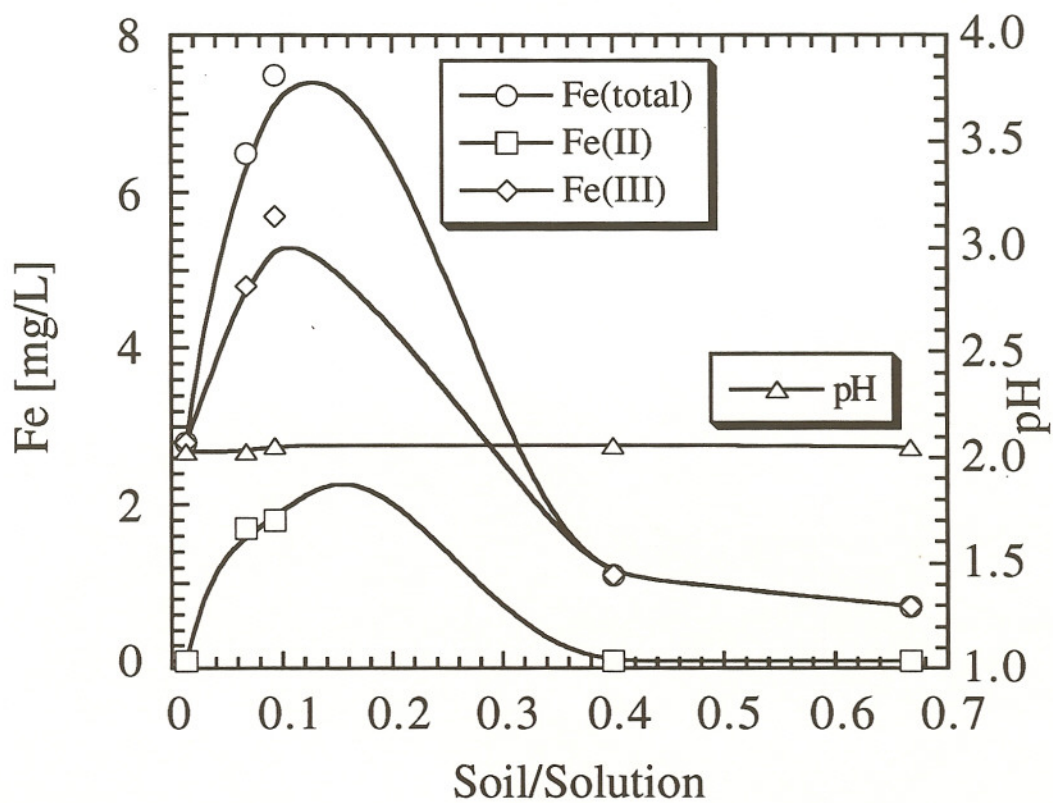


Figure 4.14 The concentration of iron leached, associated with reduction reaction of Cr(VI), with respect to soil/solution ratio. Soil = Sassafras sandy loam; Volume of solution = 0.1 L; I = 0.01 M simulated ground water; Temperature = 25 °C; Reaction time = 48 hours.

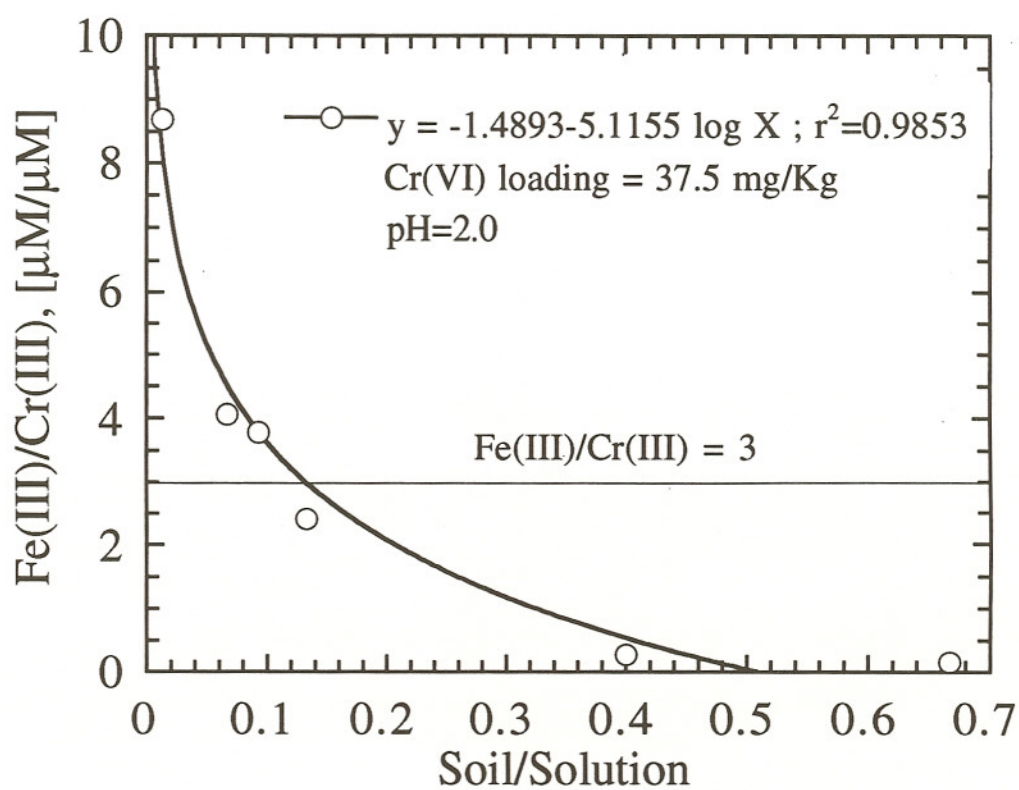


Figure 4.15 The ratio of Fe(III) oxidized to Cr(III) reduced with respect to soil/solution ratio. pH = 2.0; Cr(VI) loading = 37.5 mg/ Kg soil.

4.1.5 The Effect of Temperature on Cr(VI) Reduction

It is frequently reported that temperature is one of the most important variables in soil kinetic studies (Barrow and Saw, 1975; Evans and Jurinak, 1976; Sparks and Jardine, 1981; Ogwada and Sparks, 1986; Amacher, 1991; Lin, 1992). Figure 4.16 shows the rate of Cr(VI) reduction by Sassafras sandy loam at various temperatures ranging from 4 °C to 45 °C. Chemical reaction rates generally increase with increasing temperature (Weber, 1972). The results indicate that Cr(VI) was removed much faster at higher temperature (45 °C) than at lower temperature (4 °C). At 45 °C, Cr(VI) was removed completely from solution after 4 hours of reaction, while at 4 °C only about 55 % of Cr(VI) was removed even after 50 hours reaction. A portion of Cr(VI) removal may be reduction to Cr(III) and the rest may be adsorption onto the soil surface. Figure 4.17 shows the rate of Cr(III) formation with respect to temperature. The result demonstrates clearly the temperature effect on Cr(VI) reduction, the higher the temperature, the more the Cr(VI) is reduced.

Rate constants and half-life time of Cr(III) formation calculated using the first-order relationship [equation (4.3) and (4.4), respectively], plotted in Figure A-7 of Appendix A, are listed in Table 4.4. The rate of Cr(III) formation increased exponentially which is Arrhenius-type of temperature dependence (Figure 4.18) and follows the empirical "common rule" that reaction rates increase by a factor of 2-3 for each of 10 °C rise in temperature (Weber, 1972). Therefore, the temperature dependence of the reaction rate of Cr(VI) reduction can be described by the well-known Arrhenius equation.

$$\frac{d \ln(k)}{dT} = \frac{E_a}{RT^2} \quad (4.10)$$

Equation (4.10) can be integrated to obtain

$$k = Ae^{-E_a/RT} \quad (4.11)$$

or, in logarithmic form

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad (4.12)$$

where k is the rate constant; A is the Arrhenius frequency factor (sec^{-1}); R is the universal gas constant ($8.314 \text{ J/mole}^\circ\text{K}$); T is the absolute temperature, $^\circ\text{K}$ ($= ^\circ\text{C} + 273.15$); E_a is the activation energy. A linear plot of equation 4.12, $\ln(k)$ versus $1/T$, yields the activation energy, E_a , from the slope, E_a/RT (Figure 4.19 and Table 4.4). Experimental values of activation energy are found to range from a few Kcal/mole (ca. 10 KJ/mole) to 25 Kcal/mole (100 KJ/mole) (Stumm and Morgan, 1981).

The magnitude of the activation energy is often used as a direct criteria to distinguish between diffusion-controlled and chemical reaction-controlled kinetics (Weber, 1971). Low activation energies ($<42 \text{ KJ/mole}$) usually indicate that reaction is diffusion-controlled, whereas higher activation energies indicate chemical-controlled processes (Sparks, 1985, 1986, 1989). It is very logical that an energy barrier must be overcome to break a chemical bond in a chemical reaction. On the other hand, diffusion requires no chemical bond breaking for reaction, so energy barriers are low (Amacher, 1991). The activation energy of the Cr(VI) reduction by Sassafras sandy loam is 58.7 KJ/mole ($= 14.0 \text{ Kcal/mole}$). This relatively high activation energy indicates that chemical reaction processes, either in solution or at the

soil surface, control the Cr(VI) reduction reaction and a chemical reaction is the rate limiting step. The values of activation energies of various reactions have been reported elsewhere. Activation energies for pesticide sorption on soils were found to range from 6.7 to 26.4 KJ/mole (Haque et al., 1968; Leenheer and Ahlrichs, 1971; Khan, 1973), while E_a values for the oxidation of pyrite ranged from 57 to 92 KJ/mole (McKibben and Barnes, 1986; Wiersma and Rimstidt, 1984; Lin, 1992). Usually diffusion-controlled kinetics occurs under static or low agitation conditions, but under vigorous mixing conditions, diffusion is no longer limiting (Amacher, 1991).

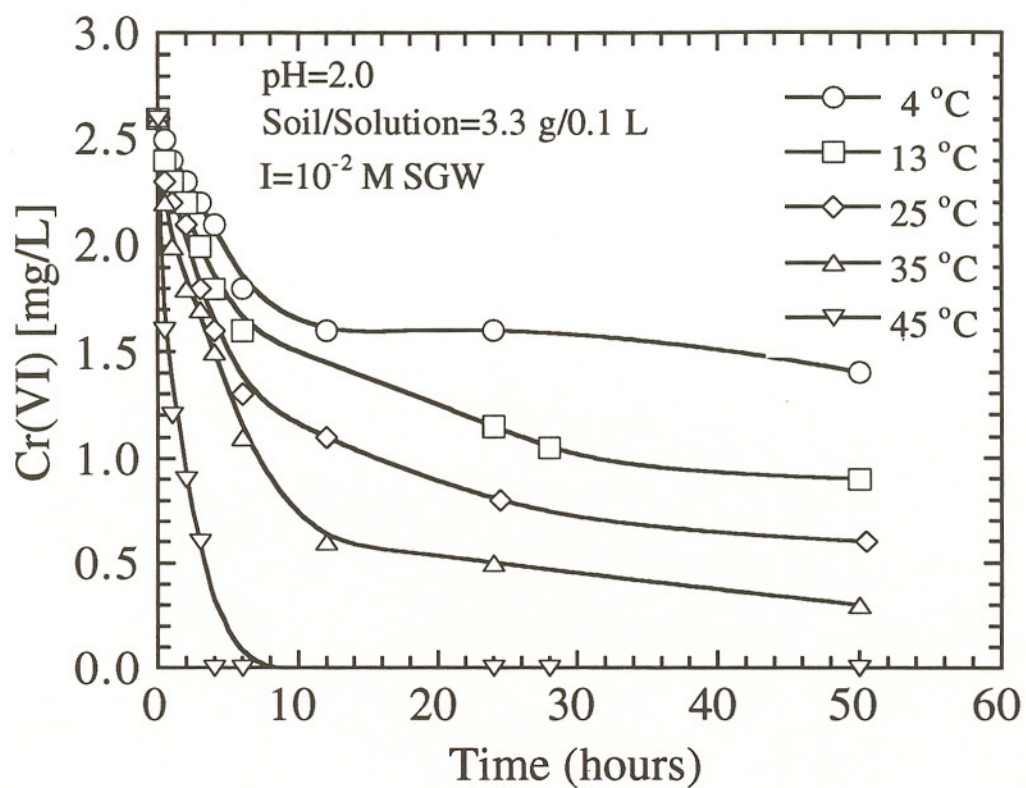


Figure 4.16 The rate of Cr(VI) reduction by Sassafras sandy loam at various temperatures. Initial Cr(VI) concentration = 2.6 mg/L; I = 0.01 M simulated ground water; Soil/solution ratio = 3.3 g/0.1 L; pH = 2.0.

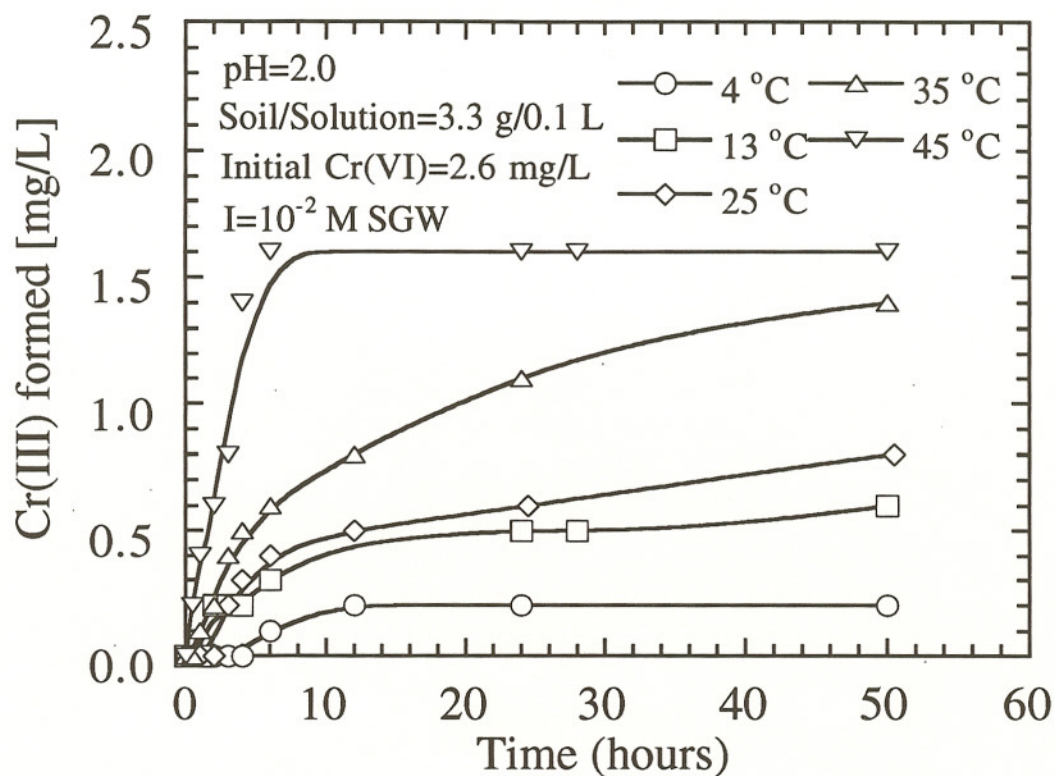


Figure 4.17 The rate of Cr(III) formation at various temperatures. Initial Cr(VI) concentration = 2.6 mg/L; I = 0.01 M simulated ground water; Soil/solution ratio = 3.3 g/0.1 L; pH = 2.0.

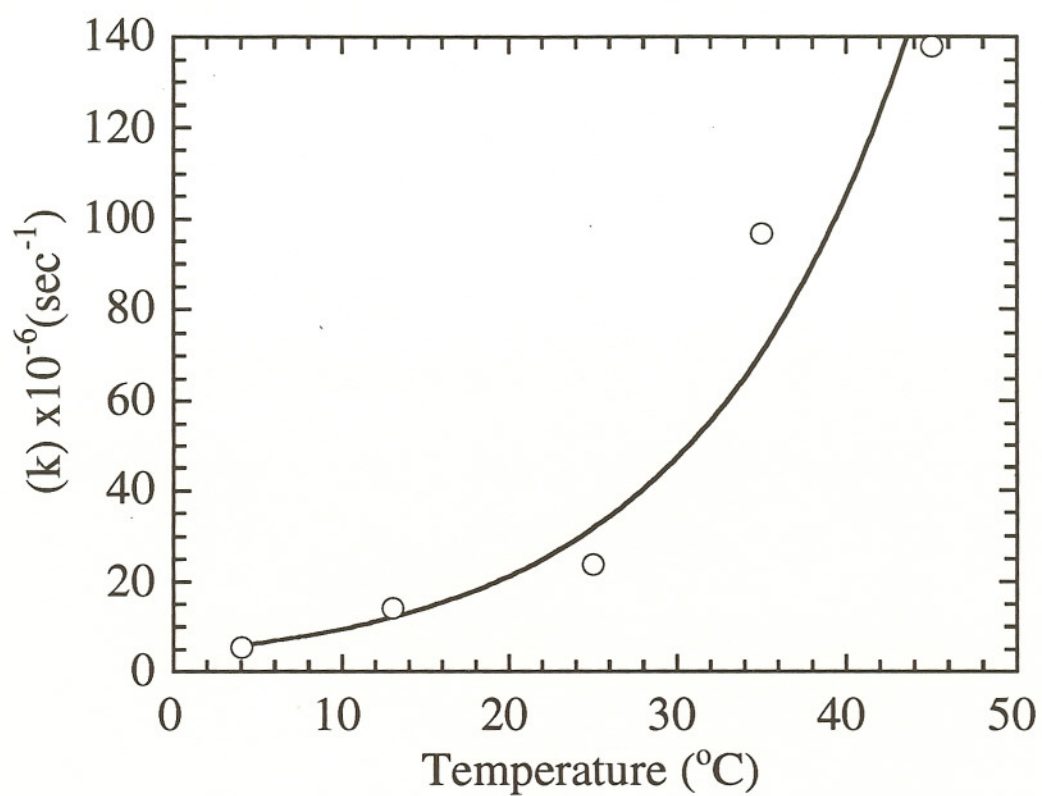


Figure 4.18 The temperature dependence of rate constant, k , for Cr(VI) reduction by Sassafras sandy loam. Initial Cr(VI) concentration = 2.6 mg/L; $I = 0.01$ M simulated ground water; Soil/solution ratio = 3.3 g/0.1 L; pH = 2.0.

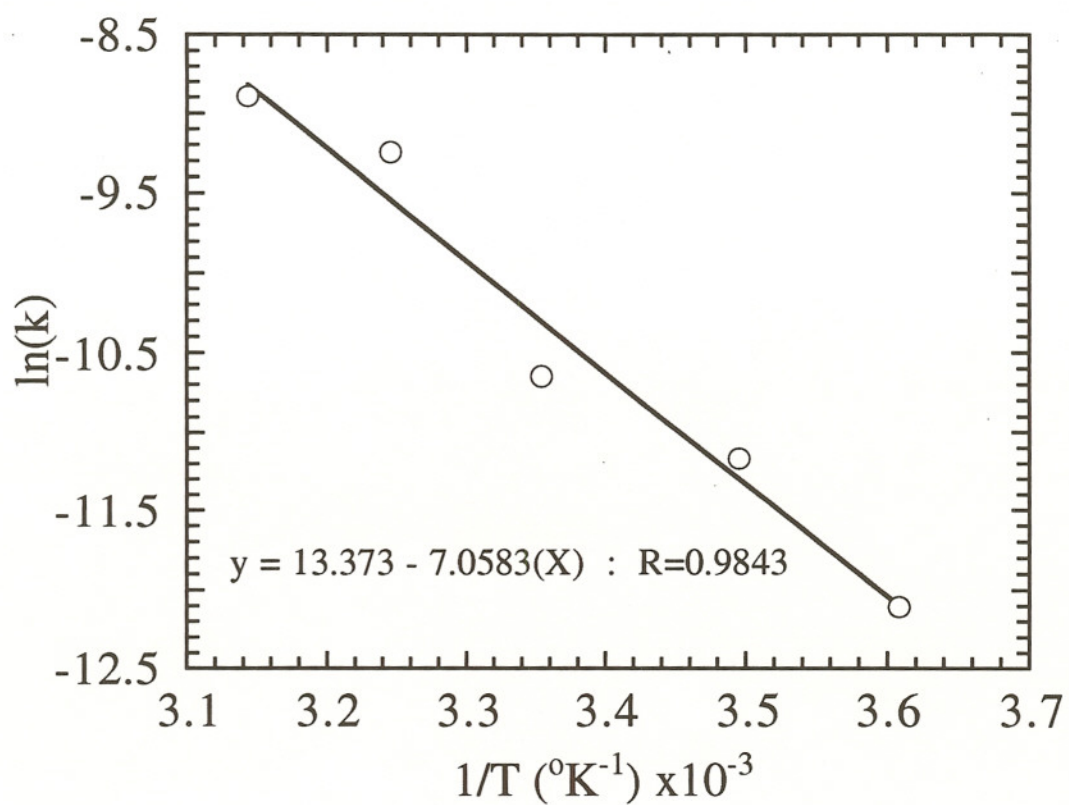


Figure 4.19 The temperature dependence of rate constants plotted by Arrhenius equation. Soil used = Sassafras sandy loam; pH = 2.0; Initial Cr(VI) concentration = 2.6 mg/L; Soil/solution = 3.3 g/0.1 L; I = 0.01 M simulated ground water.

Table 4.4 Rate constants and activation energies for Cr(VI) reduction by Sassafras sandy loam at different temperatures.

Temperature °K	Rate Constant k, (1/sec)	Half-life $t_{1/2}$, (hour)	Activation Energy (KJ/mole)*
277.15	5.539×10^{-6}	34.76	58.7 (=14.0 Kcal/mole)
286.15	1.411×10^{-5}	13.64	
298.15	2.384×10^{-5}	8.08	
308.15	9.676×10^{-5}	1.99	
318.15	1.380×10^{-4}	1.40	

Experimental conditions :

- Initial Cr(VI) = 5×10^{-5} M (2.6 mg/L)
- pH=2.0
- I= 10^{-2} M Simulated ground water
- Soil/Solution = 3.3 g Sassafras sandy loam/0.1 L

* : Frequency factor (A) = 640497 (1/sec), R = 0.9843

4.1.6 Cr(VI) Reduction by Soil Organic Matter

4.1.6.1 Chemistry of Soil Humic Acids

Information on the chemical and functional properties of humic acids (HA) is important for the understanding of their origin and for the evaluation of their role in speciation, transport, immobilization, bioavailability, biogeochemical cycling of organic compounds and metal ions in the environment (Senesi and Sakellariadou, 1994). However, the identification of the HA functional groups is a difficult task.

Many researchers reported that the functional groups which respond to acid-base titrations are mainly carboxylic (-COOH), phenolic ($\phi\text{-OH}$), and alcoholic (R-OH) (Grant, 1977; Peschel and Wildt, 1988; Schulthess, 1985; Wershaw et al., 1981; Wershaw, 1993). FT-IR (Fourier Transform Infrared) spectroscopy analysis of humic acids identified possible functional groups present in Aldrich and Sassafras humic acids (Figure 4.20 a, b).

The infrared spectra of Sassafras HA were recorded as KBr pellets on a Mattson Alpha Centauri FT-IR in the Department of Chemistry, University of Delaware and that on Aldrich humic acids were adopted from Schulthess' thesis (Schulthess, 1985). The frequency range of aromatics, amides, aldehydes, and carboxylic acid functional groups are superimposed on the figures. Although the IR scans are too complex to identify individual absorbance (or transmittance) peaks, at least they give peaks within the frequency range scanned. These FT-IR scans show

that the humic acids examined here have aromatic, phenolic and carboxylic groups as expected.

The carboxylic and phenolic groups in humic acids are responsible for the acidic nature of HA (Borggaard, 1974; Schulthess, 1985; Leenheer et al., 1995). Because humic acids are polydisperse mixtures of natural organic polyelectrolytes, the individual carboxylic acids and phenols have different acid dissociation constants (Borggaard, 1974; Ochs et al., 1994). The reactions of humic acids are assumed to be:



where A^- is carboxyl group (COO^-) and ROH is alcoholic ($-OH$) or phenolic ($\phi-OH$) group. The acidity constants for these reactions fall in groups each associated with an "average" acidity constant ($p\bar{K}$) described as:

$$\bar{K}_{a,COOH_1} = \frac{[H^+][HA^-]}{[H_2A]} \quad (4.16)$$

$$\bar{K}_{a,COOH_2} = \frac{[H^+][A^{2-}]}{[HA^-]} \quad (4.17)$$

$$\bar{K}_{a,OH} = \frac{[H^+][RO^-]}{[ROH]} \quad (4.18)$$

An acid-base titration would yield the information on the average acidity constants of humic acids (Borggaard, 1974; McCallum and Midgley, 1975; Takamatsu and Yoshida, 1978). Figure 4.21 shows the titration curve for Aldrich and Sassafras

humic acid. Although it may be somewhat rough, the plot of $\Delta\text{Vol}/\Delta\text{pH}$ against ΔpH can be used to estimate $p\bar{K}$ values simply (Figure 4.24.a and b). In the figures, the maxima correspond to equivalence points while the minima correspond to $p\bar{K}$ values of carboxylic and phenolic groups in humic acid (Borggaard, 1974; Schulthess, 1985). Results indicate that there are three distinguishable equivalence points and three $p\bar{K}$ values. The first two points probably correspond to two types of carboxylic groups and the third one corresponds to phenolic OH (Borggaard, 1974). Table 4.5 gives the $p\bar{K}$ values on humic acids extracted from various soils. The $p\bar{K}$ values estimated in this study agree with those presented in the literature (listed in Table 4.5).

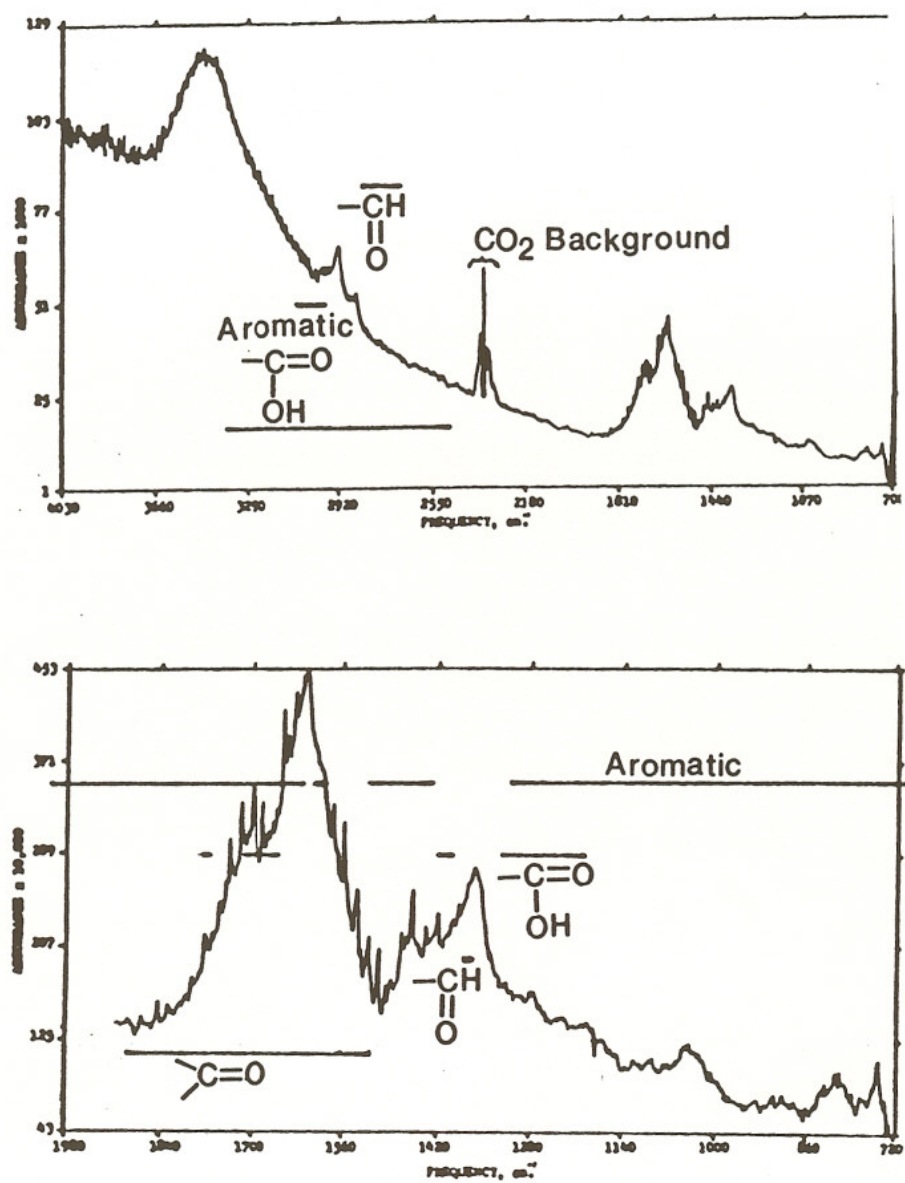


Figure 4.20a FT-IR spectra of Aldrich humic acid.

