

Removal of Hexavalent Chromium from a Contaminated Soil by Electroremediation

by

Christian O. Marks

B.Sc.E., University of New Brunswick

Submitted to the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degree of

Master of Science in Mechanical Engineering

at the

Massachusetts Institute of Technology

February 1997

© Massachusetts Institute of Technology 1997. All rights reserved.

Author.....

Department of Mechanical Engineering

January 17, 1997

Certified by.....

Ronald F. Probst

Ford Professor of Engineering

Thesis Supervisor

Accepted by.....

Ain A. Sonin

Chairman, Departmental Committee on Graduate Students

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

APR 16 1997

LIBRARIES

Removal of Hexavalent Chromium from a Contaminated Soil by Electroremediation

by

Christian O. Marks

Submitted to the Department of Mechanical Engineering
on January 17, 1997, in Partial Fulfillment of the
Requirements for the Degree of Master of Science in
Mechanical Engineering

Abstract

Hexavalent chromium is a class A carcinogen by inhalation. High levels of chromium contamination of soils exist in numerous sites as a result of depositing chromite ore processing residue. Electroremediation is well suited for the removal of hexavalent chromium from soils in situ. This thesis studies the removal of hexavalent chromium from a contaminated soil by electromigration. In an experiment at pH 13 using a sodium hydroxide purging solution, a 95 % removal of hexavalent chromium was achieved, although at a high energy cost. Several experiments operated at lower pH and constant current resulted in a lower energy expenditure. Sodium carbonate addition to the soil improved hexavalent chromium removal and reduced energy expenditure further. In one experiment, 85 % of 2300 ppm (moist soil weight) hexavalent chromium was removed at an energy expenditure of less than 1250 kWh/m³ of soil, by the addition of sodium carbonate to the soil. operation at low current densities (below 10 A/m²) with pH controlled between 10 and 12 is key to reducing energy consumption.

Thesis Supervisor: Ronald F. Probst
Title: Ford Professor of Engineering

Acknowledgments

First and foremost, I would like to thank my thesis advisor, Professor Ronald F. Probst, for having given me the opportunity to work on this research. His leadership has been both challenging and motivating. I feel that I have benefited greatly by learning from Professor Probst, a man of the highest scientific intellect and experience. My sincerest gratitude goes out to Dr. R. Edwin Hicks for all his help, guidance and support. I would also like to express my appreciation to the students, staff and faculty of the Fluid Mechanics Laboratory for making it such a pleasant place. In particular, I would like to thank John Dzenitis for introducing me to the experiments and for his patience in explaining to me the basics of electroremediation research. I am also appreciative of Mr. Dick Fenner and the staff of the Pappalardo Laboratory for their assistance in machining parts for my experimental apparatus. I would especially like to thank Mrs. Virginia Brambilla for all the warmth she brought to the Fluid Mechanics Laboratory. Finally, I would like to express my gratitude to my family and friends, here at MIT and elsewhere, for their love and support.

Contents

1. Introduction	11
2. Theory and Background	16
2.1 Electromigration.....	16
2.2 Electroosmosis	17
2.3 Electrophoresis	18
2.4 Electrode Reactions	19
2.5 Diffusion	20
2.6 Electroremediation Process	20
2.7 Soil Properties.....	21
2.8 Chemistry	23
2.8.1 Dissolution and Precipitation.....	23
2.8.2 Chromium.....	25
3. Experiments	28
3.1 Batch Tests	28
3.2 Small Cell Tests	30
3.3 Large Cell Tests	32
4. Results and Discussion	35
4.1 Batch Tests.....	35
4.2 Small Cell Tests	48
4.3 Large Cell Tests	62
5. Conclusions and Future Work	71
6. References	74

List of Figures

Figure 2.1: Electromigration of charged ions in solution subjected to an electric field.	16
Figure 2.2: Electroosmosis of a pore solution in a clay soil subjected to an electric field..	18
Figure 2.8.1: Solubility Diagram of Aluminum.....	25
Figure 2.8.2: Domains of dissolved hexavalent chromium Ions as a function of pH and concentration.	26
Figure 3.2: Small Test Cell.....	30
Figure 3.3: Large Test Cell.....	33
Figure 4.1.1: Batch Test 1a, hexavalent chromium dissolution	38
Figure 4.1.2: Batch Test 1b, hexavalent chromium dissolution	38
Figure 4.1.3: Batch Test 2a, hexavalent chromium dissolution	39
Figure 4.1.4: Batch Test 2b, hexavalent chromium dissolution	39
Figure 4.1.5: Batch Test 3a, hexavalent chromium dissolution	40
Figure 4.1.6: Batch Test 3b, hexavalent chromium dissolution	40
Figure 4.1.7: Batch Test 3a: comparison of aluminum and hexavalent chromium dissolution at pH 10.	41
Figure 4.1.8: Batch Test 3a: comparison of aluminum and hexavalent chromium dissolution at pH 12.	41
Figure 4.1.9: Batch Test 4, hexavalent chromium dissolution	42
Figure 4.1.10: Batch Test 4, aluminum dissolution	42
Figure 4.1.11: Batch Test 4, comparison of aluminum and hexavalent chromium dissolution in water.....	43
Figure 4.1.12: Batch Test 4 , comparison of aluminum and hexavalent chromium dissolution in 0.1 M sodium carbonate solution.	43
Figure 4.1.13: Batch Test 5, hexavalent chromium dissolution with various sodium carbonate additions.....	45
Figure 4.1.14: Batch Test 5, aluminum dissolution with various sodium carbonate additions.	45
Figure 4.1.15: Batch Test 8, hexavalent chromium dissolution with various sodium carbonate additions.....	46
Figure 4.1.16: Batch Test 8, aluminum dissolution with various sodium carbonate additions.	46
Figure 4.1.17: Batch Test 7, hexavalent chromium dissolution at pH 10.5 with various solutions.....	47
Figure 4.1.18: Batch Test 7, percent hexavalent chromium dissolution at pH 10.5 with various solutions.....	47
Figure 4.2.1: Small Cell Test 2, the relationship between temperature and power.	49
Figure 4.2.2: Small Cell Test 2, hexavalent chromium and aluminum removal	50
Figure 4.2.3: Small Cell Tests, conductivity as a function of time.	51
Figure 4.2.4: Small Cell Tests, conductivity as a function of time.	51
Figure 4.2.5: Small Cell Tests, conductivity as a function of time.	52
Figure 4.2.6: Small Cell Tests, hexavalent chromium removal	53
Figure 4.2.7: Small Cell Tests, hexavalent chromium removal	53
Figure 4.2.8: Small Cell Tests, % hexavalent chromium removal.....	54
Figure 4.2.9: Small Cell Tests, % hexavalent chromium removal.....	55
Figure 4.2.10: Small Cell Tests, aluminum removal	55
Figure 4.2.10: Small Cell Tests, aluminum removal	56
Figure 4.2.12: Small Cell Tests, remediation efficiency.	57
Figure 4.2.13: Small Cell Tests, remediation efficiency.	57

Figure 4.2.14: Small Cell Tests, remediation efficiency.....	58
Figure 4.2.15: Small Cell Tests, distribution of hexavalent chromium in the pore solution at the end of electroremediation.	59
Figure 4.2.15: Small Cell Tests, distribution of hexavalent chromium remaining in the soil at the end of electroremediation.	59
Figure 4.2.17: Small Cell Tests, current efficiency.....	60
Figure 4.2.18: Small Cell Tests, current efficiency.....	61
Figure 4.3.1: Large Cell Tests, soil conductivity versus time.....	63
Figure 4.3.2: Large Cell Test 1, pH versus time at various positions.....	63
Figure 4.3.3: Large Cell Test 2, pH versus time at various positions.....	64
Figure 4.3.4: Large Cell Tests, current efficiency.....	64
Figure 4.3.5: Large Cell Tests, voltages applied across the soil and across the electrodes.	65
Figure 4.3.6: Large Cell Test 1, aluminum concentrations in the pore water as a function of time in various positions.	67
Figure 4.3.7: Large Cell Test 1, hexavalent chromium concentrations in the pore water as a function of time, in three positions.....	67
Figure 4.3.8: Large Cell Test 2, aluminum and hexavalent chromium concentrations in the pore water as a function of time, halfway between cathode and anode	68
Figure 4.3.9: Large Cell Tests, hexavalent chromium and aluminum removal	68
Figure 4.3.10: Large Cell Tests, electroremediation efficiency.	70
Figure 4.3.11: Large Cell Tests, concentration of undissolved hexavalent chromium remaining in the soil after remediation in various positions.....	70

List of Tables

Table 2.7 Soil Composition (after drying and sieving).....	22
Table 2.8.1. Common hexavalent chromium ions [Deltcombe et al. 1966].	26
Table 2.8.2: Hexavalent Chromium Precipitates, [CRC 1981]	27
Table 3.1: Dissolution kinetics batch test parameters.....	29
Table 3.2: Small cell electromigration test parameters.....	31
Table 3.3: Large cell electromigration test parameters.....	34
Table 4.1.1: Single sample batch test results (with unsieved moist soil).....	36
Table 4.1.2: Single sample batch test results (with dried and sieved soil)	36
Table 4.1.3: Batch Test 6, composition of extraction solution.	48
Table 5.1: Upper and Lower Bounds on Control Parameters.	73

Nomenclature

c	molar concentration, mol / m ³
D	diffusion coefficient, $D = \nu RT$, m ² / s
E	electric field strength, V / m
F	Faraday's constant, 96487 C / mol
I	current, A
K _{sp}	solubility constant
R	universal gas constant, 8.3143 J / mol K
T	absolute temperature, K
u _d	diffusion velocity, $u = (D/c)\nabla c$, m / s
u _m	electromigration velocity, $u = \nu zFE$, m / s
u _o	electroosmosis velocity, $u = \epsilon\zeta E / \mu$, m / s
v	ion mobility, mol s / kg
z	valence number of ion
ε	permittivity of the solution, 6.93 x 10 ⁻¹⁰ C / V m (for 298 K water)
μ	fluid viscosity, kg / m s
ζ	zeta potential of the soil surface, V

Subscripts

j with reference to species j

Acronyms

COPR	Chromite Ore Processing Residue
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DC	Direct Current
EDTA	Ethylenediaminetetra-acetic Acid
EPA	United States Environmental Protection Agency
ICP	Inductively Coupled Plasma Spectrophotometer
NJDEP	New Jersey Department of Environmental Protection

1. Introduction

With the increasing concern with soils and groundwater contaminated by heavy metals, a variety of new cleanup technologies are being developed. One of the most promising of these technologies is electroremediation.

Contamination of soils and groundwater with heavy metals has resulted from various activities including the following: application of industrial waste, application of fertilizers and pesticides, mining operations, smelting operations, battery production, metal plating and finishing operations, vehicle emissions, and fly ash [Peters and Shem 1995].

Most contaminated sites are condemned and surface runoff is diverted away from the contaminated area to reduce the spreading of contamination [Erdogan 1992]. In some cases the contaminated soil is excavated and transported to special landfill sites where the contaminants can be contained more effectively. This technique has several disadvantages including the need for regulatory approval of transport, high costs, liability issues, and its lack of permanence [Pamukcu 1992]. Techniques that actually detoxify the soil either in situ or ex situ would be more permanent than simple contaminant containment technologies. The most established of these detoxification techniques is excavation followed by incineration (for organic contaminants) or soil washing (for heavy metals) [Dzenitis 1996]. Since significant costs and risks of spreading contamination are associated with excavation, considerable efforts are being made to develop other effective techniques for in situ remediation of soils.

The in situ remediation techniques include the following: solidification or stabilization, bioremediation, vitrification, volatilization, pump and treat, and electroremediation [Arman 1992]. Stabilization is achieved by mixing a stabilizing agent into the soil with an auger. Stabilizing agents include portland cement, lime, fly ash, calcium chloride, bentonite, sodium silicate, and polymers. This technique is restricted to solid wastes and requires long term monitoring and maintenance since the solid is not completely impermeable and may break down. It is however sufficiently permanent to be a widely practiced technique. Solidification is similar to stabilization. It renders the contaminant into an immobile solid by altering the soil chemical conditions. In this technique precautions must be taken to prevent chemical conditions from changing in a way that the solidification process could reverse. Bioremediation involves activating microorganisms in the soil to destroy hazardous chemicals. This technique is effective for a number of organic contaminants.

In situ, it requires low contaminant concentrations and a porous soil. Vitrification occurs by heating the soil to its melting temperature with an electric current. After subsequent cooling the soil becomes a glass-like solid encapsulating any contaminants. Vitrification is very costly and is therefore limited to only the most toxic contaminants such as radioactive wastes. Volatilization of contaminants is achieved by injecting steam into the soil. This technique can be effective in porous soils, but may only remediate some relatively volatile organic compounds. There are a number of pump and treat technologies in practice, and they all involve pumping water through the soil by means of a system of wells to remove dissolved or liquid contaminants permanently. Pump and treat may spread some contamination outside the treatment zone if wells are not placed appropriately, which requires a precise knowledge of the sites hydrological conditions. It also requires a uniform permeability to be effective.

Electroremediation functions by moving the contaminants through the soil with an electric field. Placing electrodes into the ground establishes an electric field. Two phenomena move the contaminants. The first is electroosmosis where the surface charge of soil particles induces a charge in the pore water which subsequently flows in the direction of the electric field removing dissolved contaminants by the resulting drag force on them. Electroosmosis is most effective in low porosity soils with relatively large surface charge such as clays. The second is electromigration where charged particles dissolved in the pore water migrate towards the electrode of opposite charge. Electromigration is most effective in removing easily solubilized ionic contaminants including many metals.

Historically, electroremediation and electroosmosis, in particular, was first applied to the dewatering of soil and sludge [Casagrande 1949]. Electromigration has also been applied in geochemical exploration [Shmakin 1985], [Smith 1993], [Talapatra 1986].

Electroremediation offers several advantages over other methods in decontaminating soils. It is able to remediate soils of low porosity unlike vaporization or pump and treat. The electric field controls the movement of contaminants, preventing dispersion of contaminants outside the area of treatment. The contaminated soil solution is easily extracted at the point of collection. This solution is also relatively concentrated in comparison with pump and treat remediation, reducing the volume needed to be treated. The remediation of the soil is permanent. Control of soil pH and dissolving the contaminant present the greatest difficulties of the electroremediation process. In many cases, electroremediation may be the most cost effective method for soil cleanup depending on the particular contaminant concentration and the soil chemistry. A soil contaminated with hexavalent

chromium is ideally suited for electroremediation, since hexavalent chromium dissolves easily at high pH where other metals tend to precipitate.

Chromium is a major contaminant in numerous sites throughout the United States of America, including a number of Superfund sites. Hexavalent chromium is ranked 18th on the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Priority List of Hazardous Substances. Sources of chromium waste include metal-plating, steel fabrication, paint and pigment production, wood treatment, leather tanning, and chromium mining and milling [McIntosh 1995]. Chromium contamination is of particular concern in Hudson County, New Jersey, which was a major processing area of chromium for the United States until about 1965. More than two million tons of alkaline chromate bearing slag were disposed of in the state of New Jersey. This slag, known as chromite ore processing residue (COPR), was used as general fill for voids and to raise low lying areas. Frequently the bright yellow chromate forms a crust on soil surfaces [James 1996]. Chromium contamination of soil sites from chromium production ranges from 500 to 70,000 ppm [Peters and Shem 1995].

Chromium in soils occurs in several oxidation states. The hexavalent form is a class A human carcinogen by inhalation and an acute irritant to living cells. Most trivalent compounds of chromium are very insoluble and non-toxic. Furthermore, the human body requires some trivalent chromium as a nutrient for activating insulin [James 1996].

The Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response is considering screening levels for hexavalent chromium of 140 mg/kg in soil and 19 mg/kg in groundwater. An electromigration method for decontamination can reduce the hexavalent chromium concentration to these levels. The New Jersey department of Environmental Protection (NJDEP) proposes a stricter standard of 15 mg/kg in soil. This lower level of hexavalent chromium contamination can also be achieved by an electroremediation method if the chromium removal stage of remediation is followed by a second stage, in which ferrous iron is moved into the soil by electromigration for the reduction of the remaining hexavalent chromium to the less hazardous trivalent form.

A number of authors have studied the removal of heavy metals from soil by electromigration including the following: Peters and Shem [1995], Pamukcu and Wittle [1992], McIntosh and Huang [1995], Wong [1995], Acar and Alshawabkeh [1993], Hicks and Tondorf [1994].

In the past few years the understanding of the electroremediation processes has improved dramatically and significant improvements have resulted in laboratory experiments. The development of numerical models has aided considerably in advancing this research [Jacobs et al. 1994], [Probstein and Hicks 1993], [Shapiro and Probstein 1993], [Shapiro et al. 1989], [Dzenitis 1996]. The development of this technology is now at a stage where applying this understanding to successful field testing could become a focus. Some limited field testing has been done with mixed success by the Geokinetics company in the Netherlands [Lageman 1993]. A more detailed overview of the status of electroremediation technology is given by Chambers [1991], and Acar et al. [1995].

The primary purpose of this thesis is to show how an electromigration method can remove hexavalent chromium from a soil in laboratory experiments. The soils to be studied come from a COPR contaminated site in New Jersey and contain up to 6000 ppm of hexavalent chromium and considerably more trivalent chromium. The first goal is to remove a large portion of hexavalent chromium from the soil. The second goal is to achieve this removal at a low energy expenditure. In a field test, which is planned for the spring of 1997, the removal of chromate by electromigration will be followed by a second stage in which ferrous iron would be moved into the soil by electromigration to reduce the remaining chromium from the hexavalent to the trivalent form in an oxidation-reduction reaction (redox). This thesis focuses on the first stage of remediation in which chromate is removed from the soil. Taylor [1997] discusses the redox stage of the electroremediation process for a COPR contaminated site.

In previous experimental work on electroremediation it was discovered that an accurate understanding of the relevant chemistry and particularly the soil chemistry is the key challenge to improving the effectiveness and efficiency of this technology [Dzenitis 1996], [Shapiro et al. 1989]. Therefore, experimental testing will be especially concerned with measurement and analysis of the relevant chemical parameters. Batch tests were performed to determine soil chemistry and to test the effects of varying chemical conditions such as pH. One-dimensional electromigration tests were performed in a small cylindrical shaped cell to test chromate removal under varying chemical and physical conditions. Finally, more elaborate electromigration tests were carried out in a larger box shaped cell that simulates field conditions more accurately.

Chapter 2 discusses the theory behind the transport phenomena and the chemistry relevant to the electroremediation of a soil contaminated with hexavalent chromium. Chapter 3 summarizes the procedures and describes the apparatus for the batch tests and electromigration experiments. Chapter 4 presents the results of these experiments and discusses them in relation to the goals

outlined for this thesis. Chapter 5 summarizes the conclusions gained from the experiments and identifies areas for potential improvement.

2. Theory

The purpose of this chapter is to give a brief description of the theory of each of the phenomena relevant to electroremediation and remediation of chromium contaminated soils by electromigration. An electric field applied to a soil induces the following phenomena in the pore solution: electromigration, electroosmosis, electrophoresis, and chemical reactions at the electrodes. More details on the theory of electroremediation are given by the following authors: Acar and Alshawabkeh [1993], Dzenitis [1996], Jacobs et al. [1994], Probstein and Hicks [1993], Probstein [1994], Shapiro and Probstein [1993].

2.1 Electromigration

Electromigration is the transport of a charged ion in solution under the action of an electric field. In this migration, electroneutrality must be satisfied at every point in the system as expressed in equation 1,

$$\sum_j^n z_j c_j = 0 \quad (1)$$

where z_j is the valence number of ion j , c_j is the concentration of ion j , and n is the total number of ion species. Therefore, for every positive ion that migrates toward the cathode there must be a negative ion moving in the opposite direction or another positive ion replacing it, and vice versa for negative ions, as illustrated in figure 2.1. Furthermore, this neutrality principle requires that in electromigration either positive ions must be generated or negative ions destroyed at the anode and vice versa at the cathode through oxidation-reduction reactions.



Figure 2.1: Electromigration of charged ions in solution subjected to an electric field.

The electromigration velocity (u) is proportional to the electric field strength (E) and the ionic charge number of the ion (z) by the following relation:

$$u = vzFE \quad (2)$$

where v is the mobility of the ion and F is Faraday's constant. Ionic migration is on the order of 1-80 cm/day under an electric field of 1 V/cm [Acar et al. 1995]. Migration is the dominant transport mechanism in electroremediation and is considerably faster than electroosmosis. The respective ionic mobilities of hydrogen and hydroxide are about four and two times as high as for other common ionic species. These ions have relatively high values because of their rapid association and dissociation with water molecules [Acar and Alshawabkeh 1993]. The distribution of current among species in the pore solution can be described by the following equation:

$$I_j = \frac{z_j v_j c_j}{\sum_{i=1}^n z_i v_i c_i} I \quad (3)$$

where I_j refers to the current contributed by ion number j , z_j is the valence number of ion j , v_j is its effective mobility and c_j is its concentration. I is the total current passing through the solution and n is the number of ionic species present in the solution. The effective ion mobility is affected by soil porosity and increases with pore size. The ratio of the current (I_j) carried by the contaminant ion to the total current (I) defines the current efficiency. Based on these relations, it becomes clear that in order to have a high current efficiency during removal of a given contaminant species, it must have a high concentration in the pore solution compared to other species. The polarity and magnitude of charge (z) changes for metals as a function of pH as will be discussed later. As a result, pH changes can arrest migration of certain species and even reverse the direction of migration in some cases.

2.2 Electroosmosis

In soils with a large surface charge, such as clays, an opposite charge will be induced in the pore water adjacent to the surface of the soil particle. This thin layer of charged fluid called the diffuse double layer will begin to flow if an electric field is imposed on the soil. Since clays typically have a negative surface charge, the double layer obtains a positive charge and flows toward the cathode. The flow of the double layer causes the rest of the pore water to flow because of the drag force it exerts. In order for this flow to be significant enough for the transport of contaminants, the pore size of the soil must be micrometer sized or smaller. Electroosmosis is illustrated in figure 2.2.

In electroosmosis, the liquid velocity is given by the Helmholtz-Smoluchowski relation

$$u = \epsilon \zeta E / \mu \quad (4)$$

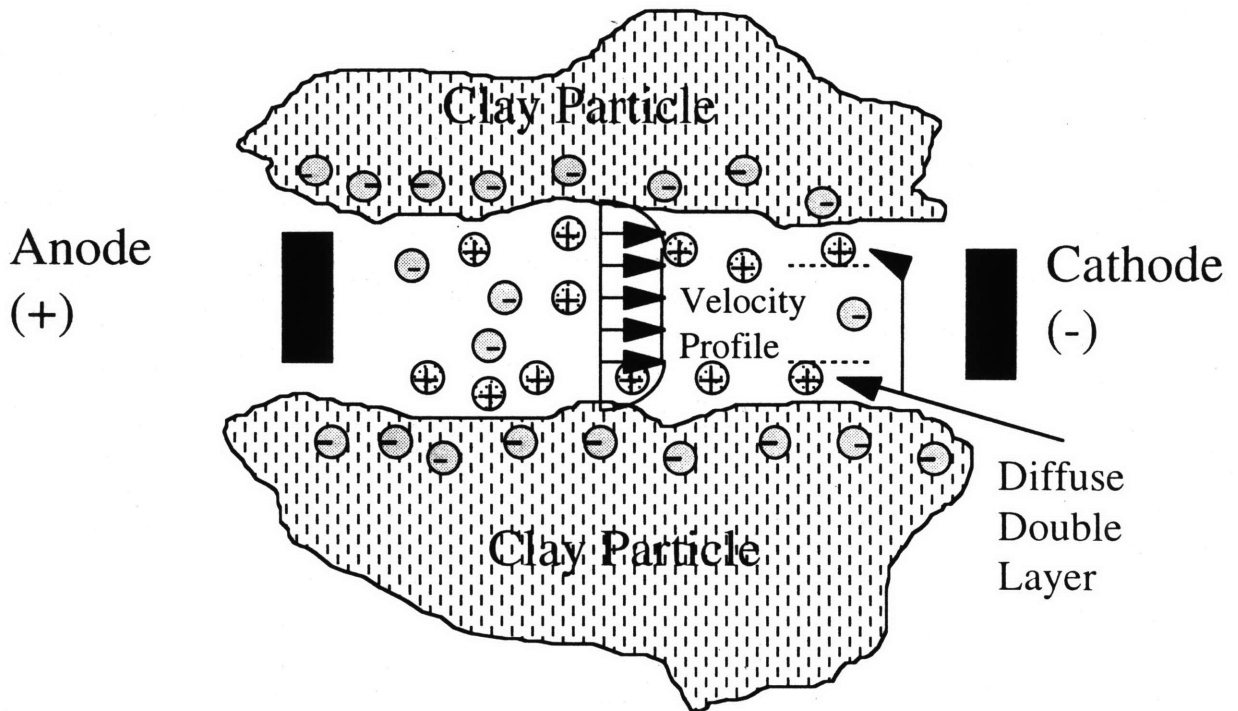


Figure 2.2: Electroosmosis of a pore solution in a clay soil subjected to an electric field.

where ϵ is the permittivity of the solution, ζ is the zeta potential of the soil, E is the applied electric field strength, and μ is the fluid viscosity,.