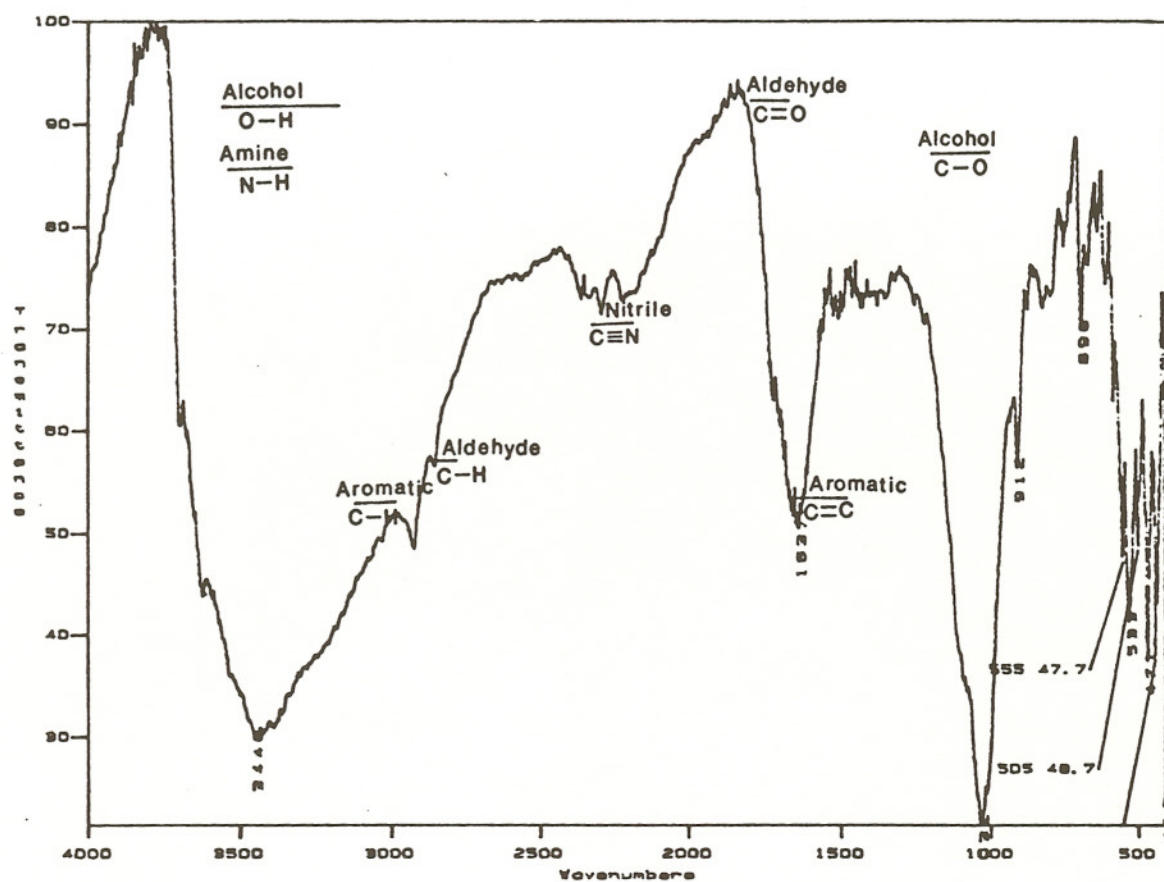


Figure 4.20b FT-IR spectra of Sassafras humic acid.

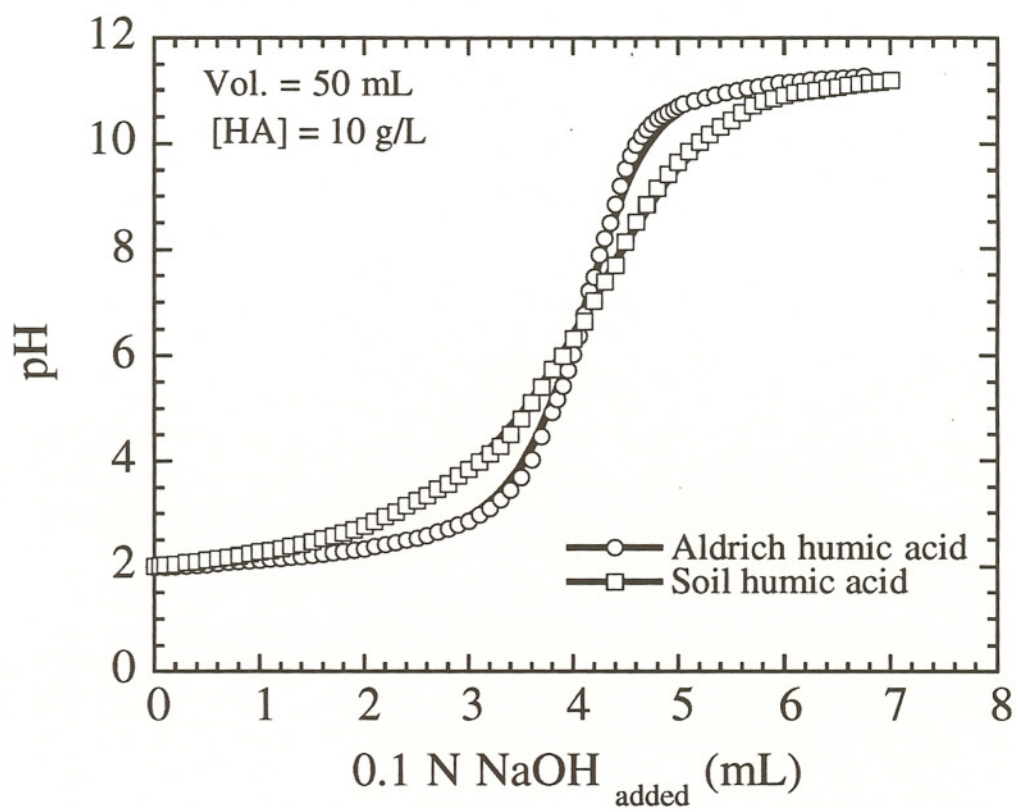


Figure 4.21 Titration of humic acids and HCl mixture with 0.1 N NaOH. $I = 0.1$ M NaNO_3 ; Temperature = 25 °C.

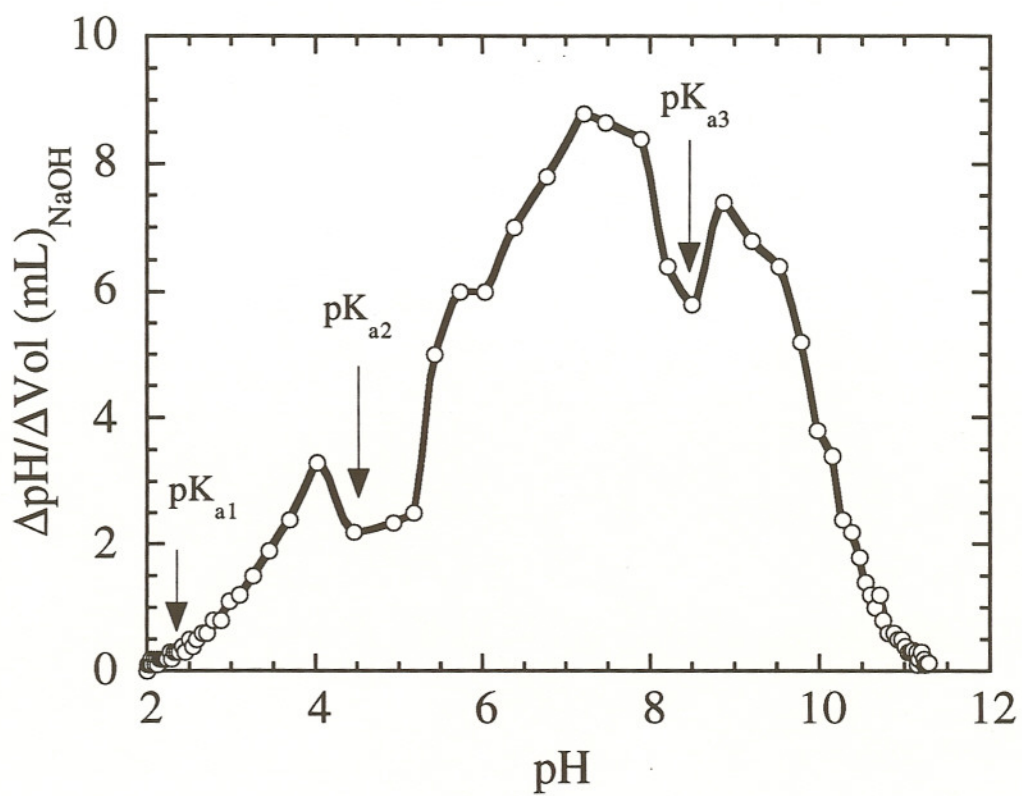


Figure 4.22a Titration analysis of Aldrich humic acid plotted $\Delta\text{pH}/\Delta\text{Volume}$ against pH.

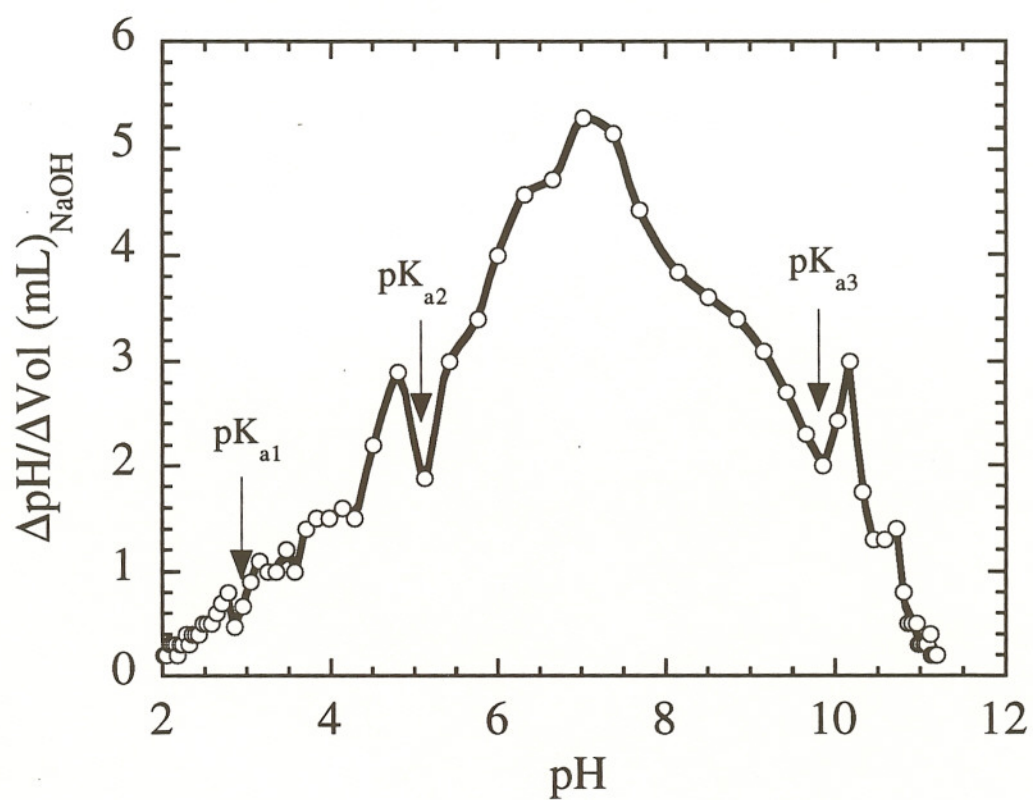


Figure 4.22b Titration analysis of Sassafras humic acid plotted $\Delta\text{pH}/\Delta\text{Volume}$ against pH.

Table 4.5 Average acidity constants ($\overline{pK_a}$) values of various soil humic acid
Ionic Strength = 0.1 N.

Name of Humic Acid	$\overline{pK_{a1}}$	$\overline{pK_{a2}}$	$\overline{pK_{a3}}$	Reference
Skarild A1	2.8 ± 0.2	5.1 ± 0.2	9.4 ± 0.3	Borggaard (1974)
Skarild A2	3.0 ± 0.3	5.1 ± 0.2	9.5 ± 0.3	Borggaard (1974)
Sdr. Vissing	2.8 ± 0.2	5.0 ± 0.3	9.7 ± 0.4	Borggaard (1974)
Stavning	3.4 ± 0.2	4.9 ± 0.1	9.6 ± 0.2	Borggaard (1974)
Aldrich	2.15	4.6	8.6	Schulthess (1985)
Aldrich	2.3	4.5	8.5	Present study
Sassafras sandy loam	2.9	5.1	9.8	Present study

A titration analysis would indicate the acidity content of humic acids in equivalents per gram humic acids (Schulthess, 1985). Assuming n equivalent acidic functional groups per mole humic acids, an average molecular weight (MW) can be estimated by:

$$MW = \frac{HA(gram)}{Acid(equiv.)} \times \frac{n(equiv. Acid) \times 1000}{HA(mole)} \quad (4.19)$$

where n is equivalent number and reported values ranging from 0.43 to 2.00 (Schnitzer and Hansen, 1970; Machesky, 1993).

By calculation, 0.1 mL of 0.1N NaOH corresponds to 0.02 meq per gram of humic acids. The carboxylic functional groups of Aldrich humic acids consumed 4.4 mL of base up to the second equilibrium point (at pH 7.2 in Figure 4.22.a), the content of carboxylic groups in humic acids were estimated as much as 0.88 meq/g humic acids. The COOH contents in Sassafras humic acids was estimated as 0.85 meq/g corresponding to the base consumption of 4.25 mL using same procedures (Figure 4.22.b). Typical values range from 1.5 to 10 meq/g humic acids (Stevenson, 1982; Tipping, 1993). Therefore, molecular weights of Aldrich and Sassafras humic acids estimated by equation (4.19) were ranging from 490 to 2270 g/mole and from 506 to 2353 g/mole corresponding to n values ranging from 0.45 to 2.00, respectively. The molecular weight of humic substances generally ranges from 300 to 30,000 g/mole (Stumm and Morgan, 1981).

Although it seems unreasonable to discuss the solubility of humic acids due to its polydispersed character, humic acids show different concentrations depend on solution pH. Therefore, knowing the concentration of humic acids (denoted

"apparent" solubility) may be useful to understand the behavior of humic acid: (Tipping, 1993). The "apparent" solubility diagram for humic acids is shown in Figure 4.23.

The oxidation state (or oxidation number) is a hypothetical concept which represents a charge that atom would have if the ion or molecule were to dissociate. The concept of oxidation state is useful tool for balancing stoichiometry of redox reactions (Stumm and Morgan, 1981). It is impossible to relate the oxidation state of humic substances to molecular structure due to complexity of function groups. Stumm and Morgan (1981) suggested an indirect measure for estimation of " average" oxidation state, which is expressed by:

$$\text{"Average" oxidation state} = \frac{4(TOC - COD)}{TOC} \quad (4.20)$$

This relation can be rearranged as:

$$\frac{COD}{TOC} = 1 - 0.25(\text{average oxidation state}) \quad (4.21)$$

Where, TOC (total organic carbon) is expressed in mole C/liter and COD (chemical oxygen demand) in mol O₂/liter. Figure 4.24 shows the relationship between oxygen demand and mean oxidation state of organic carbon estimated by equation (4.25) on various organic substances. The average oxidation state of Aldrich and Sassafras humic acid obtained were +2.28 and +2.4, respectively.

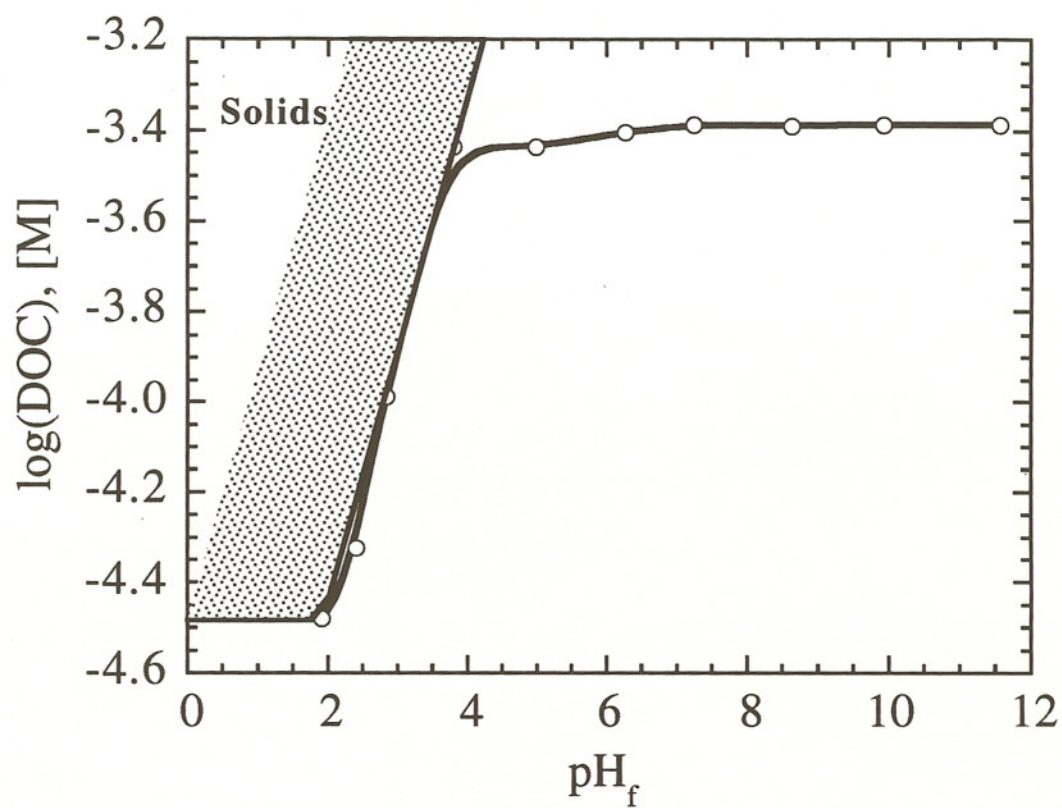


Figure 4.23 The apparent solubility of Sassafra humic acid as a function of pH.
Temperature = 25 °C; I = 0.1 M NaNO₃.

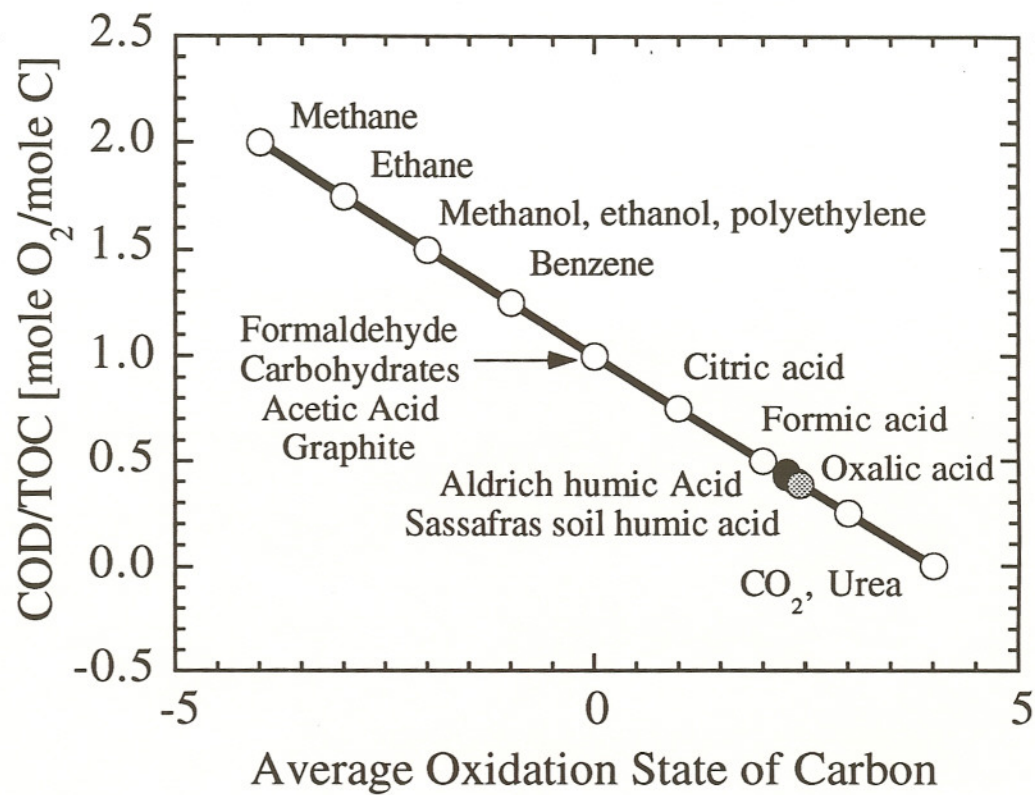


Figure 4.24 Oxygen demand and average oxidation state of organic carbon
(modified from Stumm and Morgan, 1981).

4.1.6.2 Reduction of Cr(VI) by Soil Organic Matter

Figure 4.25 shows the production of Cr(III) by reduction reaction of Cr(VI) with soil humic acid with respect to pH. The figure indicates that Cr(III) formation from Cr(VI) reduction by humic acids decreases as pH increases. Through the Cr(VI) reduction reaction, organics in either soluble or solid form of humic acid such as carboxylic group would be oxidized. In Figure 4.25, it is speculated that the DOC (dissolved organic carbon) value, the difference between blank and with Cr(VI) may indicate the portion of organic groups oxidized by Cr(VI) reduction reaction. Such oxidation of organic groups in humic acids proceeded up to pH 6.7, after which Cr(III) formation did not take place.

Figure 4.26 shows the change of Cr associated either with the oxidation of soil humic acid or with the adsorption onto humic acid surfaces as a function of pH. In the figure, the fact that the maximum consumption of DOC was recorded at pH 4.5 even though Cr(III) production, i.e., Cr(VI) reduction was highest at pH 2. The low DOC consumption at $\text{pH} < 2$ is due to the low amount of Cr(VI) adsorption onto humic acid. Cr(VI) tends to adsorb onto humic acid only small amount at very low pH (< 2), increase as pH increased up to pH 2 to 3, and then decrease with increasing pH. The result indicates that dominant Cr(VI) reduction might take place at the surface of solid humic acid rather than with soluble humic acid at pH 2. Then, Cr(VI) reduction with soluble humic acid becomes dominant as pH increased up to pH 4.5 (redox reaction controlled). Above pH 4.5, DOC consumption decreased sharply and stopped at around pH 7 due to the high solubility of humic acid (solubility controlled).

Figure 4.27 is a logarithmic plot of the ratio of the consumption of DOC to Cr(III) production with respect to solution pH change for the Cr(VI) reduction. The ratio increased sharply in the low pH region ($\text{pH} < 4$) and then decreased slowly or remained constant at $\text{pH} > 4$. The possible explanation for this is: at very low pH (ca. pH 2) the concentration of DOC was very low due to the precipitation of humic acid, while Cr(III) production was high (Figure 4.25). These conditions resulted in a low ratio of DOC consumption to Cr(III) production. As pH increased up to pH 4, the concentration of DOC increased and Cr(III) production decreased, which led the increase of the ratio. Above pH 4, the concentration of DOC would keep increasing due to the partitioning of humic acid (Figure 4.23) but the consumption of organic carbon decreased, and the production of Cr(III) decreased, which resulted in decrease or stagnation in the ratio.

The apparent oxidation state of soil humic acid (e.g., Sassafras humic acid) is about +2.3 (Figure 4.24) and in the solution of $< 10^{-4}$ M Cr(VI), only HCrO_4^- needs be considered in the pH range 1-5 (Beattie and Haight Jr, 1972). Thus, the reduction of Cr(VI) by humic acids can be expressed stoichiometrically.



Figure 4.28 demonstrates the schematic illustration of Cr(VI) reduction by humic acids for the acidic condition described in equation (4.22). In the figure, Cr(VI) may bind to humic acid by ligand exchange and then electron transfer reaction occur between humic acid and Cr(VI) - humic acids donate $3 e^-$ to 1 mole of Cr(VI). Subsequently, Cr(III), the reduced species of Cr, may dissociate from humic acid and dissociated carboxyl group of humic acids may be mineralized to carbon dioxide.

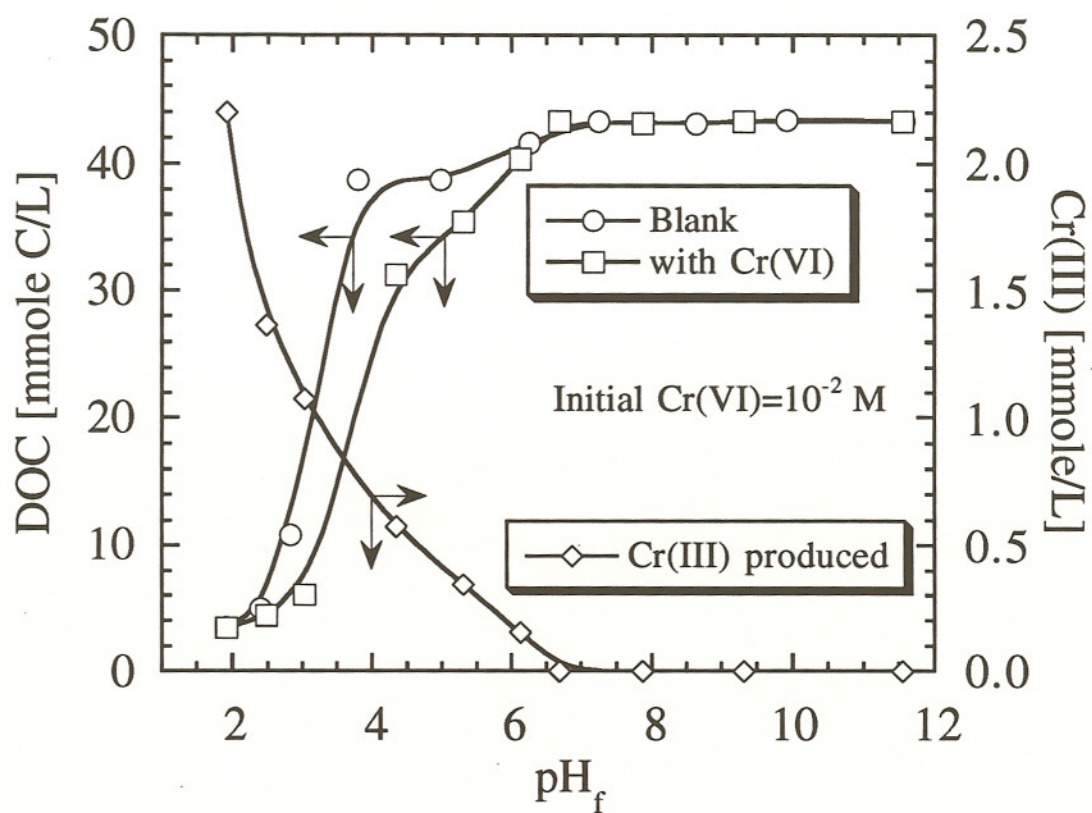


Figure 4.25 The reduction of Cr(VI) with soil humic acid at various pH values. Initial Cr(VI) = 1×10^{-2} M; I = 0.1 M NaNO₃; Temperature = 25 °C; Initial DOC = 43.3 mmole/L; Reaction time = 24 hours.