Since the soil from the New Jersey site is not a clay, it is expected that pore size will be too large and zeta potential too low for electroosmosis to be significant in the investigation. Several investigators found that electroosmosis is best suited for remediating saturated silts or clays contaminated with relatively soluble organic compounds such as benzene, toluene, xylene, phenols, and chlorinated solvents.

2.3 Electrophoresis

Electrophoresis occurs when charged colloidal particles migrate toward an oppositely charged electrode under an applied electric field. Electrophoresis generally does not occur in soils because the particles are too large to have sufficient mobility, consequently it is not included in studies of electroremediation.

2.4 Electrode Reactions

The current flowing between the electrodes will cause electrolysis of water to occur on the electrode surfaces. Hydrogen ions are produced at the anode and hydroxyl ions at the cathode by the following reactions:



These reactions will affect pH directly. If a pH change is not desired during the remediation the electrode must be rinsed with an appropriate solution to neutralize the hydrogen or hydroxyl ions generated. Using a buffer solution in the electrode well also reduces pH changes. Since the amount of ions produced is proportional to the current, a reduction in the current will also slow pH changes. If pH is allowed to change freely it may fall below 2 at the anode and rise above 12 at the cathode [Acar and Alshwabkeh 1993]. Furthermore, an acid and base front will migrate into the soil from the anode and the cathode respectively. These fronts will eventually meet and a sharp discontinuity in the pH will arise at that location. At this discontinuity, conductivity will be very low and precipitation may occur, arresting migration [Probstein and Hicks 1993]. Acar and Alshwabkeh [1993] observed the clogging of soil pores by precipitation of calcium carbonate and calcium hydroxide, preventing transport of lead. Furthermore, pH changes could dramatically affect dissolution and precipitation of various complexes present in the soil, as will be discussed later.

There are a number of other possible reactions that may occur at the electrodes such as the precipitation of metal hydroxides, illustrated in equation 7 for a divalent metal "M". In general these reactions are undesirable since they could foul the electrode surface. They should be avoided as much as possible by conditioning the electrode rinse solution. Redox reactions may also attack the electrodes and therefore electrode materials should be chosen carefully. Carbon is an inexpensive electrode material with good stability, except at high currents. Some special titanium alloys and platinum are still better electrode materials but are very costly.



2.5 Diffusion

The velocity of ion transport by diffusion at a particular location is described by the following equation:

$$u = (D/c)\nabla c \quad (8)$$

where c is the molar concentration, and D is the diffusion coefficient which is defined by the Nernst-Einstein relation

$$D = vRT \quad (9)$$

where v is the ion mobility, R is the gas constant and T is the temperature. Mass flux by diffusion is usually at least one order of magnitude less than that of migration [Acar et al. 1995]. Since the diffusion rate is proportional to the concentration gradient it may increase as steeper gradients are created by electromigration, thus slowing the electromigration rate.

2.6 Electroremediation Process

The first step in an electroremediation treatment must be an investigation of the soil and the site. Electromigration treatment can be effective if the soil has a medium or high porosity and is contaminated with a heavy metal or several chemically similar heavy metals of relatively high concentration. Electroosmosis treatment can be effective, if the soil has very low porosity and high zeta potential such as a clay.

An electromigration treatment can only be successful if the contaminant can be dissolved easily, because only dissolved ions can be moved out of the soil. The solubility of metals varies greatly with pH, and the appropriate control of pH may be sufficient in dissolving the contaminant. In some cases, the pH may fall into the required range as a result of electrolysis at the electrodes. In other cases, it may require the addition of a chemical such as sodium hydroxide or acetic acid. It is very important that the pH does not vary excessively throughout the system, because it could lead to the dissolution of an element in one place and its reprecipitation in another place of different pH, thereby possibly clogging soil pores and thus seriously hindering contaminant transport. Another method for dissolving metal contaminants is by the use of chelating agents such as EDTA. Any chemical additives should be non-toxic. A key factor in choosing a dissolution enhancement method is that it should dissolve much more of the contaminant metal than other non-toxic metals that may be present in the soil, in order to achieve a high current efficiency during migration. The cost of these enhancing agents can be a significant factor in the overall remediation cost. A high

degree of saturation of the soil with water aids in dissolving contaminants as well as improving ion mobility during migration.

The electric field is established with a DC power source connected to electrodes placed in the soil up to several meters apart. If the electrode is rinsed it must be placed inside a well. The wells are typically surrounded by a membrane or geotextile to prevent large hydraulically driven flows through the soil or erosion of the well walls. Electrodes must be spaced close enough that the migration time of the contaminant to the electrode is significantly faster than the time of it potentially reaching the groundwater by gravity driven flows or diffusion. The migration rate is proportional to the voltage gradient. Therefore, to achieve an efficient use of power, voltage drops across the electrode wells should be minimized by an electrode well fluid of sufficient ionic strength. Higher current densities increase energy expenditure without improving the contaminant removal efficiency [Acar et al. 1995], because the energy expenditure is proportional to the square of the current while the contaminant flux is directly proportional to the current and the current efficiency is not proportional to current as stated in equation 3.

The final step in the electroremediation process is the treatment of the contaminant waste solution pumped out at the electrode well. There are a variety of standard treatment methods including adsorption, precipitation, electrodeposition, and ion exchange. Ouki and Neufeld [1989] studied the interactions of chromium with activated carbon. A practical method for treatment of hexavalent chromium is its reduction to the trivalent form by ferrous iron and its subsequent precipitation.

2.7 Soil Properties

Positively charged ions such as those of many heavy metals are strongly sorbed to negatively charged surfaces. The sorption is strongest in soil particles with a particularly high negative charge such as certain clays which are the same soils that are best suited for electroosmosis, as mentioned earlier. The amount of sorption varies widely among cations but is most influenced by size and valence. In electroremediation, an acid front that migrates through the soil from the anode typically desorbs metal species. If the heavy metal forms a negatively charged complex as hexavalent chromium does, adsorption is less prevalent, since soil particles tend to have a negative surface charge. Aluminum oxides, iron and some other soil colloids have positively charged surfaces and do adsorb chromate ions in a manner similar to adsorbing sulfate and phosphate ions. It has been shown experimentally that large phosphate concentrations can

greatly reduce chromate adsorption [Bartlett and James 1988]. Hsieh et al. [1989], as well as McIntosh and Huang [1995] discuss the sorption of trivalent and hexavalent chromium onto clays.

Soils have a natural pH buffering capacity that varies among soils. A large buffering capacity can be a serious obstacle if remediation requires a low pH to desorb the contaminants. In other cases a large buffering capacity can be beneficial if pH changes and especially sharp pH discontinuities are undesirable.

The structure of soil particles tends to break down at very low or high pH, resulting in a decrease in soil porosity. This decrease in porosity adversely affects electromigration by reducing ion mobility. Above pH 12 much of the breakdown of soil particles would be due to the dissolution of alumina which are an important piece of the ring structure of clay particles. The heating and flow of electrical current in electroremediation may further contribute to the breakdown of soil particles.

The particles in a soil are typically very irregular and vary greatly in size, which results in a wide range in the pore size between soil particles. A standard “pump and treat” or “soil washing” remediation technique would only wash out the contaminants from the larger pores, whereas an electromigration technique might also remove contaminants from the smallest crevices and pores, because the electric field acts directly on the contaminant ion. A more serious factor in soil heterogeneity is that contaminants are very non-uniformly distributed in it. In the case of COPR contamination, the chromate frequently forms small clumps dispersed throughout the soil, mostly in the top layers. Particle size affects chromate dissolution rate [Hsieh et al. 1990], since dissolution rate is proportional to surface area. In addition to the chromate clumps (typically up to

Table 2.7: A COPR Soil Composition (after drying and sieving)

Species	Concentration (ppm)
Aluminum	22,500
Calcium	112,500
Total Chromium	15,000
Hexavalent Chromium	5040
Iron	95,000
Lead	800
Magnesium	25,000
Sodium	100

1/4 inch in diameter), the COPR soils investigated contained quickly dissolving chromate dust and chromium layers precipitated on the surfaces of rocks. This heterogeneity presents a serious problem in conducting small scale laboratory experiments with a good repeatability.

This thesis is concerned with soils contaminated with chromite ore processing residue (COPR). The major metal species in this soil are chromium (trivalent and hexavalent), iron, aluminum, calcium and magnesium. The exact findings of a laboratory analysis of a characteristic batch of soil is given in table 2.7. The hexavalent chromium in the soils used in the experiments ranged from 2000 to 6000 ppm. As a result of the chromite ore processing method, the residue has a high pH. The soils typically have a pH near 10 and a relatively high porosity.

2.8 Chemistry

The chemistry of the system especially pH strongly affects the efficiency and effectiveness of the remediation process. The system pH is typically chosen based on the solubility of the contaminant metal. Heavy metals usually form a negatively charged species at high pH and a positively charged species at low pH. Most metals such as cadmium, lead, iron, and trivalent chromium are more soluble at low pH and form positively charged species. Some metals such as hexavalent chromium and aluminum are most soluble at high pH and form negatively charged species. If several metals are to be remediated simultaneously, then it is very important that they dissolve under the same chemical conditions. Similarly, it will be impossible to avoid removing non-toxic metals that behave like the toxic metal being removed. For example, efforts to remove hexavalent chromium will also remove aluminum, because they dissolve in the same pH range. The removal of non-toxic metals such as aluminum would add to the cost of the remediation, especially if chelating agents are to be used. Therefore, the concentration of these non-toxic metals in the contaminated soil may determine the feasibility of a proposed electroremediation.

2.8.1 Dissolution and Precipitation

A detailed model of dissolution kinetics is presented by Hering [1995]. Cusseler et al. [1983] idealized the dissolution process into three steps. In the first step, the acid or other reagents diffuse to the surface of the solid; in the second, they react with the surface; in the third the dissolved solid diffuses away from the surface. The first and third step are physical processes, and

so are affected by physical factors like stirring and temperature. The second step is a chemical process, and so is influenced by changes in reaction stoichiometry. The goal in electroremediation is to maximize contaminant dissolution, while minimizing dissolution of non-toxic complexes.

In electroremediation the only physical factor improving dissolution that may be altered is the temperature of the soil which increases due to ohmic heating. Temperatures of up to 50 °C have been reported in field tests. This temperature is high enough to significantly improve dissolution kinetics.

The dissolution of calcium chromate may be expressed stoichiometrically as follows:



$$K_{sp} = [CrO_4^{2-}][Ca^{2+}] \quad (11)$$

where K_{sp} is the solubility constant and $[CrO_4^{2-}]$ and $[Ca^{2+}]$ are the dissolved chromate and calcium concentrations, respectively.

The reaction stoichiometry may be altered to favor dissolution in variety of ways. Decreasing the ratio of soil mass to water volume decreases the dissolved contaminant concentration. Therefore, saturating the soil with water will be helpful. If the electromigration rate removing the dissolved species out of the soil is increased, the dissolution rate should also increase. A change in redox potential could result in a change in stoichiometry by converting the species to another oxidation state. An example of this mechanism would be the reduction of hexavalent chromium to trivalent chromium by ferrous iron. The reduction in the hexavalent chromium concentration would encourage the dissolution of more hexavalent chromium. In the experiments conducted for this thesis sodium carbonate was added to the solution to improve the solubility of calcium chromate. In this case, the carbonate would precipitate out dissolved calcium, which would result in more calcium chromate dissolving.

Concentration and especially pH govern dissolution and precipitation of metals. The solubility of various species as a function of pH and its concentration can be shown in a solubility diagram. The solubility diagram for aluminum is given in figure 2.8.1. The dissolved ions of aluminum are colorless and its precipitates are white. A solubility diagram plots lines of concentrations versus pH above which precipitates begin to form. The optimum pH for the electroremediation of hexavalent chromium is between 10 and 12. This range is well above the range in which iron and lead are soluble, and below the range of high aluminum dissolution, while still within a range of high chromate dissolution. A variety of techniques using acids and bases at

the electrodes have been tried for conditioning the soil pH to the desired range [Weeks and Pamukcu 1995], [Ramsey and Reed 1995], [Acar et al. 1995], [Acar and Alshawabkeh 1993], [Hicks and Tondorf 1994], [Probstein and Hicks 1993]. In many experiments described in this thesis, sodium carbonate, a good pH buffer, is applied for pH conditioning.

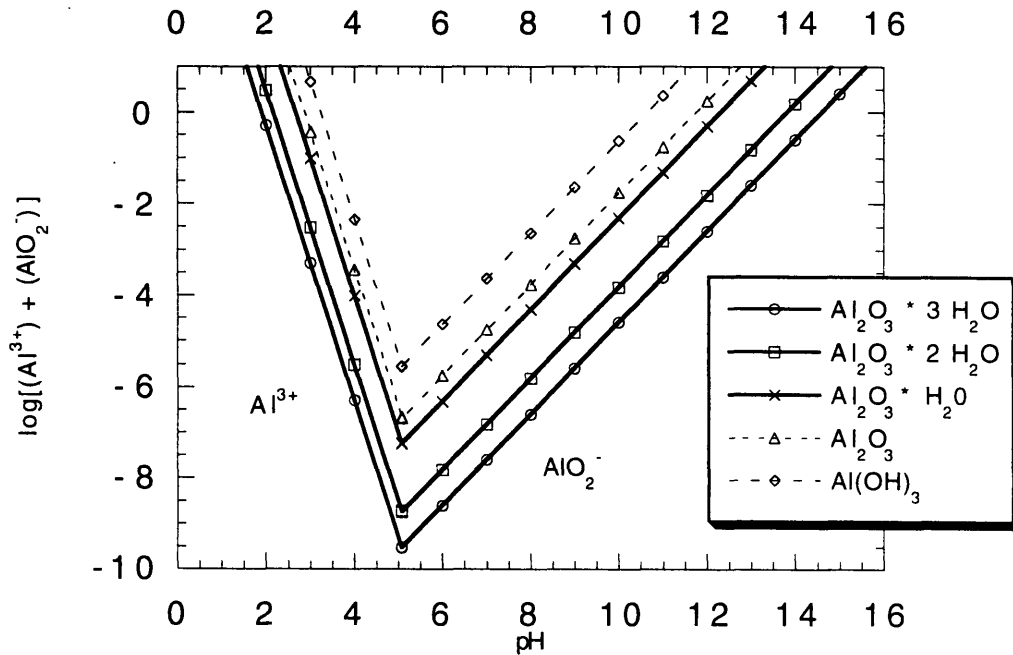


Figure 2.8.1: Solubility Diagram of Aluminum

There is a group of chemicals, called chelating agents, that have a very strong affinity for metals and will form soluble charged complexes with them. Chelating agents such as EDTA have been employed to achieve good dissolution rates for electroremediation even at pH's where heavy metals are normally very sparingly soluble [Peters and Shem 1995], [Wong 1996].

2.8.2 Chromium

Chromite ore is in the trivalent form of chromium: $FeCr_2O_4$. This complex is very insoluble and in order to process the chromium ore it is converted to the hexavalent form, which is much more soluble. This conversion is achieved by a roasting process in which Na_2CO_3 and/or $CaCO_3$ are added to the ore, which results in the high pH of the residue. The hexavalent form of chromium is a strong oxidizer, which generally results in its reduction in most field conditions. Most of the

chromium in the COPR soil is in the trivalent form, but because of the high chromium and carbonate concentration a large fraction remains in the hexavalent form.

Figure 2.8.2 shows the domains of the dissolved forms of hexavalent chromium, and table 2.8.1 contains their colors and names.

Table 2.8.1. Common hexavalent chromium ions [Deltcombe et al. 1966].

Substance Name	Chemical Formula	Color
Chromic acid	H_2CrO_4	orange-red
Acid chromate ion	$HCrO_4^-$	orange
Dichromate ion	$Cr_2O_7^{2-}$	orange
Chromate ion	CrO_4^{2-}	yellow

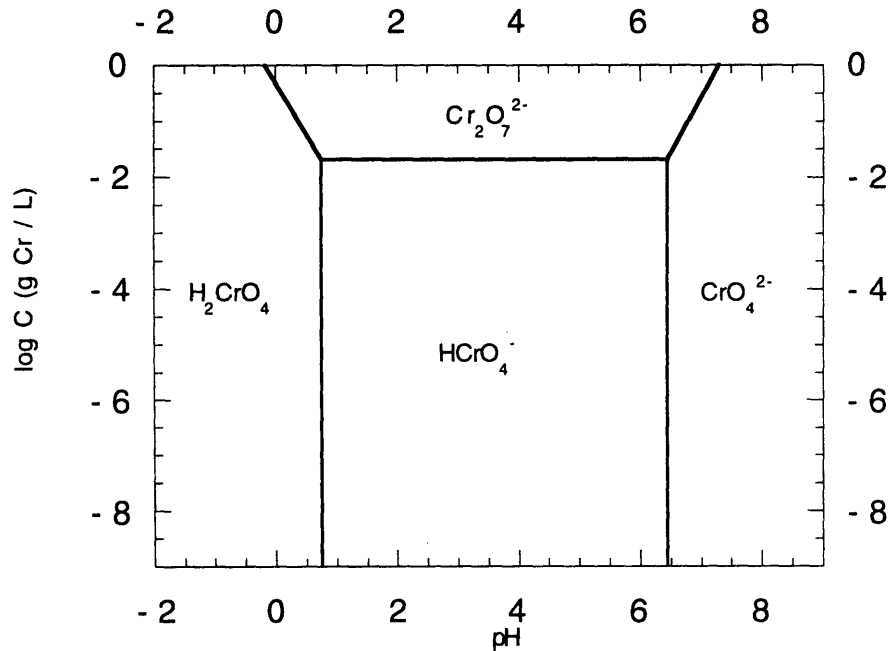


Figure 2.8.2: Domains of dissolved hexavalent chromium ions as a function of pH and concentration.

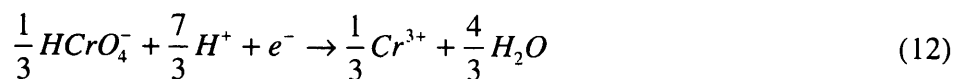
The COPR soils are very alkaline and therefore contain hexavalent chromium in the CrO_4^{2-} form, called chromate. Although chromate is very soluble, much of the hexavalent chromium in the soil is present in the form of precipitates. Table 2.8.2 lists the hexavalent chromium precipitates and their solubilities. An investigation by James [1994] indicated that most of the hexavalent chromium

Table 2.8.2: Hexavalent Chromium Precipitates, [CRC 1981]

Substance	Color	Solubility (g/100 cc)	
		Cold Water	Hot Water
BaCrO ₄	Yellow	0.00034	0.00044
CaCrO ₄	Yellow	16.3	18.2
K ₂ CrO ₄	Yellow	62.9	79.2
Na ₂ CrO ₄	Yellow	50	126
PbCrO ₄	Yellow	0.0000058	insoluble
CrO ₃	Red	61.7	67.45

in COPR soils is probably in a complex of intermediate solubility such as CaCrO₄. Hexavalent chromium complexes are typically yellow in color, and trivalent chromium complexes are typically green in color. Trivalent forms of chromium such as Cr₂O₃ and Cr(OH)₃ are very insoluble except at very low pH.

Next to the removal of chromium from the soil, the reduction of the toxic hexavalent form to the less toxic sparingly soluble trivalent form presents the most permanent form of remediation. The reduction of hexavalent chromium is inhibited by hydroxides and manganese oxides, as well as a high pH [James 1996]. James [1994] found that hexavalent chromium was not reduced and trivalent chromium was not oxidized in COPR soils unless chemical agents were added. He found ferrous iron to be the most effective at reducing hexavalent chromium, and Mn²⁺ to be slightly less effective. At low pH, lactic acid was also able to reduce the hexavalent chromium. For the planned electromigration field test at a COPR contaminated site, Taylor [1997] has examined a reduction of residual hexavalent chromium as a second phase of decontamination that should follow the chromate removal phase. He suggests the use of ferrous iron at a low pH with the following two half-reactions:



It has been proposed as a second phase only after removal of most hexavalent chromium because reduction is most effective on lower concentrations of contaminants. Also, a large concentration of hexavalent chromium would lead to a large amount of precipitation of the reduced species, possibly enough to clog soil pores completely, preventing the reducing agent from reaching other contaminated areas [Taylor 1997].

3. Experiments

A variety of batch tests were conducted to determine the dissolution kinetics of chromium and other elements in the soil. Electromigration tests were conducted in a small cylindrical cell and a larger box shaped cell that more closely simulates field testing conditions. The apparatus and procedures for the experiments are described in the following sections.

3.1 Batch Tests

Hexavalent chromium in a soil was extracted by an alkaline digestion similar to EPA method 3060A and subsequently measured on a spectrophotometer to determine the total hexavalent chromium present in the soil initially [James et al. 1995] [Vitale et al. 1994]. In this digestion method a 0.28 M Na_2CO_3 - 0.5 M NaOH solution was added to the soil at a 20 to 1 solution volume to soil mass ratio, in a 500 mL beaker. The solution was stirred and heated to maintain a temperature of 90 °C for at least one hour on a stirrer hotplate. The samples were centrifuged or passed through a filter prior to the spectrophotometer measurement. Soil samples were between 10 and 30 grams minimum to reduce the variability introduced by the heterogeneity of the chromate distribution in the soil. The repeatability error in soil digestion measurements was as low as 10 %, but reached up to 20 %, due to the very heterogeneous nature of the soil. The spectrophotometer measured hexavalent chromium with errors below 10 %.

The batch tests for determining dissolution under different conditions were similar to the digestion method except for varying the solutions employed, lowering the temperatures and using longer times. Several simple batch test were done to determine total dissolution under various conditions. In these tests a solution sample was taken at the end of the test only. The numbers of these total chromium dissolution tests are designated with a "T". The parameters that were investigated are listed together with the results in tables 4.1.1 and 4.1.2, in chapter 4.1.

In order to quantify the dissolution kinetics, similar batch tests were done, in which samples were taken at different times as dissolution advanced. For batch tests attempting to quantify the dissolution rate of chromium to model the process frequent samples were required in the first hour of the test. If the effects of varying chemical conditions were being investigated

sampling once a day for several days was sufficient. Table 3.1 lists the batch tests that were performed to investigate dissolution kinetics. In each of these tests 500 mL of solution was used and about 25 g dry weight of soil. The solutions were stirred on the hotplate at 180 rpm. In some experiments two consecutive extractions were done on the same soil under the same conditions in order to determine the effect of the initial chromate concentration in the soil on the dissolution rate. Second extractions are designated with a “b” and first extractions are designated with an “a”.

Table 3.1: Dissolution kinetics batch test parameters.

Dissolution Kinetics Test Number	Temperature (°C)	Solution 1	Solution 2	Solution 3	Solution 4
1a, 1b	35	pH 14 NaOH	pH 12 NaOH	pH 10 NaOH	pH 10 H ₂ O
2a, 2b	35	pH 13 NaOH	pH 12 NaOH	pH 11 NaOH	
3a, 3b	60	pH 14 NaOH	pH 12 NaOH	pH 10 NaOH	
4	60	0.1 M Na ₂ CO ₃	0.1 M Na ₂ HPO ₄	H ₂ O	
5	50	0.5 g/L Na ₂ CO ₃	1.0 g/L Na ₂ CO ₃	2.0 g/L Na ₂ CO ₃	10.0 g/L Na ₂ CO ₃
6	50	H ₂ O	H ₂ O		
7	50	pH 10.5 Na ₂ CO ₃	pH 10.5 NaOH	pH 10.5 Ca(OH) ₂	
8	50	0.013 g/L Na ₂ CO ₃	0.033 g/L Na ₂ CO ₃	0.067 g/L Na ₂ CO ₃	0.200 g/L Na ₂ CO ₃

Several soils from an actual COPR contaminated site were used in the various tests. For the initial tests, the soil was dried and sieved (U.S. standard No. 20 sieve), and subsequently well mixed by shaking. This processing resulted in a much more uniform soil and higher repeatability in the experiments. However, the drying alters the soil characteristics significantly from field conditions and therefore, later tests used soil as found at the site. Most notably, the chromium concentrations and the dissolution rates were higher in the dried and sieved soil.

3.2 Small Cell Tests

A schematic drawing of the small cylindrical electroremediation test cell is given in figure 3.2. The cylindrical tube contains the wet contaminated soil. At each end of the tube, there is a filter membrane disc and stainless steel screen serving as a passive electrode. These passive electrodes are used to measure the voltage across the soil because there are voltage drops in the electrode wells. The filter membranes prevent hydraulic flow through the soil while allowing ions to pass through it. A hydraulic flow through the soil would wash contaminants from the soil and skew the results. The anode and cathode are made of a carbon disc connected to a carbon rod. Should these carbon electrodes deteriorate during the course of an experiment it is possible to replace them, if the end cap is removed from the tube. The electrode wells have an inlet and an outlet connected to a gravity driven circulation system that may be used to wash the electrodes. In some experiments a pH-controller was used to maintain a constant pH in an electrode well. Sodium carbonate solutions of 2.5 - 10.0 g/L and various sodium hydroxide solutions as well as tap water were used as electrode washing solutions (see Table 3.2). The electrode well circulation system held a volume of 2 to 3 L of electrode wash solution. The electrode well solution system can be drained and the solution can be replaced with a fresh or different solution during an experiment. Also, in some tests pipe insulation was placed around the cylindrical tube and a thermocouple monitored the temperature rise in the soil due to ohmic heating. The DC power could be supplied to the electrodes at either constant voltage or constant current. Constant voltage operation was between 100 and 200 volts per meter of soil. Constant current operation was between 10 and 20 amperes per square meter. The passive electrodes are 20 cm apart and the tube has an inner diameter of 2.5 cm.

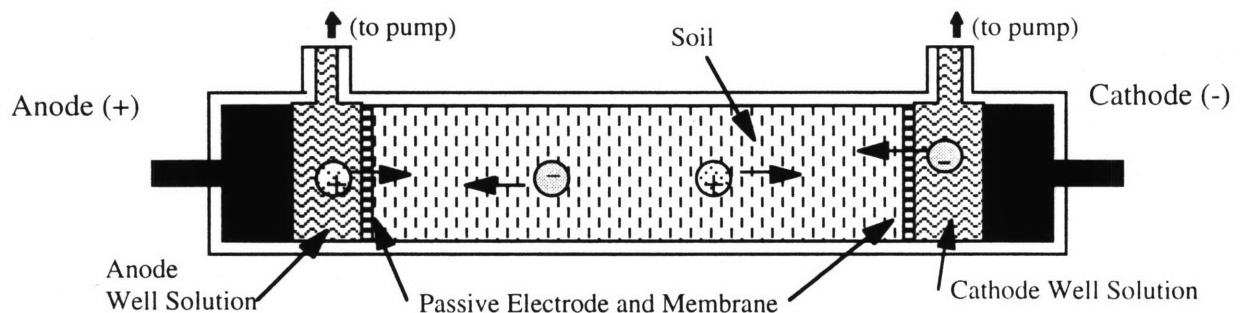


Figure 3.2: Small Test Cell

The parameters for the electromigration tests in the small cylindrical shaped cell are summarized in Table 3.2. The percentages of sodium carbonate in the soil fill solution column refer

to the amount of sodium carbonate added directly to the soil when the cell was filled. It is given as a percentage of the stoichiometrically equivalent amount of chromate present in the particular soil before remediation.

Table 3.2: Small cell electromigration test parameters.

Small Cell Test Number	Voltage Limit (V/m)	Current Limit (A/m ²)	Anode Well Solution	Cathode Well Solution	Soil Fill Solution	Soil Type	Anode Washing	Cathode Washing
1 a	500	no limit	pH 5 H ₂ O	pH 13 NaOH	H ₂ O	dried + sieved	Y	Y
1 b	500	no limit	pH 13 NaOH	pH 13 NaOH	H ₂ O	dried + sieved	Y	Y
2	500	65	pH 12 NaOH	pH 12 NaOH	H ₂ O	dried + sieved	Y	Y
3	500	70	pH 10 NaOH	pH 10 NaOH	H ₂ O	dried + sieved	Y	N
4	500	65	0.5 g/L Na ₂ CO ₃	pH 8 NaOH	H ₂ O	moist + unsieved	Y	Y
5	500	65	0.5 g/L Na ₂ CO ₃	0.5 g/L Na ₂ CO ₃	H ₂ O	moist + unsieved	Y	N
6	500	70	pH 10 NaOH	pH 12 NaOH	H ₂ O	moist + unsieved	Y	Y
7	150	no limit	10 g/L Na ₂ CO ₃	10 g/L Na ₂ CO ₃	70 % ¹ Na ₂ CO ₃	dried + sieved	Y	Y
8	200	no limit	5 g/L Na ₂ CO ₃	5 g/L Na ₂ CO ₃	186 % ¹ Na ₂ CO ₃	moist + unsieved	Y	Y
9	150	no limit	5 g/L Na ₂ CO ₃	5 g/L Na ₂ CO ₃	50 % ¹ Na ₂ CO ₃	moist + unsieved	Y	Y
10	150	no limit	10 g/L Na ₂ CO ₃	10 g/L Na ₂ CO ₃	110 % ¹ Na ₂ CO ₃	moist + unsieved	Y	Y

¹ Na₂CO₃ addition is given as a percentage of the stoichiometrically equivalent amount of chromate present in the particular soil before remediation.

After weighing, the soil was carefully filled into the tube from one end while the other end was closed off with the filter membrane and end cap. At the same time solution was added to the soil to ensure that it was saturated with water. Both the solution volume and the soil mass that were loaded into the tube were recorded. The small cell typically held 170 to 190 g of soil and 40 to 50 mL of pore solution. Since the tube volume was known the porosity of the soil could be estimated from these quantities. The porosity for the dried and sieved soil was estimated to be 25-30 % at the beginning of an experiment. After the tube was completely filled with soil, the other membrane and end cap was put in place. The end cap also contained the carbon electrode that could be replaced whenever the endcap was removed, since it deteriorated at high pH. A more detailed description of filling the small test cell is given by Wong [1996].

Using a multimeter, it was possible to measure current through the cell and voltage drops across the cell, across the electrode wells, and across the soil. The removal rates of chemicals were measured by sampling from the electrode wells. Samples were analyzed for hexavalent chromium on a spectrophotometer. Analyses for most other elements did not require knowledge of the valence state and were therefore done more reliably and efficiently on an Inductively Coupled Plasma Spectrophotometer (ICP). After a migration test was ended the cell was taken apart carefully and the soil was analyzed in sections with the alkaline digestion method described earlier to determine the distribution of hexavalent chromium remaining in the soil. The pore solution was separated from the soil by centrifugation and was also analyzed.

3.3 Large Cell Tests

A schematic drawing of the larger box shaped test cell is given in figure 3.3. As the diagram shows the arrangement of the box shaped cell apparatus is analogous to the cylindrical cell. The main difference is that the lid may be removed making it possible to take samples from the soil while a remediation test progresses. That way, the dissolved chromate concentration in the pore water can be monitored transiently. Furthermore, the distribution of pH and dissolved chromate in the soil can be measured as the test progresses. There is a chamber filled with water below the soil to simulate the groundwater in a field test. The procedure of the electromigration tests in the box shaped test cell were very similar to those in the cylindrical cell except that the chromate concentration in the pore water was monitored and chemicals such as sodium carbonate for enhancing dissolution were added directly to the soil as needed. In the cylindrical test cell any such addition of chemicals could only be done indirectly by electromigration from the electrode

wells after the test is started or when the cell was filled with soil initially. The large test cell has features to enable the placement of metal as well as carbon sheet electrodes and to allow easy replacement of the electrodes. Generally, carbon electrodes were used because they are low cost and relatively inert. In one test, a titanium alloy electrode was used to see if it would deteriorate less than a carbon electrode, but it also deteriorated. Before filling the cell with soil, the soil was weighed and filter papers and membranes were placed in the cell to reduce hydraulic flow through it. The large test cell could hold about 1000 g of soil and more than 100 mL of pore solution. The soil compartment had a length of 15 cm, a width of 13 cm, and soil was usually filled to a height of 4 cm. The circulation system that was used to wash the anode well was the same as in the small cell experiments.

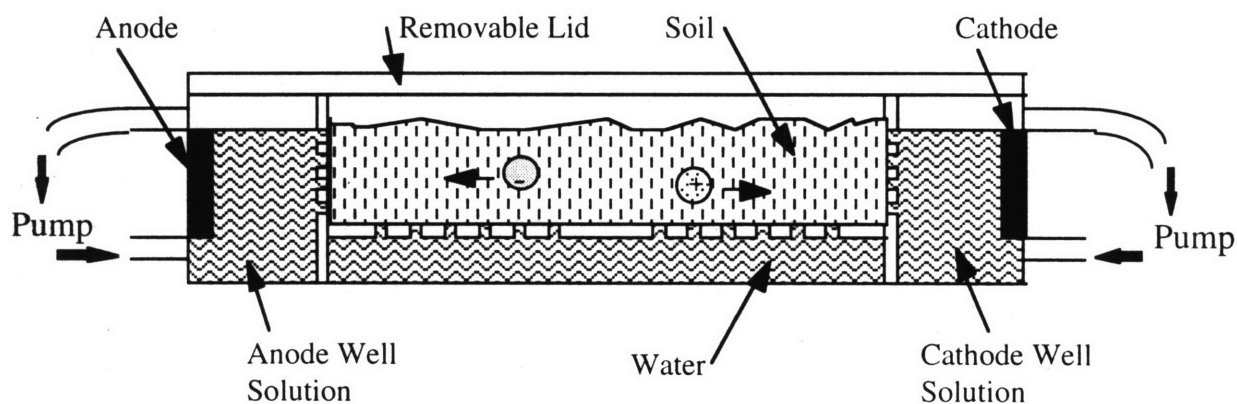


Figure 3.3: Large Test Cell

The addition of sodium carbonate to the soil for enhancing calcium chromate dissolution can be timed in several ways. The total chromate removed from the soil could be calculated and thus an estimate of the sodium carbonate that has been used up can be made, assuming that it is used at a rate of stoichiometric equivalence to the chromate dissolved. Another measurement that could be more insightful is to analyze the pore solution. If the chromate concentration in the pore solution is dropping significantly, it would imply that its dissolution rate is slowing and more carbonate may help. Generally, a combination of these measurements was used to make a judgment about carbonate addition.

The electrode well solutions were replaced periodically to prevent large pH changes. A sodium carbonate solution of 5 g/L was chosen as the solution for the electrode wells. The actions taken during large cell tests 1 and 2 are listed in table 3.3. In large cell test 2, the current was interrupted several times with the intention of increasing the concentration of hexavalent chromium in the pore water. The carbon anode electrode tended to deteriorate with time and was replaced

Table 3.3: Large cell electromigration test parameters.

Time (hours)	Total Na ₂ CO ₃ added to Soil (% stoichiometric Cr ⁶⁺)	Experiment Interruption (hours current off)	Fresh Anode Electrode	Well Solution Replacement (5 g/L Na ₂ CO ₃)
Large Cell 1:				
0	10	0	titanium	Anode
18.5	10	0	-	Anode
28.5	10	0	titanium	-
51.5	10	0	titanium	Anode (10 g/L)
82	50	0	titanium	Anode
101	50	0	carbon	-
128	50	0	carbon	Anode
Large Cell 2:				
0	8.5	0	carbon	Anode
5	18.5	0	-	-
20.5	28.5	0	-	Anode
43	28.5	0	-	Anode
68	28.5	0	carbon	Anode
88	40	0	carbon	Cathode, Anode
107	60	34	-	-
129	60	0	carbon	Anode
152	60	11	-	Anode
171	60	112	carbon	Cathode, Anode
189.5	60	0	carbon	Anode
219.5	60	0	carbon	Anode
243.5	60	0	carbon	Anode
287	60	23	carbon	Anode
319.5	60	0	carbon	Anode

almost daily. The cathode electrode did not deteriorate and was not replaced during the experiments. In large cell test 1, the cathode was placed directly into the soil to determine the effect of operating without a cathode well.

4. Results and Discussion

This chapter will present the results obtained from the experiments and discuss them with respect to the objectives of the research. The main goal of the research is to remove hexavalent chromium from a soil effectively; that is to remove most of it from the contaminated soil. The secondary goal is to do this removal with a high efficiency; that is to expend a small amount of electrical energy per mole of hexavalent chromium removed.

4.1 Batch Tests

There were two types of batch tests. The first type involved taking only one sample from the solution at the end of the tests to investigate total chromium dissolution. The second type of batch test involved taking solution samples periodically over time to investigate dissolution kinetics. Tables 4.1.1 and 4.1.2 summarize the results of the first type of batch test and their numbers are designated with a "T". The batch tests in Table 4.1.1 used soil directly from the site, while the tests in table 4.1.2 used the same soil after it was dried and sieved (US standard no. 30 sieve) to make it more uniform. These tests make it evident that the trivalent chromium is only sparingly soluble even at very low pH. Furthermore, the results in table 4.1.1 indicate that the following factors increase hexavalent chromium dissolution:

- increasing the water to soil mass ratio
- increasing the pH by sodium hydroxide addition
- adding sodium carbonate
- heating the solution
- increasing dissolution time

Adding sodium carbonate and heating seem to have the strongest effects on the dissolution rate of hexavalent chromium from the COPR enriched soil. The results of table 4.1.2 indicate that the distribution of the chromium in the soil is very non-uniform and it is therefore difficult to achieve a high repeatability in the batch tests. This variability can be reduced by taking larger samples of soil. Furthermore the relative amount of chromate in the soil increased as a result of drying and sieving. The reason for this increase is probably that more chromium is found among the finer particles. A similar result was discovered by Hsieh [1989].

Table 4.1.1: Single sample batch test results (with unsieved moist soil)

Test #	Cr tot. (ppm)	Cr hex. (ppm)	Stir	Temp. (C)	Time (h)	Solvent (M)	Solv. V/ Soil M (mL/g)
Lab	16000	3200					
T1		2400	slow	>65	1	0.5 NaOH	20
T2	496		fast	20	4	70% HNO ₃	14.6
T3	2810		fast	20	25	99% H ₂ SO ₄	11.6
T4		2400	slow	>80	1.5	0.5 NaOH	20
T5		1175	fast	20	24	0.5 NaOH	20
T6		319	fast	20	17.5	H ₂ O	6.3
T7		1000	slow	40	17	H ₂ O	31
T8		510	none	20	55	0.5 NaOH	4.9
T9		144	none	20	55.5	H ₂ O	4.6
T10		508	none	20	209	H ₂ O	5.6
T11		207	none	20	209	H ₂ O	5.7
T12		1340	none	20	209	0.5 NaOH	6.5
T13		636	none	20	209	0.5 NaOH	2.3
T14	2746	2746	slow	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	24

Table 4.1.2: Single sample batch test results (with dried and sieved soil)

Test #	Soil Mass (g)	Cr hex. (ppm)	Stir	Temp. (C)	Time (h)	Solvent (M)	Solv. V/ Soil M (mL/g)
T15	2.55	4480	slow	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	19.6
T16	2.5	6396	slow	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	20
T17	0.976	4918	none	20	142	0.5 NaOH 0.28 Na ₂ CO ₃	22.5
T18	1.08	3667	none	20	142	0.5 NaOH	19.4
T19	1.02	2157	none	20	142	H ₂ O	19.6
T20	2.5	1764	slow	<40	3	0.5 NaOH 0.28 Na ₂ CO ₃	20
T21	2.46	764	slow	<40	3	H ₂ O	20.3
T22	2.5	4752	slow	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	20.4
T23	2.5	4774	slow	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	19.6
T24	10.08	3750	med.	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	10
T25	10	4500	med.	>80	1	0.5 NaOH 0.28 Na ₂ CO ₃	10

The parameters for the dissolution kinetics tests are presented in table 3.1 in chapter 3.1. The rest of this section discusses the results from these tests which are graphed in figures 4.1.1 to 4.1.19

The purpose of batch tests 1 to 3 was to determine the effect of pH on the dissolution of hexavalent chromium and aluminum, as well as the effect of initial hexavalent chromium concentration in the soil on its dissolution rate. The results are displayed in figures 4.1.1 to 4.1.8. The plots indicate a very high initial dissolution rate and a gradual slowing of the rate, which is due to the changing stoichiometry of the solution but may also indicate that a portion of the chromate salts is less easily soluble. James [1994] found that 50 % of the chromate in the COPR soils he investigated was in an easily soluble form. The pH 10 and the H₂O extraction had similar results, because the soil has a pH close to 10 even without adding base. The figures for the first extractions indicate that increasing pH significantly increases dissolution. After the first extraction, the soils no longer contain the same amount of chromate salts since the different solutions dissolved different amounts. As was discovered in the single sample batch tests, the dissolution rate is affected by the amount of undissolved chromate salts relative to the solution volume. This effect dominates the second extraction. According to the length of these tests, it should be possible to clean a COPR soil in about ten days by electromigration, because contaminant dissolution limits removal rate. As will be seen in the next section, cleaning a COPR soil in a laboratory cell takes much longer. The reason for this discrepancy is that the solution to soil ratio is much lower in an electromigration test than in a batch test. Furthermore, stirring breaks up slowly dissolving chromate clumps in the batch tests. Figure 4.1.7 and 4.1.8 compare aluminum and hexavalent chromium dissolution rates. Hexavalent chromium dissolves significantly faster than aluminum, especially at pH 10. The lower dissolution rate of aluminum at pH 10 is of great advantage, since according to theory, the current efficiency depends on the concentration of the contaminant ion relative to other dissolved ions.

As explained in chapter 2, carbonate addition should increase the dissolution rate of calcium chromate by forming calcium carbonate precipitate, and phosphate addition should improve hexavalent chromium dissolution by reducing its adsorption to positively charged soil colloids. Batch test 4 investigated these effects and its results are presented in figures 4.1.9 and 4.1.10. Clearly, sodium carbonate results in the largest increase in dissolution of hexavalent chromium. Unfortunately, sodium carbonate also significantly enhances the dissolution of aluminum, but to a lesser extent than it enhances hexavalent chromium dissolution, as figures 4.1.11 and 4.1.12 show.

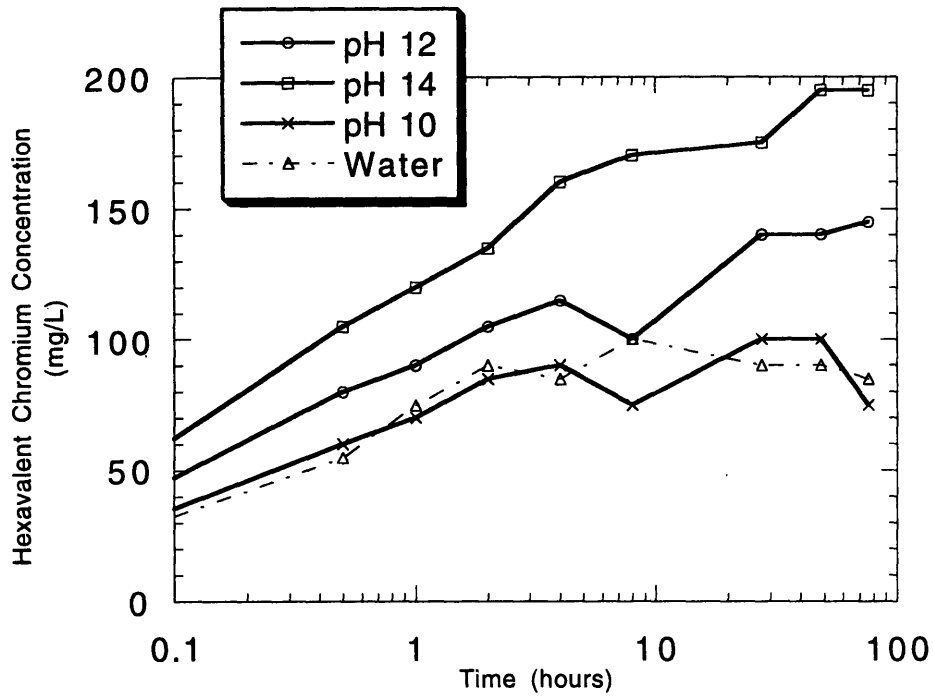


Figure 4.1.1: Batch Test 1a, hexavalent chromium dissolution (first extraction).

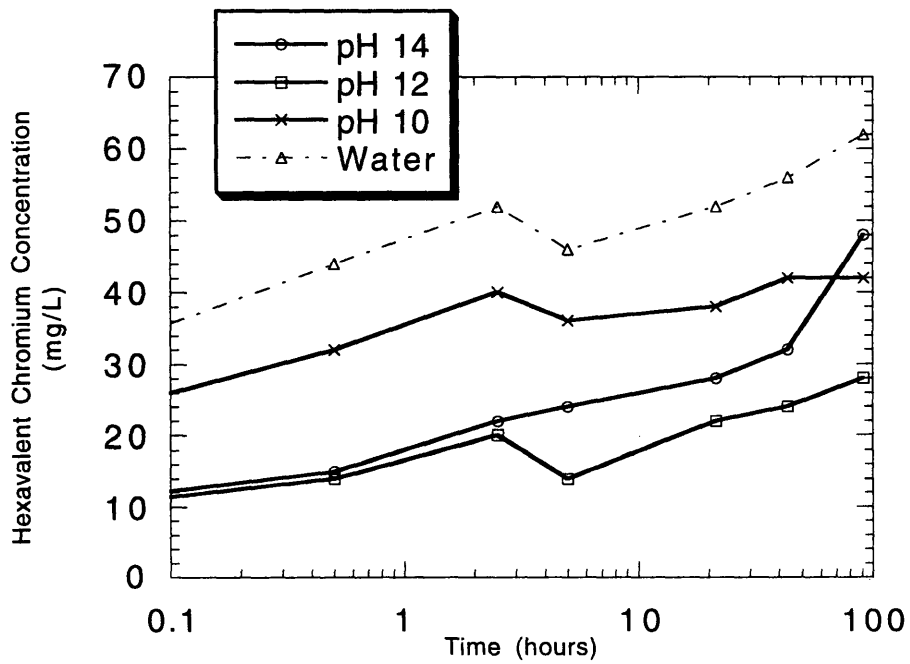


Figure 4.1.2: Batch Test 1b, hexavalent chromium dissolution (second extraction).