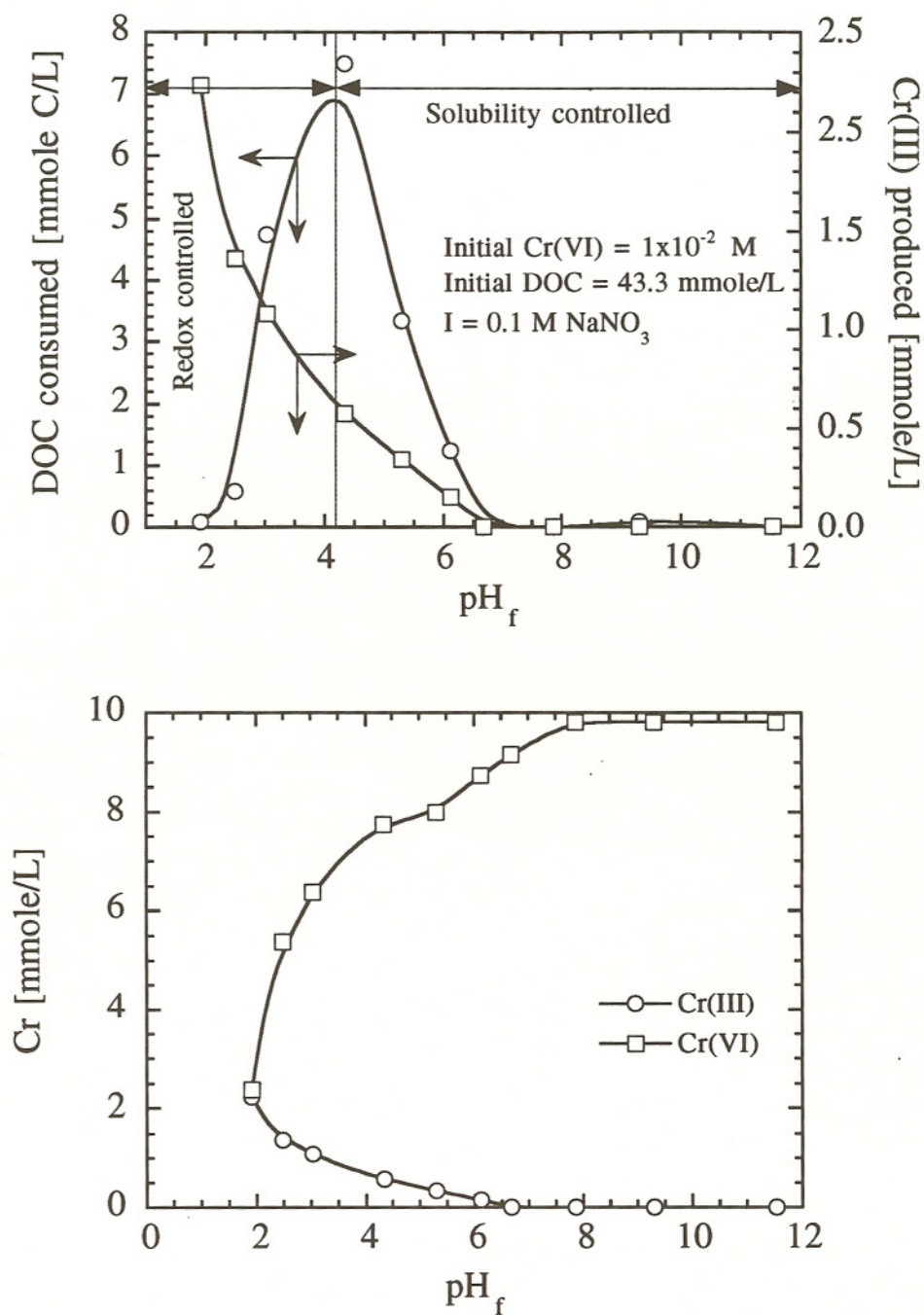


Figure 4.26 The change of Cr concentration and DOC consumption associated with the oxidation of soil humic acid as a function of pH. Temperature = 25 °C.

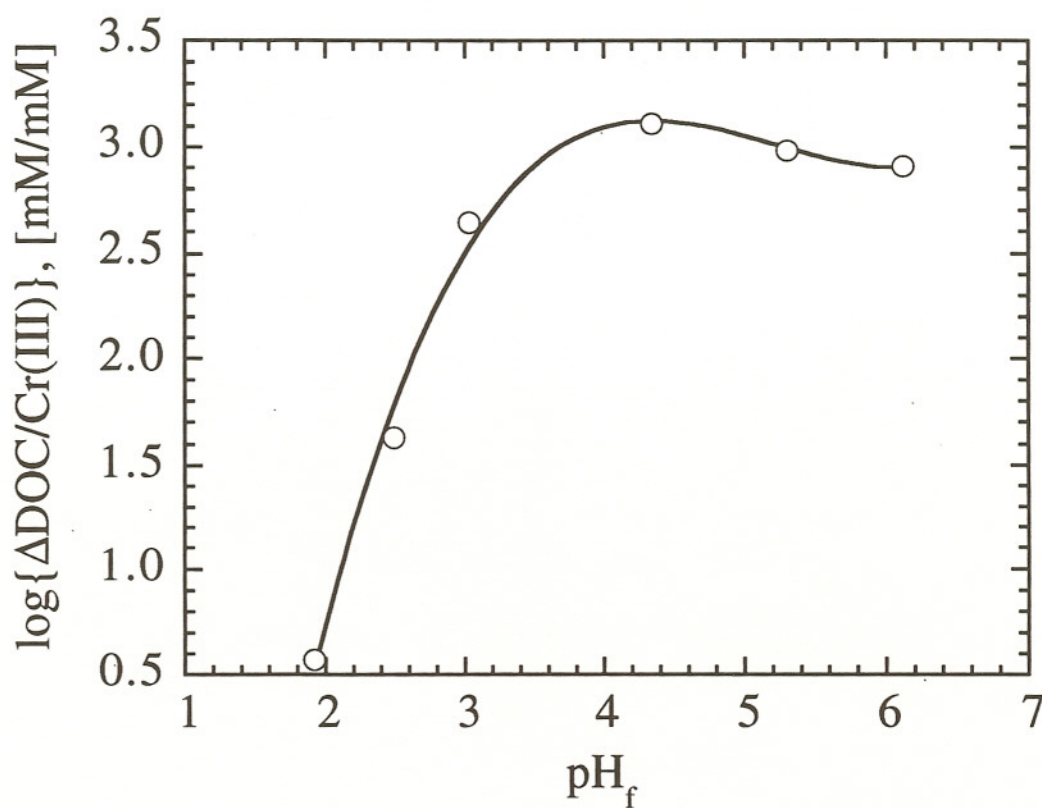
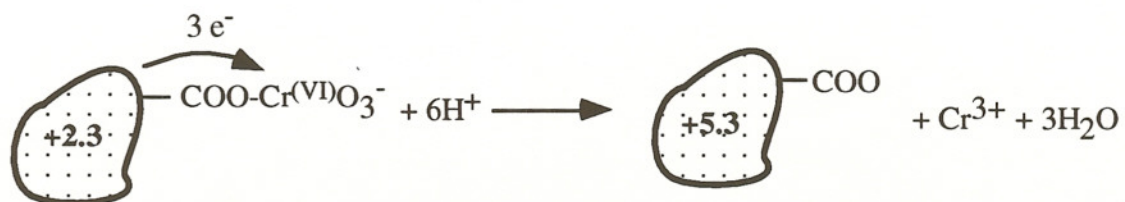
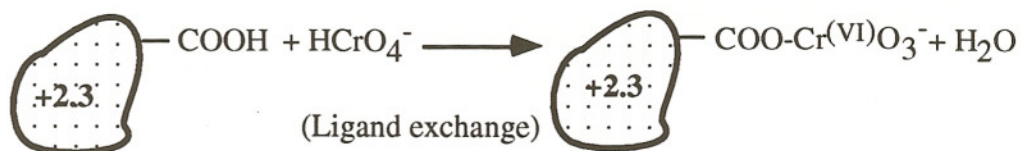


Figure 4.27 Ratio of the consumption of dissolved organic matter to Cr(III) production by Cr(VI) reduction reaction at various pH conditions. Initial Cr(VI) = 1×10^{-2} M; I = 0.1 M NaNO₃; Temperature = 25 °C; Initial DOC = 43.3 mmole/L.



[Electron transfer (Redox) and Cr(III) detachment (dissociation)]

or



(CO₂-Mineralization)

Figure 4.28 Schematic illustration on Cr(VI) reduction with the solid form of humic acid at acidic pH. Numbers in the lump indicate apparent oxidation number of soil humic acids.

4.2 Oxidation Reactions of Chromium(III) in Subsurface Soils

4.2.1 Effect of Soil Mn Content on Cr(III) Oxidation Capacity of Soils and the Rates of Cr(III) Oxidation

The potential of soils to oxidize Cr(III) was measured and expressed as "Cr(III) oxidation capacity". Figure 4.29 demonstrates the Cr(III) oxidation capacity (mg Cr/Kg soil) of New Jersey soils with respect to manganese content (%) extracted by three different methods. The figure shows that the oxidation capacity of Cr(III) by soils is proportional to manganese content of soils, i.e., the oxidation capacity of soils increased as manganese content increased. When Cr(III) oxidation capacity and manganese content were compared, the following relationships were obtained:

$$\text{Cr(III) oxidation capacity (mg/Kg)} = 1002.3 \times (\text{Mn content in soil, \%}) + 128.58$$

$$r^2 = 0.9280: \text{ sodium citrate-bicarbonate dithionite method} \quad (4.28.a)$$

$$\text{Cr(III) oxidation capacity (mg/Kg)} = 4156.4 \times (\text{Mn content in soil, \%}) + 149.88$$

$$r^2 = 0.9110: \text{ acid ammonium oxalate method} \quad (4.28.b)$$

$$\text{Cr(III) oxidation capacity (mg/Kg)} = 201.6 \log(\text{Mn content in soil, \%}) + 488.7$$

$$r^2 = 0.9720: \text{ perchloric-nitric acids method} \quad (4.28.c)$$

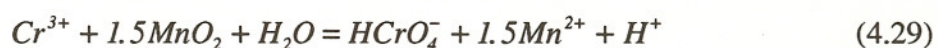
Figure 4.29 The relationship between Cr(III) oxidation capacity and Mn content in soils extracted by perchloric-nitric acids (acid), sodium citrate-bicarbonate - dithionite (DCB), and acid ammonium oxalate (oxalate).

The kinetics of Cr(III) oxidation by soils with various Mn oxides content are shown in Figure 4.30. It has been suggested that Cr(III) may possibly be adsorbed by manganese oxides in the first step of oxidation by Mn, followed by oxidized to hexavalent Cr (Bartlett and James, 1979). Manganese minerals have large surface areas and have tendency of being charged negatively at all except very acidic conditions (McKenzie, 1977). It has been reported that the pH_{zpc} of $\delta\text{-MnO}_2$ is 2.8 (Stumm, 1992). However, Cr tends to not accumulate in Mn oxide nodules, relative to the whole soil, to the extent of Co, Ni, V, or Pb. This might be due to the oxidation of Cr(III). Once Cr(III) was oxidized to Cr(VI) anion, Cr is no longer adsorbed by the Mn minerals and will leach from the system (Bartlett and James, 1979).

In fact, the extent of Cr(III) oxidation was clearly differentiated between three high manganese content soils (Boonton Union county loam, Washington loam, and Hazen gravelly loam) and two low manganese content soils (Rockaway stony loam and Birdsboro silt loam). However, within either of the two groups of soils with high or low manganese content, there was no significant difference. Bartlett and James (1979) reported that 0.01% (100 $\mu\text{g/g}$) manganese oxide in soil was enough for efficient oxidation of Cr(III) to Cr(VI). The production of Cr(VI) for these five soils showed a fast reaction at an early stage, followed by a slower reaction until they reached to pseudo-equilibrium states. This could be due to the exhaustion of "active" manganese species for Cr(III) oxidation. Throughout the study, the mechanisms limiting the rate are difficult to explain, but Figure 4.31 demonstrates that Cr(III) oxidation is closely related to manganese dissolution. The dissolution rates of manganese were also rapid for an initial period in the Cr solutions, followed by a

slower rate with increasing time. The ranges of reaction time for the rapid rate that were estimated up to about 10 hours were the same as the rate of Cr(III) oxidation (Figure 4.30). This result implies that an initial fast reaction between Cr(III) and manganese oxide in soil may be due to acidic dissolution of manganese oxides. $\text{MnO}_2(\text{s})$ dissolves more rapidly in low pH solution (Murray, 1975). After the period of fast reaction, the Cr(VI) species produced result in a decrease in the reactivity of manganese oxides and eventually decrease the rates of both Cr(III) oxidation and manganese dissolution (Eary and Rai, 1987). An other possible mechanism has suggested is that the decreased rates could only occur if only reactive surface was "used up" as the reaction proceeded (Amacher and Baker, 1982). They also postulated that ion competition for adsorption sites between Cr(III) and Mn(II) might inhibit Cr(III) oxidation. Fendorf and Zasoski (1992) suggested that a surface alteration induced by Cr(III) at $\text{pH} > 3.5$ could inhibit oxidation, but a finite amount of Cr(III) is oxidized prior to a surface alteration.

A possible overall stoichiometric reaction involving MnO_2 and Cr(III) would be expressed by the following reaction (Bartlett and James, 1979; Amacher and Baker, 1982; Eary and Rai, 1987; Fendorf and Zasoski, 1992).



In equation (4.29), Cr(III) will have a different form of species: Cr^{3+} at $\text{pH} < 3$, CrOH^{2+} at pH of 3.0-4.7 (Rai et al., 1987), and $\text{Cr}(\text{OH})_3$ at $\text{pH} > 5$ (Fendorf and Zasoski, 1992). The predicted reaction stoichiometric ratio of Mn(II) to Cr(VI) is 1.5:1. Figure 4.32 shows the ratio of Mn to Cr(VI) in solution for five soils. In this figure, the soluble form of manganese was regarded as Mn(II) since Mn(II) ion is the only significant soluble ion, as Mn(IV) is very insoluble and Mn(III) ion

disproportionates to Mn(IV) and Mn(II) ion (Schmitt and Sticher, 1991). At pseudo-equilibrium state, the values range from 0.9 to 1.3 which are a little less than 1.5. The reason may be due to high initial Cr(III) concentration. Eary and Rai (1987) suggested that Mn to Cr(VI) ratio decreased with increasing Cr(III) concentration. In their research, the slopes of Mn(II) to Cr(VI) ratio decreased from 1.53 to 0.28 at pH 4 as Cr(III) concentration increased from 1.9×10^{-5} M to 38.5×10^{-5} M. However, the determination of the reaction stoichiometries of Cr(III) oxidation in soils is extremely difficult because reactions involved, such as Cr(III) oxidation, Cr(VI) adsorption, and Mn redox processes with other soil components, are inter-related and the distinction of individual processes is impossible. The effect of Cr(III) concentration on oxidation reaction will be considered later.

The rate constants for Cr(III) oxidation for the five soils were calculated using first order kinetics (equation 4.2-4.3). Figure A-8 in Appendix A shows the logarithmic plots for Cr(III) oxidation. Rates constants which were estimated are listed in Table 4.6. The plot of rate constants with respect to manganese contents is presented as Figure 4.33, which shows that reaction rate linearly increased as manganese content increased. The relationship is expressed as:

$$\text{Rate Constant } (hr^{-1}) = -0.007 + 0.203x(\text{Mn content, \%}) : r^2 = 0.9952 \quad (4.30)$$

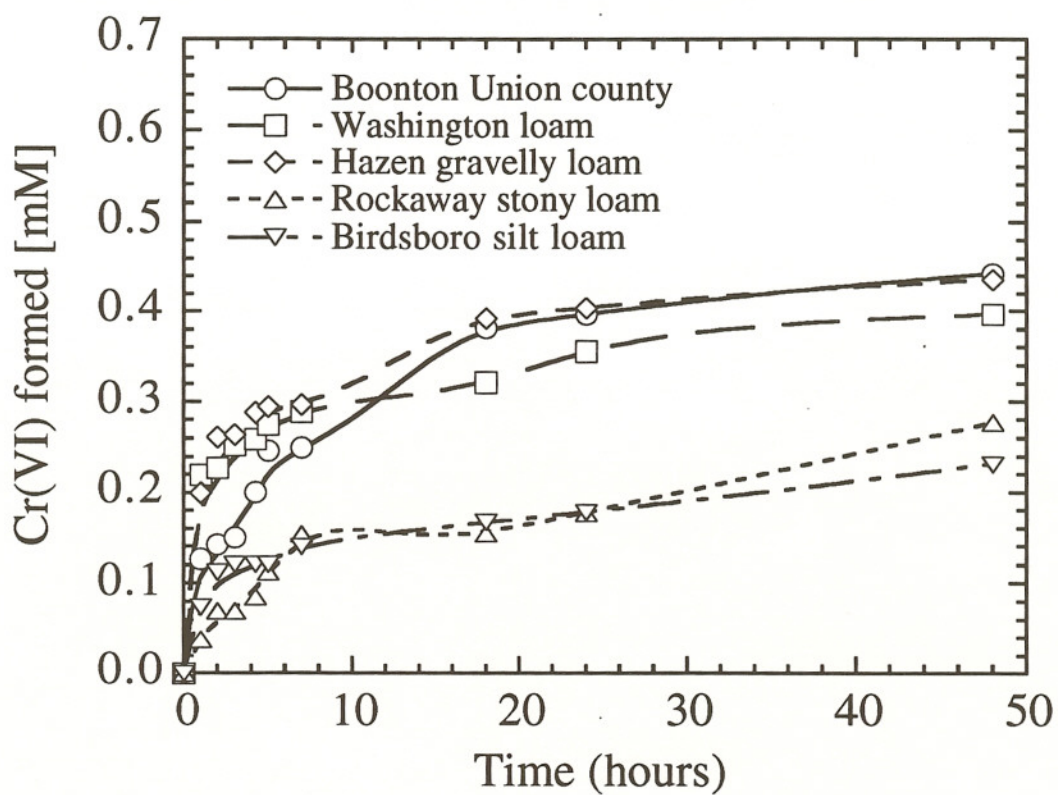


Figure 4.30 Kinetics of Cr(III) oxidation by five soils. pH = 2.0; Temperature = 25 °C; Initial Cr(III) concentration = 1 mM $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Soil/Solution = 0.1; I = 0.1 M NaNO_3 .

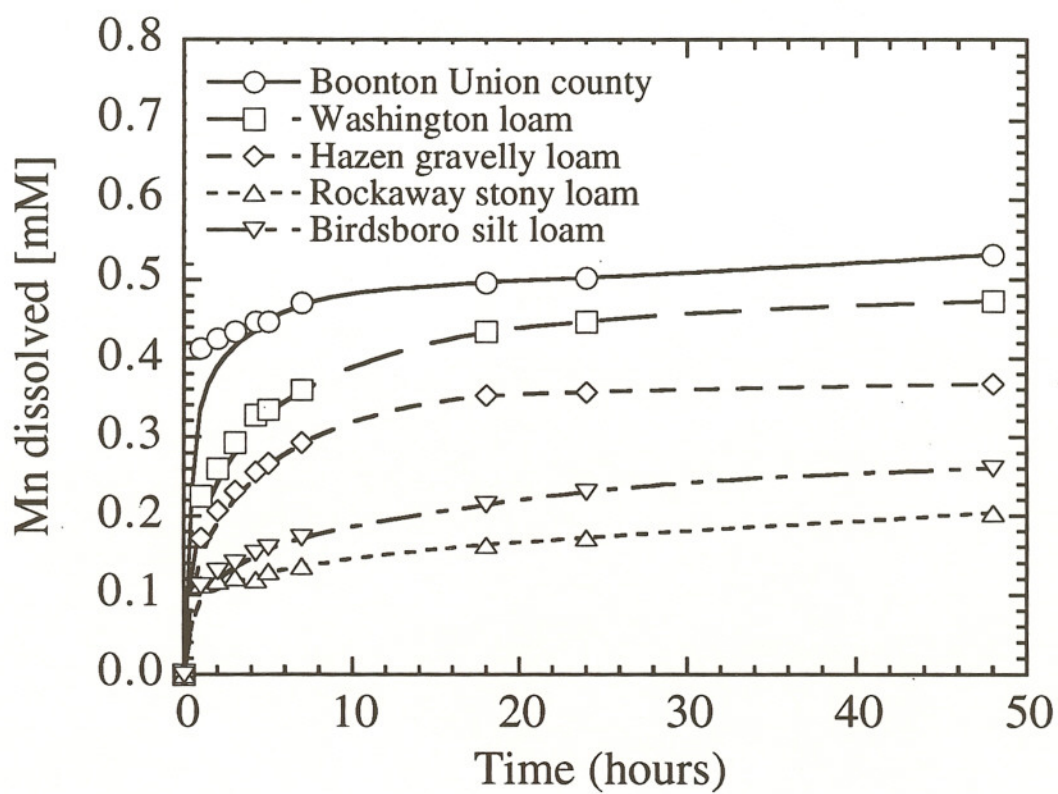


Figure 4.31 The dissolution of manganese associated with Cr(III) oxidation for five soils. pH = 2.0; Temperature = 25 °C; Initial Cr(III) concentration = 1 mM $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Soil/Solution = 0.1; I = 0.1 M NaNO_3 .

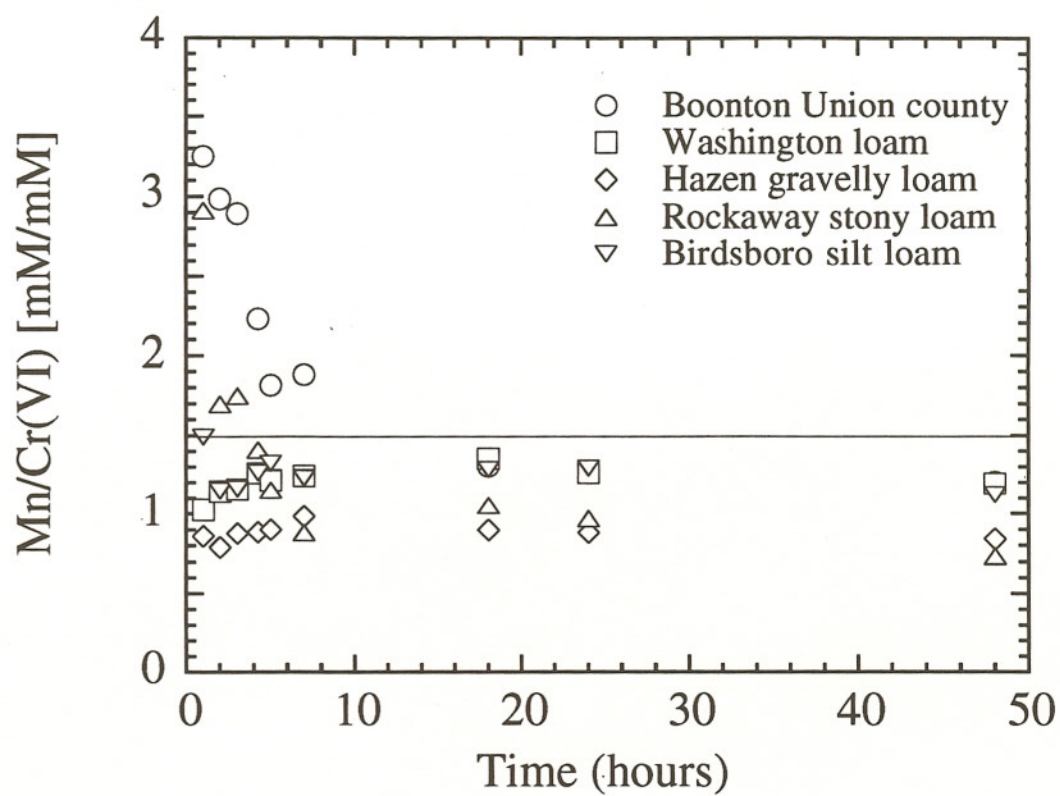


Figure 4.32 The ratio of soluble Mn to Cr(VI) produced in Cr solution. pH = 2.0; Temperature = 25 °C; Initial Cr(III) concentration = 1 mM $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Soil/Solution = 0.1; I = 0.1 M NaNO_3 .

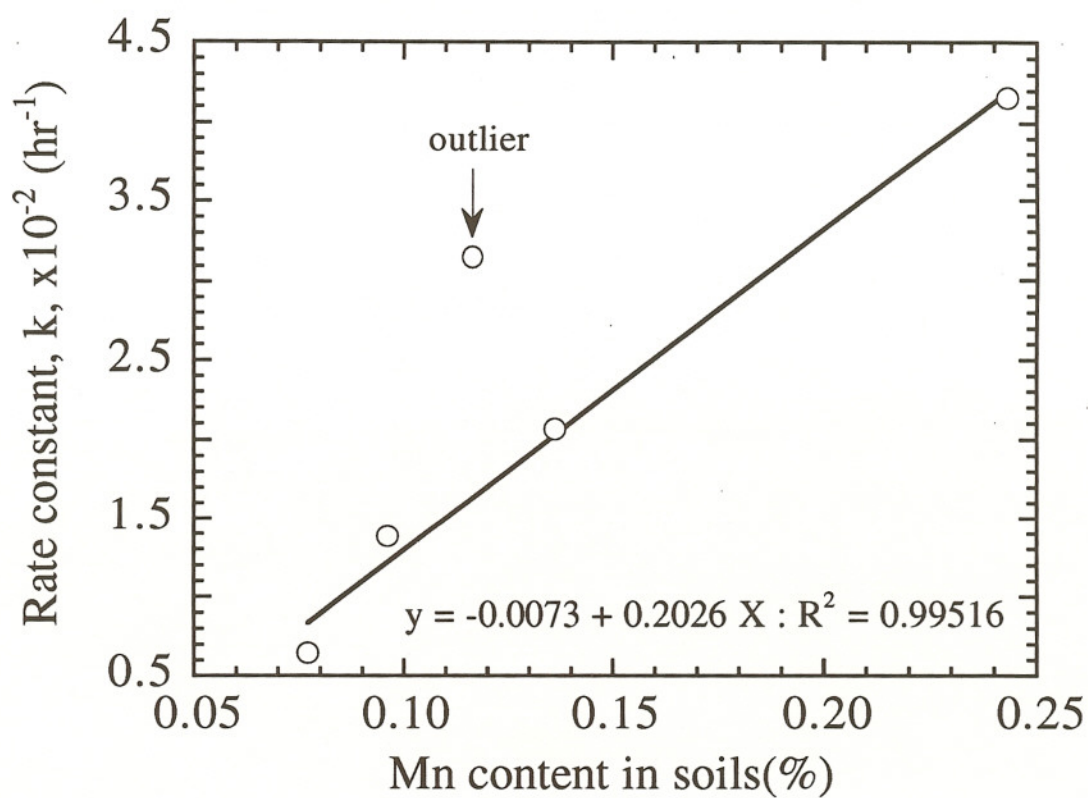


Figure 4.33 The relationship of the rate constants of Cr(III) oxidation to manganese content in soils. pH = 2.0; Temperature = 25 °C; Initial Cr(III) concentration = 1 mM $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Soil/Solution = 0.1; I = 0.1 M NaNO_3 .

Table 4.6 First-order rate constants for Cr(III) oxidation by five soils.

Soil Name	k (1/hr)	t _{1/2} (hr)	r ²
Boonton Union county	4.16x10 ⁻²	16.66	0.9648
Washington loam	2.07x10 ⁻²	33.48	0.9792
Hazen gravelly loam	3.20x10 ⁻²	21.63	0.9559
Rockaway stony loam	1.39x10 ⁻²	49.86	0.9643
Birdsboro silt loam	8.45x10 ⁻³	82.82	0.9687

Experimental conditions:

- Solution pH = 2.0
- Temperature = 25 °C
- Initial Cr(III) concentration = 1 mM Cr(NO₃)·9H₂O
- Soil/Solution = 0.1
- I = 0.1 M NaNO₃

4.2.2 Effect of Dissolved Oxygen and Temperature on Cr(III) Oxidation

The kinetics of Cr(III) oxidation for 10^{-3} M Cr(III) solution by Washington loam for various temperatures (5-45 °C) are shown in Figure 4.34. At each temperature, the measured concentrations of dissolved oxygen in the solutions aerated with air or deaerated with N_2 are plotted in Figure A-9 in Appendix A. In the 10^{-3} M Cr(III) solution at pH 2.0, no Cr(VI) was formed at the experimental temperatures even after a week of aeration. Schroeder and Lee (1975) observed that about 3 % of a 2.4×10^{-6} M Cr(III) was oxidized to Cr(VI) by aeration over 2 weeks in buffered solution with pH 5.5 - 9.9 and in natural lake waters. However, Eary and Rai (1987) reported that no aqueous Cr(VI) was detected in 1.9×10^{-5} M Cr(III) solution by approximately 8.0 ppm dissolved oxygen at pH 4.0 - 12.5 after 24 hours reaction. Consequently, from these results it is speculated that dissolved oxygen has little effect on the Cr(III) oxidation reactions in solution and should be considered insignificant in Cr(III) oxidation by soils. On the other hand, it indicates that Cr(III) oxidation occurs by direct reaction with manganese oxides in soil.

Figure 4.34 shows the change of Cr(VI) formation over time. The amount of Cr(III) oxidized increases rapidly during the first 8 hours and then decreases. This trend is more distinct at higher temperature. The changes of Mn concentration in Cr solution at various temperatures are plotted in Figure 4.35. The rate of Mn leaching from soil is fast up to about 8 hours and then is retarded. This result exactly matches the rate of Cr(III) oxidation, which may be explained if the rate of Cr(III) oxidation is totally dependent on available Mn. However, at lower temperatures (5 - 25 °C),

Cr(III) oxidation was almost constant or still increased after 8 hours reaction. The Cr(VI) changes shown at temperature of 35 and 45 °C could be due to the reduction of Cr(VI) which was formed from oxidation of Cr(III) by soil. Bartlett and James (1979) observed the reduction of Cr(VI) oxidized by moist, moist and limed, and air-dried Raynham silt loam after 24 hours reaction. They implied that the Cr was oxidized by the soil, reduced, and then could be reoxidized. The result in Figure 4.36 demonstrates that increasing temperature may promote the reduction of Cr(VI) by soil. However, below 25 °C, the reduction of Cr(VI) may not occur or may occur very slowly.

Generally, manganese solubility increases with increasing reducing conditions (Schmitt and Sticher, 1991). However, the difference in the dissolution of manganese was not observed clearly in this study. The results were almost the same under both aerated and deaerated conditions.

The rate of Cr(III) oxidation by Washington loam at various temperatures was evaluated using a first-order kinetic equation for the aerated and deaerated 10^{-3} M Cr(III) solution (Figure A-10 in Appendix A). The results are listed in Table 4.7 and plotted in Figure 4.36. Figure 4.37 shows an Arrhenius equation plot of rate constants. Activation energies of Cr(III) oxidation by Washington loam were calculated by equation (4.12). The activation energies of Cr(VI) formation by Washington loam for the aerated and deaerated Cr(III) solution were evaluated as 81.3 and 83.0 KJ/mole (= 19.5 Kcal/mole), respectively. These higher values of activation energy (> 42 KJ/mole) demonstrate that Cr(III) oxidation reaction may be controlled by chemical reaction processes (Sparks, 1985, 1986, 1989). Amacher and Baker (1982) obtained an activation energy of Cr(III) oxidation by δ -MnO₂ of 14.9 Kcal/mole. These results

imply that the Cr(III) oxidation by Washington loam may be more difficult than by δ -MnO₂.

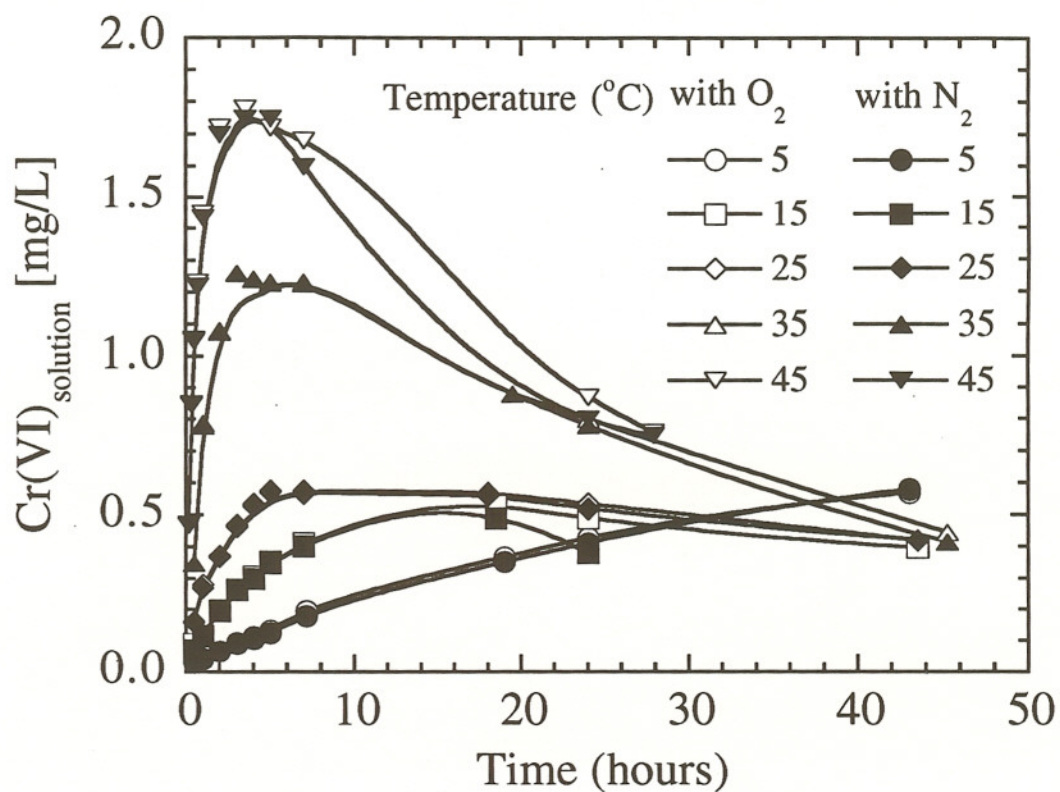


Figure 4.34 Effect of dissolved oxygen and temperature on the rate of Cr(VI) formation by Washington loam. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; pH = 2.0; I = 0.1 M NaNO_3 ; Soil/Solution = 50 g/1.5 L.

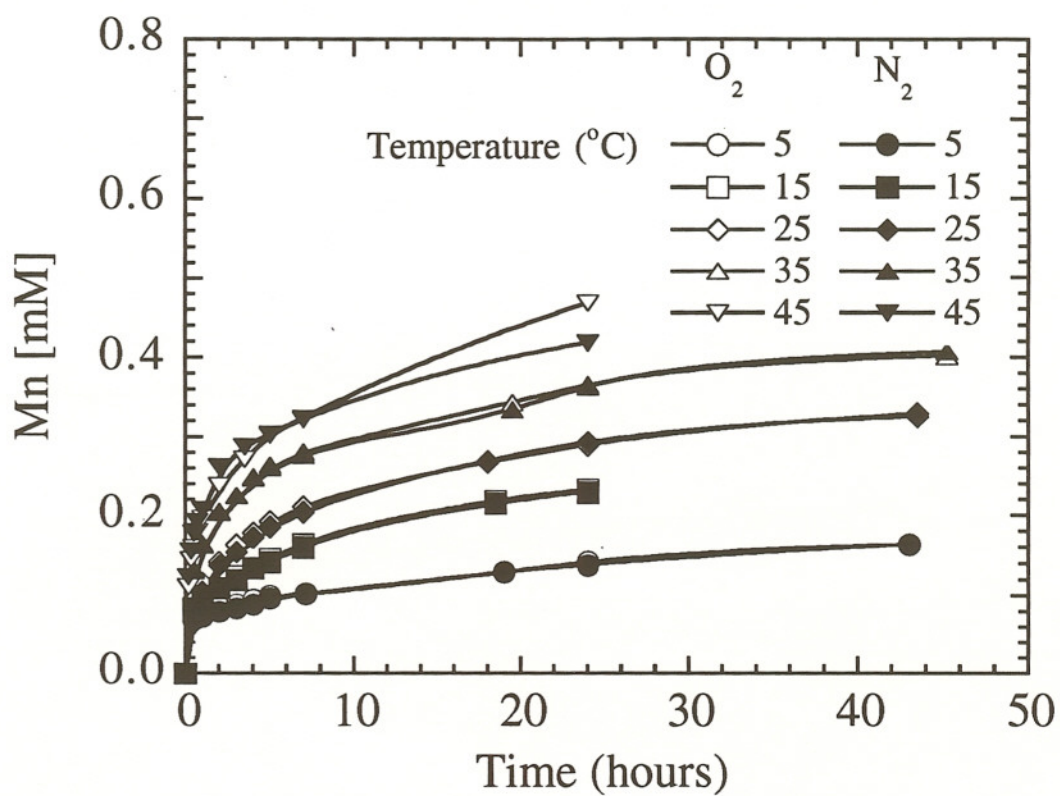


Figure 4.35 The rate of Mn dissolution from Washington loam in Cr(III) solution. Initial Cr(III) = 10^{-3} M $Cr(NO_3)_3 \cdot 9H_2O$; pH = 2.0; I = 0.1 M $NaNO_3$; Soil/Solution = 50 g/1.5 L.

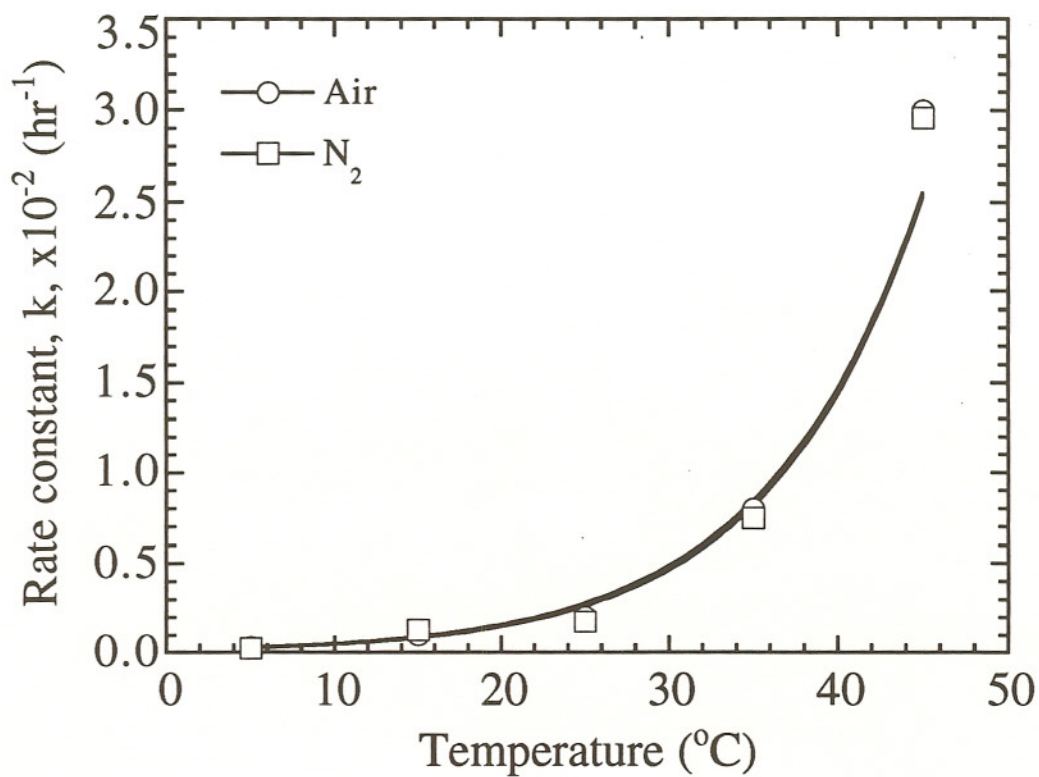


Figure 4.36 The rate constants of Cr(VI) formation by Washington loam at various temperatures. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; pH = 2.0; I = 0.1 M NaNO_3 ; Soil/Solution = 50 g/1.5L.

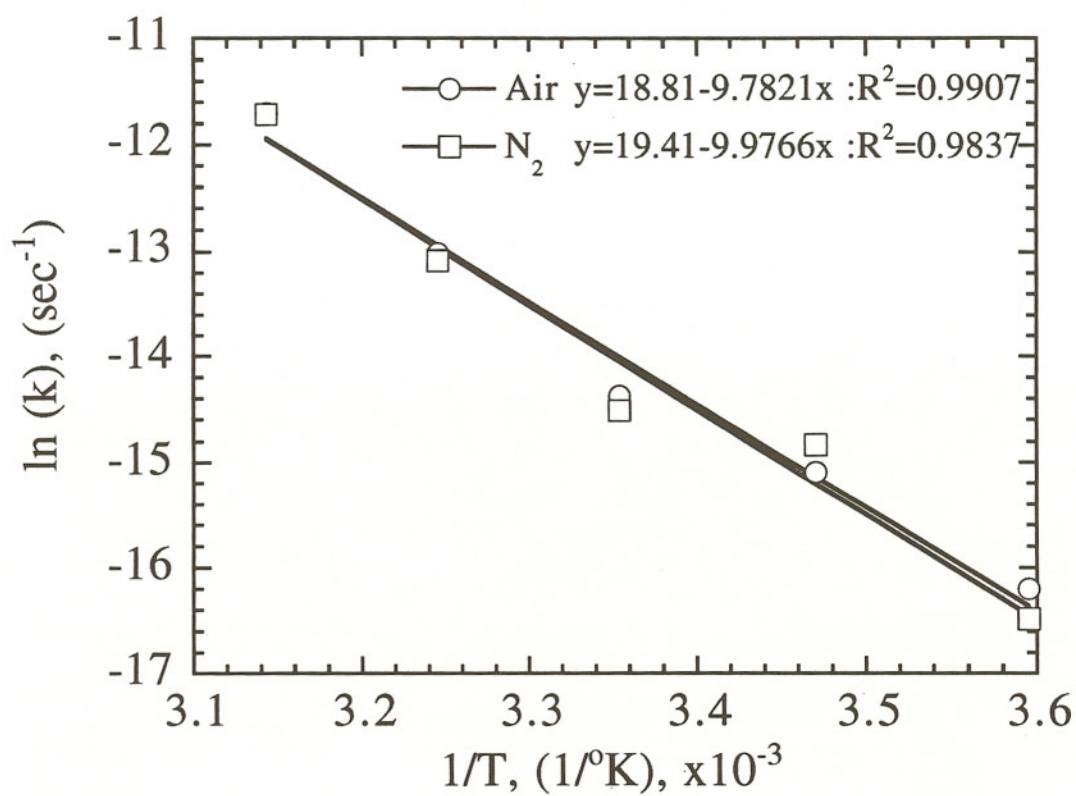


Figure 4.37 The temperature dependence of the rate constants of Cr(VI) formation plotted by the Arrhenius equation. Soil = Washington loam; Initial Cr(III) = 10^{-3} M $Cr(NO_3)_3 \cdot 9H_2O$; pH = 2.0; I = 0.1 M $NaNO_3$; Soil/Solution = 50 g/1.5 L.

Table 4.7 Rate constants of Cr(VI) formation by Washington loam at different temperatures in the aerated and deaerated Cr(III) solution.

	Temperature (°K)	Rate Constant, k (1/sec)	t _{1/2} (day)	r ²	E _a (KJ/mole)
Air	278.15	9.17x10 ⁻⁸	87.51	0.9905	81.3 (= 19.4 Kcal/mole)
	288.15	2.78x10 ⁻⁷	28.88	0.9712	
	298.15	5.72x10 ⁻⁷	14.02	0.9525	
	308.15	2.22x10 ⁻⁶	3.61	0.9529	
	318.15	8.33x10 ⁻⁶	0.96	0.9257	
N ₂	278.15	6.94x10 ⁻⁸	115.52	0.9926	83.0 (= 19.6 Kcal/mole)
	288.15	3.61x10 ⁻⁷	22.21	0.9818	
	298.15	5.00x10 ⁻⁷	19.25	0.9545	
	308.15	2.08x10 ⁻⁶	3.85	0.9550	
	318.15	8.22x10 ⁻⁶	0.98	0.9239	

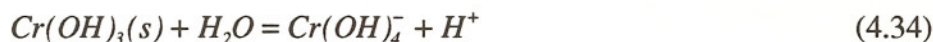
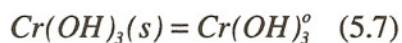
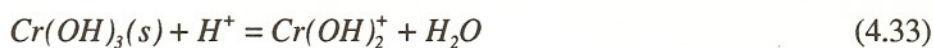
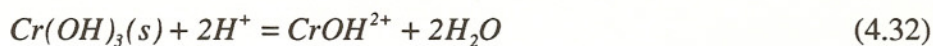
Experimental Conditions:

- Initial Cr(III) = 10⁻³ M Cr(NO₃)₃·9H₂O
- pH = 2.0
- I = 0.1 M NaNO₃
- Soil/Solution = 50 g Washington loam/1.5 L

4.2.3 Effect of pH and Cr(III) Concentration on Cr(III) Oxidation

Changes of pH affect the distribution of chemical forms by influencing solubility, sorption and redox processes (Delfino and Lee, 1971).

Figure 4.38 shows the solubility of $\text{Cr}(\text{OH})_3(\text{s})$, precipitated from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, with respect to pH values. The measured Cr(III) concentrations are above the detection limit ($= 10^{-6.72} \text{ M}$) at the low pH range (2.5 - 6.5) and high pH range (> 10). In the intermediate range, Cr(III) concentrations are close to detection limit. These results indicate that $\text{Cr}(\text{OH})_3(\text{s})$ exhibits amphoteric behavior (Rai et al., 1987). In the absence of carbonates, the formation of Cr(III) hydroxo-complexes can be attributed to the changes of Cr (III) concentrations with pH changes. Rai et al. (1987) reported several forms of Cr(III) hydroxo species, which are given in equation (4.31) - (4.35).



These reactions indicate that the plots of $\log [\text{Cr(III)}]$ vs. pH in equations (4.31) - (4.35) will have slopes of -3, -2, -1, 0, and +1, respectively. The slopes found in Figure 4.38 are -2.6, -1.2, 0, and 1.1. These values indicate that dominant Cr(III) species are Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$, and $\text{Cr}(\text{OH})_4^-$.

The effect of pH on Cr(III) oxidation has been studied by a few researchers (Bartlett and James, 1979; Amacher and Baker, 1982; Eary and Rai, 1987). Bartlett and James (1979) and Eary and Rai (1987) reported that the oxidation of Cr(III) in soil and by β -MnO₂(s) increased with decreasing pH. Likewise, Amacher and Baker (1982) discovered that the rate of Cr(III) oxidation by δ -MnO₂ increased with pH up to pH = 5.5 and thereafter, the rates did not change much. The effect of pH on Cr(III) oxidation by Washington loam is shown in Figure 4.39. At low pH more Cr(VI) is produced than at higher pH. After 24 hours of reaction the amount of Cr(VI) production at pH lower than 3 was about 25 μ M which is 10 times greater than that at pH higher than 5.3. The rates of Cr(III) oxidation were fast at incipient reaction and slowed gradually. Clearly, these results match those of manganese dissolution shown in Figure 4.40. The dissolution of manganese was obviously dependent upon solution pH. The Mn concentrations in solution for pH 2.50 and 5.30 at 24 hours were about 250 μ M and 25 μ M, respectively. These values are 10 times different, the same difference as the case of Cr(III) oxidation. The rate constants of Cr(III) oxidation by Washington loam are calculated by first order kinetic expression of equation 4.3 (Figure A-11 in Appendix A). Table 4.8 lists the rate constants of Cr(III) oxidation at various pH values. Figure 4.41 shows the relation of the rate constant to Cr(III) oxidation and solution pH. The figure shows that the rate constant of Cr(III) oxidation seems to have three different slopes rather than one linear relationship over the pH range. The equations explaining the relationship are described as follows:

$$k = (3.9 \times 10^{-3}) [H^+]^{(0.0053)} : (\text{pH} < 3.5) \quad (4.36)$$

$$k = (5.8 \times 10^{-2}) [H^+]^{(0.433)} : (3.5 \leq \text{pH} \leq 5.4) \quad (4.37)$$

$$k = (7 \times 10^{-4}) [H^+]^{(0.0768)} : (\text{pH} > 5.4) \quad (4.38)$$

where k is the rate constant of Cr(III) oxidation by soil, $[\text{hr}^{-1}]$. The absolute value of $\log(k)/\text{pH}$ in the low pH region ($\text{pH} < 3.5$) is smaller than that in the pH range of 3.5 - 5.4, demonstrating that there is an inhibition of Cr(III) oxidation by soil. Eary and Rai (1987) indicated that the extent of Cr(III) oxidation at low pH is limited probably by the strong adsorption of the resulting anionic Cr(VI) species, which inhibits contact between the active oxidizing sites on the $\beta\text{-MnO}_2(\text{s})$ surface and the Cr(III) species. Amacher and Baker (1982) reported that at pH 1, the rate of oxidation approached a zero order reaction. They explained this with the concept of pH_{ZPC} (zero point of charge), the pH at which the surface of a solid is electrically neutral. For Washington loam pH_{ZPC} is about 2.85. The pH_{ZPC} of $\delta\text{-MnO}_2$ was reported as about 2.5 to 2.8 (Amacher and Baker, 1982; Stumm, 1992). Above the pH_{ZPC} , a surface could be negatively charged due to OH^- groups. On the contrary, below that pH, a surface could be positively charged due to the excess of protons adsorbed onto surfaces. These positively charged surfaces tend to repel the Cr(III) ions, e.g., $\text{Cr}(\text{OH})^{2+}$, and readily adsorb negatively charged Cr(VI) ions. Therefore, Cr(III) can not approach the active surface for oxidation. In addition, adsorbed Cr(VI) ions may inhibit the reaction of manganese with Cr(III) in solution. It was reported that $\delta\text{-MnO}_2$ has a strong affinity for various cationic metals (Morgan and Stumm, 1964; Posselt et al., 1968; Loganathan and Burau, 1973; Zasoski and Burau, 1988). Although this study did not cover very low pH ($\text{pH} < 1$), the slope at pH less than 3.5 clearly indicates the inhibition effect on Cr(III) oxidation. At pH above 5, the oxidation of Cr(III) was found to be a very slow process and was limited by the adsorption of positive chromium species and the precipitation of $\text{Cr}(\text{OH})_3$ (Milacic and Stupar, 1995). It has been reported that the oxidation of Cr(III) by manganese dioxide is slow, with half-times of several years (Katz and Salem, 1994).

The depletion of Cr(III) from solution by soil at various pH conditions was studied. Figure 4.42 shows that the extent of Cr(III) removal by soil increased with increasing pH. The depletion of Cr(III) may be governed by three chemical physical mechanisms: adsorption, precipitation, and oxidation to Cr(VI). The total amount of Cr(III) depleted by soil can be expressed:

$$\text{Cr(III)}_{\text{depl}} = \text{Cr(III)}_{\text{added}} - \text{Cr(III)}_{\text{sol}} \quad (4.39)$$

where

$\text{Cr(III)}_{\text{depl}}$ = the amount of Cr(III) removed from solution at any time,

$\text{Cr(III)}_{\text{added}}$ = the amount of Cr(III) initially present in the solution,

$\text{Cr(III)}_{\text{sol}}$ = the amount of Cr(III) remaining in the solution at any time.

In equation (4.39), $\text{Cr(III)}_{\text{depl}}$ term consists of Cr(VI) oxidized and Cr(III) adsorbed or precipitated, that is,

$$\text{Cr(III)}_{\text{depl}} = \text{Cr(III)}_{\text{ads}} + \text{Cr(III)}_{\text{ppt}} + \text{Cr(VI)}_{\text{oxid}} \quad (4.40)$$

$$\text{Cr(VI)}_{\text{oxid}} = \text{Cr(VI)}_{\text{ads}} + \text{Cr(VI)}_{\text{sol}} \quad (4.41)$$

where

$\text{Cr(III)}_{\text{ads}}$ = the amount of Cr(III) adsorbed onto soil,

$\text{Cr(III)}_{\text{ppt}}$ = the amount of Cr(III) precipitated,

$\text{Cr(VI)}_{\text{oxid}}$ = The amount of Cr(VI) oxidized by soil,

$\text{Cr(VI)}_{\text{ads}}$ = the amount of Cr(VI) adsorbed onto soil, and

$\text{Cr(VI)}_{\text{sol}}$ = the amount of Cr(VI) remaining in the solution after reaction.

It is almost impossible to distinguish the quantity of Cr(III) adsorbed, Cr(III) precipitated and Cr(VI) adsorbed by the analytical methods used for this study. Those terms are, however, strongly dependent upon solution pH. Lee (1994) reported that below pH 2.0 the adsorption of Cr(III) onto Washington loam was almost zero, in

the range of pH 2.0-6.0 the amount of Cr(III) adsorption increased from 20 % to 95 % and Cr(VI) adsorption was about 10 % at pH 6.5. Therefore, the terms of Cr(II) adsorbed and Cr(III) precipitated could be ignored and the term of Cr(III) depletion could be the same as Cr(VI) oxidized at pH less than 2. However, as pH increased the amount of Cr(VI) adsorbed and Cr(III) oxidized become smaller and smaller. Thus, in the range of pH > 3, Cr(III) depletion is limited by Cr(III) adsorption and precipitation. The rates of Cr(III) depletion by Washington loam at various pH conditions, estimated by first order kinetics (Figure A-12 in Appendix A), are listed in Table 4.9. Figure 4.43 shows the relation of Cr(III) depletion rate to pH. The results indicate that Cr(III) depletion rate increases exponentially as pH increases due to high potential of Cr(III) adsorption and precipitation. The relationship is expressed as:

$$k = (2.274 \times 10^{-5})e^{(1.883 \text{ pH})}; r^2 = 0.9961 \quad (4.42)$$

where, k = the rate constant of Cr(III) depletion, hr⁻¹.

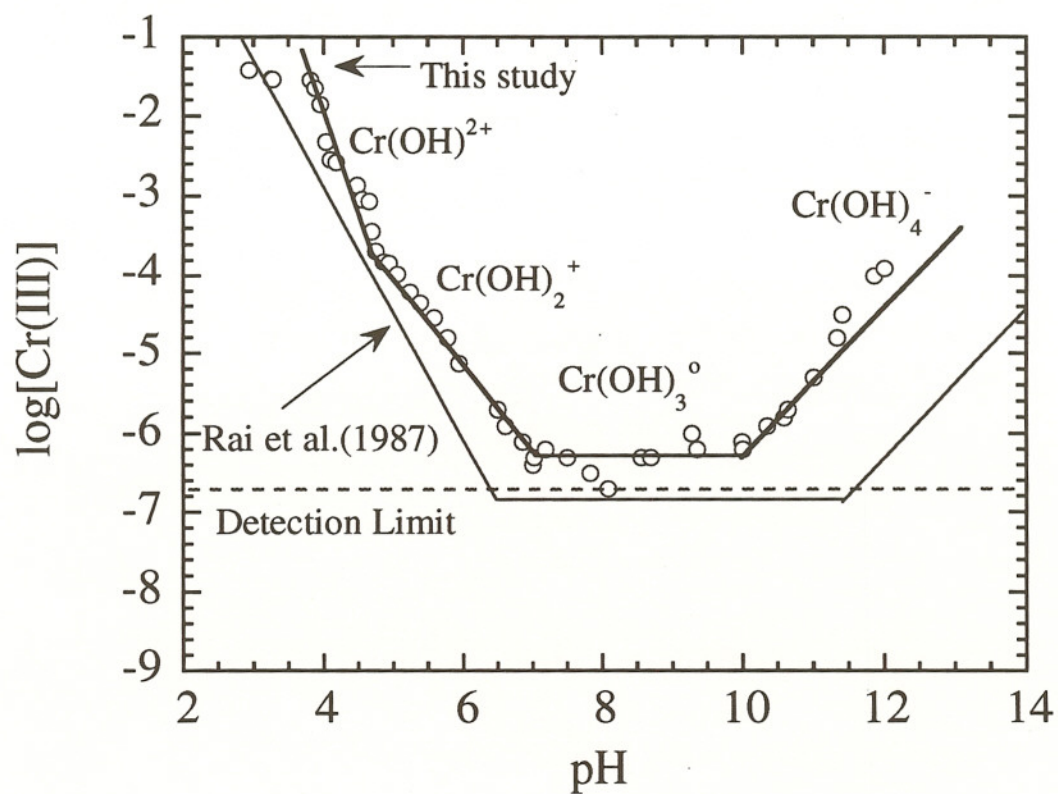


Figure 4.38 Solubility of Cr(III) as a function of pH. Cr(III) concentrations were measured in 0.22 μm filtrates from N_2 -equilibrated $\text{Cr(OH)}_3(\text{s})$ suspensions. pH was adjusted by 0.1 N HNO_3 or 0.1 N NaOH . Temperature = 25 $^\circ\text{C}$; $I = 0.1 \text{ M NaNO}_3$.

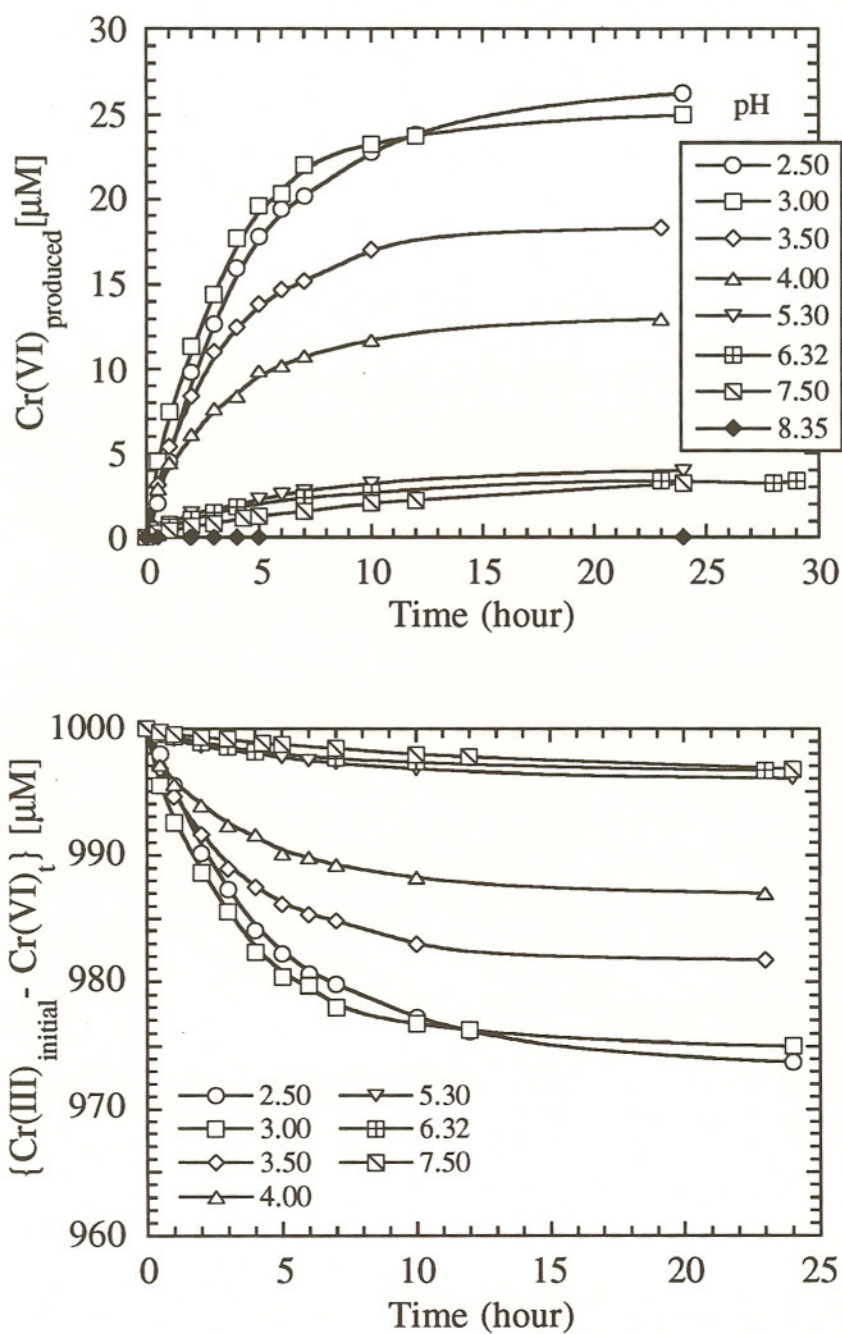


Figure 4.39 The kinetics of Cr(III) oxidation by Washington loam at various pHs. Initial $\text{Cr(III)} = 10^{-3} \text{ M Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Temperature = 25°C ; $\text{I} = 0.1 \text{ M NaNO}_3$; Soil/Solution = $50 \text{ g}/1.5 \text{ L}$.