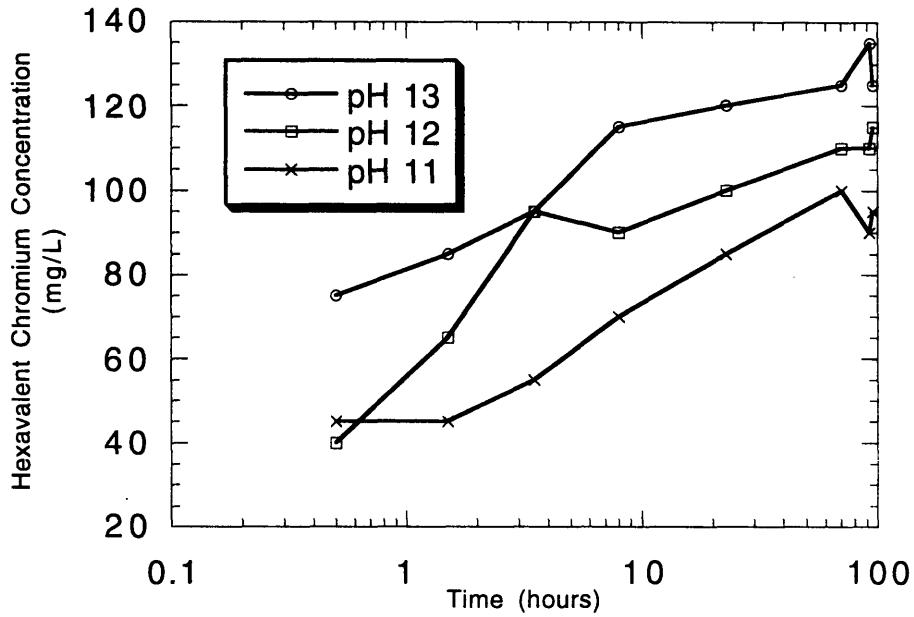


Figure 4.1.3: Batch Test 2a, hexavalent chromium dissolution (first extraction).

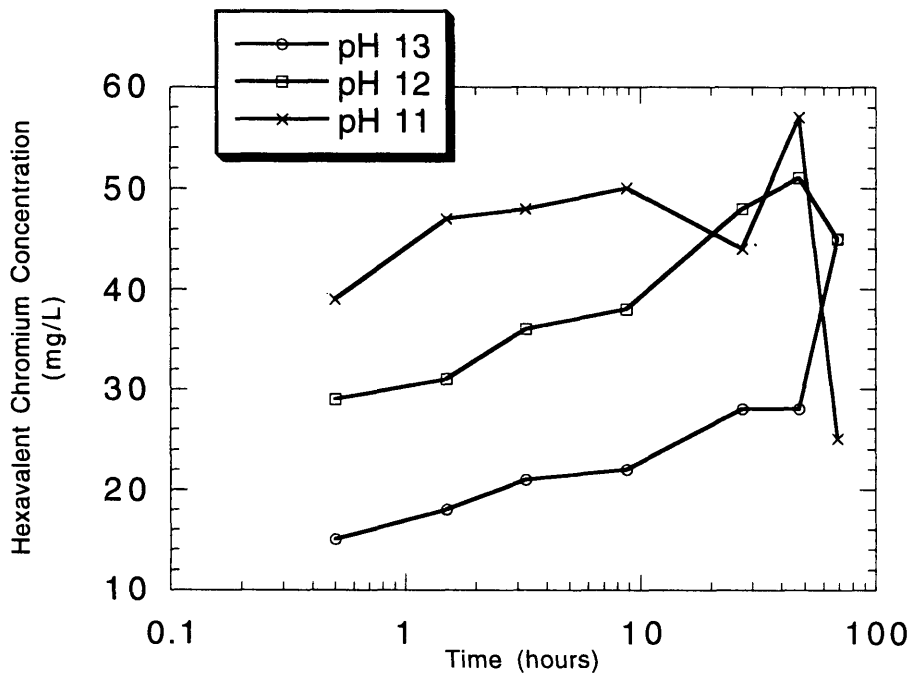


Figure 4.1.4: Batch Test 2b, hexavalent chromium dissolution (second extraction).

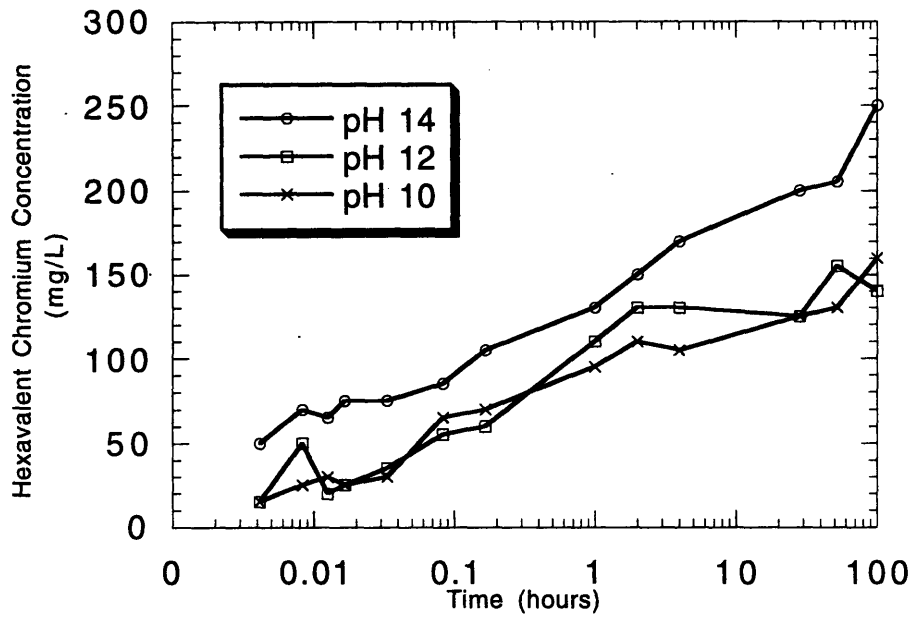


Figure 4.1.5: Batch Test 3a, hexavalent chromium dissolution (first extraction).

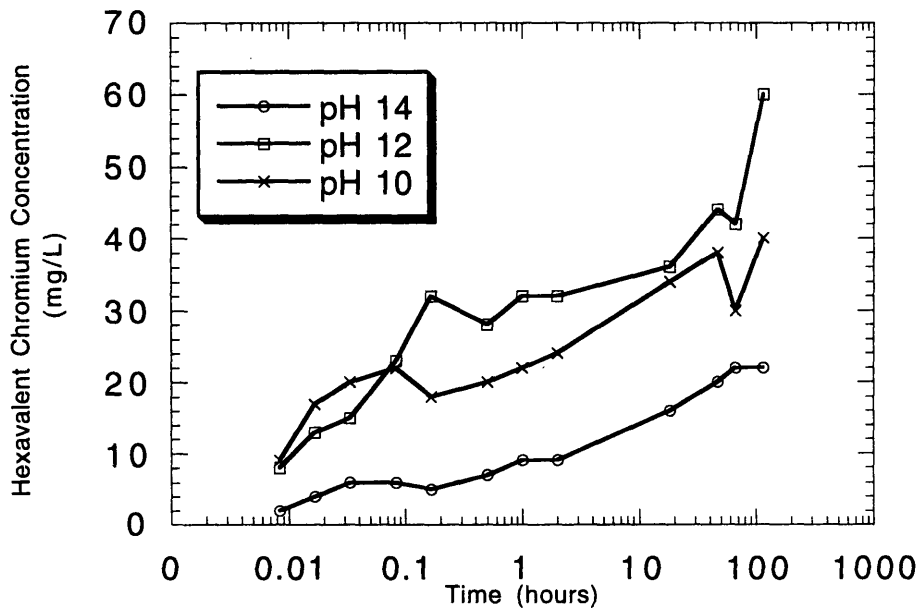


Figure 4.1.6: Batch Test 3b, hexavalent chromium dissolution (second extraction).

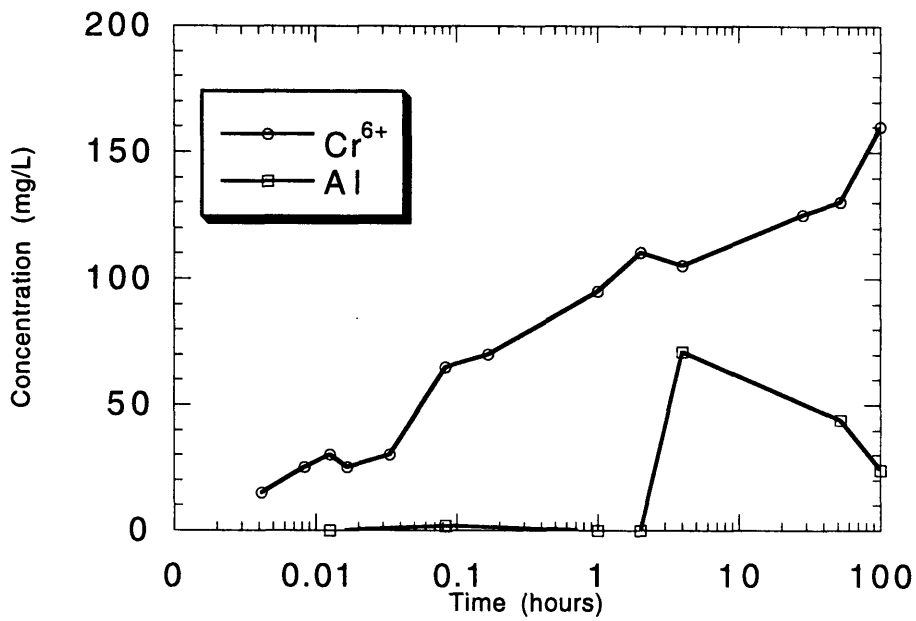


Figure 4.1.7: Batch Test 3a: comparison of aluminum and hexavalent chromium dissolution at pH 10.

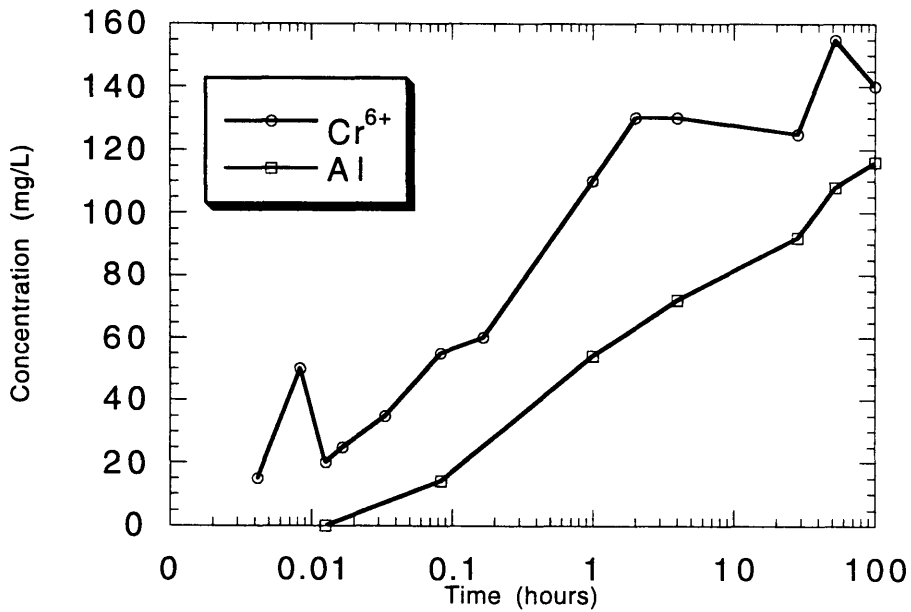


Figure 4.1.8: Batch Test 3a: comparison of aluminum and hexavalent chromium dissolution at pH 12.

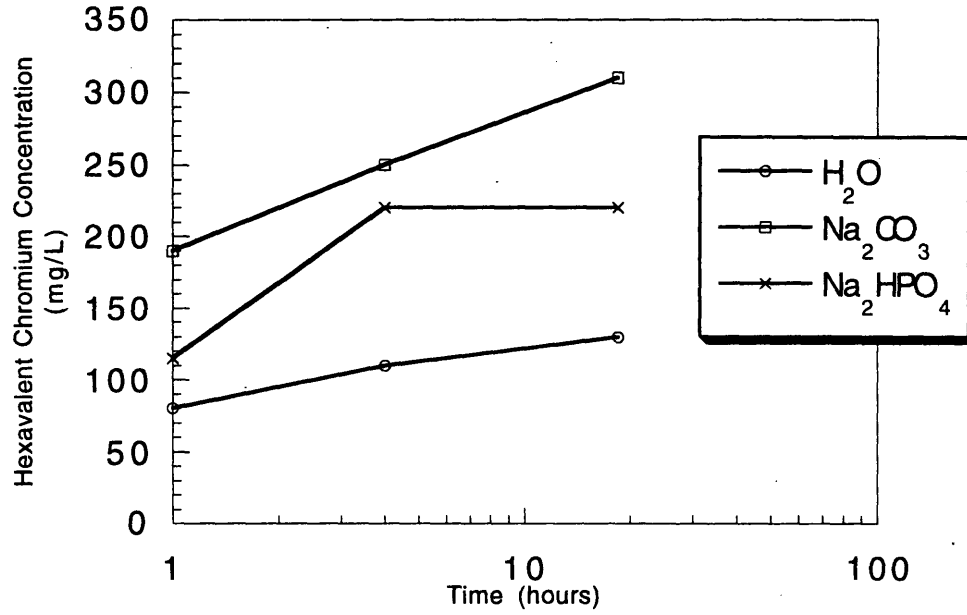


Figure 4.1.9: Batch Test 4, hexavalent chromium dissolution.

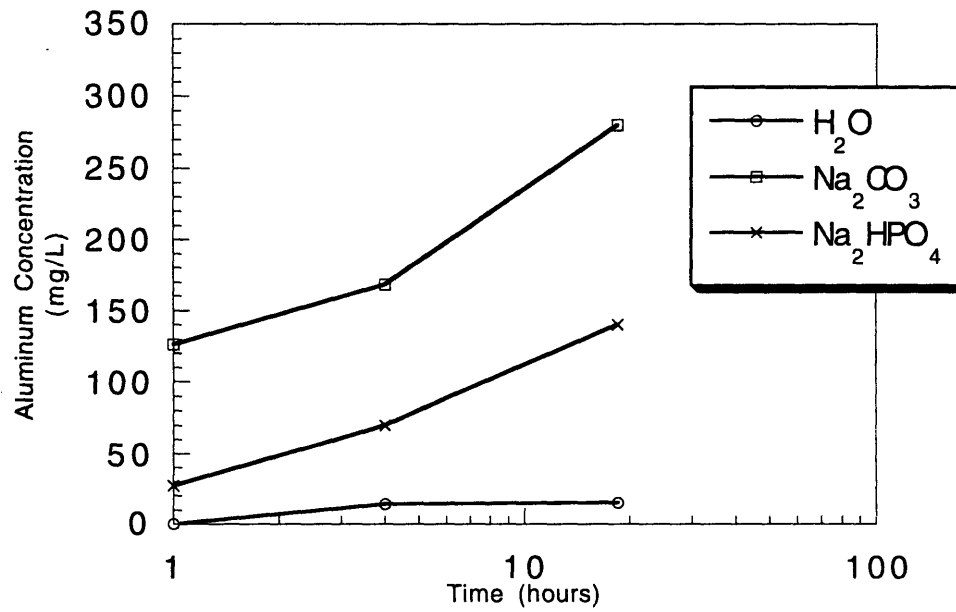


Figure 4.1.10: Batch Test 4, aluminum dissolution.

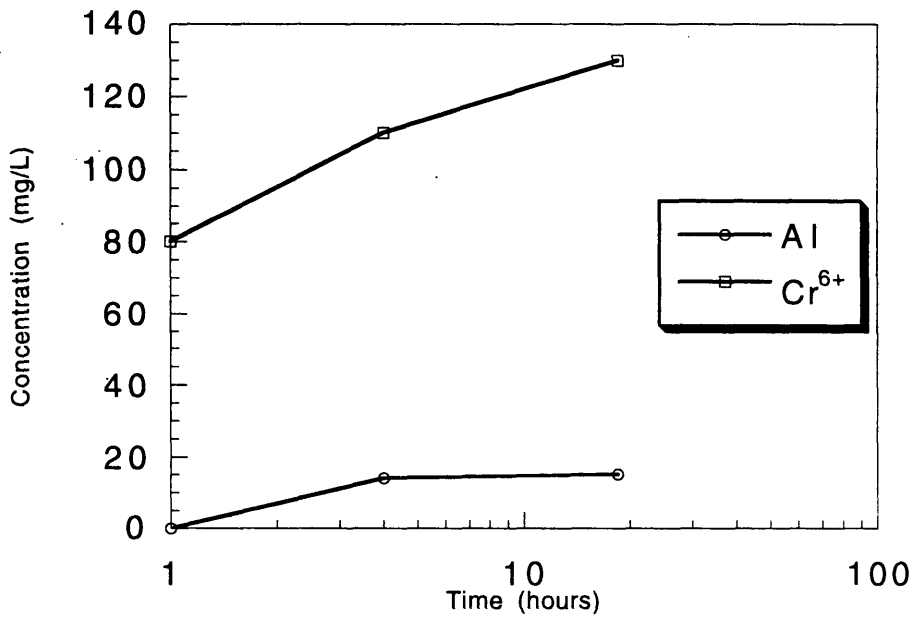


Figure 4.1.11: Batch Test 4, comparison of aluminum and hexavalent chromium dissolution in water.

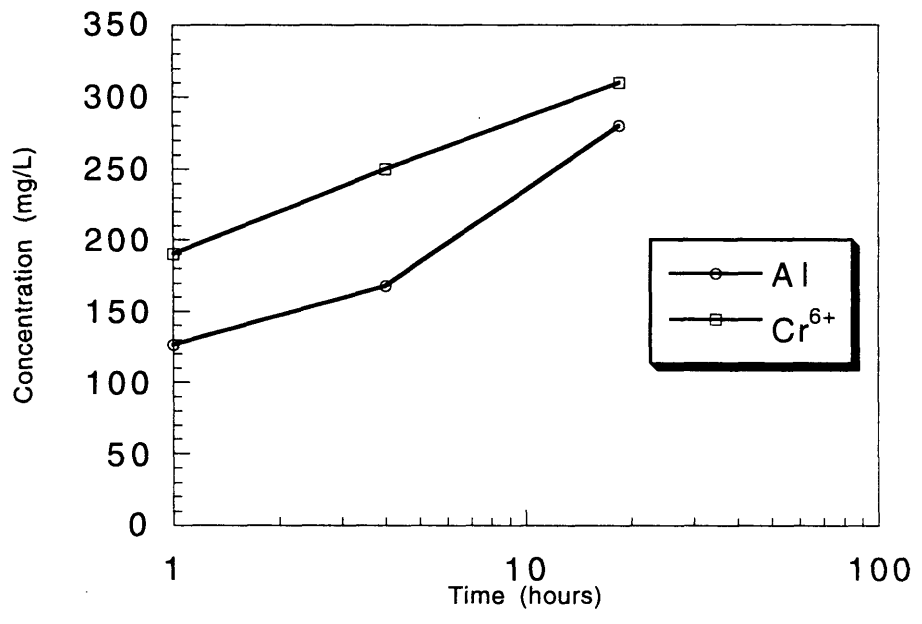


Figure 4.1.12: Batch Test 4, comparison of aluminum and hexavalent chromium dissolution in 0.1 M sodium carbonate solution.

Sodium carbonate was further investigated in batch test 5 and 8. The results are in plotted in figures 4.1.13 to 4.1.16. As the figures indicate, hexavalent chromium dissolution increases if the sodium carbonate concentration is increased. However, variability in the soil has a stronger effect on dissolution than small increases in sodium carbonate concentration. More importantly, aluminum dissolution is low for low sodium carbonate concentrations that still enhance hexavalent chromium dissolution. In contrast, more concentrated sodium carbonate solutions do significantly increase aluminum dissolution, probably because of a pH effect. The important conclusion from this observation is that sodium carbonate concentrations in the pore water during a remediation test should be kept relatively low.

Batch test 7 intended to discover if the enhancing effect of sodium carbonate resulted from a pH increase associated with it or the action of the carbonate on the calcium. Three different solutions of nearly equal pH were compared in figures 4.1.17 and 4.1.18. The concentration of hexavalent chromium, for the sodium hydroxide sample drops after a day because the pH of the solution started to drop by equilibration with carbon dioxide in the atmosphere. The results indicate that carbonate enhances dissolution but that pH has an even stronger effect. Certainly, the advantage of sodium carbonate as a pH buffer becomes apparent in this experiment. Furthermore, sodium carbonate is more likely to be approved for field use because it is much safer to handle than sodium hydroxide.

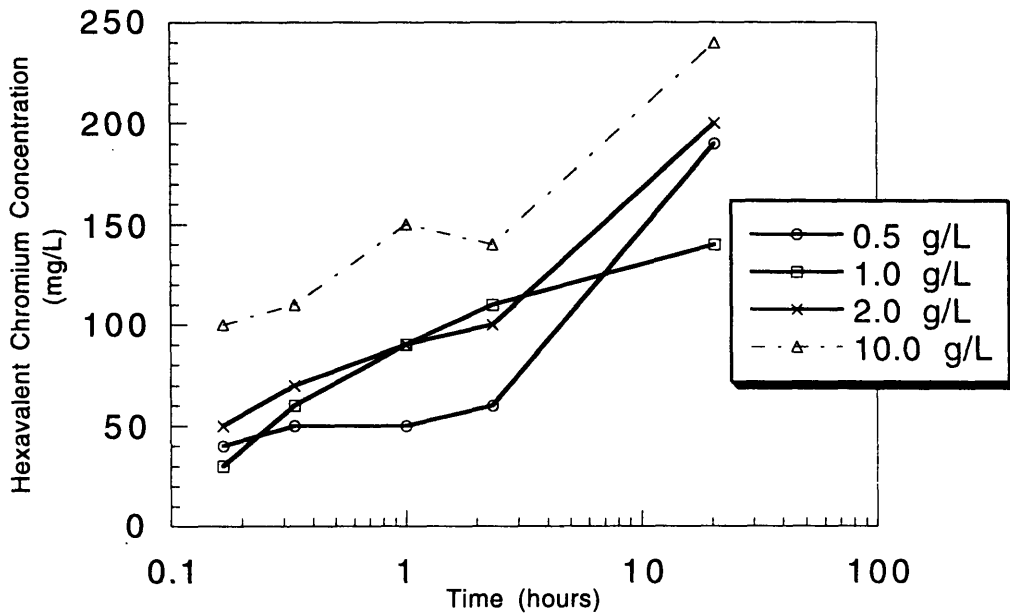


Figure 4.1.13: Batch Test 5, hexavalent chromium dissolution with various sodium carbonate additions.

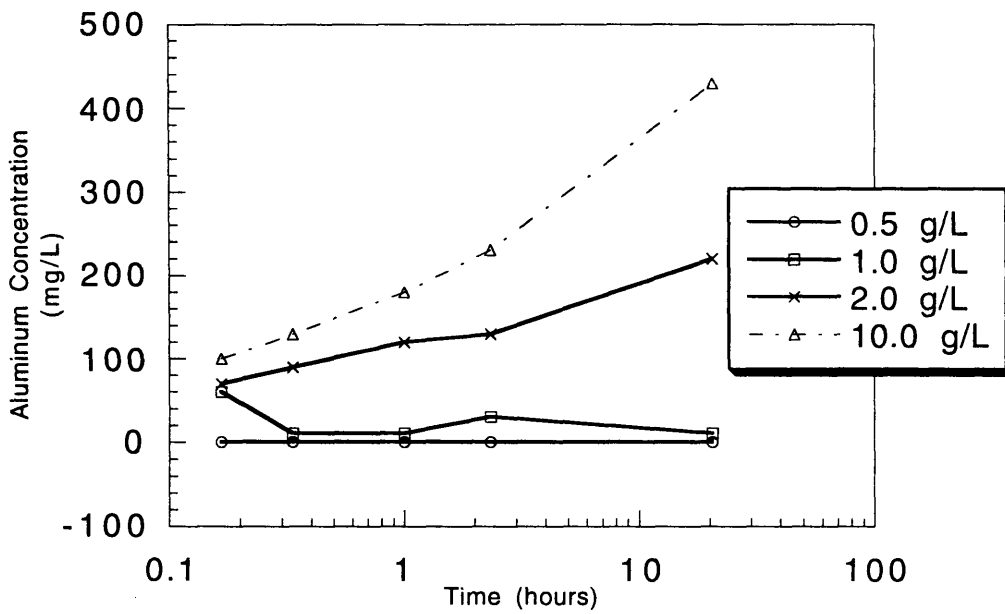


Figure 4.1.14: Batch Test 5, aluminum dissolution with various sodium carbonate additions.

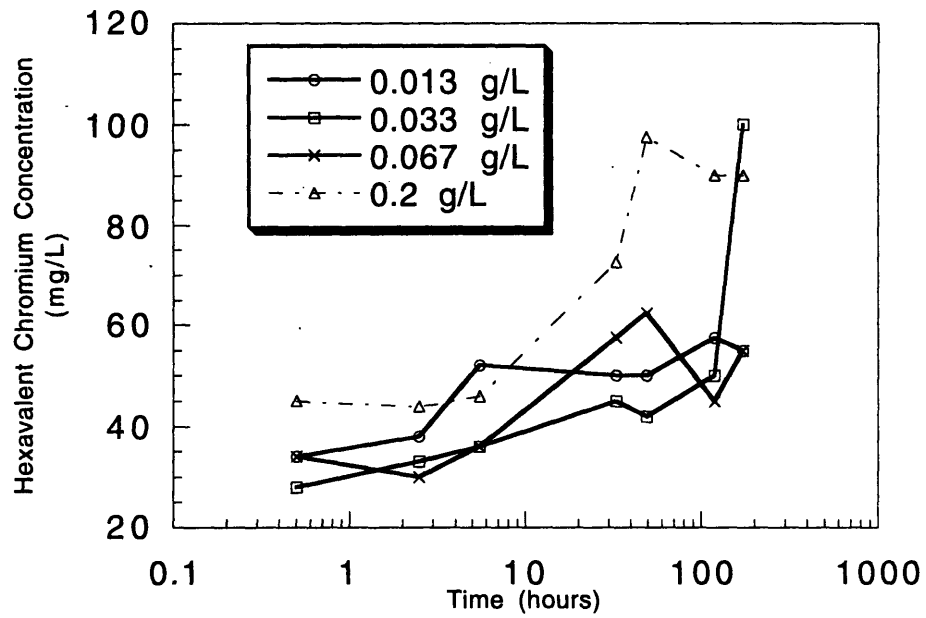


Figure 4.1.15: Batch Test 8, hexavalent chromium dissolution with various sodium carbonate additions.

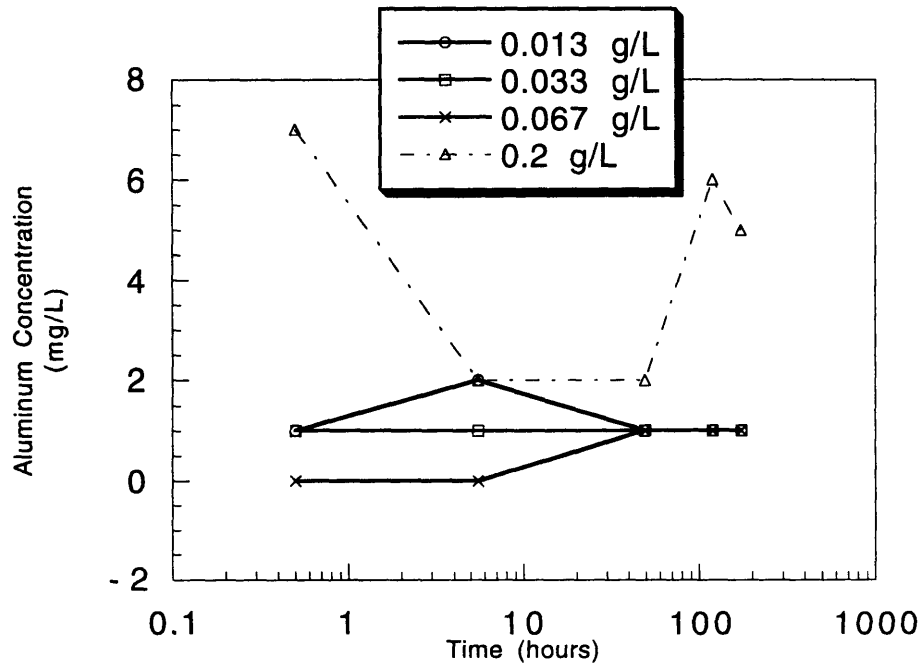


Figure 4.1.16: Batch Test 8, aluminum dissolution with various sodium carbonate additions.

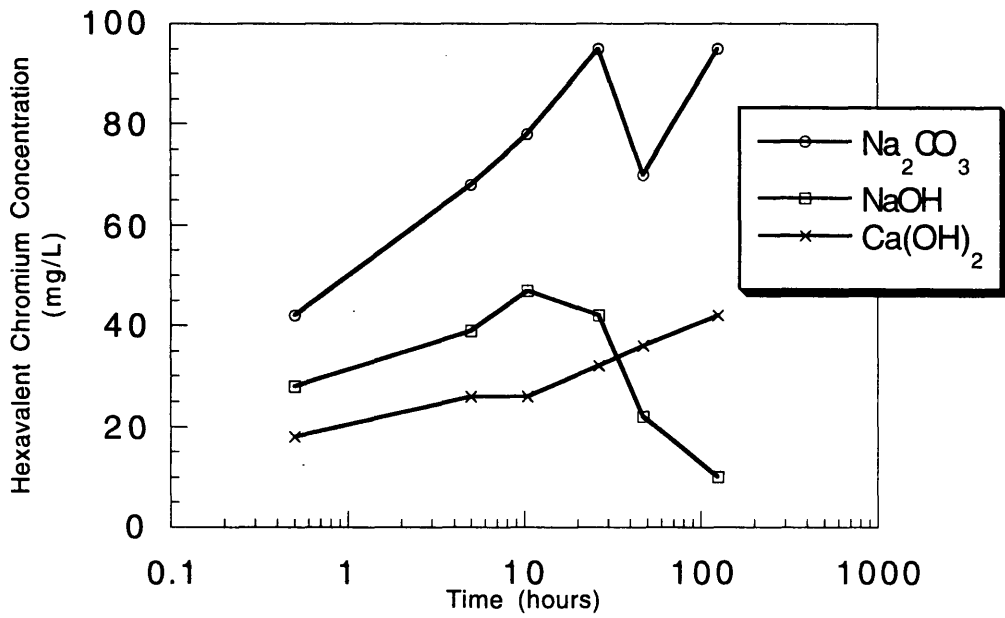


Figure 4.1.17: Batch Test 7, hexavalent chromium dissolution at pH 10.5 with various solutions.

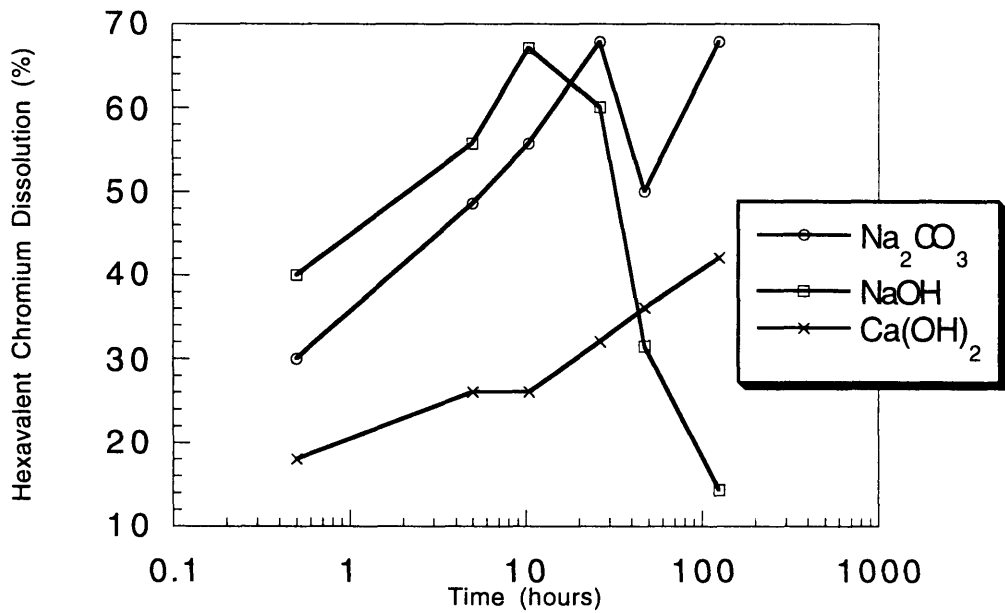


Figure 4.1.18: Batch Test 7, percent hexavalent chromium dissolution at pH 10.5 with various solutions.

Based on the literature reviewed for this thesis, it was assumed that most of the hexavalent chromium in the COPR soils was in the calcium chromate form. The purpose of batch test 6 was to verify the likelihood of this assumption. The extraction solution of batch test 6 used only distilled water and soil without the addition of chemicals so that the solution should reflect the composition of the easily soluble substances in the soil. Table 4.1.3 lists the concentrations of dissolved substances detected in the solution. Based on this analysis it is likely that most of the easily soluble hexavalent chromium precipitate is present as a calcium chromate salt. It is also noteworthy that large amounts of calcium from a source other than calcium chromate is dissolving at this pH (close to 10). Calcium hydroxide dissolves below pH 11.5 and may be present in the soil. In the migration experiments, the dissolution of this additional calcium will require sodium carbonate additions to be larger than estimates based on chromate dissolution alone.

Table 4.1.3: Batch Test 6, composition of extraction solution.

Substance	Concentration (mg/L)	
	Sample 1	Sample 2
Cr ⁶⁺	42.5	30
Al	72	67
Ca	215	294
Na	22	23
K	1	1

4.2 Small Cell Tests

The purpose of the small cell tests was to test various electroremediation schemes for their relative effectiveness and efficiency. Figure 4.2.1 shows a plot of temperature on the top outside surface of the Plexiglas tube of small test cell with pipe insulation around the tube section, and the electric power supplied during the experiment versus time. This plot demonstrates that the electrical energy is converted to heat by ohmic heating as expected from theory. With the insulation on the test cell the soil temperature quickly reached nearly 60 °C, as has been reported in some field tests. The drop in power with time is due to a rise in the soil conductivity that occurs as more ions are dissolved in the pore solution, which increases its ionic strength. The ions dissolving into the pore water are primarily aluminate and chromate complexes. The removal of these ions from the soil by migration is plotted in figure 4.2.2. The lower removal of aluminum is a reflection of its lower dissolution rate as well as its lower migration rate due to the aluminate ion's lower charge of minus

one. The chromate ion has a charge of minus two. The removal rate slows gradually as a result of a slowing in dissolution of the chromate.

Plots of soil conductivity versus time for the small cell tests are given in figures 4.2.3 to 4.2.5. In experiment 1a the pH of the anode and cathode wells differed considerably and gradually a pH jump developed in the soil resulting in a low conductivity region. By increasing the pH at the anode and allowing some time for diffusion this pH jump was eliminated and the conductivity began to increase when the current was restarted as seen in the plot for cell 1b. Dzenitis [1996] discusses the development of pH jumps in detail. Dissolving of chromate and aluminate complexes is the primary reason for conductivity increases, which tends to occur more rapidly in tests at higher pH such as cell 1b and cell 2. The high initial conductivities of cell 7, 8, and 9 are due to the sodium carbonate solution that was added directly to the soil. As was discovered in the batch tests much of the chromate is in the calcium chromate form in the soil. Therefore, when it dissolves the calcium will complex with the carbonate and precipitate out of solution according to equation 14, so the dissolution of calcium chromate does not lead to conductivity increases.

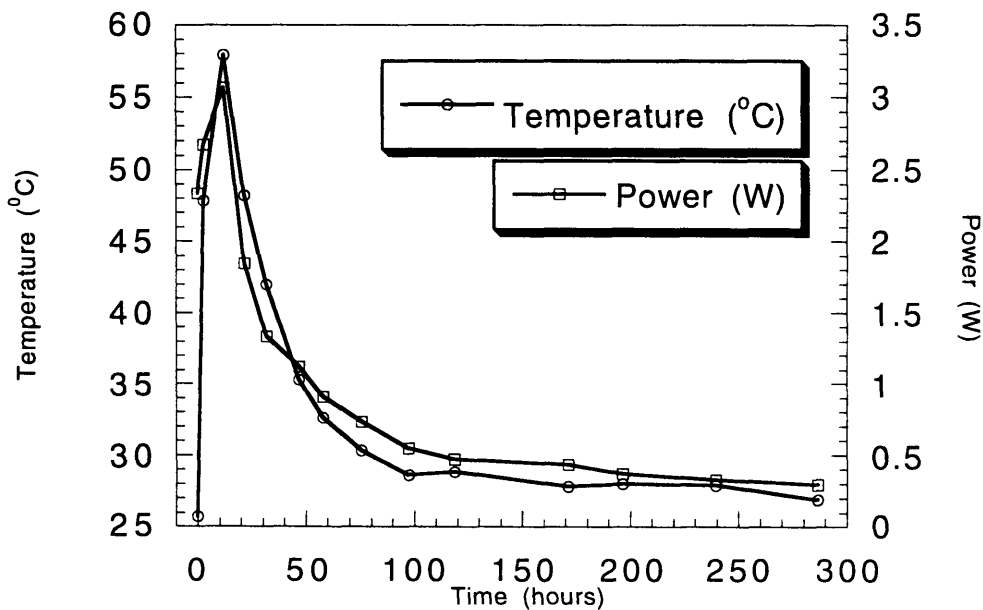
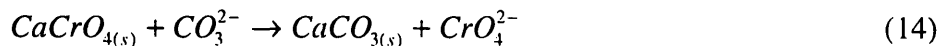


Figure 4.2.1: Small Cell Test 2, the relationship between temperature and electrical power.

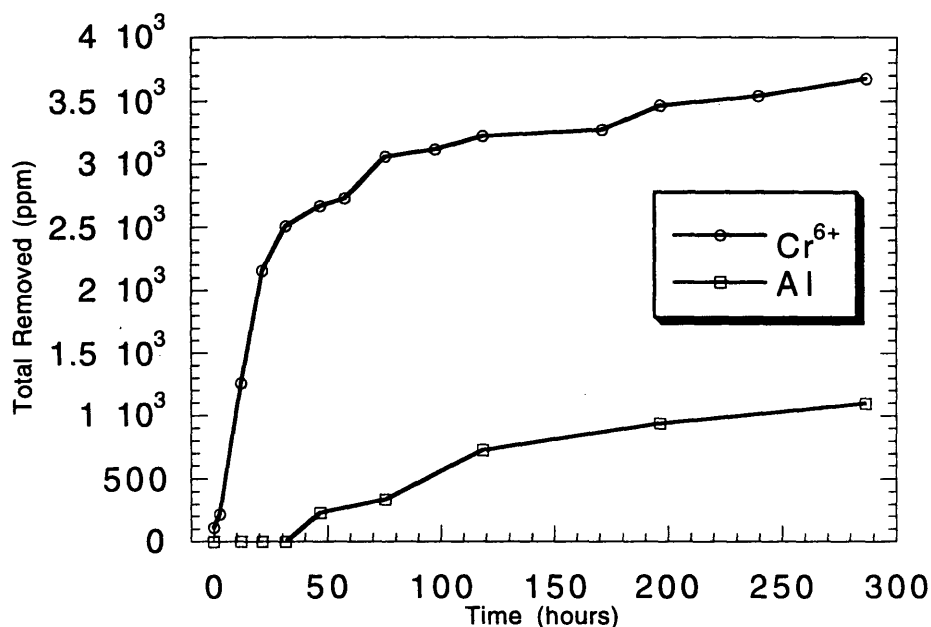


Figure 4.2.2: Small Cell Test 2, hexavalent chromium and aluminum removal.



If hydrogen ions migrate into the soil from the anode, they will react with carbonate ions to form bicarbonate ions according to reaction 15, reducing the ionic strength by one half, which could explain some of the gradual conductivity drops that were observed in cells 7, 8, and 9. A drop in pH in the soil would also result in a drop in the soil conductivity. In most small cell experiments the pH in the cathode well tended to fall especially in later stages of the experiment, which is evidence of hydrogen ions migrating there from the anode. Although it was not possible to verify the pH inside the cell during the small cell tests, it is unlikely that a pH drop caused the conductivity decreases in cells 7, 8 and 9, because sodium carbonate is a pH buffer.

During some of the small cell experiments conductivity decreases also occurred from precipitation of another complex which is suspected to be alumina. This white precipitate was seen to be deposited on the anode in cell 3 and 5. Along the length of the cell, the pH inside the cell typically decreased towards the anode and the aluminum concentration increased due to migration. Both of these factors could combine to favor precipitation of alumina near the anode in the soil and on the anode surfaces. If precipitation occurred on the anode surface itself it reduced conductivity dramatically, which would reduce the fraction of the applied voltage acting on the soil, thus reducing the migration rate. Replacing the anode could partially restore the conductivity.

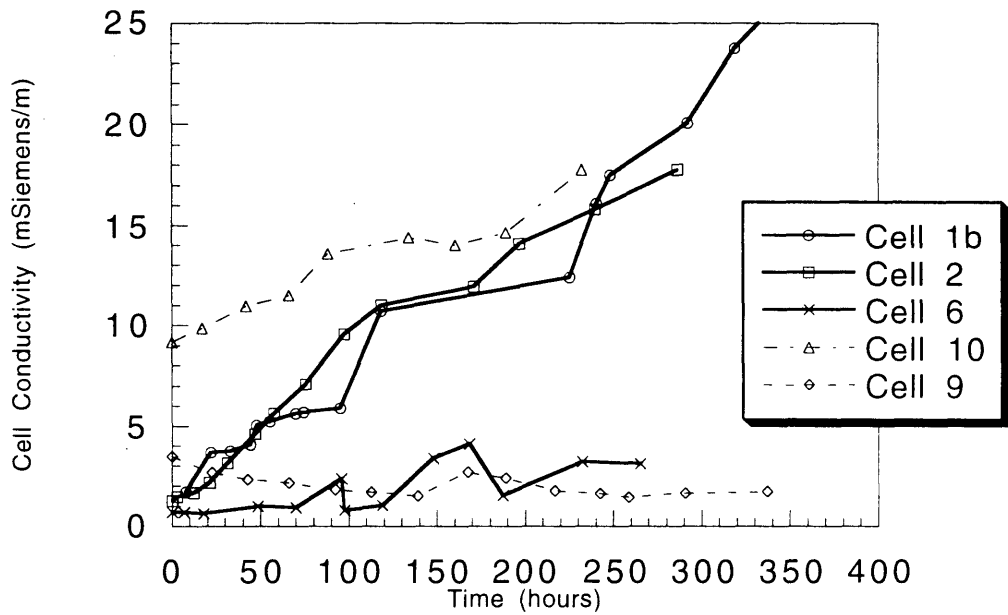


Figure 4.2.3: Small Cell Tests, conductivity as a function of time.

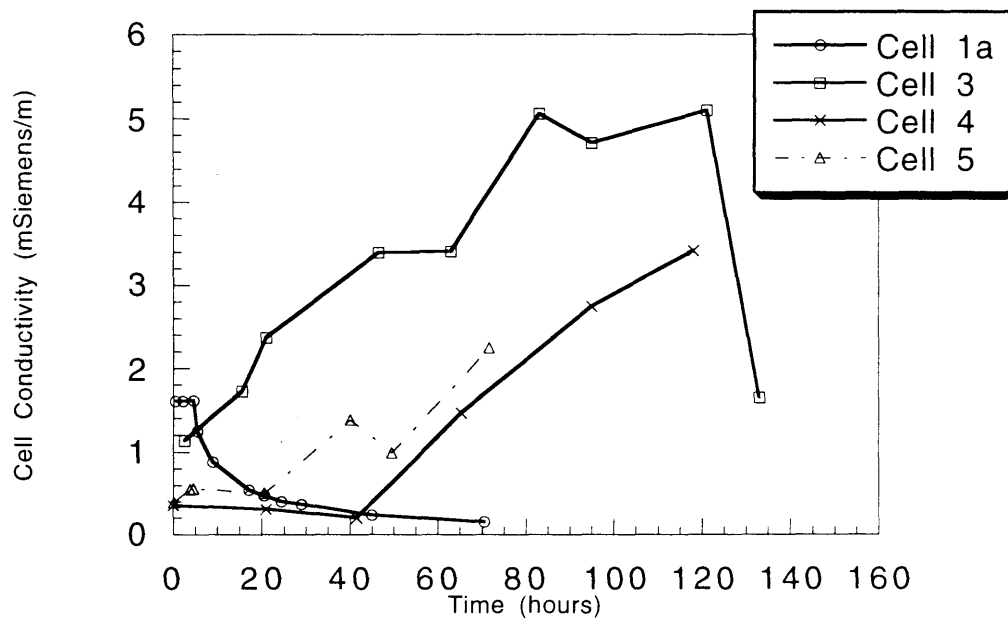


Figure 4.2.4: Small Cell Tests, conductivity as a function of time.

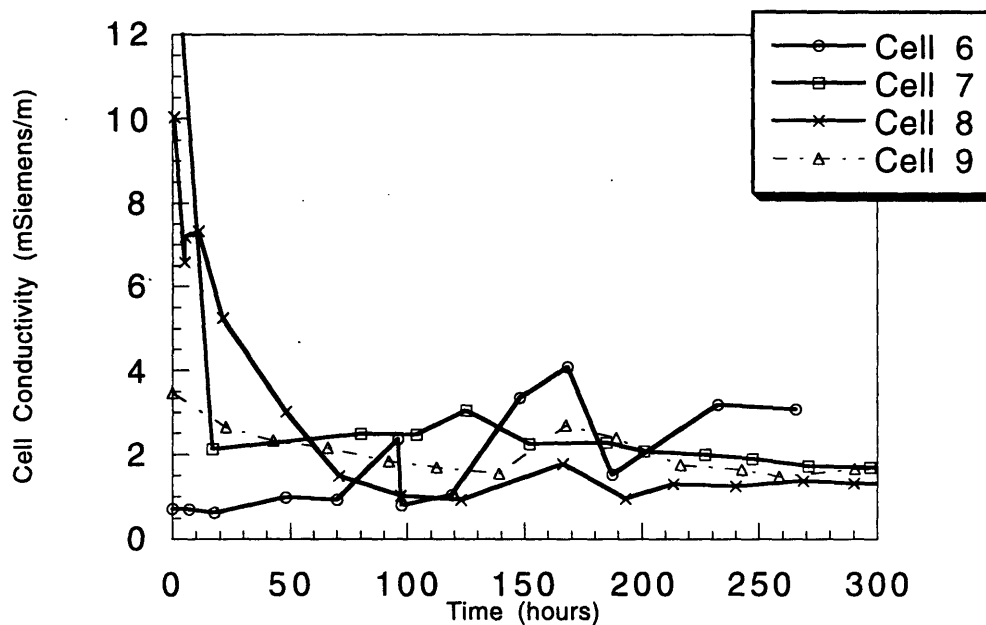


Figure 4.2.5: Small Cell Tests, conductivity as a function of time.

It is interesting to note the differences in conductivity curves as a function of sodium carbonate added to the soil. If a low amount was added such as in cell 7 and 9, the conductivity drops quickly at the beginning and then stabilizes. If a large amount of sodium carbonate is added such as in experiment 10, the conductivity increases, probably due to increased aluminum dissolution as the batch tests showed. In cell 8, there was a large amount of sodium carbonate added and the soil was allowed to soak in this solution before starting the migration. As a result, the concentration of aluminum in the pore solution was probably even higher than in cell 10, and when the current was turned on it may have combined with a drop in pH in the anode well to produce a low conductivity zone near the anode by aluminum precipitation. Clearly, the amount of sodium carbonate added in cells 8 and 10 was excessive.

Figures 4.2.6 and 4.2.7 plot the hexavalent chromium removal versus time. Cells with a higher pH and a higher current or voltage display a much higher removal rate, particularly at the beginning of a remediation. In cell 7, the anode and cathode polarities were accidentally reversed at the beginning of the experiment (second and third day), which resulted in the nearly flat section at the beginning of the removal plots for cell 7. If this horizontal piece of the curve were removed from the plot as if the reversal of the poles had never occurred, the removal plots for cell 7 would closely resemble those of cell 9.