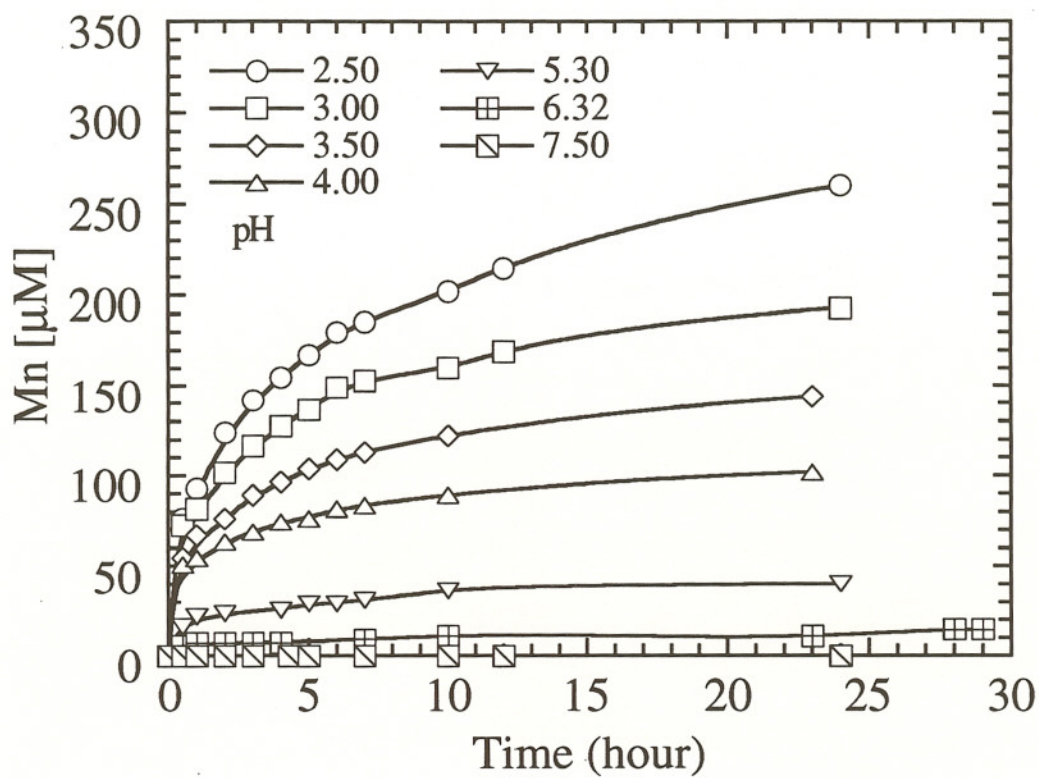


Figure 4.40 The dissolution of Mn in Cr(III) solution at various pHs. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Temperature = 25 °C; I = 0.1 M NaNO_3 ; Soil/Solution = 50 g/1.5 L.

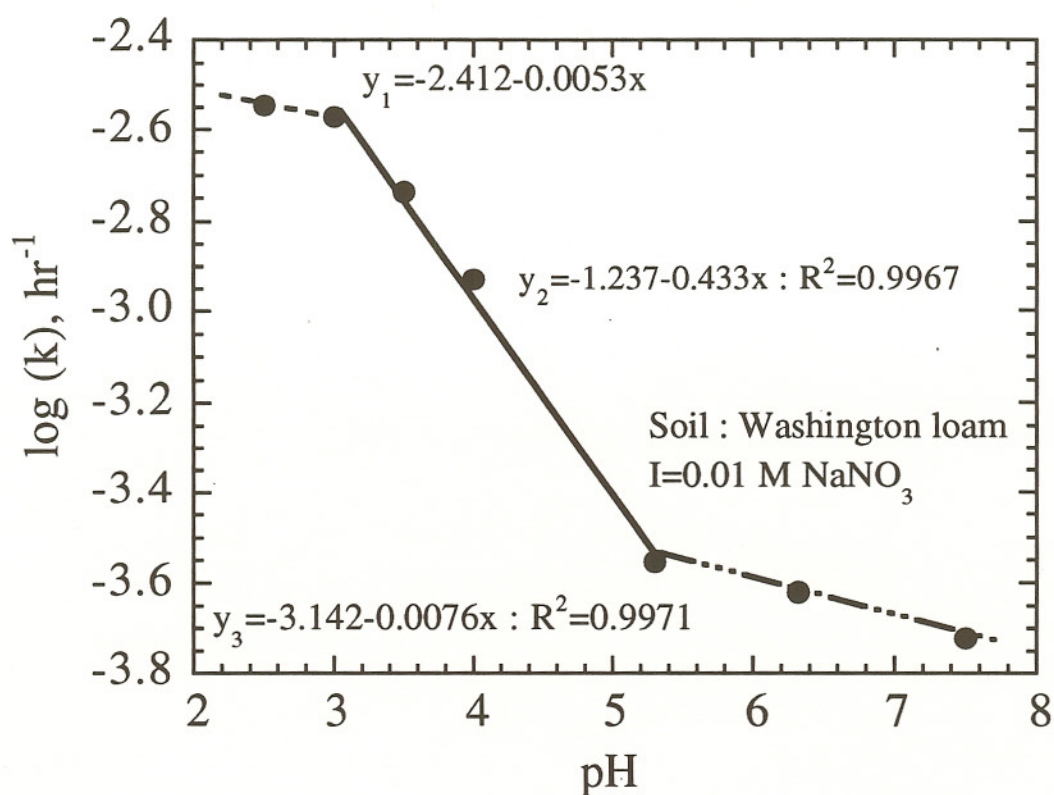


Figure 4.41 Relation of the rate constant of Cr(III) oxidation by Washington loam to solution pH. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Temperature = 25 °C; I = 0.1 M NaNO₃; Soil/Solution = 50 g/1.5 L.

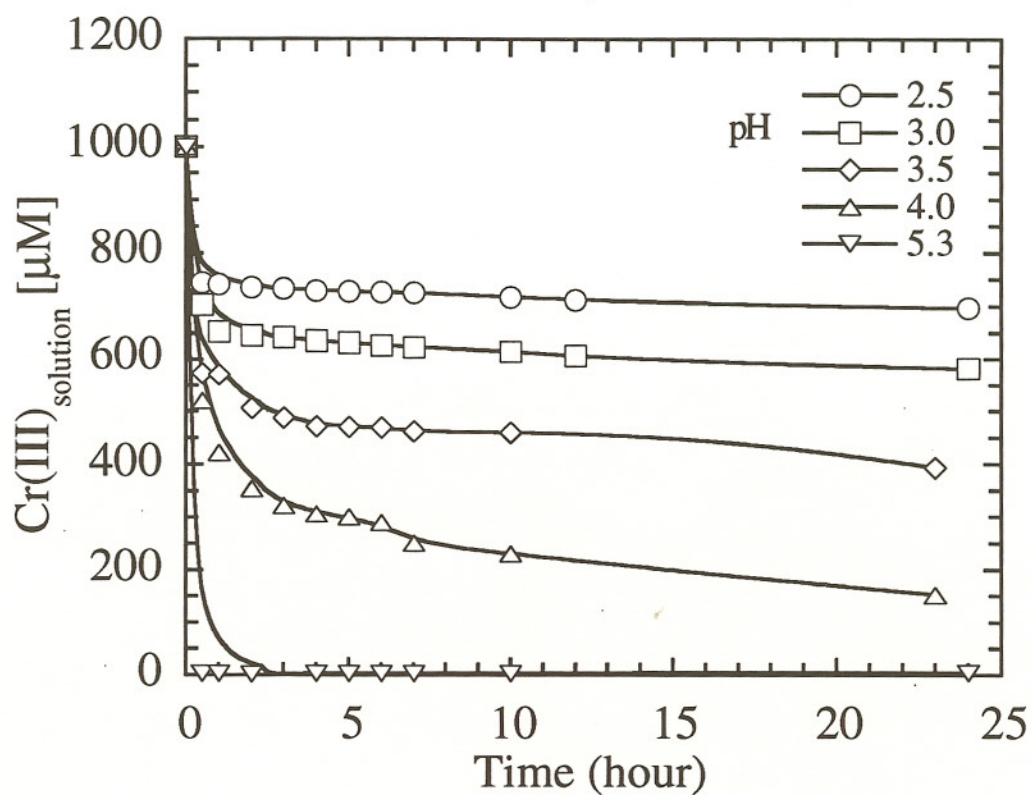


Figure 4.42 Change of Cr(III) concentration as a function of time at various pH values. Soil used = Washington loam; Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Temperature = 25 °C; $I = 0.1$ M NaNO_3 ; Soil/Solution = 50 g/1.5 L.

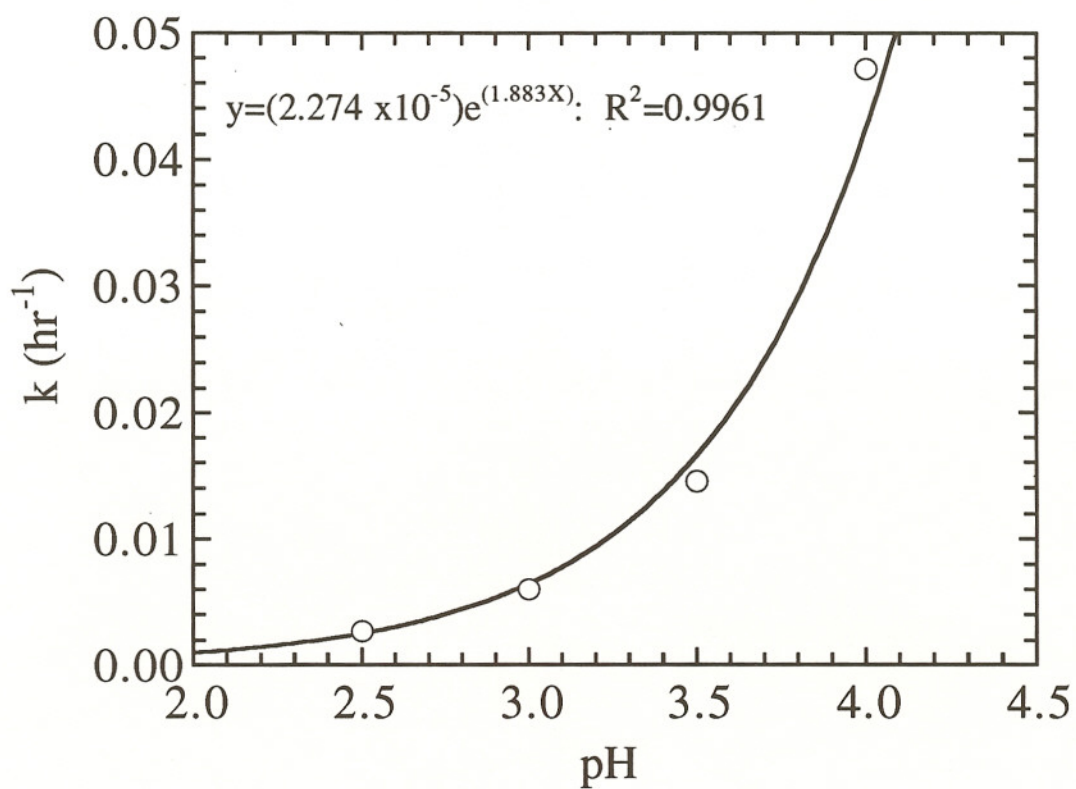


Figure 4.43 The relation of Cr(III) depletion rate to pH. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Temperature = 25°C ; $I = 0.1$ M NaNO_3 ; Soil/Solution = 50 g/1.5 L.

Table 4.8 The rate constants for Cr(VI) formation by Washington loam at various pH values.

pH	k (1/hr)	t _{1/2} (day)	r ²
2.50	2.85x10 ⁻³	10.14	0.9699
3.00	2.68x10 ⁻³	10.79	0.9735
3.50	1.84x10 ⁻³	15.70	0.9608
4.00	1.18x10 ⁻³	24.45	0.9732
5.30	2.80x10 ⁻⁴	103.14	0.9725
6.32	2.36x10 ⁻⁴	122.37	0.9623
7.50	1.86x10 ⁻⁴	155.26	0.9932

Experimental conditions:

- Soil used : Washington loam
- Temperature : 25 °C
- Initial Cr(III) concentration : 10⁻³ M Cr(NO₃)·9H₂O
- I = 0.1 M NaNO₃
- Soil/solution = 50 g/1.5 L

Table 4.9 The rate constants for Cr(III) depletion by Washington loam at various pH values.

pH	k, (1/hr)	$t_{1/2}$, (day)	r^2
2.5	2.74×10^{-3}	10.54	0.9583
3	6.05×10^{-3}	4.77	0.8597
3.5	1.45×10^{-2}	1.99	0.8710
4	4.72×10^{-2}	0.61	0.9250

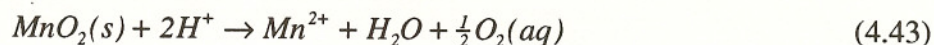
Experimental conditions:

- Soil used : Washington loam
- Temperature : 25 °C
- Initial Cr(III) concentration : 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
- $I = 0.1$ M NaNO_3
- Soil/solution = 50 g/1.5 L

Figure 4.44 illustrates the oxidation of Cr(III) with varying initial Cr(III) concentrations from the equilibrium study over the pH range of 2.0 - 5.0 in a 0.1 M NaNO₃ matrix. The result indicates that at pH 2.5 (slightly less than pH_{zpc}), Cr(VI) production is at a maximum. Above pH 3, the amount of Cr(VI) production decreased as the solution pH was increased. As the initial Cr(III) concentrations was increased, the amount of Cr(VI) production increased and then remained constant. These relationships are expressed in Figure A-13 in Appendix A and Table 4.10, which demonstrates that the amount of Cr(VI) produced was logarithmically related to Cr(III) concentration. This demonstrates, presumably, that Cr(VI) production may be limited, even for high loading concentrations of Cr(III), like for a Cr waste depository site.

Fendorf and Zasoski (1992) studied Cr(III) oxidation by δ -MnO₂ at pH in the range of 3 - 5 in a 0.1 M NaNO₃ matrix. They reported that at pH values less than 3.5, MnO₂ gave the maximum potential oxidizing capacity for Cr(III). This study, however, showed the decrease of Cr(VI) production at pH < 2.5 was greater than pH $\geq$ 2.5. These are clearly demonstrated in Figure 4.45. This figure shows Cr(VI) production is the maximal at pH $\approx$ 2.5 for Cr(III) addition range of 260-2600 μ g and pH $\approx$ 3 for the range of 26-180 μ g. The production of Cr(VI) decreased rapidly below pH 2.5 and above pH 2.5 to 3.0. These phenomena could be explained by the electrical charge of the soil surface as mentioned earlier in this section. Through all the results of Cr(III) oxidation as a function of Cr(III) concentration and pH, it is suggested that the production of Cr(VI) by soil will be very low in the natural soil-solution system in which soil pH is greater than 5.0.

Amacher and Baker (1982) and Fendorf and Zasoski (1992) proposed that from the stoichiometry of the Cr(III) oxidation reaction by MnO_2 , 1.5 Mn(II) should be formed for each Cr(VI) produced. Figure 4.46 shows the ratio of Mn to Cr(VI) produced as a function of pH and initial Cr(III) concentrations added. The results demonstrate that the ratio decreased as either pH or initial Cr(III) concentration increased. At a constant pH, Mn to Cr(VI) ratio decreases with increasing Cr(III) concentration. As a similar trend, at a constant Cr(III) concentration, the ratio decreased with increasing pH. This result indicates that the dissolution of manganese is significantly dependent upon pH change. Ratios above the dotted line indicating the expected stoichiometry demonstrate that an excess dissolution of Mn over that expected from Cr(III) oxidation. The reason that a greater amount of Mn dissolved over the stoichiometric ratio of 1.5 was due to the acidic dissolution of Mn oxides in soil as follows (Eary and Rai, 1987):



Fendorf and Zasoski (1992) suggested that the limitation in Cr(III) oxidation must not be thermodynamic, assuming that the reaction stoichiometry of equation (4.29) was correct. From the thermodynamic viewpoint, the reaction should proceed to a greater extent at higher pH values and at higher reactant concentrations. However, these phenomena were not observed in this study. Therefore, Cr(III) oxidation by soil is not limited thermodynamically.

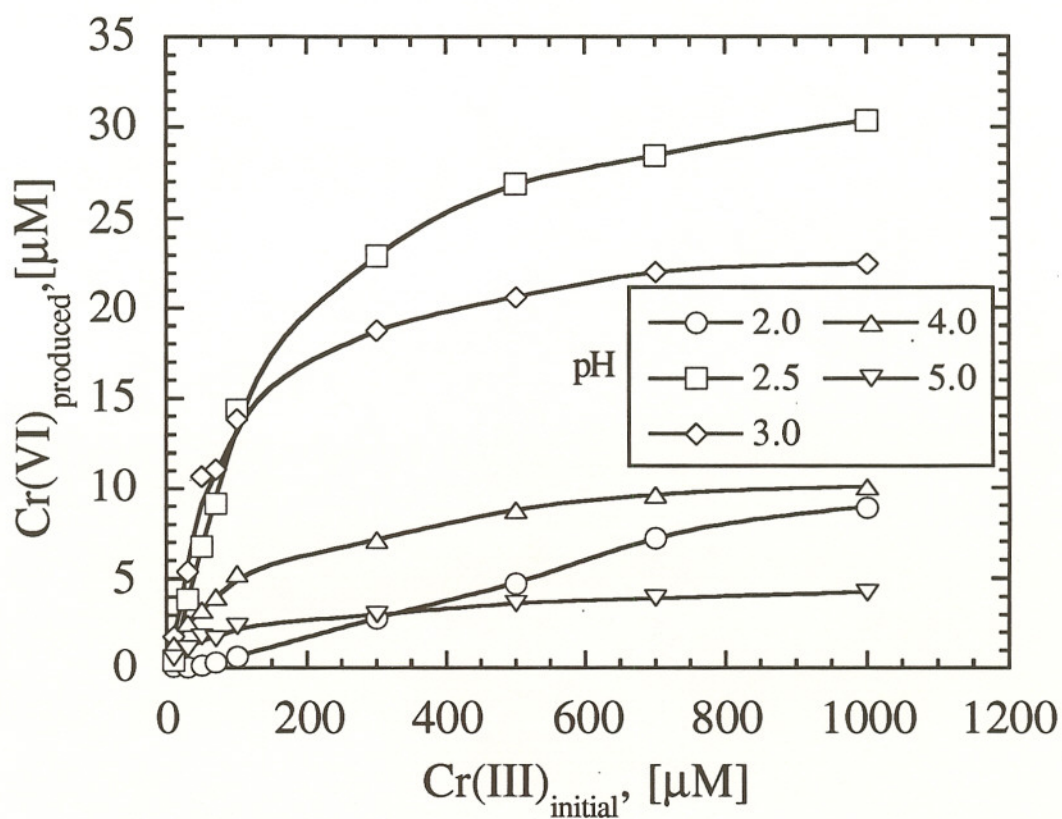


Figure 4.44 Cr(III) oxidized by a soil as a function of Cr(III) concentration added at various pH values. Temperature = 25 °C; I = 0.1 M NaNO₃; Soil = Washington loam; Soil/solution = 2.0 g/50 mL.

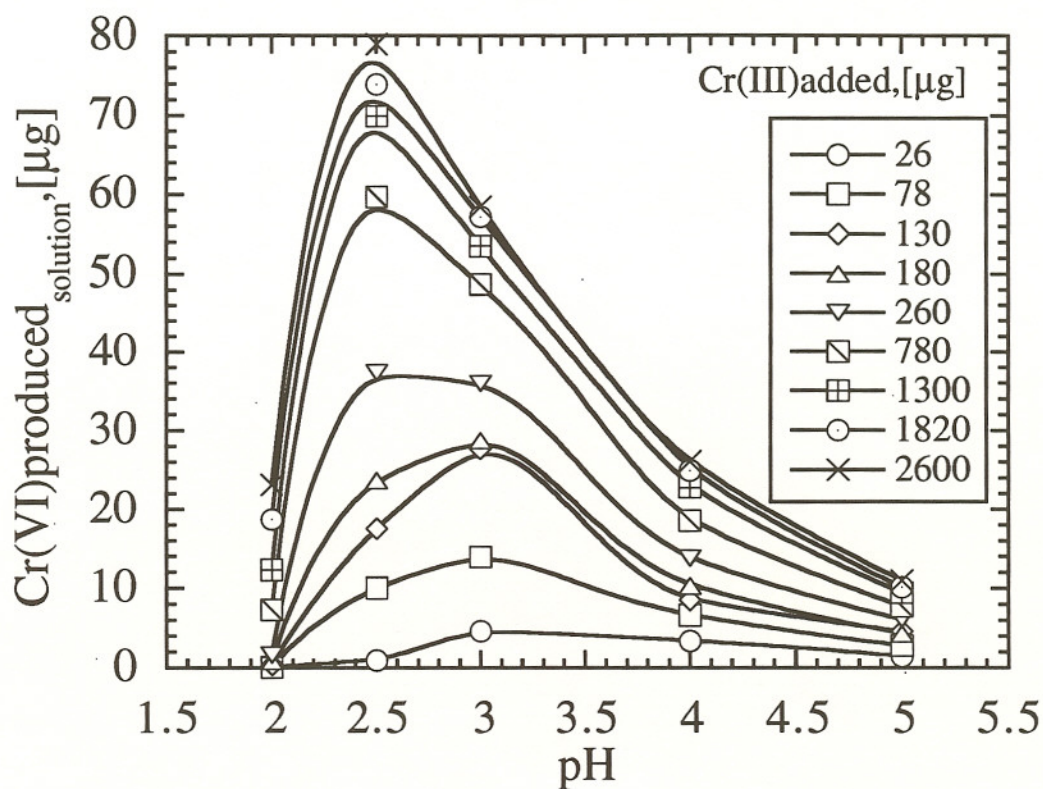


Figure 4.45 Cr(VI) production by a soil as a function of pH at various initial Cr(III) concentrations. Temperature = 25 °C; I = 0.1 M NaNO₃; Soil = Washington loam; Soil/solution = 2.0 g/50 mL.

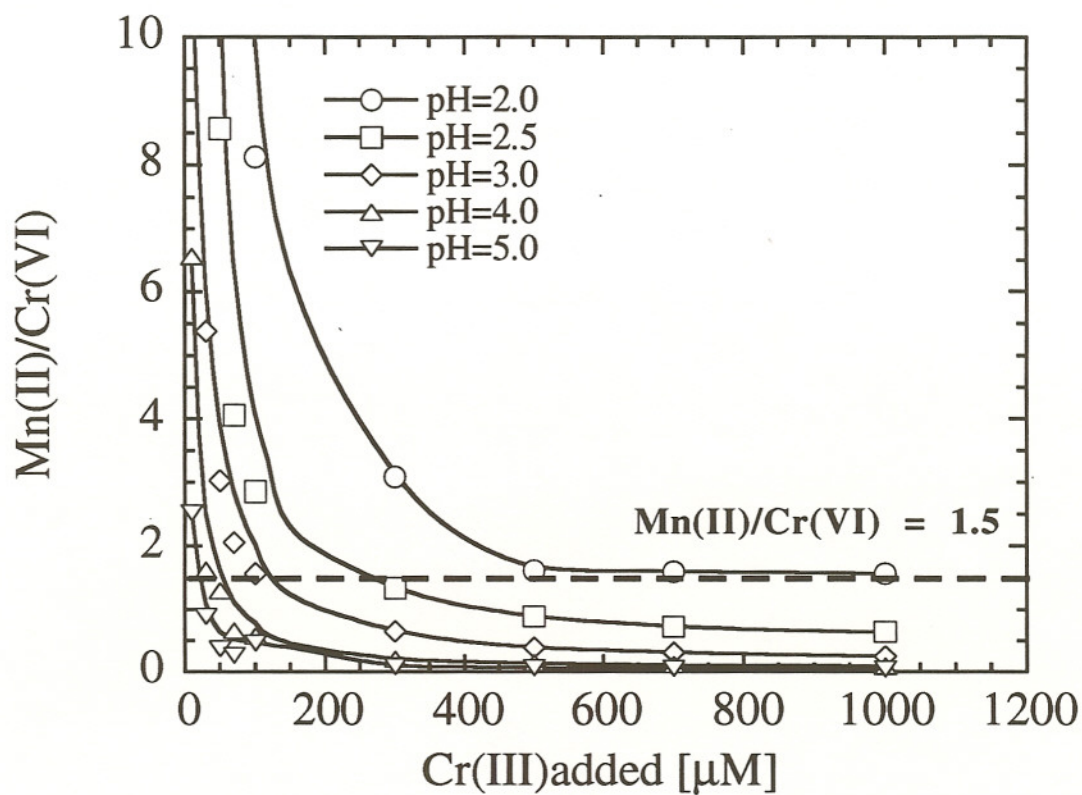


Figure 4.46 The ratio of Mn dissolved to Cr(VI) produced as a function of Cr(III) concentration and pH. Temperature = 25 °C; I = 0.1 M NaNO_3 ; Soil = Washington loam; Soil/solution = 2.0 g/50 mL.

Table 4.10 The relation of Cr(VI) produced to initial Cr(III) added.

pH	Linear expression *	r ²
2.0	$\text{Cr(VI)}_{\text{pro}} = -22.31 + 11.694[\log\{\text{Cr(III)}_{\text{add}}\}]$	0.8932
2.5	$\text{Cr(VI)}_{\text{pro}} = -68.39 + 43.396[\log\{\text{Cr(III)}_{\text{add}}\}]$	0.9885
3.0	$\text{Cr(VI)}_{\text{pro}} = -35.00 + 28.295[\log\{\text{Cr(III)}_{\text{add}}\}]$	0.9916
4.0	$\text{Cr(VI)}_{\text{pro}} = -15.95 + 12.260[\log\{\text{Cr(III)}_{\text{add}}\}]$	0.9908
5.0	$\text{Cr(VI)}_{\text{pro}} = -6.04 + 4.938[\log\{\text{Cr(III)}_{\text{add}}\}]$	0.9921

- * $\text{Cr(VI)}_{\text{pro}}$ = the amount of Cr(VI) produced by oxidation,
 $\text{Cr(III)}_{\text{add}}$ = the amount of Cr(III) added in the beginning of experiment.

Experimental conditions:

- Soil = Washington loam
- Soil/solution = 2.0 g/50 mL
- Temperature = 25 °C
- I = 0.1 M NaNO₃

4.2.4 Effect of Soil to Solution Ratio on Cr(III) Oxidation

The effect of the ratio of soil to solution, weight/weight, assuming that the specific gravity of solution is 1, on the rates of Cr(III) oxidation by soil is shown in Figure 4.47. A two-fold increase of soil resulted in almost two-fold increase of aqueous Cr(VI) production. Eary and Rai (1987) reported similar results that an order of magnitude increase in the β -MnO₂ surface area brought out an order of magnitude increase in the amount of Cr(VI) production. The increase of soil or Mn oxide surface area can provide more Mn available for Cr(III) oxidation. The production of Cr(VI), shown in Figure 4.47, is initially very rapid and slows down significantly after 8 hours, typical results observed in the oxidation of Cr(III). These nonlinear rates of Cr(III) oxidation were also observed in the Cr(III) oxidation by manganese oxides (Eary and Rai, 1987; Schroeder and Lee, 1975).

Figure 4.48 shows the dissolution of manganese from a soil with and without Cr(III) oxidation. The result indicates that the dissolution of manganese has a similar nonlinear trend with Cr(III) oxidation by soil, i.e., manganese was dissolved rapidly in the beginning of the reaction and then slowed down. This was already explained in Section 4.2.3. Also, the data in Figure 4.48 demonstrate that higher soil to solution ratio results in greater manganese dissolution, since the dissolution rate of minerals are dependent upon the concentration of the appropriate surface species (Wieland et al., 1988).

It was found that the oxidation of Cr(III) expedited the dissolution of manganese. But in some cases, dissolution was inhibited in the presence of inorganic

species such as Ca^{2+} and HPO_4^{2-} (Stone and Morgan, 1984a). The reductive dissolution of manganese oxides was studied by Stone and co-workers (Stone and Morgan, 1984a, 1984b; Stone, 1987; Ulrich and Stone, 1989; Stone and Ulrich, 1989). The dissolution of a mineral is sum of chemical and physical reaction steps (Herin and Stumm, 1990). However, they demonstrated that the dissolution rate is controlled by the rate of chemical reactions on the mineral surface rather than transport processes.

The rate constants were estimated by the first order kinetic equation (equation 4.3) for various ratio of soil to solution. Table 4.11 and Figure 4.49 show a summary of the rate constants and the plot of them as a function of soil-to-solution ratio. The data in Figure 4.49 demonstrate that the reaction rate constants are linearly related to the ratio of soil-to-solution. It is, therefore, speculated that higher soil/solution ratio can accomplish more Cr(III) oxidation than can a lower one. The relation of Cr(III) oxidation to soil/solution ratio for various initial Cr(III) concentration is clearly shown in Figure 4.50 and Table 4.12. The production of Cr(VI) increased as soil/solution ratio or initial Cr(III) concentration was increasing. The relationship of the fraction of Cr(VI) production to the soil/solution ratio is summarized in Figure 4.51.

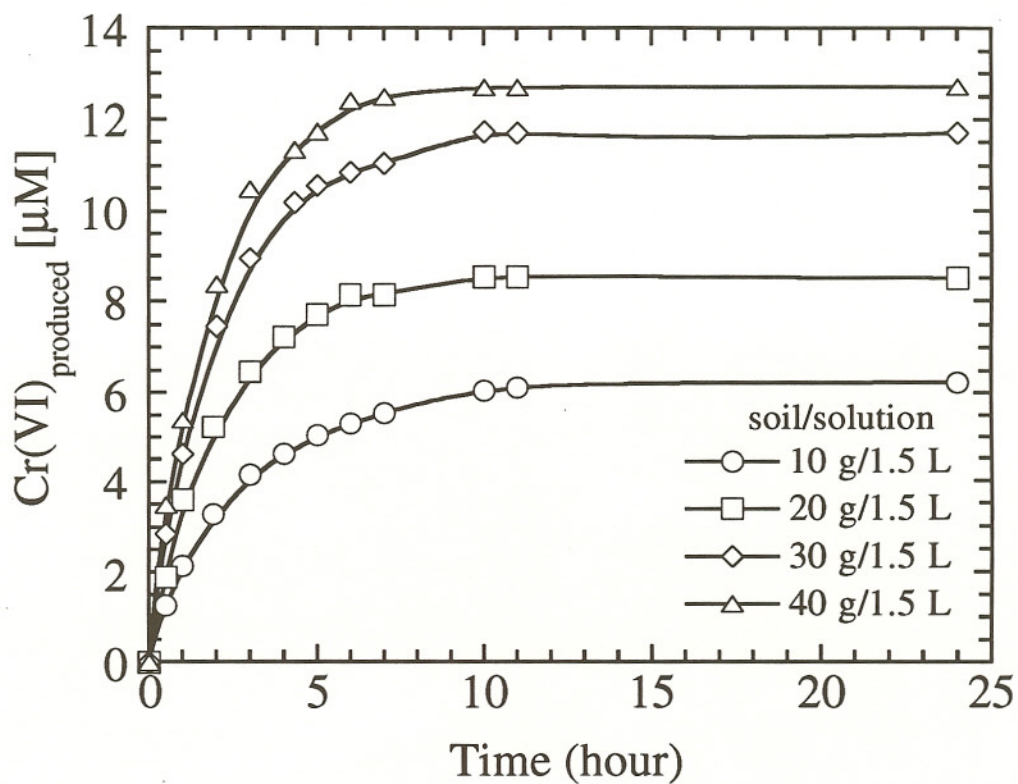


Figure 4.47 The kinetics of Cr(VI) production as a function of time at various soil concentrations. Soil = Washington loam; Initial Cr(III) = 10^{-3} M; pH = 2.0; Temperature = 25 °C; I = 0.1 M NaNO₃.

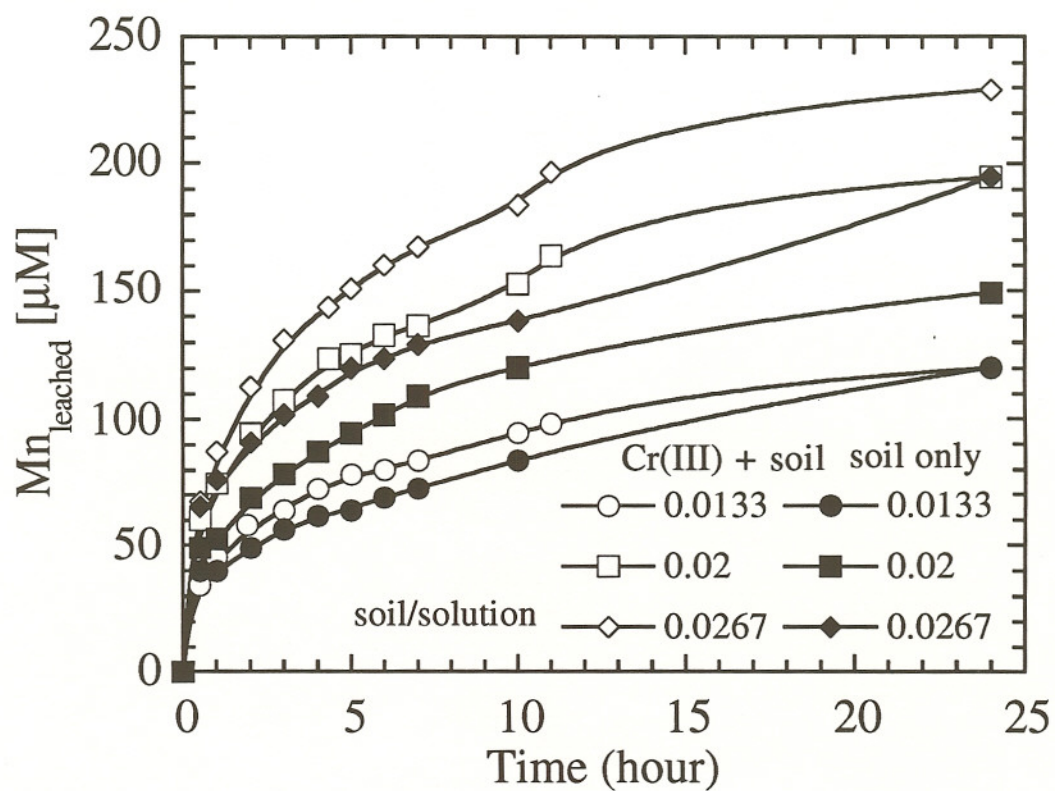


Figure 4.48 The dissolution of Mn associated with Cr(III) oxidation reaction as a function of time at various soil concentrations. Soil = Washington loam; Initial Cr(III) = 10^{-3} M; pH = 2.0; Temperature = 25 °C; I = 0.1 M NaNO_3 .

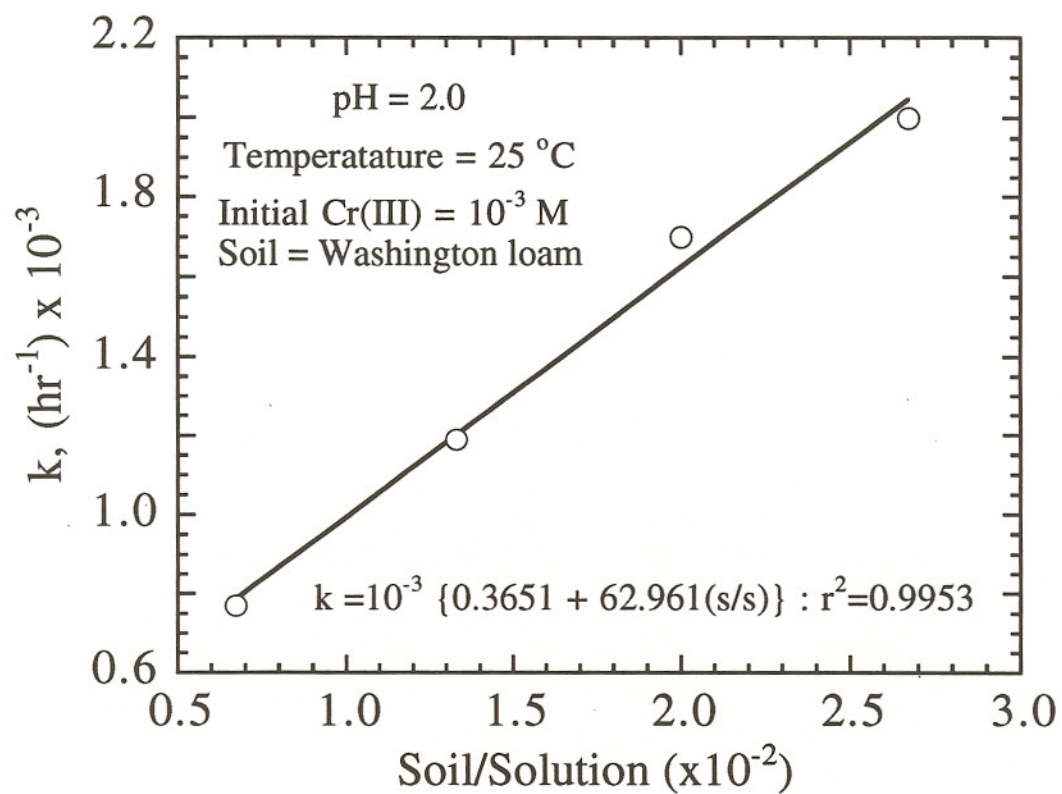


Figure 4.49 The relation of the rate constant of Cr(III) oxidation to soil/solution ratio. Soil = Washington loam; Initial Cr(III) = 10^{-3} M; pH = 2.0; Temperature = 25 °C; I = 0.1 M NaNO₃.

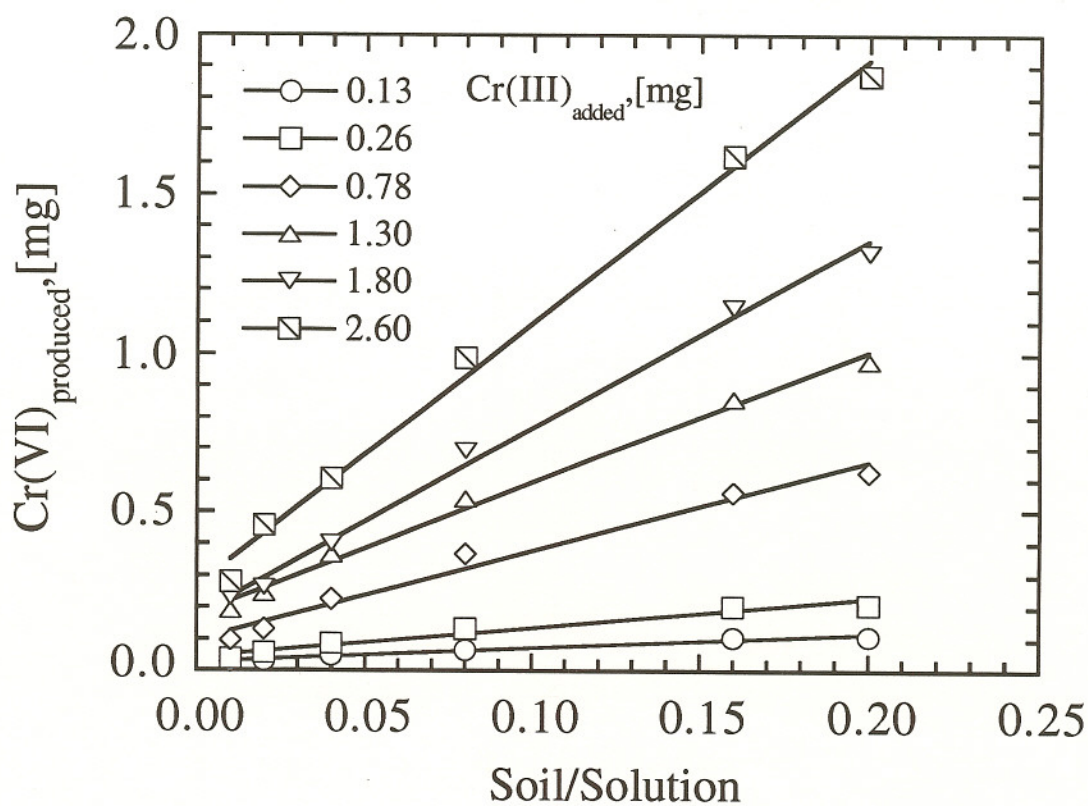


Figure 4.50 The relation of Cr(VI) production to soil/solution ratio for various initial Cr(III) concentrations. Soil = Washington loam; Temperature = 25 °C; pH = 2.0; I = 0.1 M NaNO₃; Volume of solution = 50 mL.

Table 4.11 The first order rate constants vs. the ratio of soil to solution

Soil/Solution	k, (hr ⁻¹)	t _{1/2} , (day)	r ²
0.0067	7.7x10 ⁻⁴	37.5	0.9605
0.0133	1.2x10 ⁻³	24.3	0.9502
0.0200	1.7x10 ⁻³	17.0	0.9373
0.0267	2.1x10 ⁻³	14.1	0.9378

Experimental conditions:

- Volume of solution = 1500 mL
- Temperature = 25 °C
- pH = 2.0
- Soil = Washington loam
- Initial Cr(III) = 10⁻³ M Cr(NO₃)₃·9H₂O
- I = 0.1 M NaNO₃

Table 4.12 The relation of Cr(VI) production to soil/solution ratio for various initial Cr(III) concentrations.

Cr(III) _{added} [mg]	Cr(VI) produced [mg] vs. Soil/Solution ratio*	r ²
0.13	$y = 26.90 + 456.4 x$	0.9878
0.26	$y = 43.36 + 928.2 x$	0.9817
0.78	$y = 97.77 + 2802.6 x$	0.9895
1.30	$y = 178.35 + 4150 x$	0.9963
1.80	$y = 175.29 + 5897.9 x$	0.9976
2.60	$y = 269.65 + 6260.2 x$	0.9970

* : x = soil/solution ratio, [g/g]; y = Cr(VI) produced, [mg]

Experimental conditions :

- Soil = Washington loam
- pH = 2.0
- Temperature = 25 °C
- I = 0.1 M NaNO₃

4.2.5 Effect of Ionic Strength on Cr(III) Oxidation

Because ionic strength will affect activity coefficients and change electrocharge balance in solution, effects on surface charge and properties arise when reactions involve a solid surface such as soil (Fendorf and Zasoski, 1992). The effect of ionic strength on the Cr(III) oxidation reaction by soil is presented in Figure 4.52. Since these experiments were conducted at pH 2.5, which is near the pH_{zpc} of Washington loam (ca.2.8), ionic strength should have little effect on the surface charge. However, increased ionic strength in solution, via increasing $NaNO_3$ concentration, lowered the oxidation of Cr(III), which is probably due to a decrease in the ionic activity of Cr(III) (Amacher and Baker, 1982). These results differ from those of Fendorf and Zasoski (1992), which were conducted above the pH_{zpc} , at which pH the surface maintained a negative charge. They reported that greater ionic strengths enhanced oxidation. However, the effect was small and could be ignored in dilute solutions (Amacher and Baker, 1982; Himenz, 1986; Stumm and Morgan, 1981). In association with the Cr(III) oxidation process in various ionic strength conditions, manganese was also dissolved and the stoichiometry of Mn dissolved to Cr(VI) produced is presented in Figure 4.53 as a function of initial Cr(III) concentration. The ratio of Mn to Cr(VI) in solution decreases logarithmically as Cr(III) loading increases. However, the effect of ionic strength on the ratio is small even though there are slight differences at low Cr(III) concentration.

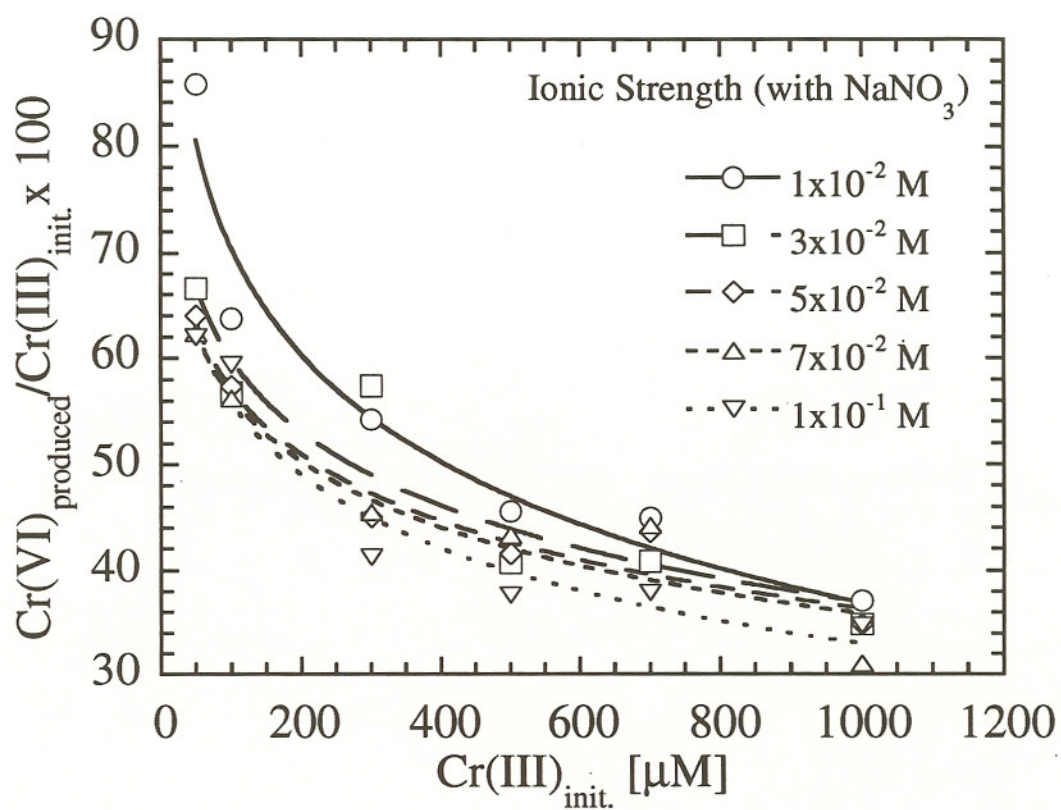


Figure 4.52 The effect of ionic strength on Cr(III) oxidation process. Soil = Washington loam; Soil/solution = 2.0 g/50 mL; Temperature = 25 °C; pH = 2.5.

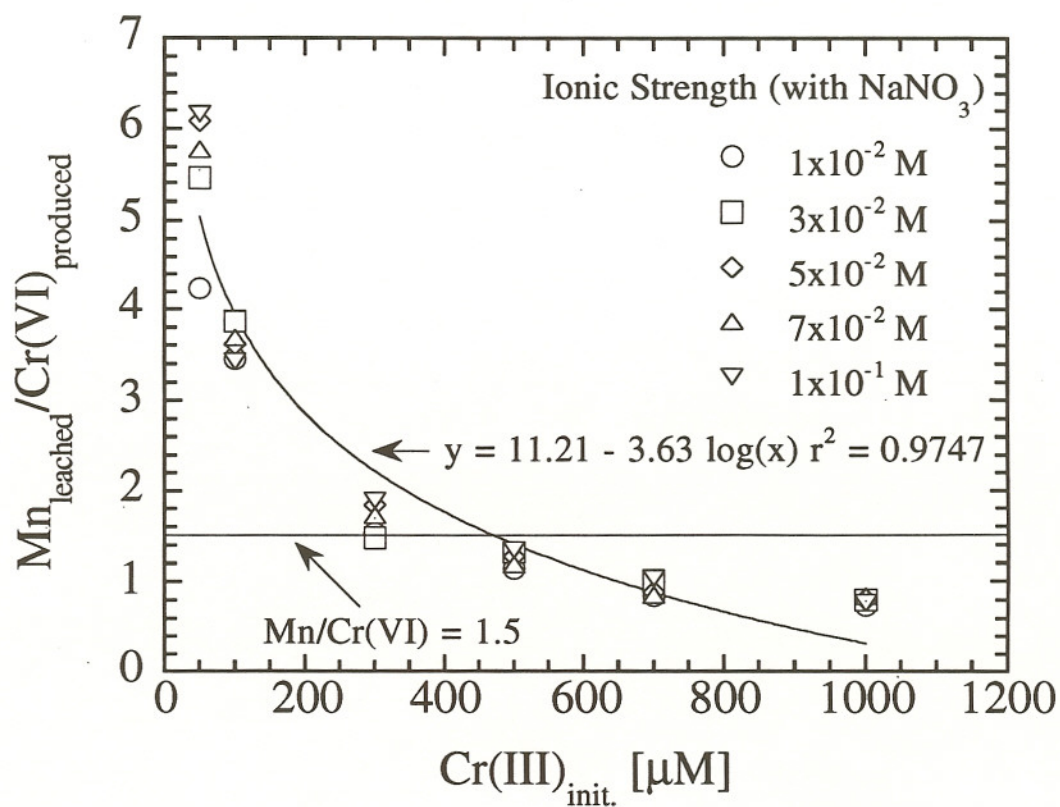


Figure 4.53 The effect of ionic strength on the stoichiometry of Mn dissolved to Cr(VI) produced at various Cr(III) concentrations. Soil = Washington loam; Soil/solution = 2.0 g/50 mL; Temperature = 25 °C; pH = 2.5.

4.3 Summary

This study shows that the reduction processes of Cr(VI) in subsurface soil are influenced by soil pH, iron or organic matter content of soil, and reduction conditions induced by deoxygenation of soil. Examination of Cr(VI) reduction in two different solution matrices, 0.01 M NaNO₃ and simulated ground water, Cr(VI) reduction could not occur in the absence of strong reductants such as Fe(II) or organic matter even under a nitrogen atmosphere, a likely reduced environment.

The Cr(III) formation from Cr(VI) reduction reaction by soils is related to iron content of soils. The amount of Cr(III) formed at pH 2.0 with six soils decreased in the order: Boonton Bergen county loam > Sassafras sandy loam > Lakewood sandy loam > Dunellen sandy loam > Hazen gravelly loam > Freehold sandy loam (B horizon). The order of amorphous iron content in soils is: Boonton Bergen county loam > Sassafras sandy loam > Freehold sandy loam > Lakewood sandy loam > Hazen gravelly loam > Dunellen sandy loam.

The reduction of Cr(VI) by soils occurred only at very acidic conditions (pH < 4). The rate constants of Cr(VI) reduction by soils were proportional to n th power of H⁺ concentration. The values of n ranged from 0.204 to 0.570 depending on the soil. Also, Cr(VI) could be reduced readily by soils with high organic matter content under acidic and more reducing conditions, such as low oxygen content.

The amount of Cr(VI) reduced increases as soil concentration increases because higher soil concentration gave more "active" sites for Cr(VI) reduction. At

the same Cr(VI) loading onto soil, the amount of Cr(VI) reduced by soil (mg/Kg) decreases with increasing soil/solution ratio. This could be due to a surface alteration either by CrO_4^{2-} or by Cr(III) adsorption, which would inhibit the dissolution of the putative reductant, Fe(II), from the soil surface.

Temperature was one of the most important variables in the kinetics of Cr(VI) reduction. The rate of Cr(III) formation from the reduction reaction increased exponentially with temperature which is an Arrhenius-type of temperature dependence. The activation energy value of 58.7 KJ/mole for Sassafras sandy loam indicated that chemical reaction processes are the rate-limiting step for Cr(VI) reduction by soil.

Cr(VI) is reduced readily at acidic condition by soil humic acids and the dominant Cr(VI) reduction might occur at the surface of solid humic acid rather than with soluble humic acid at very low pH (pH 2), whereas soluble humic acid becomes more predominant reductant for Cr(VI) reduction as pH increased up to pH 4.5. The average oxidation state of soil humic acids is about +2.3. Therefore, the reduction reaction of Cr(VI) by humic acids can be stoichiometrically expressed as:



Through the study of Cr(III) oxidation by soils at various experimental conditions, the following results were found:

The oxidation capacity and rate constant of soil for oxidation was linearly related to the manganese content in soil as determined by sodium dithionite-citrate-bicarbonate extraction. The relationship was expressed by:

Cr(III) oxidation capacity (mg/Kg) = $1002.3 \times (\text{Mn content in soil, \%}) + 128.58$

$$r^2 = 0.9280$$

It was found that dissolved oxygen did not affect significantly the Cr(III) oxidation reaction in solution alone and Cr(III) oxidation occurred by direct reaction with manganese oxides in soil.

The Cr(III) oxidation reaction by soil was totally dependent on available Mn, which was promoted by increasing temperature. The activation energy for Cr(III) oxidation by Washington loam estimated by the Arrhenius equation was about 82 KJ/mol, which demonstrates that Cr(III) oxidation reaction may be controlled by chemical reaction processes.

The reaction rate of Cr(III) oxidation was significantly dependent upon pH and had three different ranges with different variations of reaction rate constants with pH. At pH less than 3.5, some inhibition effect on Cr(III) oxidation by adsorption of anionic Cr(VI) species onto the surface was dominant and at pH above 5, the oxidation of Cr(III) was a very slow process since the reaction was limited by the adsorption of positive chromium species and the precipitation of $\text{Cr}(\text{OH})_3$.

The production of Cr(VI) resulting from Cr(III) oxidation was increased as initial Cr(III) concentration and the ratio of soil to solution increased. The reaction rate constant was linearly related to the soil/solution ratio.

The effect of ionic strength on Cr(III) oxidation was insignificant and the ratio of Mn to Cr(VI) in solution was decreased logarithmically as Cr(III) loading increased.

Chapter 5

CONCLUSIONS

5.1 Major Findings

Through examination of Cr(VI) reduction in two different solution matrices, 0.01 M NaNO₃ and simulated ground water, Cr(VI) reduction could not occur in the absence of strong reductants such as Fe(II) or organic matter even under a nitrogen atmosphere, a likely reduced environment.

The Cr(III) formation from the Cr(VI) reduction reaction in soils is related to the iron content of soils and occurs only at very acidic conditions (pH < 4). Also, Cr(VI) can be reduced readily by soils with high organic matter content under an acidic and more reducing condition, such as low oxygen content.

The amount of Cr(VI) reduced increases as soil concentration increases because higher soil concentrations give more "active" sites for Cr(VI) reduction. At the same Cr(VI) loading onto soil, the amount of Cr(VI) reduced by soil (mg/Kg) decreases with increasing soil/solution ratio. This is due to a surface alteration, either by CrO₄²⁻ or Cr(III) adsorption, which would inhibit the dissolution of the reductant, Fe(II), from the soil surface.

Temperature was one of the most important variables in the kinetics of Cr(VI) reduction. The rate of Cr(III) formation from the reduction reaction increases

exponentially, an Arrhenius-type of temperature dependence. The activation energy value of 58.7 KJ/mole for Sassafras sandy loam indicated that chemical reaction processes are the rate-limiting step for Cr(VI) reduction by soil.

Cr(VI) is reduced readily at acidic pH by soil humic acids and dominant Cr(VI) reduction might occur at the surface of solid humic acid rather than with soluble humic acid at very low pH (pH 2). Soluble humic acid is the more predominant reductant for Cr(VI) reduction as pH increase up to pH 4.5. The average oxidation state of soil humic acids is about +2.3. Therefore, the reduction reaction of Cr(VI) by humic acids can be stoichiometrically expressed as:



Through the study of Cr(III) oxidation by soils at various experimental conditions, the following results were found:

The oxidation capacity and rate constant of soil is significantly related to the manganese content in soil and sodium dithionite-citrate-bicarbonate extraction shows the linear correlation. The relationship was expressed by:

$$\text{Cr(III) oxidation capacity (mg/Kg)} = 1002.3 * (\text{Mn content in soil, \%}) + 128.58$$

$$r^2 = 0.9280$$

Dissolved oxygen did not affect significantly the Cr(III) oxidation in solution, and Cr(III) oxidation occurs by direct reaction with manganese oxides in soil. Therefore, Cr(III) oxidation by soil is totally dependent on the amount of available Mn, which is enhanced by increasing temperature.

The activation energy for Cr(III) oxidation by Washington loam estimated by the Arrhenius equation is about 82 KJ/mol, which demonstrates that Cr(III) oxidation may be controlled by a chemical reaction.

The reaction rate constant for Cr(III) oxidation had three different values depending on the pH range. At pH less than 3.5, some inhibition effect on Cr(III) oxidation from the adsorption of anionic Cr(VI) species produced at the surface was dominant. At pH above 5, the oxidation of Cr(III) was a very slow process since the reaction was limited by the adsorption of positive chromium species and the precipitation of $\text{Cr}(\text{OH})_3$.

The production of Cr(VI) by Cr(III) oxidation increases with initial Cr(III) concentration and as the ratio of soil to solution increases. The reaction rate constant is linearly related to the soil/solution ratio.

The effect of ionic strength on Cr(III) oxidation is insignificant and the ratio of Mn to Cr(VI) in solution decreases logarithmically as Cr(III) loading increased.

Based on the results for Cr redox reactions by New Jersey soils, it is concluded that Cr redox reactions may not occur in chromium-contaminated sites due to soil pH (about 5.5 - 6.).