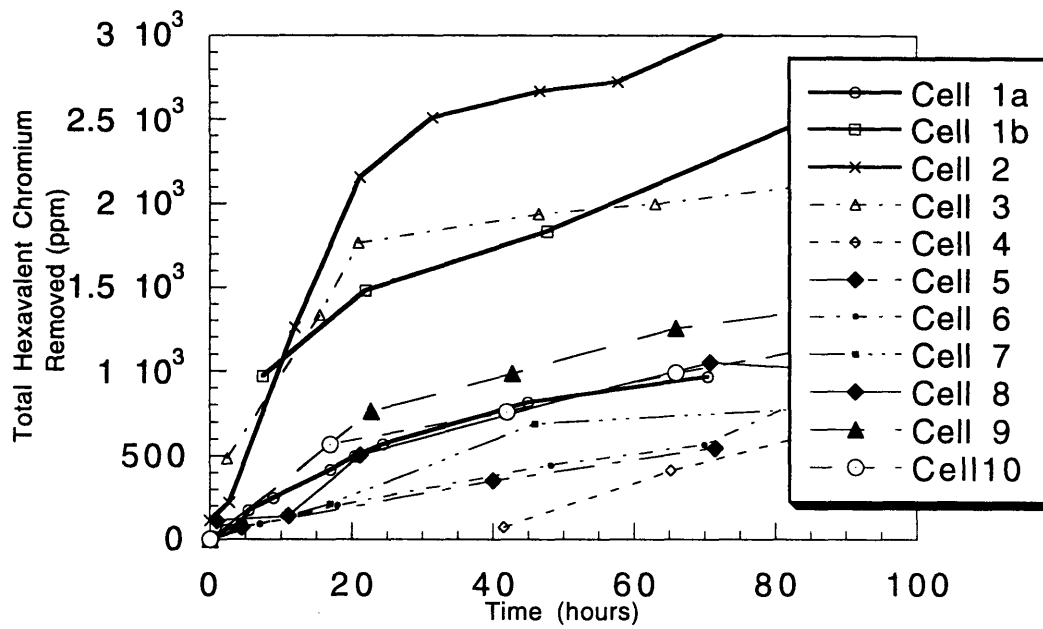


Figure 4.2.6: Small Cell Tests, hexavalent chromium removal.

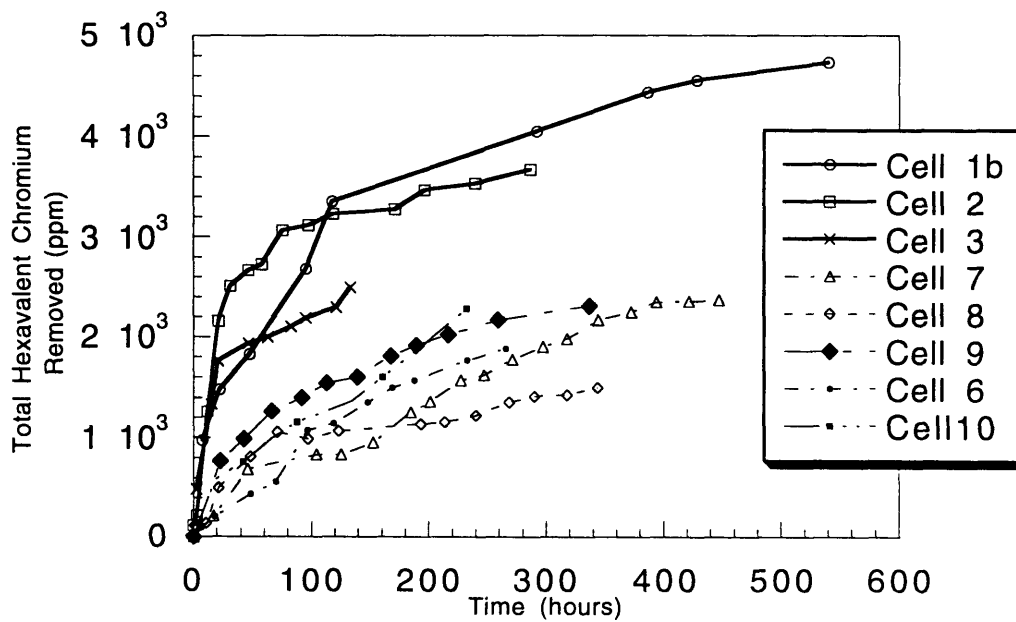


Figure 4.2.7: Small Cell Tests, hexavalent chromium removal.

Figures 4.2.8 and 4.2.9 show the hexavalent chromium removal as a percent of the total hexavalent chromium present in the soil initially, since the goal of a soil remediation would be stated as a percent removal or a reduction to a certain concentration level. Furthermore, the batch tests demonstrated that the amount of chromate salts present in the soil initially affects the dissolution rate significantly. Therefore, percentage chromate removal is a much more valid basis of comparison for electroremediation tests.

Figures 4.2.10 and 4.2.11 show the total aluminum removal from the soil for various tests, but they do not indicate clear trends, because the amounts of aluminum that precipitated due to pH variations is not accounted for. The anode pH briefly dropped as low as 8.5 in several tests due to unreliable pH control. At pH below 10 the solubility of aluminate is greatly reduced as figure 2.8.1 shows. Aluminum precipitation was not a factor in cell 2 and 9, which indicate a higher removal of aluminum when sodium carbonate is applied to the soil. The batch tests also indicated this enhancement of aluminum dissolution by sodium carbonate. Aluminum precipitation likely occurred in cell 8, because it removed less aluminum than cells 7 and 9 despite a larger sodium carbonate addition, initially.

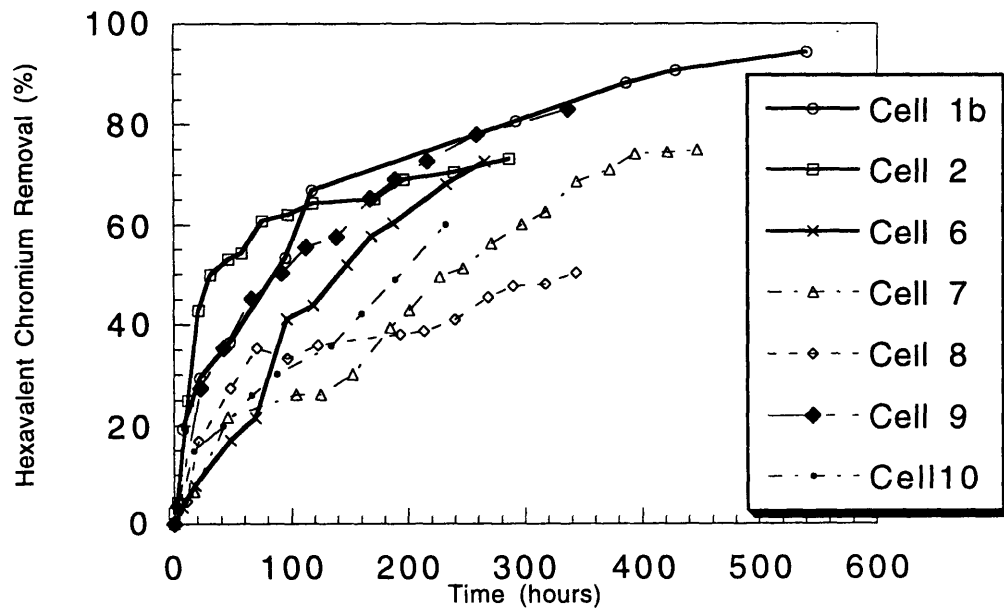


Figure 4.2.8: Small Cell Tests, % hexavalent chromium removal.

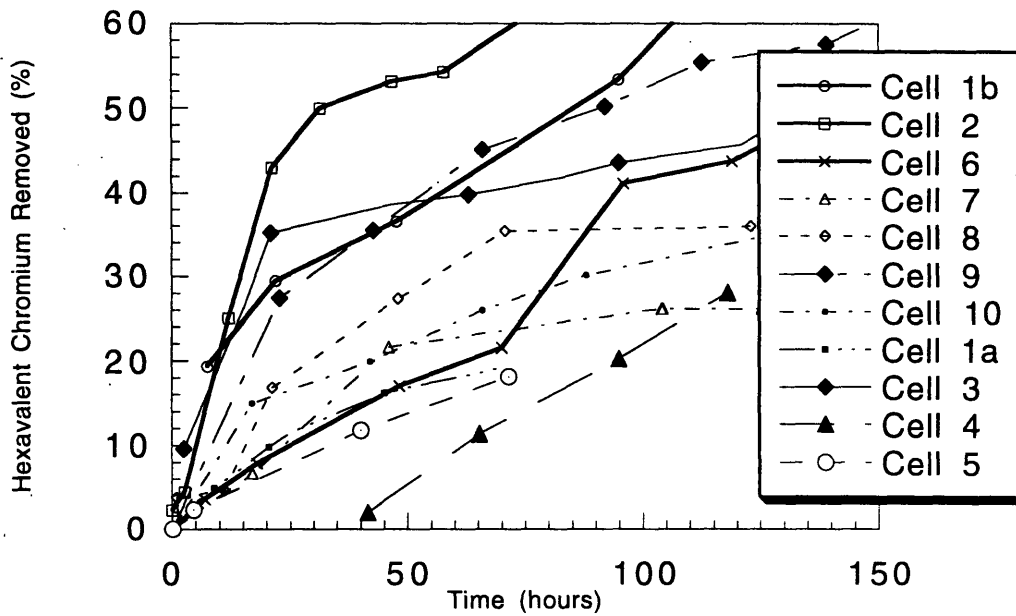


Figure 4.2.9: Small Cell Tests, % hexavalent chromium removal.

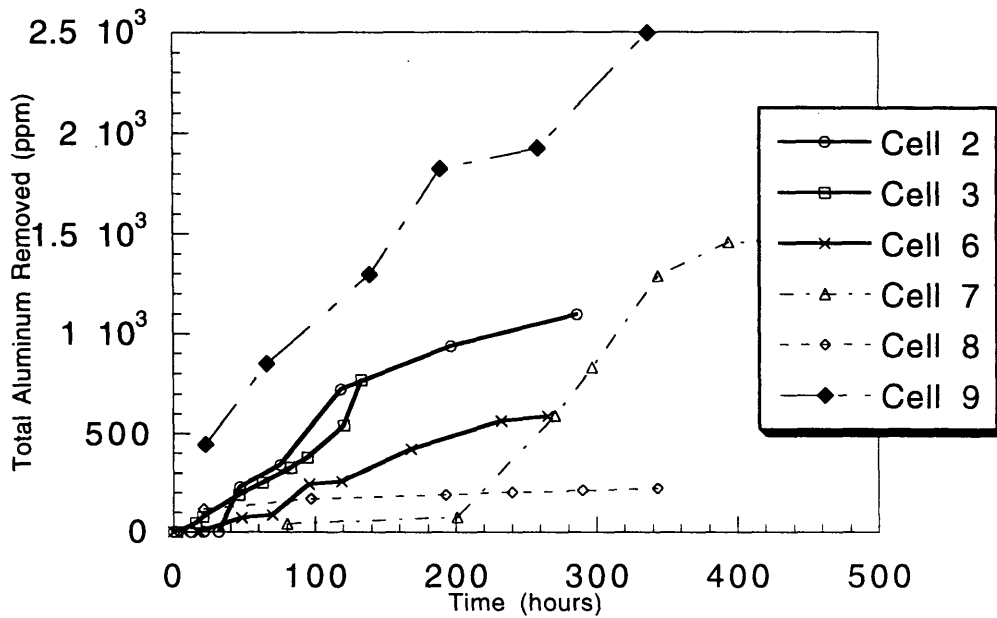


Figure 4.2.10: Small Cell Tests, aluminum removal.

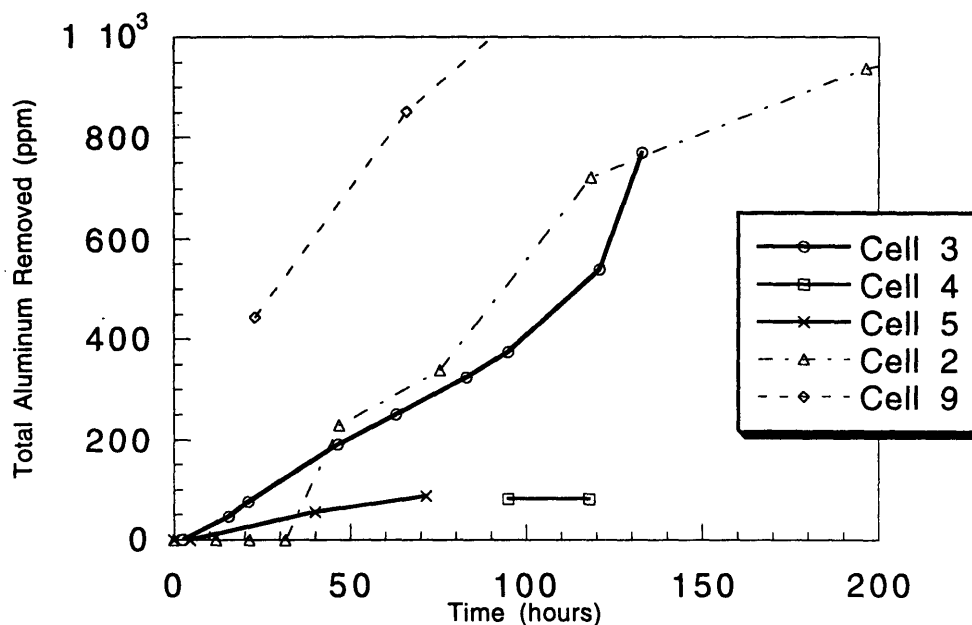


Figure 4.2.10: Small Cell Tests, aluminum removal.

An important operating cost in electroremediation is electrical energy. In chapter 2, remediation efficiency was defined as the chromate removed relative to the energy expended. To determine the relative efficiencies of the small cell tests, figures 4.2.12, 4.2.13 and 4.2.14 were plotted. These plots indicate that despite their lower chromate removal rate, cells operated at lower currents are more efficient. Also, a small initial addition of sodium carbonate improves efficiency, as the plot of cell 9 indicates. The result for cell 8 lies below those of cells 7 and 9, because a precipitate prevented migration, as described earlier (refer to figures 4.2.10 and 4.2.7). The results of cell 10 and cell 8 imply that a large sodium carbonate addition to the soil or soaking of the soil at the beginning of a remediation experiment has a detrimental effect. It contrast cell 7 and 8 show that interrupting the current temporarily during a later stage of an experiment when chromate removal rate has become low can improve it slightly when current is turned back on.

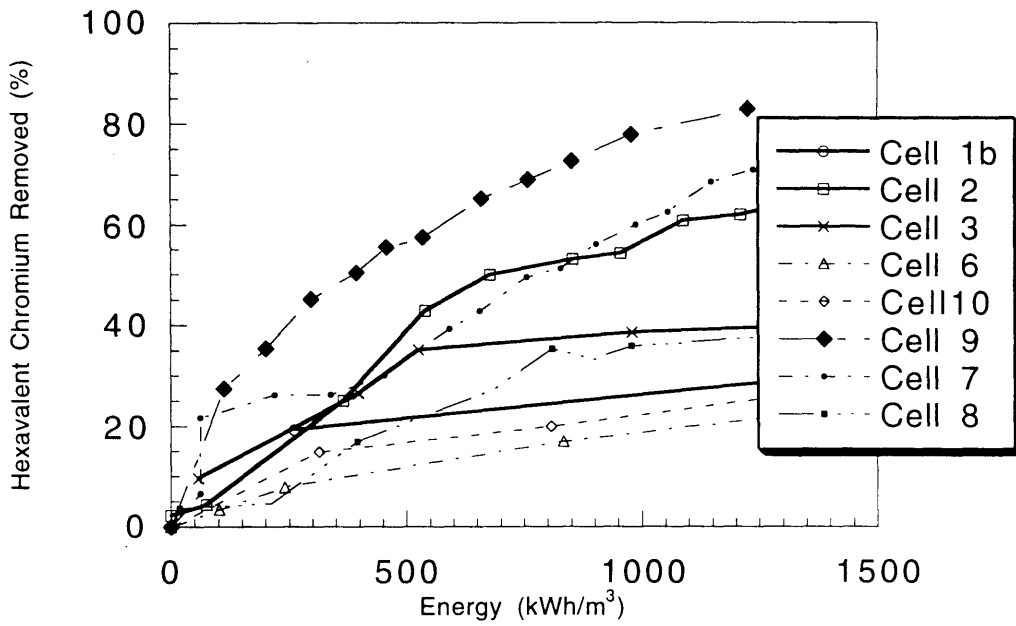


Figure 4.2.12: Small Cell Tests, remediation efficiency.

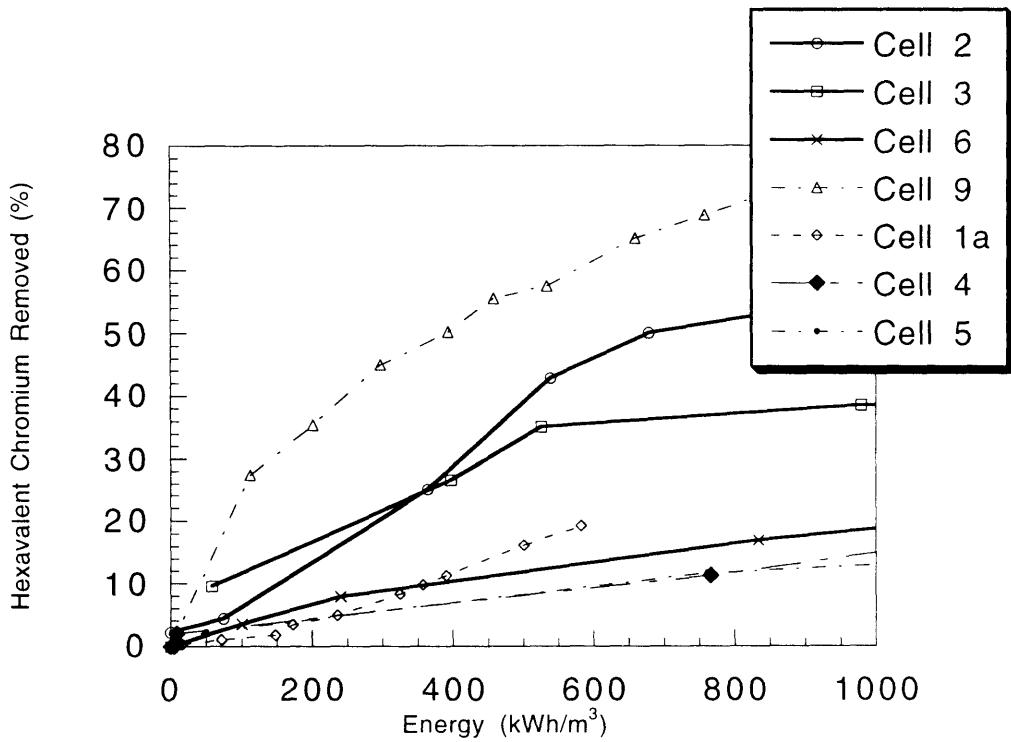


Figure 4.2.13: Small Cell Tests, remediation efficiency.

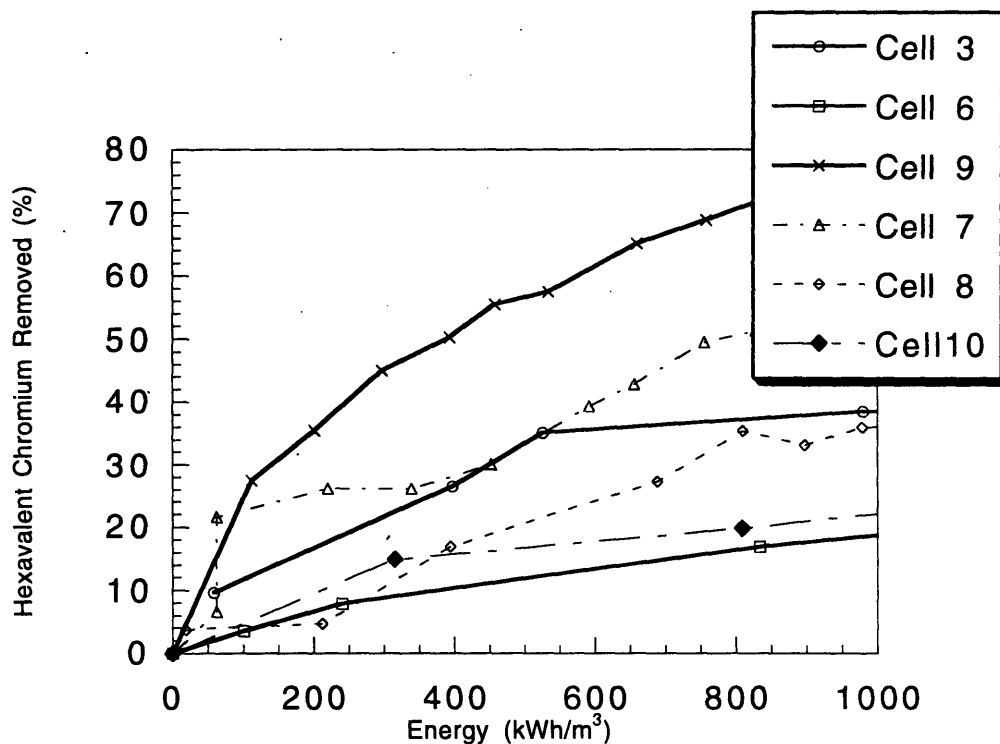


Figure 4.2.14: Small Cell Tests, remediation efficiency.

Figures 4.2.15 and 4.2.16 give the hexavalent chromium distribution that remained in the soil and the pore water after the remediation. The undissolved hexavalent chromium in the soil tends to increase towards the anode (figure 4.2.16). Several kinetic factors explain the decrease in dissolution rate towards the anode. The first factor is that the chromate concentration in the pore water increases towards the anode (figure 4.2.15), which can be explained by imagining a series of control volumes along the cell. The control volumes near the anode would decrease in chromate concentration only slowly since chromate ions that move out of the volume toward the anode will mostly be replaced by chromate ions coming from the cathode side of the volume; the control volumes near the cathode would decrease in chromate concentration more quickly because chromate ions that move out of the volume toward the anode would mostly be replaced by hydroxide ions or carbonate ions coming from the cathode side of the volume. The second factor is that the pH and carbonate concentrations decrease from cathode to anode, by the same migration mechanism. The inconsistent distribution of cell 7 resulted from the reversal in the electric poles that occurred during part of the remediation.

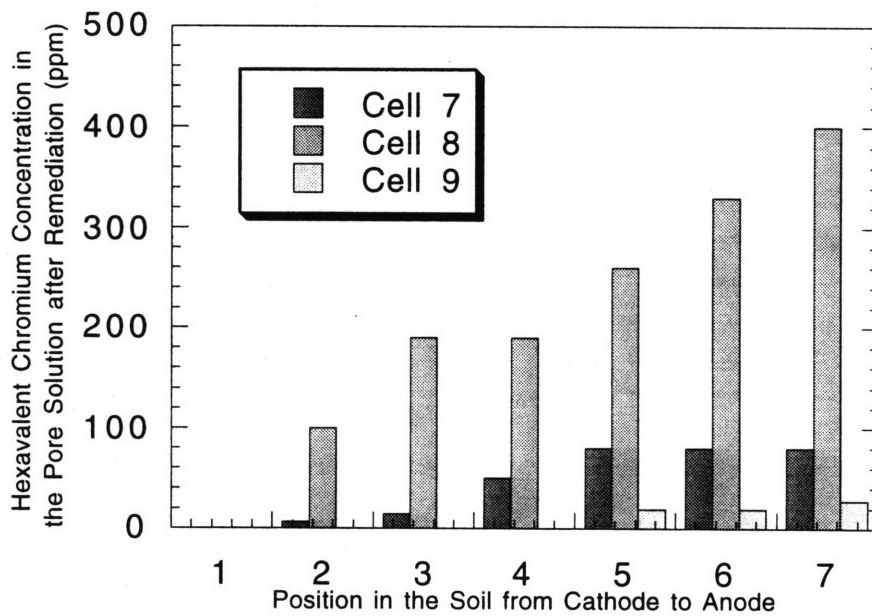


Figure 4.2.15: Small Cell Tests, distribution of hexavalent chromium in the pore solution at the end of electroremediation.

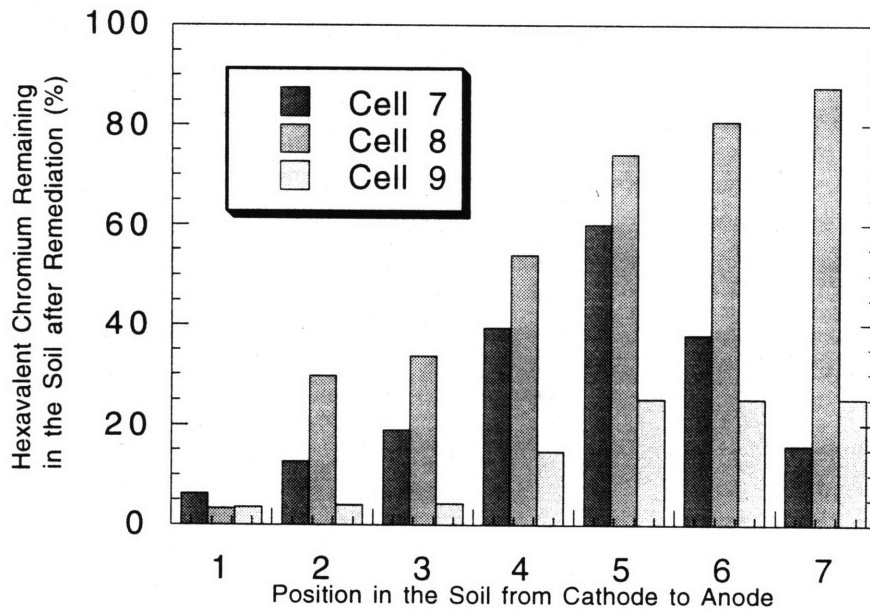


Figure 4.2.15: Small Cell Tests, distribution of hexavalent chromium remaining in the soil at the end of electroremediation.

Theoretically, a current efficiency of 100 % occurs when all of the current is carried by chromate ions and its corresponding cation (see also section 2.1). Therefore, the current efficiency may be calculated by plotting the amount of charge moved by the chromate ions removed versus the amount of charge passed by the electrical current. The amount of charge carried by the chromate ions is measured in equivalents of chromate. An equivalent of chromate is defined as one mole of chromate removed multiplied by two, because each chromate ion has a charge of minus two. The current passed is measured in Faradays. One Faraday is 96500 Coulombs, and a Coulomb is an Ampere-second. Since for every chromate ion that is removed at the anode, its corresponding cation is removed at the cathode, a current efficiency of 100 % means that one equivalent of chromate requires two Faradays of charge to be passed. Figures 4.2.17 and 4.2.18 give plots of equivalents chromate removed versus charge passed for the small cell tests. The decreasing slope of the plots corresponds to a decrease in current efficiency. A sharp decrease in the slope occurs in several plots and occurs nearly at the same time as aluminum begins to appear in the anode well. The addition of sodium carbonate to the soil did not produce the increases in current efficiency that they were intended to produce, because far too much sodium carbonate was added at once, resulting in much of the current moving carbonate rather than chromate ions.

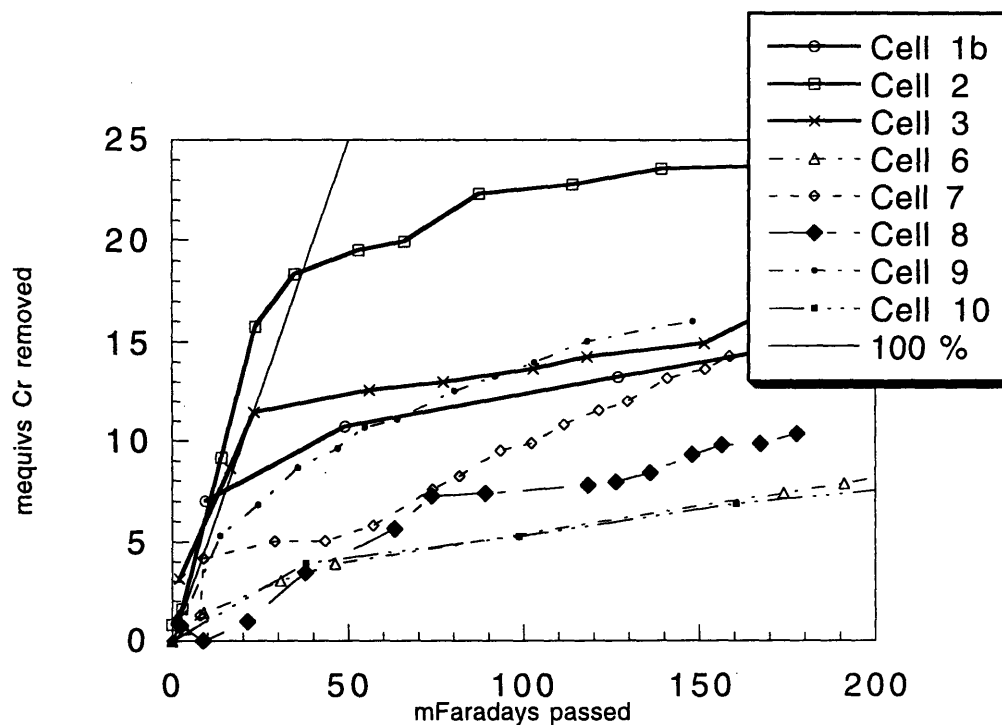


Figure 4.2.17: Small Cell Tests, current efficiency.

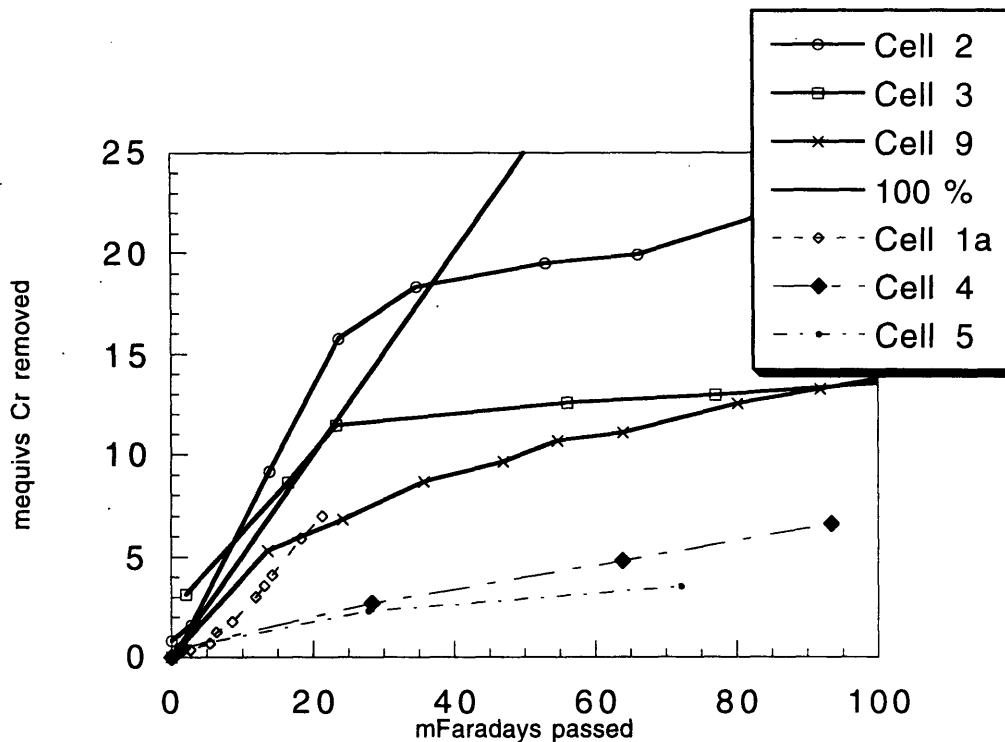


Figure 4.2.18: Small Cell Tests, current efficiency.

Calcium and magnesium were measured in the cathode well during several experiments. In the NaOH experiments, the calcium removal at the cathode did not match the chromate removal at the anode with sufficient consistency to make a conclusion on their stoichiometric relationship. In the Na₂CO₃ experiments, calcium and magnesium removal rates were very low in comparison to chromate removal, which demonstrates the Na₂CO₃ to be very effective at precipitating calcium out of solution.

The soil tended to collapse slightly in the tube during the longer experiments indicating a breakdown in the soil structure and a decrease in the porosity. Aluminum dissolution causes most of the breakdown in the soil structure. Theoretically, decreases in porosity lead to decreases in ion mobility.

4.3 Large Cell Tests

Based on the small cell tests, it was concluded that in order to control the electroremediation process better and to improve understanding of its subprocesses requires having access to the soil and pore fluid while an experiment is ongoing. The large cell apparatus allows sampling of the soil and addition of chemicals to the pore fluid during an experiment. Also, the larger soil volumes of the large cell reduce some of the error due to soil variability. Two large cell tests were performed. Figures 4.3.1 to 4.3.13 summarize the results for these two experiments.

The first large cell ran at a constant voltage of 200 V/m and the second at a constant current of almost 10 A/m². Initially, cell 1 and 2 had 8 and 10 % Na₂CO₃ (stoichiometric equivalent of hexavalent chromium) added to the soil, respectively, which resulted in relatively high initial conductivities. Figure 4.3.1 indicates the conductivity of cell 1 to rise very rapidly and the conductivity falling slightly in cell 2. The rapid rise in cell 1 was a result of the soil pH rising rapidly. As explained in the theory section, a rise in pH increases the dissolution of aluminum which increases the ionic strength and thus increases conductivity. The rise in conductivity reinforces itself, because it increases current thus increasing the rate of electrolysis at the cathode, which further increasing the pH. Based on this theory, several measures were taken in cell 2 to prevent the pH from rising rapidly in the soil. In cell 2 a well was placed at the cathode, while in the first large cell test the cathode was placed directly into the soil. The well at the cathode increased the solution volume slowing pH rises due to electrolysis. Furthermore, experiment 2 ran at a much lower constant current preventing the current from rising, which prevented the trend from reinforcing itself. Large cell 2 had a nearly constant conductivity plotted in figure 4.3.1. Furthermore, at 88 and 171 hours the cathode well solution was replaced with a fresh solution of 0.5 g/L Na₂CO₃, to reduce the pH which induced subsequent declines in the conductivity. Figures 4.3.2 and 4.3.3 give plots of pore solution pH versus time for the large cell tests. As expected from theory, the reduction of aluminum dissolution in cell 2 resulted in the much higher current efficiency indicated in figure 4.3.4.

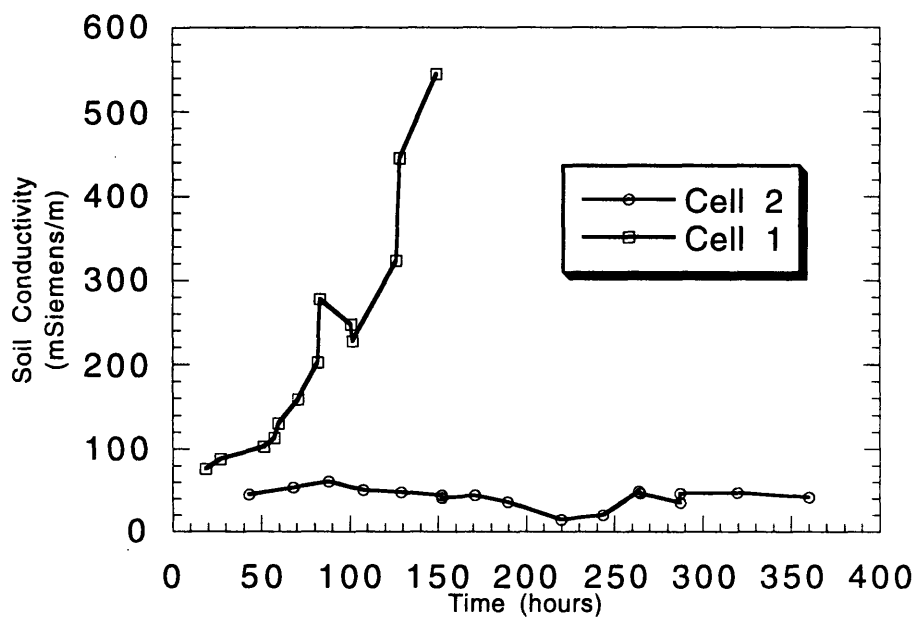


Figure 4.3.1: Large Cell Tests, soil conductivity versus time.

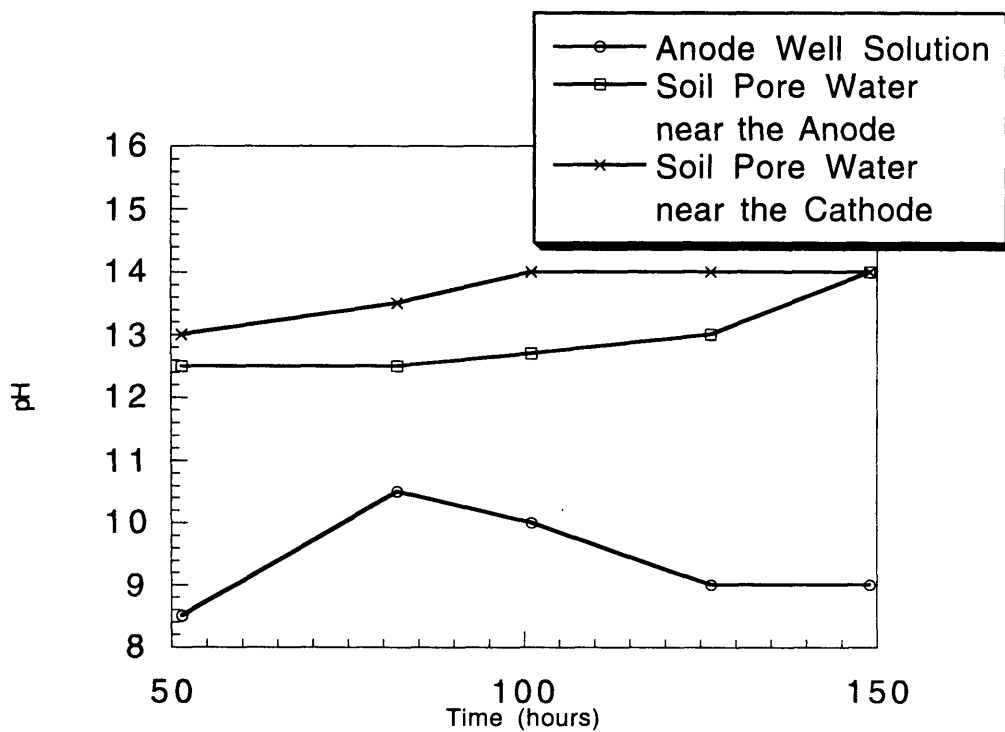


Figure 4.3.2: Large Cell Test 1, pH versus time at various positions.

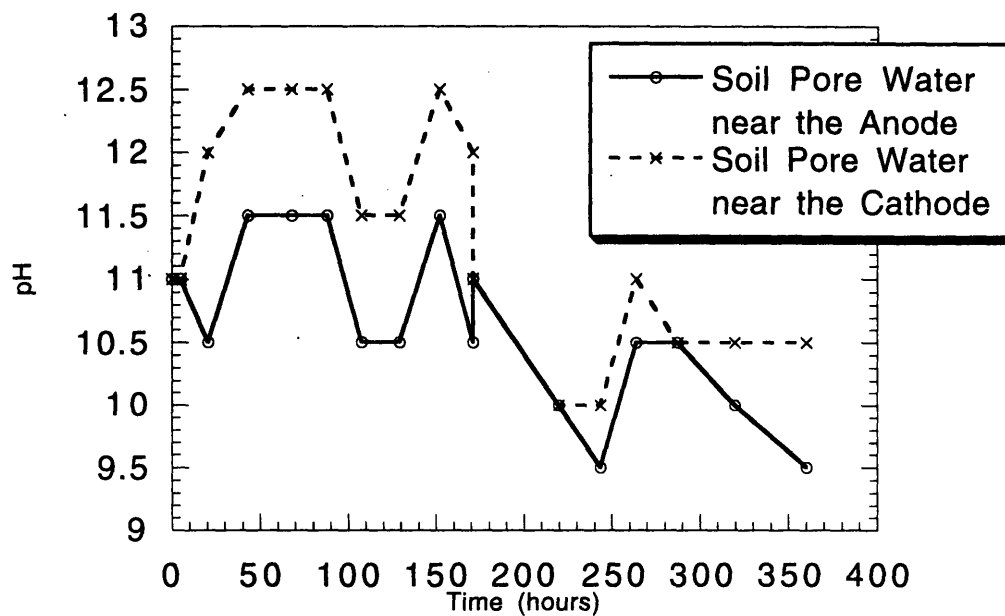


Figure 4.3.3: Large Cell Test 2, pH versus time at various positions.

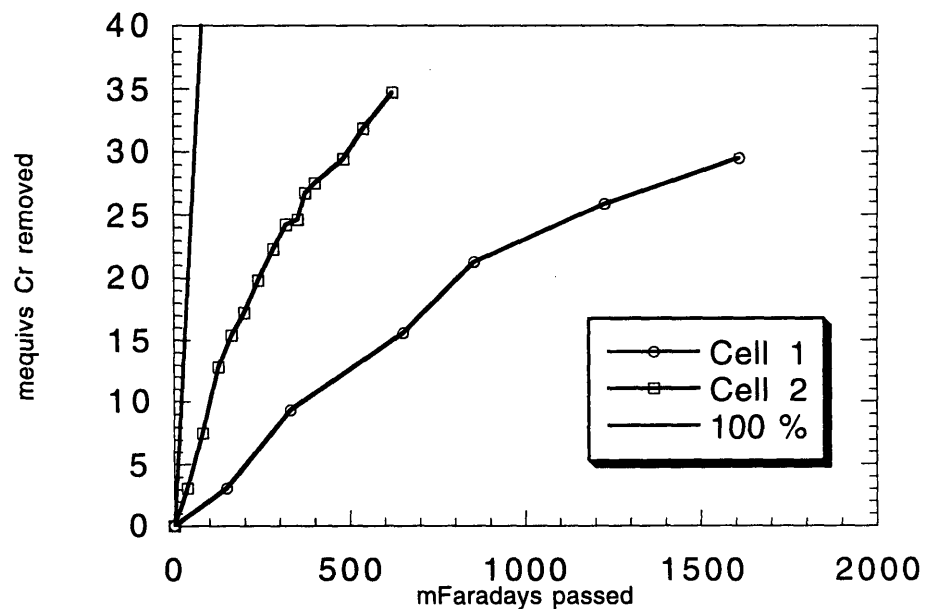


Figure 4.3.4: Large Cell Tests, current efficiency.

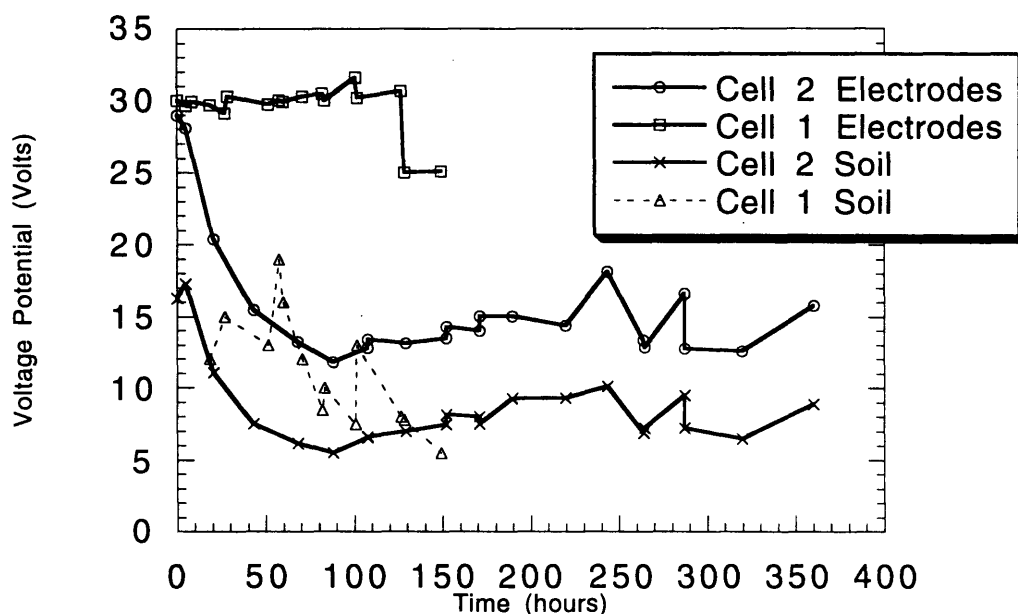


Figure 4.3.5: Large Cell Tests, voltages applied across the soil and across the electrodes.

In large cell test 1, a precipitate formed on the anode surface, which produced a large voltage drop. Furthermore, a closer investigation of the voltage distribution showed another unexpected large voltage drop across the membrane between the anode well and the soil, which is suspected to be caused by the same precipitation process occurring on the membrane as on the electrode. As a result, only a fraction of the applied voltage effectively contributed to the migration of ions through the soil. The applied voltage potential and the voltage potential across the soil are plotted in figure 4.3.5. The sharp increases in the voltage across the soil in cell 1 correspond to times when the precipitate covered anode was replaced with a clean electrode. The subsequent gradual decreases correspond to the gradual build up of precipitate on the electrode surface. Since the membrane could not be replaced during the experiment, the slowly increasing voltage loss there could not be avoided. In cell 2, the precipitation problem never appeared. The voltage curves for cell 2 thus run parallel to each other and mirror the conductivity plot.

From analysis of the white precipitate it was concluded that it was an aluminum compound, such as aluminum oxide (Al_2O_3). The precipitation occurs when a large pH gradient causes large amounts of aluminum to dissolve near the cathode and, subsequent to migrating towards the anode, to precipitate near it. The solubility diagram of aluminum presented in section 2.8.1 shows that this mechanism is likely to occur if a pH gradient from 9 to 12 exists, and if the dissolved

aluminate concentration is sufficiently high. An analogous clogging of the soil pores due to calcium precipitation near the cathode is reported by Acar and Alshawabkeh [1993] to hinder transport of lead in an electroremediation experiment at low pH.

Figures 4.3.6 to 4.3.8 show the dissolved chromate and aluminate concentrations in the pore water for both large cell tests. The dissolved aluminate levels for cell 2 are considerably lower than for cell 1, and therefore the concentration did not cause significant precipitation such as occurred in cell 1. The continuous rise in aluminum concentration in cell 1 reflects the rise in the pH. A sodium carbonate addition caused the spike in chromate concentration near 100 hours of cell 1. Similarly, a combination of sodium carbonate addition and interrupting the current caused the spike in figure 4.3.8 at 110 hours. In cell 2, the current was interrupted again at 152, 171 and 287 hours, which unexpectedly resulted in drops in chromate concentration in the pore solution due to drops in the pH (see figure 4.3.3.). Sodium carbonate should have been added to the soil at these times if the current interruptions were to have increased chromate concentration. The pH drops probably occurred due to an equilibration of the pore solution with carbon dioxide from the atmosphere. Such an equilibration would only occur if the pH had become dominated by hydroxide rather than carbonate, since carbonate is a pH buffer. If no new sodium carbonate is added to the soil or cathode well solution, then the carbonate ions in the pore solution would gradually be replaced by hydroxide ions migrating in from the cathode. In cell 2, the sodium carbonate addition at time 88 hours was ineffective, because the sodium carbonate was added locally to the top soil layer and did not have time to diffuse downward, before migrating to the anode well. Therefore, sodium carbonate additions enhance chromate dissolution most effectively in conjunction with brief current interruptions or by adding it in the cathode well continuously with an electrode wash, as was done in several of the small cell tests.