5.2 Recommendations for Future Research

1. Because the variety of kinetic parameters of Cr redox reactions developed were obtained at laboratory conditions, it is possible that the results are

somewhat different from actual conditions. Therefore, it may be necessary to observe the Cr concentration as a function of time.

2. Development of remediation technologies, such as electro-osmosis and soilflushing, may be interesting research subject for Cr-contaminated soil.

REFERENCES

- ACGIH (1980) "Documentation of Threshold Limit Values." American Conference of Government Industrial Hygienist. Inc., 4th Ed. Cincinnati, OH.
- Ainsworth, C.C., Girvin, D.C., Zachara, J.M., and Smith, S.C. (1989) " CrO_4^{2-} Adsorption on Goethite: Effects of Aluminum Substitution." Soil Sci. Soc. Am. J., Vol.53, pp.411-418.
- Allen, H.E., Lee, S.Z., Huang, C.P., and Sparks, D.L. (1994) "The Fate and Transport of Inorganic Contaminants in New Jersey Soils." Final Report Submitted to New Jersey Department of Environmental Protection and Energy, Trenton, NJ.
- Amacher, M.C. (1991) "Methods of Obtaining and Analyzing Kinetic Data." in Rates of Soil Chemical Processes Edited by Sparks, D.L. and Suarez, D.L., SSSA Special Publication, No.27, Soil Science Society of America, Madison, WI, pp.19-59.
- Amacher, M.L. and Baker, D.E. (1982) "Redox Reactions Involving Chromium, Plutonium, and Manganese in Soils." DOE/DP/04515-1. Pennsylvania State University, University Park, PA.
- American Public Health Association (APHA) (1985) Standard Methods for the Examination of Water and Wastewater, 17th Ed. APHA, Washington D.C.
- Barcelona, M.J. and Holm, T.R. (1991) "Oxidation-Reduction Capacities of Aquifer Solids." Environ. Sci. Technol., Vol.25, pp.1565-1572.
- Barrow, N.J. and Shaw, T.C. (1975) "The Slow Reactions between Soil and Anions. II. Effect of Time and Temperature on the Decrease in Phosphate Concentration in the Soil Solution." Soil Sci., Vol.119, pp.167-177.
- Bartlett, R.J. and James, B.R. (1979) "Behavior of Chromium in Soils: III. Oxidation." J. Environ. Qual., Vol.8, pp.31-35.
- Bartlett, R.J. and James, B.R. (1988) "Mobility and Bioavailability of Chromium in Soils." in Chromium in the Natural and Human Environments, Edited by Nriagu, J.O. and Nieboer, E., John Wiley & Sons, New York, pp.267-304.
- Bartlett, R.J. and Kimble, J.M. (1976a) "Behavior of Chromium in Soils: I. Trivalent Forms." J. Environ. Qual., Vol.5, pp.379-383.
- Bartlett, R.J. and Kimble, J.M. (1976b) "Behavior of Chromium in Soils: II. Hexavalent Forms." J. Environ. Qual., Vol.5, pp.383-386.

- Beattie, J.K. and Haight, G.P. Jr. (1972) "Chromium(VI) Oxidations of Inorganic Substances." in Progress in Inorganic Chemistry Series. Inorganic Reaction Mechanisms, Edited by Edwards, J.O., Vol.17, John Wiley & Sons, New York, pp.93-145.
- Bloomfield, C. and Pruden, G. (1980) "The Behaviour of Cr(VI) in Soil under Aerobic and Anaerobic Conditions." Environ. Pollution (Series A), Vol.23, pp.103-114.
- Borggaard, O.K. (1974) "Titrimetric Determination of Acidity and pK Values of Humic Acid." Acta Chem. Scand., Vol.A 28, pp.121-122.
- Bruland, K.W. (1983) "Trace Elements in Seawater." Chemical Oceanography, Vol.8, Edited by Riley, J.P., Academic Press, New York, pp.203-204.
- Burns, L.A., Cline, D.M., and Lassiter, R.R. (1981) "Exposure Analysis and Modeling Systems (EXAMS)." User Manual and System Documentation, U.S. EPA, Athens, GA.
- Casarett, L. and Doull, J. (1980) Toxicology: The Basic Science of Poison, Doull, J., Klaassen, C.D. and Amdur, M.O. Eds. MacMillan, New York. pp.265-267, 410-412.
- Davies, J.M. (1984) "Lung Mortality among Workers Making Lead Chromate and Zinc Chromate Pigments at Three English Factories." Br. J. Ind. Med., Vol.41, pp.158-169.
- Delfino, J.J. and Lee, G.F. (1971) "Variation of Manganese, Dissolved Oxygen and Related Chemical Parameters in the Bottom Waters of Lake Mendota, Wisconsin." Water Res., Vol.5, pp.1207-1217.
- Eary, L.E. and Rai, D. (1987) "Kinetics of Chromium (III) Oxidation to Chromium (VI) by Reaction with Manganese Dioxide." Environ. Sci. Technol., Vol.21, pp.1187-1193.
- Eary, L.E. and Rai, D. (1988) "Chromate Removal from Aqueous Wastes by Reduction with Ferrous Ion." Environ. Sci. Technol., Vol.22, pp.972-977.
- Eary, L.E. and Rai, D. (1989) "Kinetics of Chromate Reduction by Ferrous Ions Derived from Hematite and Biotite at 25 °C." J. Sci., Vol.289, pp.180-213.
- Eary, L.E. and Rai, D. (1991) "Chromate Reduction by Subsurface Soils under Acidic Conditions." Soil Sci. Soc. Am. J., Vol.55, pp.676-683.
- Eary, L.E. and Schramke, J.A. (1990) "Rates of Inorganic Reactions Involving Dissolved Oxygen." in Chemical Modeling of Aqueous Systems II, Edited by Melchior, D.C. and Bassett, R.L. ACS Symp. Ser., 416. American Chemical Society, Washington, DC.

- Eary, L.E. and Zachara, J.M. (1989) "Environmental Chemistry of Chromium." Sci. Total Environ., Vol.86, pp.15-23.
- Environmental Science and Engineering (1988) "Risk Assessment for Chromium Sites in Hudson County." New Jersey Department of Environmental Protection and Energy, Trenton, NJ.
- Evans, R.L. and Jurinak, J.J. (1976) "Kinetics of Phosphate Release from a Desert Soil." Soil Sci., Vol.121, pp.205-211.
- Fendorf, S.E. and Zasoski, R.J. (1992) "Chromium(III) Oxidation by δ -MnO₂. 1. Characterization." Environ. Sci. Technol., Vol.26, pp.79-85.
- Forstner, V. and Wittmann, G.T.W. (1981) Metal Pollution in the Aquatic Environment, Springer - Verlag, New York.
- Grant, D. (1977) "Chemical Structure of Humic Substances." Nature, Vol.270, pp.709-710.
- Haque, R., Lindstrom, F.T., Freed, V.H., and Sexton, R. (1968) "Kinetic Study of the Sorption of 2,4-D on Some Clays." Environ. Sci. Technol., Vol.2, pp.207-211.
- Hering, J.G. and Stumm, W. (1990) "Oxidative and Reductive Dissolution of Minerals." in Mineral-Water Interface Geochemistry, Reviews in Mineralogy, Edited by Hochella, M.F.Jr. and White, A.F., Vol.23, The Mineralogical Society of America, Washington, DC, pp.427-465.
- Himenz, P.C. (1986) Principles of Colloid and Surface Chemistry, 2nd ed. Marcel Dekker, New York, pp.153.
- Huang, C.P. and Bowers, A.R. (1978) "The Use of Activated Carbon for Cr(VI) Removal." Prog. Wat. Tech., Vol.10, pp.45-64.
- Huang, C.P., Allen, H.E., Cheng, A.H-D., and Weng, C.H. (1991) "Environmental Fate Investigation of Chromium Contamination (Spill and Research Found)." Final Report Submitted to New Jersey Department of Environmental Protection and Energy, Trenton, New Jersey.
- Huang, C.P., Weng, C.H., Allen, H.E., and Cheng, A.H.D. (1994) "Effects of Specific Chemical Reactions on the Transformation and the Transport of Chromium in the Soil-Water System and in Concrete Walls." Final Report Submitted to New Jersey Department of Environmental Protection and Energy, P34913, University of Delaware, Newark, DE.
- IARC (1980) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol.23, pp.205-213.

- Jenne, E.A. (1968) "Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Mn and Fe Oxides." In Trace Inorganics in Water; Adv. Chem. Ser., Vol.73, pp.337-387.
- Katz, S.A. and Salem, H. (1994) The Biological and Environmental Chemistry of Chromium, VCH Publishers, New York, pp.57.
- Lee, S.Z. (1994) "Chemical Interactions Between Heavy Metals and Soils" Ph.D Dissertation of University of Delaware, Newark, DE.
- Leenheer, J.A. and Ahlrichs, J.L. (1971) "A Kinetic and Equilibrium Study of the Adsorption of Carbaryl and Parathion upon Soil Organic Matter Surfaces." Soil Sci. Soc. Am. Proc., Vol.35, pp.700-704.
- Leenheer, J.A., Wershaw, R.L., and Reddy, M.M. (1995) "Strong-acid, Carboxyl-group Structures in Fulvic Acid from the Suwannee River, Georgia. 1. Minor Structures." Environ. Sci. Technol., Vol.29, pp.393-398.
- Lin, Y. (1992) "The Kinetic Study of Chromium Reduction with Pyrite." Masters Thesis of University of Delaware, Newark, DE.
- Lindberg, R. and Hedensteirna, G. (1983) "Symptoms, Findings in Upper Airways and Effects on Lung Function." Arch. Environ. Health, Vol.38, pp.367-374.
- Machesky, M.L. (1993) "Calorimetric Acid-Base Titrations of Aquatic and Peat-Derived Fulvic and Humic Acids." Environ. Sci. Technol., Vol.27, pp.1182-1189.
- Mali, J.W.H., van Kooten, W.J., and van Neer, F.C.J. (1963) "Some Aspects of the Behavior of Chromium Compounds in the Skin." J. Invest. Derm., Vol.41, pp.111-122.
- McCallum, C. and Midgley, D. (1975) "Linear Titration Plots for the Potentiometric Determination of Mixtures of Strong and Weak Acids." Anal. Chim. Acta, Vol.78, pp.171-181.
- McKenzie, R.M. (1977) "Manganese Oxides and Hydroxides." in Minerals in Soil Environments, Edited by Dixon, B and Weed, S.B., Soil Sci. Soc. Am., Madison, WI, pp.181-192.
- McKibben, M.A. and Barnes, H.L. (1986) "Oxidation of Pyrite in Low Temperature Acidic Solutions: Rate Laws and Surface Textures." Geochim. Cosmochim. Acta, Vol.50, pp.1509-1520.
- Metcalf and Eddy Inc. (1972) Wastewater Engineering. Treatment/ Disposal/ Reuse, McGraw-Hill, New York, pp.740.

- Milacic, R. and Stupar, J. (1995) "Fractionation and Oxidation of Chromium in Tannery Waste and Sewage Sludge-Amended Soils." Environ. Sci. Technol., Vol.29, pp.506-514.
- Morgan, J.J. and Stumm, W. (1964) "Colloid-chemical Properties of Manganese Dioxide." J. Colloid Sci., Vol.19, pp.349-359.
- Murray, J.W. (1975) "The Interaction of Metal Ions at the Manganese Dioxide-solution Interface." Geochim. Cosmochim. Acta, Vol.39, pp.505-519.
- Ochs, M., Cosovic, B., and Stumm, W. (1994) "Coordinative and Hydrophobic Interaction of Humic Substances with Hydrophilic Al_2O_3 and Hydrophobic Mercury Surfaces." Geochim. Cosmochim. Acta, Vol.58, pp.639-650.
- Ogwada, R.A. and Sparks, D.L. (1986) "A Critical Evaluation on the Use of Kinetics for Determining Thermodynamics of Ion Exchange in Soils." Soil Sci. Soc. Am. J., Vol.50, pp.300-305.
- Peschel, G. and Wildt, T.H. (1988) "Humic Substances of Natural and Anthropogeneous Origin." Wat. Res., Vol.22, pp.105-108.
- Rai, D., Eary, L.E., and Zachara, J.M. (1989) "Environmental Chemistry of Chromium." Sci. Total Environ., Vol.86, pp.15-23.
- Rai, D. and Zachara, T.M. (1986) "Geochemical Behavior of Chromium Species." Research Project 2485-3, Battelle Pacific Northwest Laboratories, Richland, WA, pp.63.
- Rai, D., Zachara, J.M., Eary, L.E., Girvin, D.C., Moore, D.A., Resch, C.T., Saas, B.M., and Schmidt, R.L. (1986) "Geochemical Behavior of Chromium Species." Electric Power Research Institute, EA-4544, Palo Alto, CA.
- Rai, D., Saas, B.M., and Moore, D.A. (1987) "Chromium(III) Hydrolysis Constants and Solubility of chromium(III) Hydroxide." Inorganic Chem., Vol.26, pp.345-349.
- Rai, D., Zachara, J.M., Ainsworth, C.C., Amonette, J.E., Cowan, C.E., Szelmeckza, R.W., Resch, C.T., Schmidt, R.L., Girvin, D.C., and Smith, S.C. (1988) "Chromium Reactions in Geologic Materials." Electric Power Research Institute, EA-5741, Palo Alto, CA.
- Sass, B.M. and Rai, D. (1987) "Solubility of Amorphous Chromium(III)-Iron(III) Hydroxide Solid Solutions." Inorg. Chem., Vol.26, pp.2228-2232.
- Saleh, F.Y., Parkerton, T.F., Lewis, R.V., Huang, J.H., and Dickson, K.L. (1989) "Kinetic of Chromium Transformation in the Environment." Sci. Total Environ., Vol.86, pp.25-41.

- Schmitt, H.W. and Sticher, H. (1991) "Heavy Metal Compounds in the Soil. Occurrence, Analysis, and Biological Relevance." in Metals and Their Compounds in the Environment, Edited by Merian, E., VCH, New York, pp.313.
- Schnitzer, M. and Hansen, E.H. (1970) "Organo-metallic Interactions in Soils: 8. An Evaluation of Methods for the Determination of Stability Constants of Metal-Fulvic Acid Complexes." Soil Sci., Vol.109, pp.333-340.
- Schroeder, D.C. and Lee, G.F. (1975) "Potential Transformations of Chromium in Natural Waters." Water Air Soil Pollut., Vol.4, pp.355-365.
- Schulthess, C.P. (1985) "Effect of Heavy Metals on the Removal of Humic Substances by Clays." Masters thesis of University of Delaware, Newark, DE.
- Senesi, N. and Sakellariadou, F. (1994) "Structural and Functional Chemical Properties of Marine and Coastal Sedimentary Humic Acids." Environ. Internat., Vol.20, pp.3-9.
- Sparks, D.L. (1985) "Kinetics of Ionic Reactions in Clay Minerals and Soils." Adv. Agron., Vol.38, pp.231-266.
- Sparks, D.L. (1986) "Kinetics of Reactions in Pure and Mixed Systems." in Soil Physical Chemistry, Edited by D.L. Sparks, CRC Press, Boca Raton, FL, pp.83-178.
- Sparks, D.L. (1989) Kinetics of Soil Chemical Processes, Academic Press, San Diego, CA.
- Sparks, D.L. and Jardine, P.M. (1981) "Thermodynamics of Potassium Exchange in Soil Using a Kinetics Approach." Soil Sci. Soc. Am. J., Vol.45, pp.1094-1099.
- Stevenson, F.J. (1982) Humus Chemistry: Genesis, Composition, Reactions, John Wiley & Sons, New York, pp.350.
- Stone, A.T. (1987) "Reductive Dissolution of Manganese (III/IV) Oxides by Substituted Phenols." Environ. Sci. Technol., Vol.21, pp.979-988.
- Stone, A.T. and Morgan, J.J. (1984a) "Reduction and Dissolution of Manganese (III) and Manganese (IV) Oxides by Organics. 1. Reaction with Hydroquinone." Environ. Sci. Technol., Vol.18, pp.450-456.
- Stone, A.T. and Morgan, J.J. (1984b) "Reduction and Dissolution of Manganese (III) and Manganese (IV) Oxides by Organics. 2. Survey of the Reactivity of Organics." Environ. Sci. Technol., Vol.18, pp.617-624.
- Stone, A.T. and Ulrich, H.-J. (1989) "Kinetics and Reaction Stoichiometry in the Reductive Dissolution of Manganese (IV) Dioxide and Co(III) Oxide by Hydroquinone." J. Coll. Int. Sci., Vol.132, pp.509-522.

- Stricharchuk, G. (1990) "Buried Trouble, Metal-processing Past Haunts Jersey City, and PPG as Well." The Wall Street Journal, Eastern Ed., Vol. CCXV, No.125, A4, Wed. June 27, 1990.
- Stumm, W. and Morgan, J.J. (1981) Aquatic Chemistry, 2nd Ed., John Wiley & Sons, New York.
- Stumm, W. (1992) Chemistry of the Solid-Water Interface, Processes at the Mineral-Water and Particle-Water interface in Natural Systems, John Wiley & Sons, New York, pp.157-209.
- Suter, D., Banwart, S., and Stumm, W. (1991) "Dissolution of Hydrous Iron(III) Oxides by Reductive Mechanisms." Langmuir, Vol.7, pp.809-813.
- Takamatsu, T. and Yoshida, T. (1978) "Determination of Stability Constants of Metal-humic Acid Complexes by Potentiometric Titration and Ion-selective Electrodes." Soil Sci., Vol.125, pp.377-386.
- Tipping, E. (1993) "Modelling Ion Binding by Humic Acids." Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol.73, pp.117-131.
- Tipping, E., Backes, C.A., and Hurley, M.A. (1988) "The Complexation of Protons, Aluminium and Calcium by Aquatic Humic Substances: A Model Incorporating Binding-site Heterogeneity and Macroionic Effects." Wat. Res., Vol.22, pp.597-611.
- Ulrich, H.-J. and Stone, A.T. (1989) "Oxidation of Chlorophenols Adsorbed to Manganese Oxide Surfaces." Environ. Sci. Technol., Vol.23, pp.421-428.
- U.S.EPA (1984) Code of Federal Regulations Title 40, National Interim Primary Drinking Water Regulations, Part 141, Washington, D.C.
- Weber, W.J.Jr. (1972) Physicochemical Processes for Water Quality Control, John Wiley & Sons, New York, pp.34-36.
- Weng, C.H. (1994) "Effects of Specific Chemical Reactions on the Transformation and the Transport of Chromium in the Soil-water System and in Concrete Walls." Ph.D. Dissertation of University of Delaware, Newark, DE.
- Wershaw, R.L., Mikita, M.A. and Steelink, C. (1981) "Direct ^{13}C -NMR Evidence for Carbohydrate Moieties in Fulvic Acids." Envir. Sci. Technol., Vol.15, pp.1461-1463.
- Wershaw, R.L. (1993) "Model for Humus." Environ. Sci. Technol., Vol.27, pp.814-816.

- White, A.F. (1990) "Heterogeneous Electrochemical Reactions Associated with Oxidation of Ferrous Oxide and Silicate Surfaces." in Mineral-Water Interface Geochemistry, Reviews in Mineralogy, Vol.23, pp.467-509, The Mineralogical Society of America, Washington, DC.
- White, A.F. and Yee, A. (1985) "Aqueous Oxidation-reduction Kinetics Associated with Coupled Electron-cation Transfer from Iron-containing Silicates at 25 °C." Geochim. Cosmochim. Acta, Vol.49, pp.1263-1275.
- White, A.F., Yee, A., and Flexser, S. (1985) "Surface Oxidation-reduction Kinetics Associated with Experimental Basalt - Water Reactions at 25 °C." Chem Geol., Vol.49, pp.73-86.
- Wieland, E., Wehrli, B., and Stumm, W. (1988) "The Coordination Chemistry of Weathering: III. A Generalization on the Dissolution Rates of Minerals." Geochim. Cosmochim. Acta, Vol.52, pp.1969-1981.
- Wiersma, C.L. and Rimstidt, J.D. (1984) "Rates of Reaction of Pyrite and Marcasite with Ferric Iron at pH 2." Geochim. Cosmochim. Acta, Vol.48, pp.85-92.
- Zachara, J.M., Girvin, D.C., Schmidt, R.L., and Resch, C.T. (1987) "Chromate Adsorption on Amorphous Iron Oxyhydroxide in Presence of Major Groundwater Ions." Environ. Sci. Technol., Vol.21, pp.589-594.
- Zachara, J.M., Cowan, C.E., Schmidt, R.L., and Ainsworth, C.C. (1988) "Chromate Adsorption on Kaolinite." Clays Clay Miner., Vol.36, pp.317-326.
- Zasoski, R.J. and Bureau, R.G. (1988) "Sorption and Sorptive Interaction of Cadmium and Zinc on Hydrated Manganese Oxide" Soil Sci. Soc. Am. J., Vol.55, pp.81-87.

Appendix

THE REDOX REACTIONS OF CHROMIUM

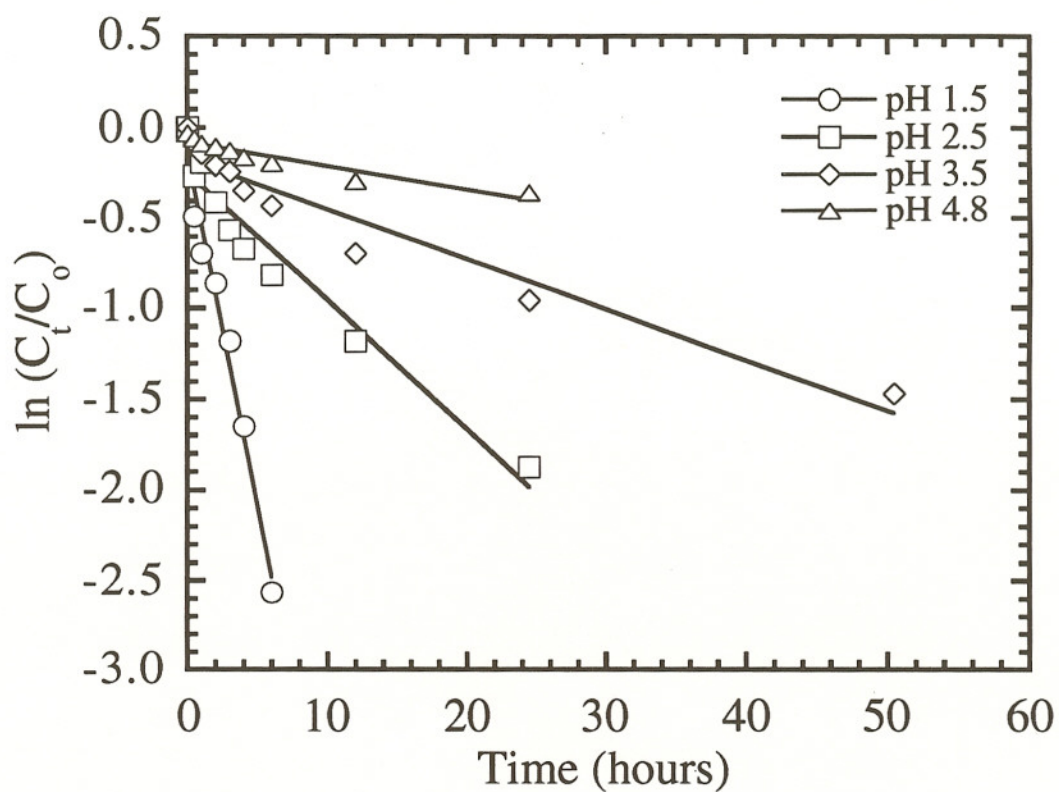


Figure A-1 Reaction rates of Cr(VI) reduction by Boonton Bergen county loam for four pH values. Temperature = 25 °C; I = 0.01 M simulated groundwater; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

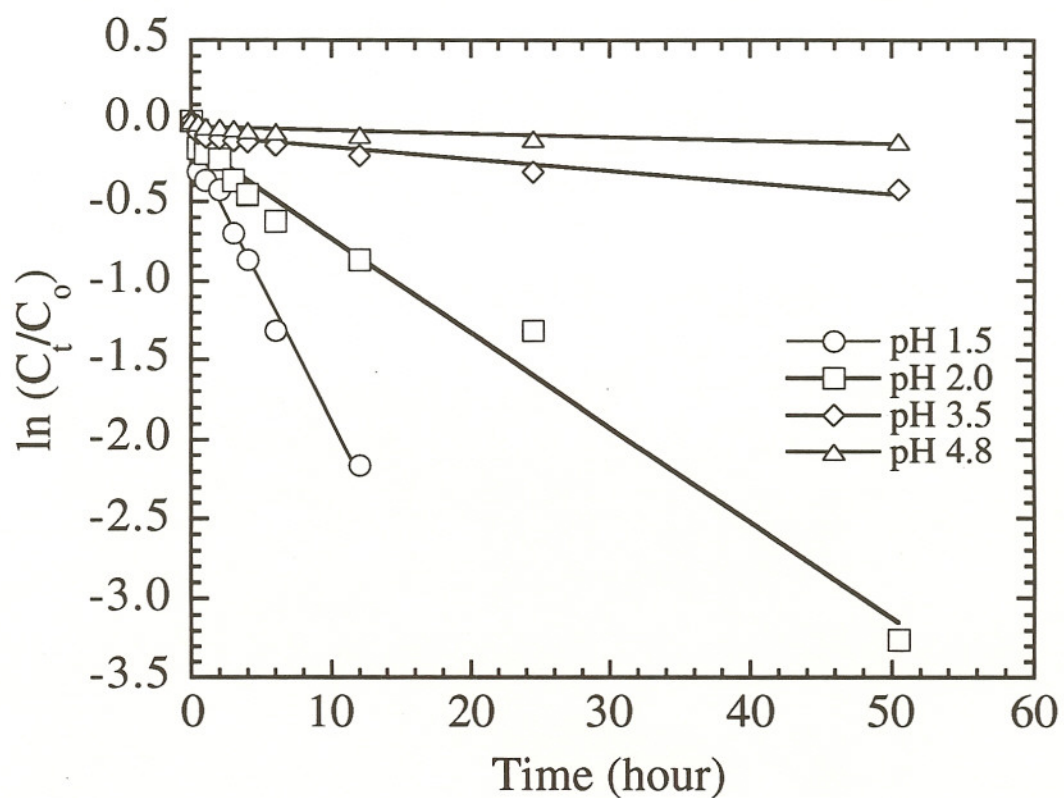


Figure A-2 Reaction rates of Cr(VI) reduction by Sassafras sandy loam for four pH values. Temperature = 25 °C; I = 0.01 M simulated groundwater; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

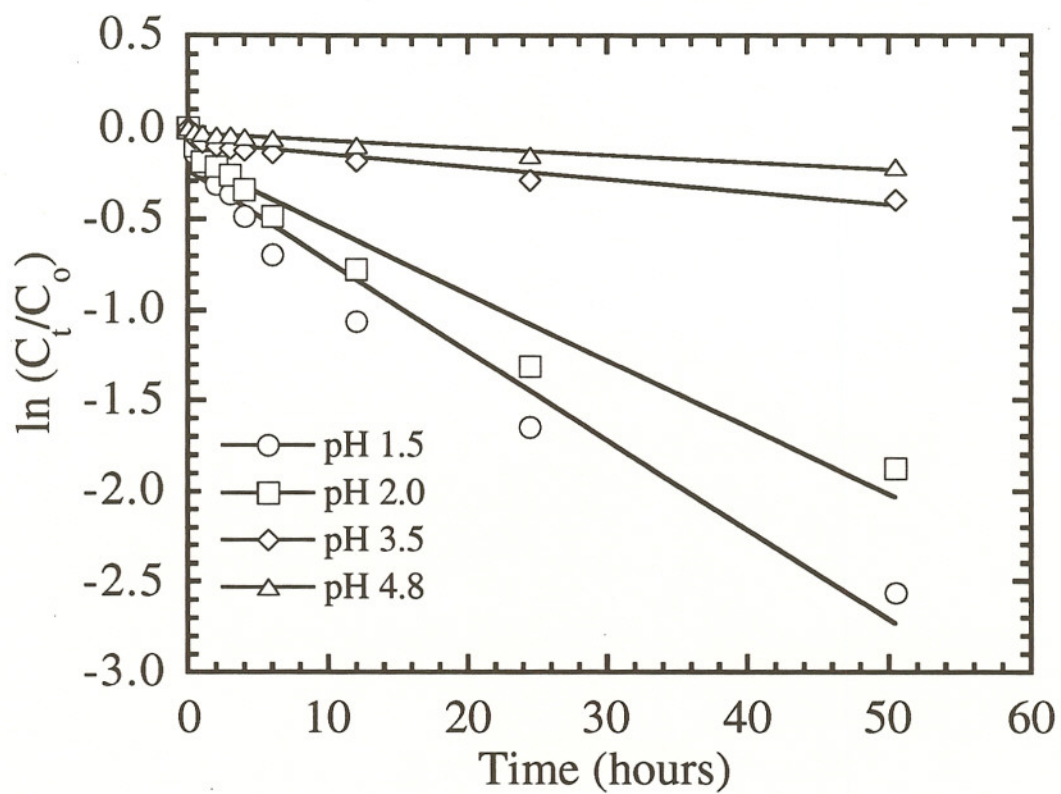


Figure A-3 Reaction rates of Cr(VI) reduction by Lakewood sandy loam for four pH values. Temperature = 25 °C; I = 0.01 M simulated groundwater; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

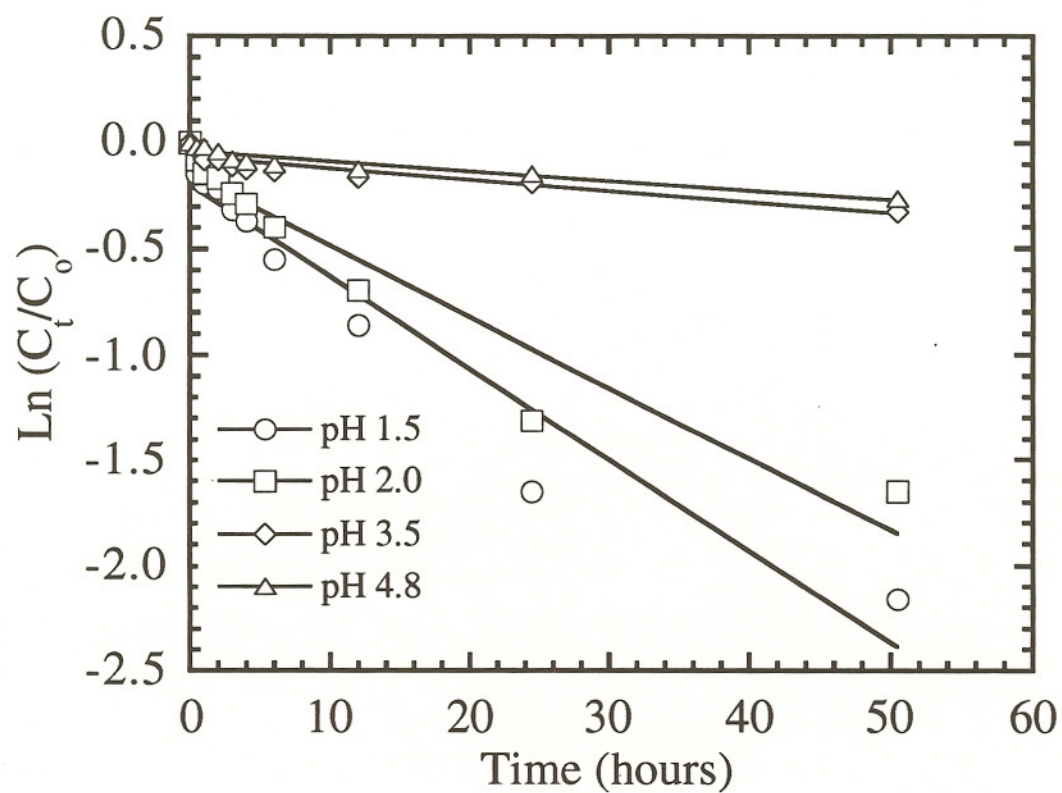


Figure A-4 Reaction rates of Cr(VI) reduction by Dunellen sandy loam for four pH values. Temperature = 25 °C; I = 0.01 M simulated groundwater; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

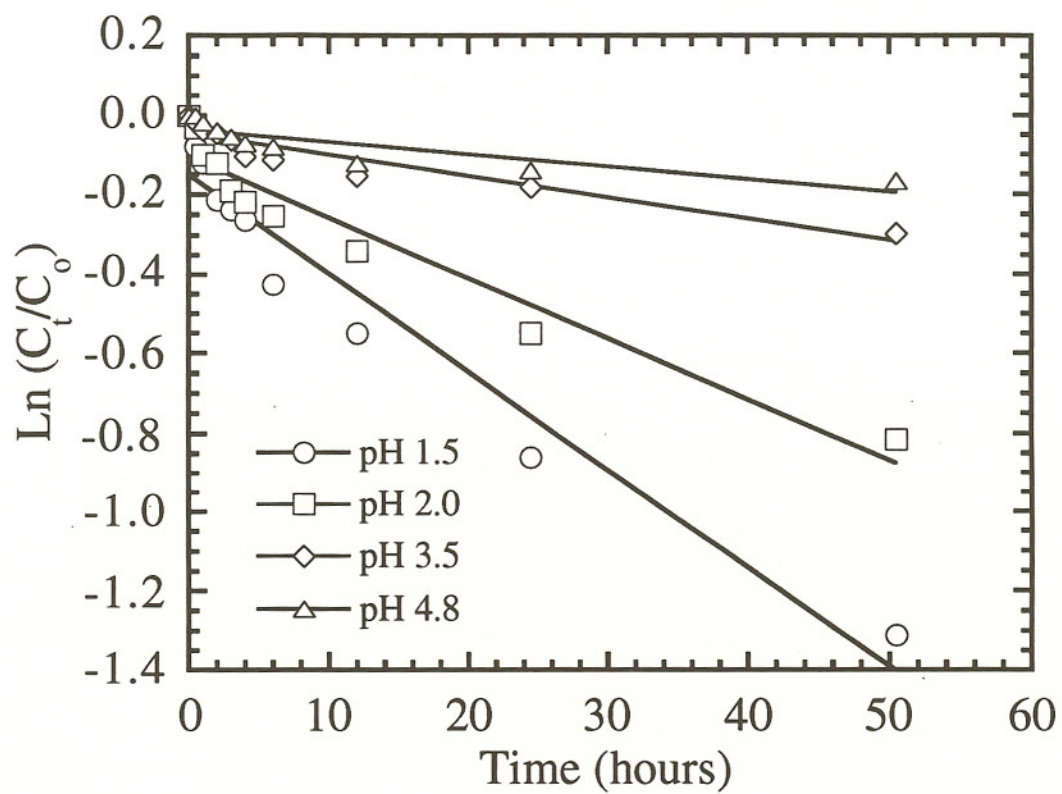


Figure A-5 Reaction rates of Cr(VI) reduction by Hazen gravelly sand for four pH values. Temperature = 25 °C; I = 0.01 M simulated groundwater; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

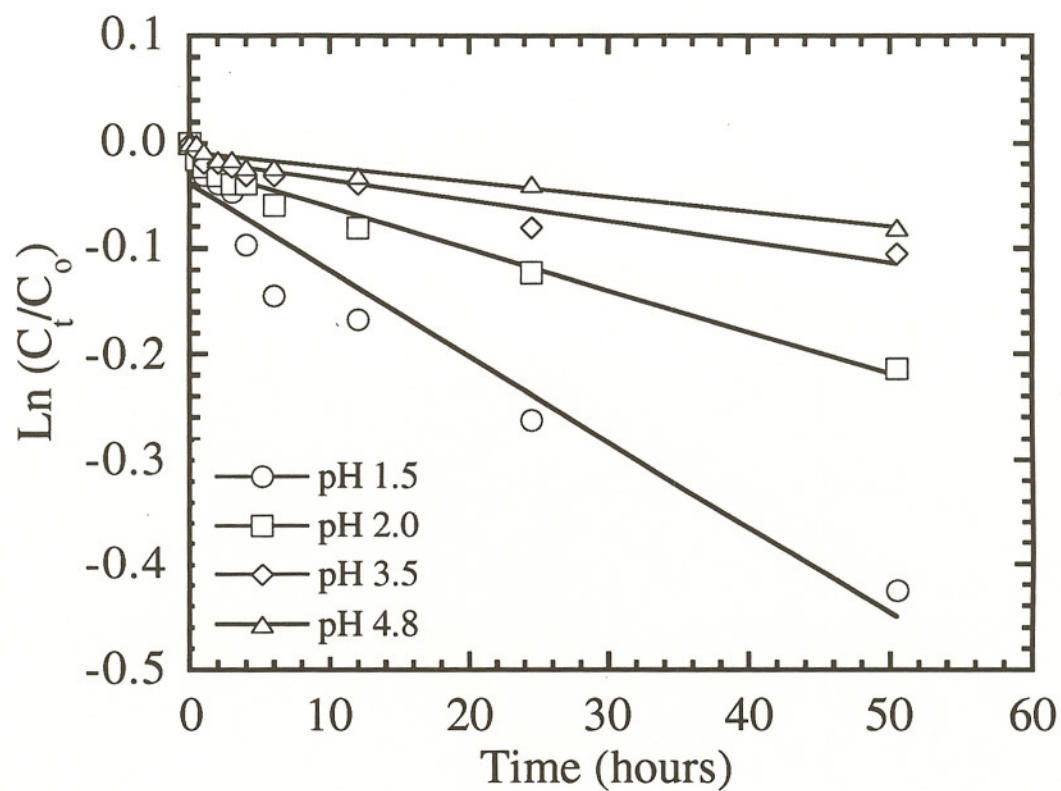


Figure A-6 Reaction rates of Cr(VI) reduction by Freehold sandy (B horizon) for four pH values. Temperature = 25 °C; I = 0.01 M simulated groundwater; Initial Cr(VI) = 5×10^{-5} M; Soil/solution = 3.3 g/0.1 L.

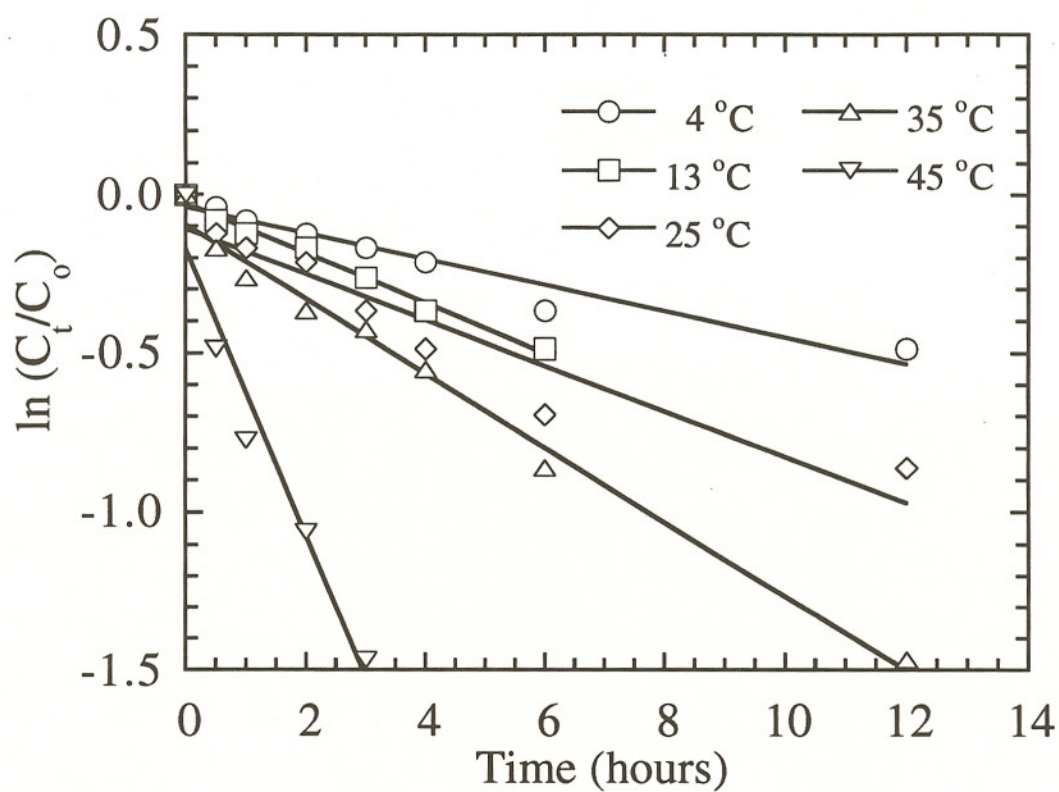


Figure A-7 The rate of Cr(VI) reduction by Sassafra sandy loam at various temperatures. Initial Cr(VI) concentration = 2.6 mg/L; I = 0.01 M simulated groundwater; Soil/solution ratio = 3.3 g/0.1 L; pH = 2.0.

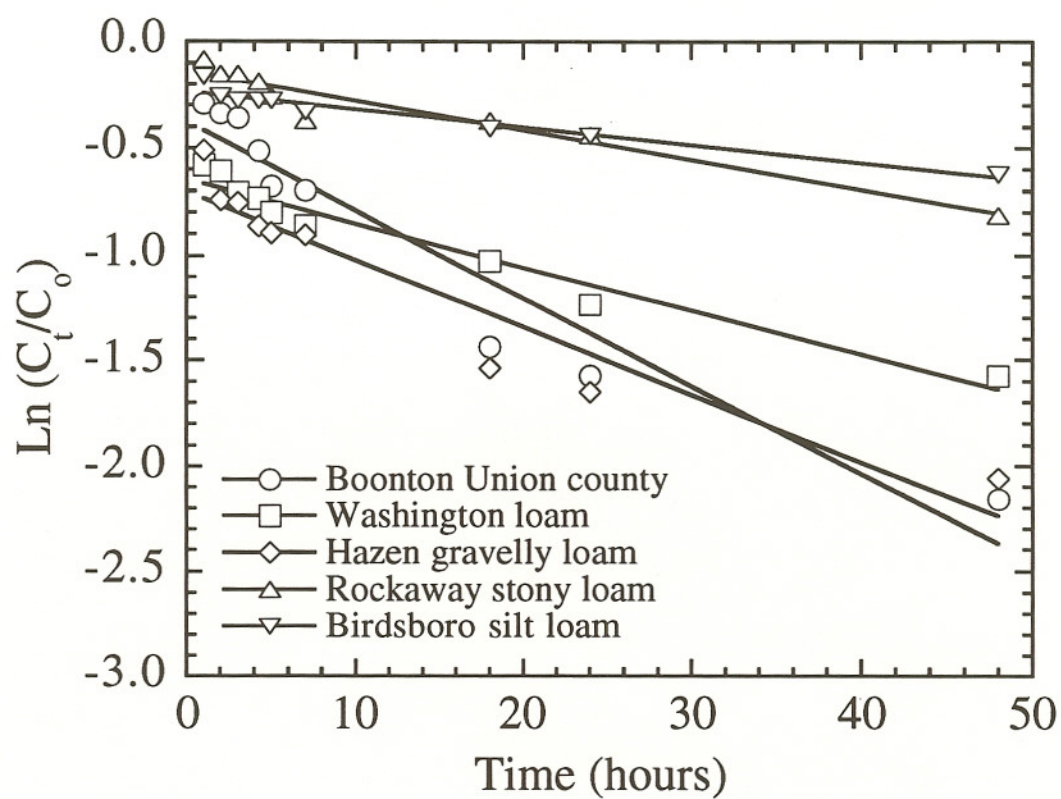


Figure A-8 First order kinetic plots of Cr(III) oxidation by soils. pH = 2.0; temperature = 25 °C; Initial Cr(III) concentration = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; I = 0.1 M NaNO_3 ; Soil/Solution = 5 g/50 mL.

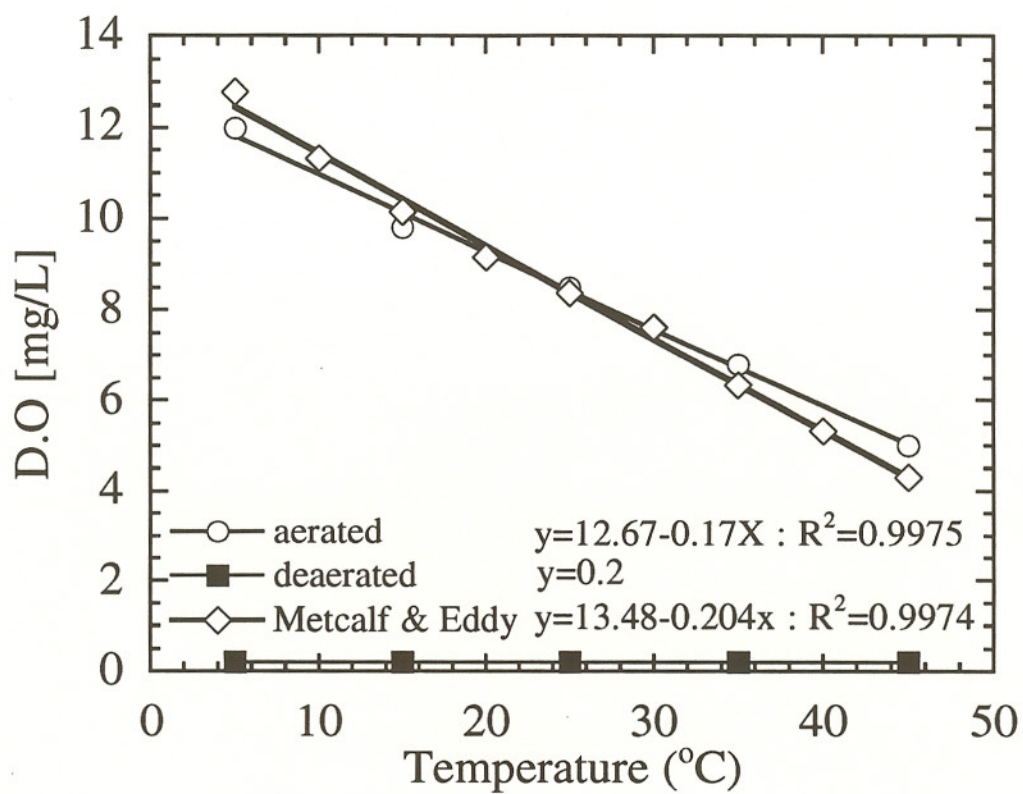


Figure A-9 Concentration of dissolved oxygen in the aerated and deaerated solutions. N₂ gas was sparged for deaeration. Data marked as diamonds were adopted from Metcalf and Eddy (1972). pH = 2.0; I = 0.1 M NaNO₃.

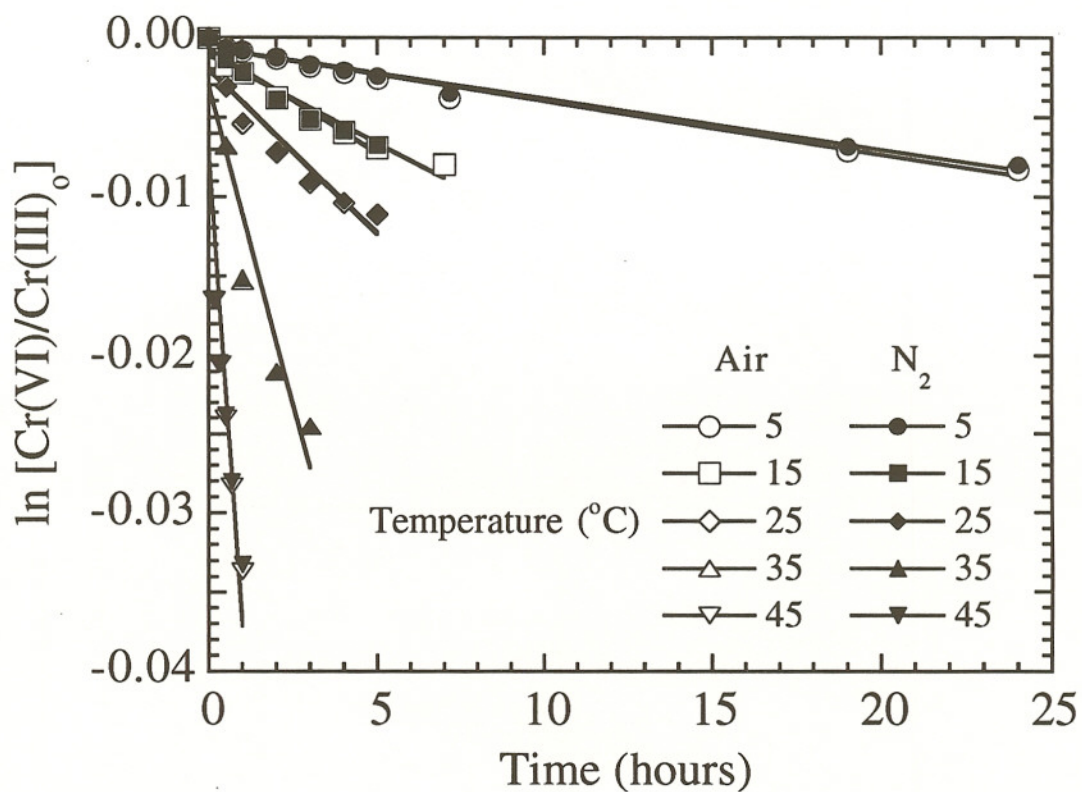


Figure A-10 The kinetics of Cr(VI) formation by Washington loam at various temperatures. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; pH = 2.0; I = 0.1 M NaNO_3 ; Soil/Solution = 50 g/1.5 L.

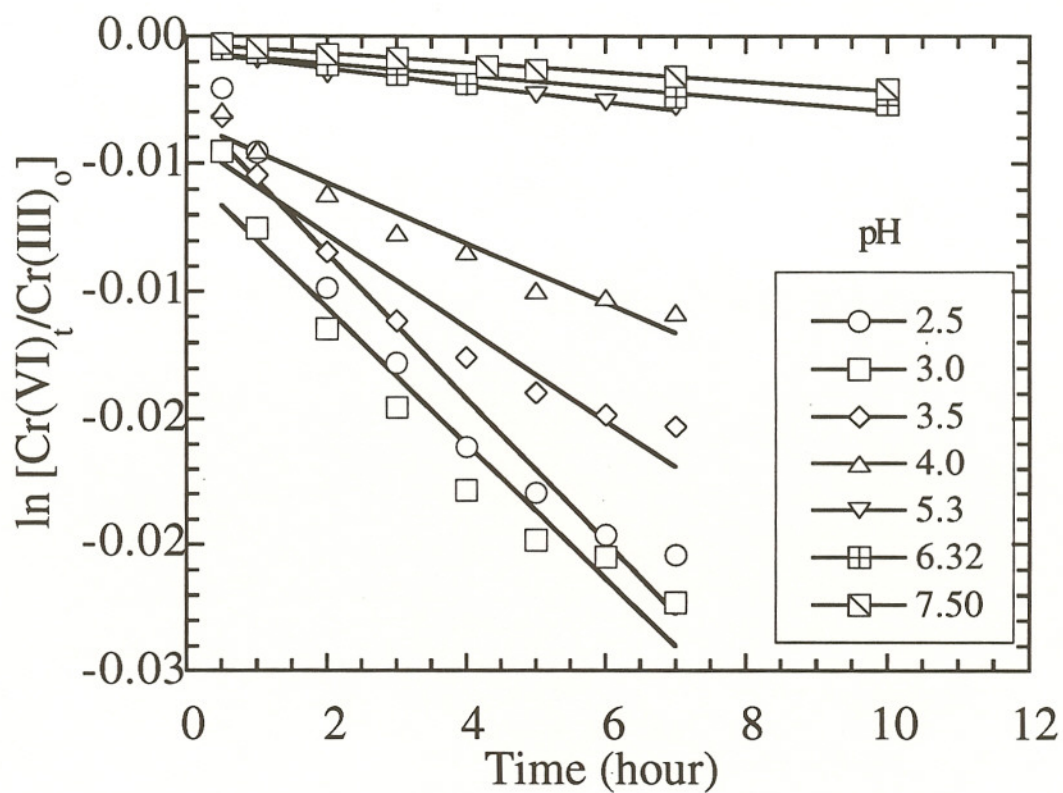


Figure A-11 The kinetics of Cr(VI) production by Washington loam at various pH values. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; I = 0.1 M NaNO_3 ; Temperature = 25 °C; Soil/Solution = 50 g/1.5 L.

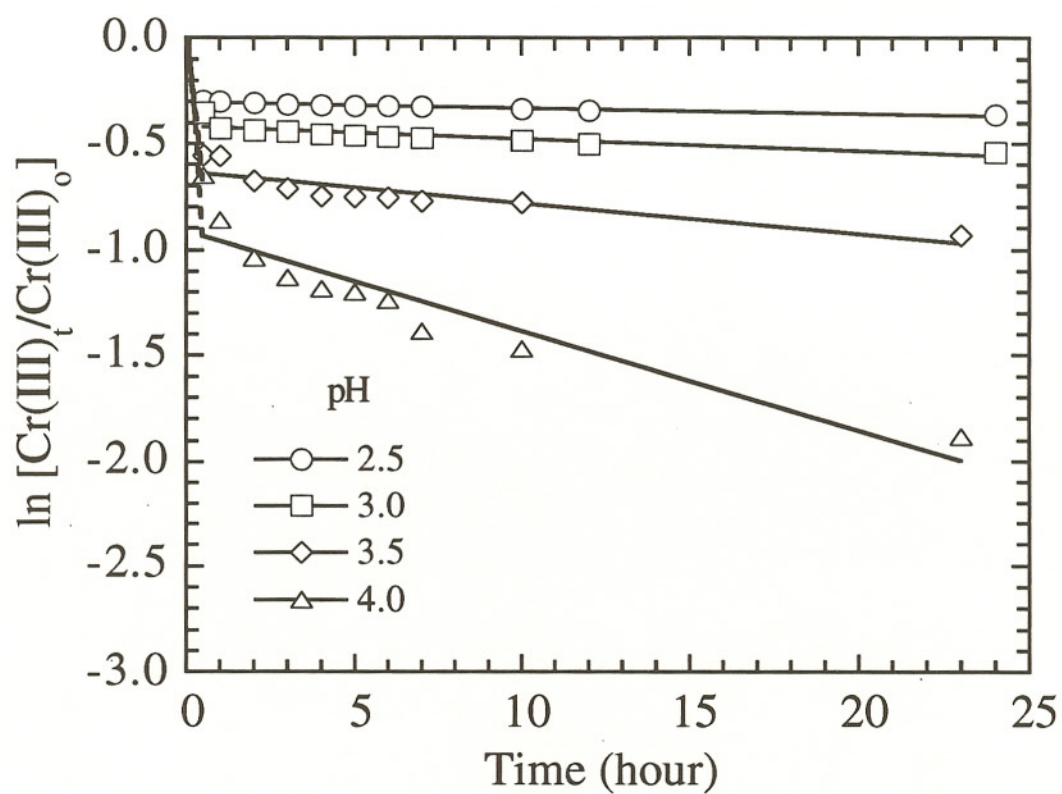


Figure A-12 The kinetics of Cr(III) depletion by Washington loam at various pHs. Initial Cr(III) = 10^{-3} M $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; $I = 0.1$ M NaNO_3 ; Temperature = 25°C ; Soil/Solution = 50 g/1.5 L.

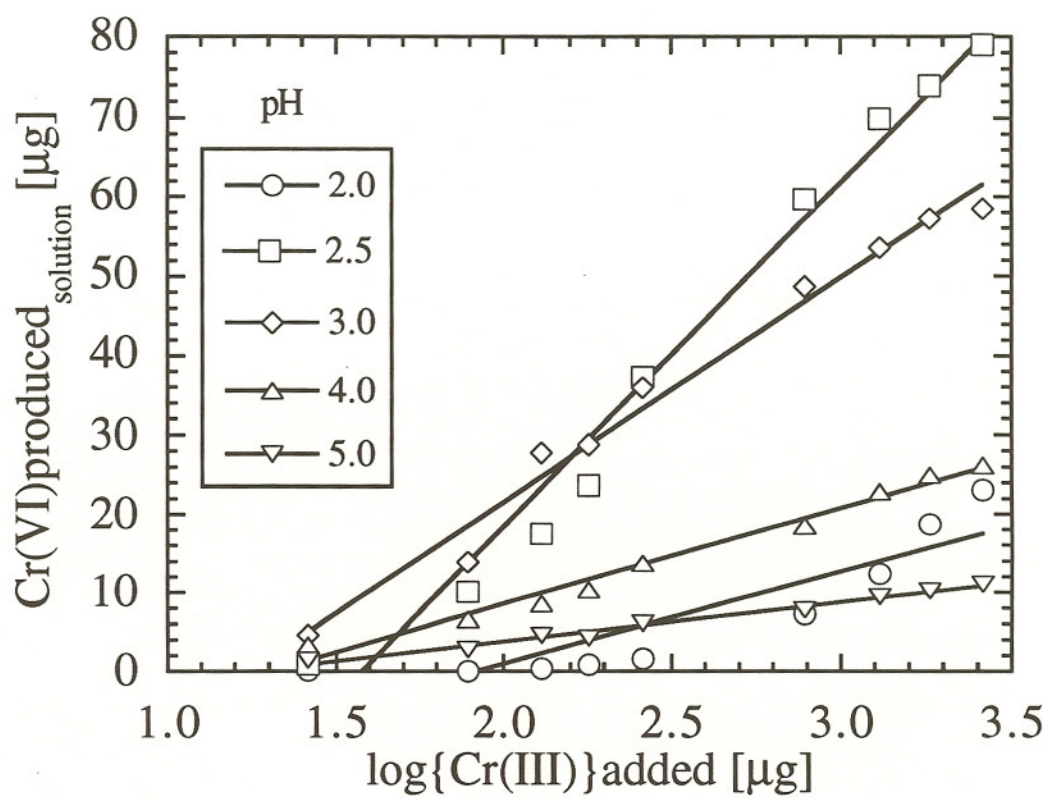


Figure A-13 The relation of Cr(III) oxidized to Cr(III) concentration added at various pH conditions. Soil = Washington loam; Soil/soilution = 2.0 g/50 mL; Temperature = 25 °C; I = 0.1 M NaNO₃.