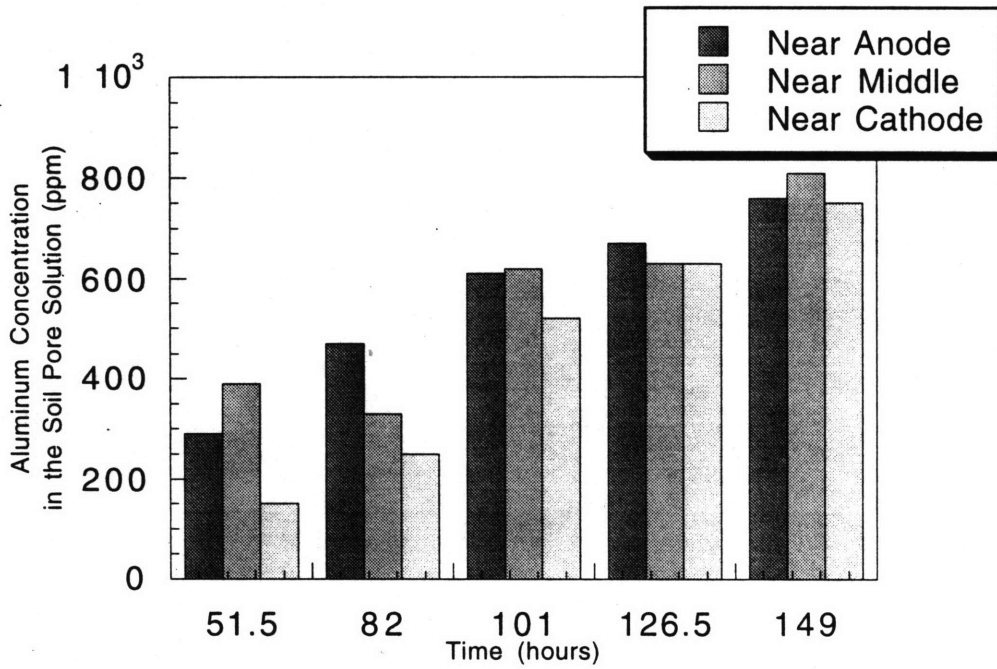


Figure 4.3.6: Large Cell Test 1, aluminum concentrations in the pore water as a function of time in various positions.

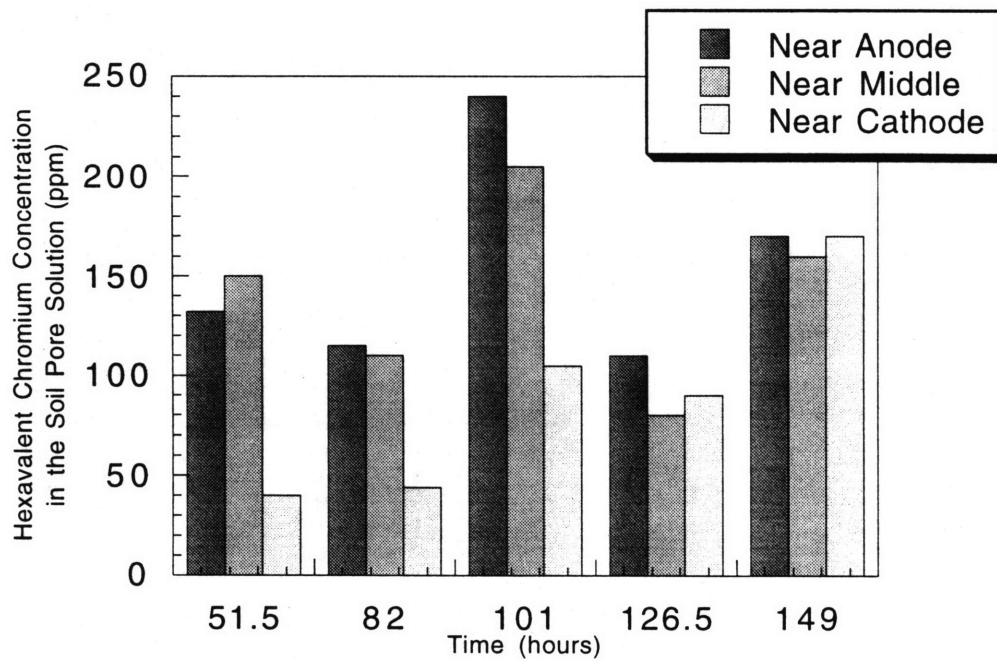


Figure 4.3.7: Large Cell Test 1, hexavalent chromium concentrations in the pore water as a function of time, in three positions.

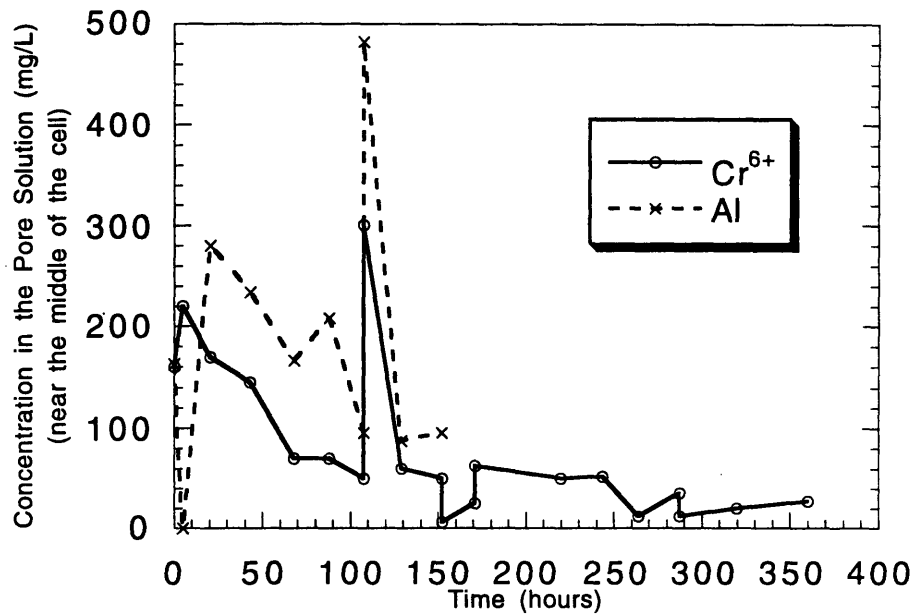


Figure 4.3.8: Large Cell Test 2, aluminum and hexavalent chromium concentrations in the pore water as a function of time, halfway between cathode and anode

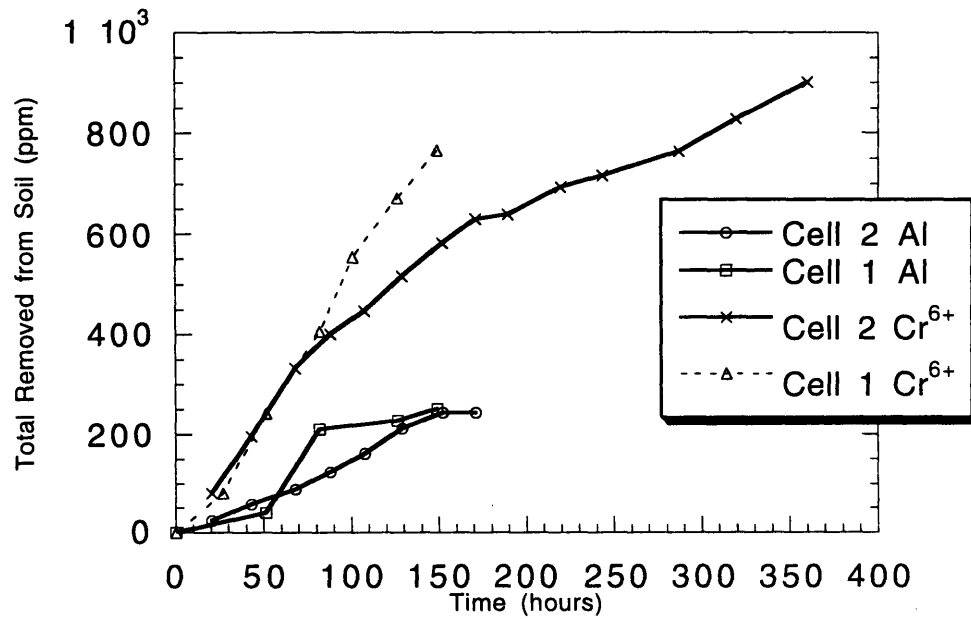


Figure 4.3.9: Large Cell Tests, hexavalent chromium and aluminum removal.

Figure 4.3.9 compares the removal rate of chromate and aluminate for the large cell tests. The chromate removal rate is considerably higher than the aluminate removal rate despite its lower concentration in the pore solution, because it has twice as much negative charge. The similarity in the hexavalent chromium removal curves initially reaffirms that the rate limiting factor in the remediation process is the dissolution of the contaminant and not the migration process, since cell 1 was operated at a much higher voltage (figure 4.3.5). The sudden decrease in the aluminum removal rate of cell 1 indicates the onset of precipitation. This time (82 hours) coincides with the addition of a large amount of sodium carbonate (50% stoichiometric equivalent of hexavalent chromium) implying that it triggered the precipitation under the prevailing pH gradient.

The percent removal of hexavalent chromium is plotted versus time and energy in figure 4.3.9 and 4.3.10 respectively. In cell 2, electromigration removed hexavalent chromium from the soil almost seven times as efficiently as in cell 1, with respect to energy consumption per unit of treated cell. This difference is very convincing evidence of the advantage of operating at a constant low current. The removal of chromate as a function of energy of large cell 2 lies below that of small cell 9, and above that of small cell 2, making it the second best result overall.

Figure 4.3.11 illustrates the distribution of the hexavalent chromium that remained in the soil after remediation. As expected, the undissolved chromate concentration increases from cathode to anode. Cell 1 removed an average of 30 % hexavalent chromium, and cell 2 an average of 40 %. These removals are not very high, but the removal in cell 2 could easily have been continued, especially if more sodium carbonate had been added to the soil.

The large test cell apparatus has a chamber filled with water located below the soil separated from it by a piece of filter paper, to simulate the groundwater. During the experiments hexavalent chromium diffused downward at a low rate, because diffusion is much slower than migration. During current interruptions of more than 48 hours however, the hexavalent chromium concentration reached a significant level. In a field test distances will be larger, while diffusion rates will remain the same, reducing the risk of groundwater contamination.

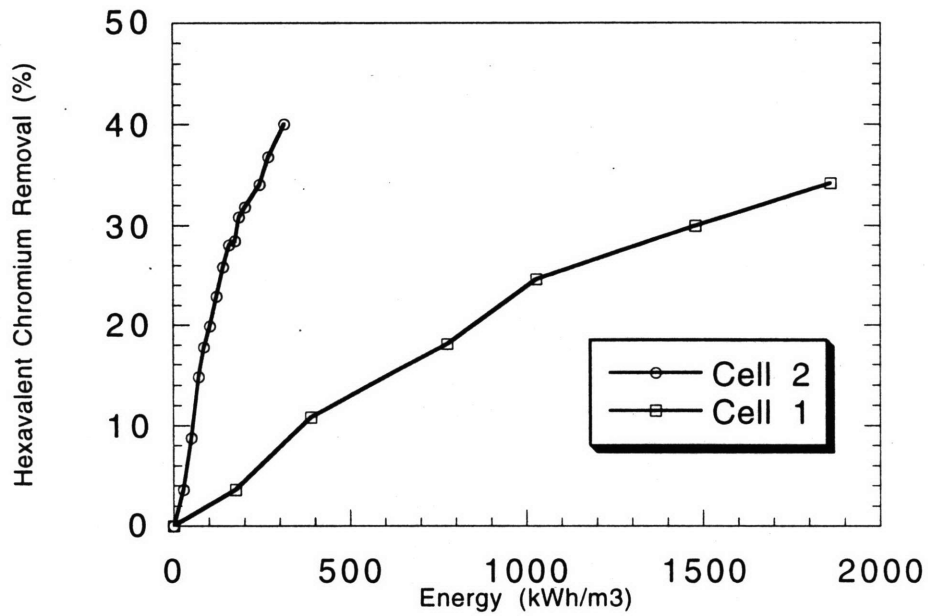


Figure 4.3.10: Large Cell Tests, electroremediation efficiency.

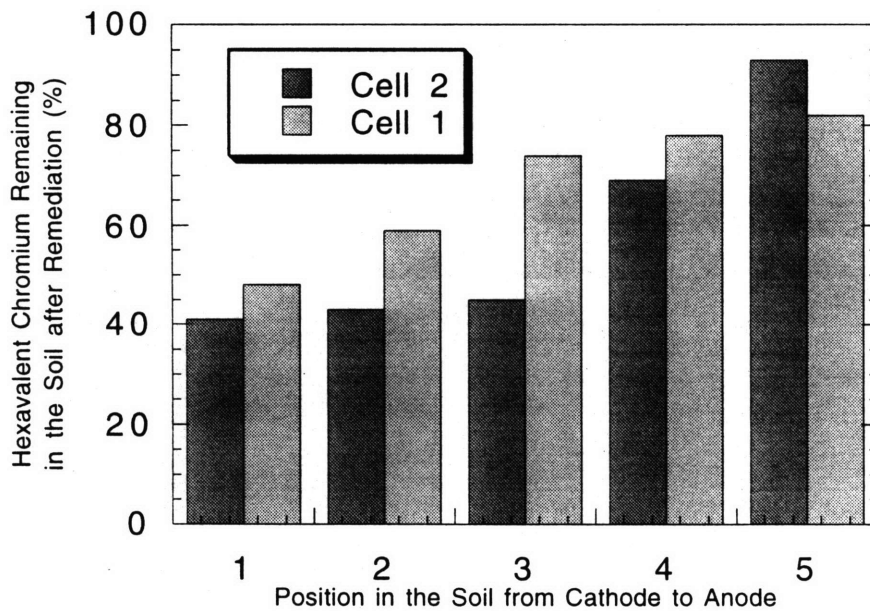


Figure 4.3.11: Large Cell Tests, concentration of undissolved hexavalent chromium remaining in the soil after remediation in various positions.

5. Conclusions and Future Work

The research for this thesis had as its primary goal to achieve a high degree of hexavalent chromium removal by electromigration from a COPR soil, and as a secondary goal to reduce the energy consumption of this electroremediation process. The removal of chromate can be subdivided into a chromate dissolving step and a chromate migration step.

In the first experiment performed at pH 13 (small cell 1a/1b), 95 % of the chromate was removed from the soil by electromigration. However, the experiment expended a very large amount of electrical energy. Experiments at lower pH reduced the energy expenditure of these experiments (small cell 2 and 3), but also lost some of the effectiveness in total hexavalent chromium removal. Subsequently, enhancing the dissolution step through the addition of sodium carbonate to the soil was investigated as a means of achieving a higher removal rate while maintaining the improvements in energy utilization by operating at a low constant current (small cell 7, 8 and 9). In small cell 9, electroremediation removed 85 % of 2300 ppm (moist soil weight) chromate, at an energy expenditure of less than 1250 kWh/m³ of soil, which represented a great improvement. Finally, two large cell tests were performed to obtain a better understanding of the individual processes involved in the remediation.

The dissolution step limits the hexavalent chromium removal rather than the migration step. Therefore, increases in applied voltage do not significantly increase removal rate, but do substantially increase energy expenditure. In order to sustain transport by migration, pH must be controlled carefully to avoid precipitation reactions that could clog soil pores or foul the electrode surfaces. If the anode pH falls below 10.5, a risk of aluminum precipitation occurs. Keeping the aluminum dissolution rate in the soil at a low level reduces this risk.

The energy expenditure can be most effectively reduced by operating at a low constant current (below 10 A/m²). Possibly, even lower energy expenditures can be achieved in the future by operating at even lower current densities. Furthermore, current efficiency improves by maximizing chromate dissolution while minimizing aluminate dissolution. The relative dissolution rates of these ions is strongly affected by pH and the addition of sodium carbonate. In the experiments performed, the best results were achieved by maintaining the soil in the range of pH 10.5 to 11.5. This pH control could most effectively be achieved by washing both the anode and cathode with a sodium carbonate buffer solution. Determining the optimal method and rate of

sodium carbonate addition should be the subject of future investigations into the electroremediation of COPR soils and could be greatly aided by the development of a more detailed numerical model of the chemistry for simulations of the remediation process. The model should include the following mechanisms affecting the carbonate concentration in the pore solution:

- equilibration with atmospheric carbon dioxide.
- reaction with hydrogen migrating into the soil from the anode to form bicarbonate.
- migration of carbonate into the soil from the cathode.
- migration of carbonate out of the soil to the anode well.
- addition of sodium carbonate directly to the top of the soil and its diffusion downward.
- precipitation with calcium and other metals present in the pore water. Calcium chromate should not be the only source of soluble calcium considered.

The experimental results allow some conclusions on the addition of sodium carbonate. Sodium carbonate should be added gradually, since high concentrations lead to excessive dissolution of aluminum. Sodium carbonate additions to the soil are more effective if the current is interrupted for a few hours to allow diffusion. Sodium carbonate in the soil can be replenished continuously by migration from the cathode well, but migration alone probably does not suffice to maintain sufficient concentration. Certainly, there should be an initial addition of sodium carbonate directly to the soil, since migration from the cathode would take too long. By the end of the first day of remediation, there should be a total sodium carbonate addition of at least 30 and less than 100 percent of the stoichiometric equivalent of chromate in the soil initially, which corresponds to 1.5 to 5 g Na_2CO_3 / kg of soil, for a 2500 ppm Cr^{6+} contamination. Monitoring the pore water for large decreases in the chromate concentration can guide sodium carbonate addition.

In summary, hexavalent chromium contamination was removed from a COPR soil effectively by electroremediation. The most important mechanisms of the process were investigated, and parameters influencing energy expenditure and removal rate were isolated to improve control of the electroremediation process. The most important of these are the operation at low current densities (10 A/m^2) and the control of pH within the range 10 to 12. Table 5.1 summarizes the ranges of control parameters that achieved the best results during experimentation.

Table 5.1: Upper and Lower Bounds on Control Parameters.

Control Parameter	Reduction of Aluminum Dissolution	Avoidance of Aluminum Precipitation	Augmentation of Chromate Dissolution
pH	< 12	> 10	> 10
Na ₂ CO ₃ Concentration	< 1 g/L	< 20 g/L	> 0.1 g/L

6. References

- Acar, Y.B., and Alshawabkeh, A.N. (1993) Principles of Electrokinetic Remediation, *Environ. Sci. Technol.*, **27** (13), pp. 2638-2647.
- Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppala, S., Bricka, M., Parker, R. (1995) Electrokinetic Remediation: Basics and Technology Status, *J. Hazard. Materials*, **40**, pp. 117-137.
- Anderson, L.D., Kent, D.B., Davis, J.A. (1994) Batch Experiments Characterizing the Reduction of Cr(VI) Using Suboxic Material from a Mildly Reducing Sand and Gravel Aquifer, *Environ. Sci. Technol.*, **28**, pp. 178-185.
- Arman, A. (1992) A Review of Remediation Technologies in the USA, in *Environmental Geotechnology*, Usmen, Acar (Eds.), Balkema, Rotterdam, pp. 385-389.
- Bartlett, R.J., James, B.R. (1988) Mobility and Bioavailability of Chromium in Soils, in *Chromium in Natural and Human Environments*, Nriagu, J.O., Nieboer, E. (Eds.), Wiley-Interscience, New York, pp. 267-304.
- Casagrande, L. (1949) *Geotechnique*, **1** (159); (1983) *J. Boston Soc. Civ. Eng.* **69** (255).
- Chambers, C.D., et al. (1991) *In Situ Treatment of Hazardous Waste Contaminated Soils*, 2nd ed., Noyes Data Corp., pp. 98-101
- CRC (1981) *Handbook of Chemistry and Physics*, 61st ed., Weast, R.C., Astle, M.J. (Eds.), CRC Press Inc., Boca Raton, Florida
- Cussler, E.L., Kopinsky, J., Weimer, J.A. (1983) The Effect of Pore Diffusion on the Dissolution of Porous Mixtures, *Chem. Eng. Sci.*, **38** (12), pp. 2027-2033.
- Deltcombe, E., deZoubov, N., Pourbaix, M. (1966) Chromium, Aluminum, in *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pourbaix, M. (Ed.), Pergamon Press, Elmsford, New York, pp. 256-271, pp. 168-176
- Dzenitis, J.M. (1996) Soil Chemistry Effects and Flow Prediction in Remediation of Soils by Electric Fields, Ph.D. dissertation, Massachusetts Institute of Technology, Mechanical Engineering Department.
- EPA (1995) Alkaline Digestion for Hexavalent Chromium, *Method 3060A*.
- Erdogan, H., Halasi-Kun, G.J. (1992) Cleanup of Contaminated Soil and Water at a Superfund Site, in *Environmental Geotechnology*, Usmen, Acar (Eds.), Balkema, Rotterdam, pp. 347-356.
- Hering, J.G. (1995) Implications of Complexation, Sorption and Dissolution Kinetics for Metal Transport in Soils, in *Metal Speciation and Contamination of Soil*, Allen, H.E., Huang, C.P., Bailey, G.W., and Bowers, A.R. (Eds.), Lewis Publishers, Boca Raton, pp. 59-86.

- Hicks, R.E., Tondorf, S. (1994) Electrorestoration of Metal Contaminated Soils, *Envir. Sci. & Technol.*, **28** (12), pp. 2203-2210.
- Hsieh, H.-N., Raghu, D., Liskovitz, J.W. (1990) An Evaluation of the Extraction of Chromium from Contaminated Soils by Soil Washing, in *Hazardous and Industrial Wastes*, Proceedings of the Twenty-Second Mid-Atlantic Industrial Waste Conference, Martin, J.P., Cheng, S.-C., Susavidge, M.A. (Eds.), Technomic Publishing Company, Inc., Lancaster, Pennsylvania, pp. 459-469.
- Hsieh, H.-N., Raghu, D., Liskovitz, J.W., Grow, J. (1989) Soil Washing Techniques for Removal of Chromium Contaminants from Soil, in *Hazardous and Industrial Wastes*, Proceedings of the Twenty-First Mid-Atlantic Industrial Waste Conference, Cole, C.A., Long, D.A. (Eds.), Technomic Publishing Company, Inc., Lancaster, Pennsylvania, pp. 651-660.
- Jacobs, R.A., Sengun, M.Z., Hicks, R.E., Probst, R.F. (1994) Model and Experiments on Soil Remediation by Electric Fields, *J. Environ. Sci. Health*, **A29** (9), pp. 1933-1955.
- James, B.R. (1996) The Challenge of Remediating Chromium-Contaminated Soil, *Environ. Sci. Technol./News*, **30** (6), pp. 248-251.
- James, B.R. (1994) Hexavalent Chromium Solubility and Reduction in Alkaline Soils Enriched with Chromite Ore Processing Residue, *J. Environ. Qual.*, **23**, pp. 227-233.
- James, B.R., Petura, J.C., Vitale, R.J., Mussoline, G.R. (1995) Hexavalent Chromium Extraction from Soils: A Comparison of Five Methods, *Environ. Sci. Technol.*, **29**, pp. 2377-2381.
- Khan, L.I., Rahman, M. (1995) Electrokinetic Decontamination of Millpond Sludge, in *Hazardous and Industrial Wastes*, Proceedings of the Twenty-Seventh Mid-Atlantic Industrial Waste Conference, Sengupta, A.K. (Ed.), Technomic Publishing Company, Inc., Lancaster, Pennsylvania, pp. 795-813.
- Lageman, R. (1993) Electroreclamation, Applications in the Netherlands, *Environ. Sci. Technol.*, **27** (13), pp. 2648-2650.
- Marshall, S. (1973) Chromium, in *Pollutant Removal Handbook*, Noyes Data Corp., Park Ridge, New Jersey, pp. 116-135.
- McIntosh, K.R., Huang, C.P. (1995) Transport of Hexavalent Chromium in Porous Media: Effect of an Applied Electrical Field, in *Hazardous and Industrial Wastes*, Proceedings of the Twenty-Seventh Mid-Atlantic Industrial Waste Conference, Sengupta, A.K. (Ed.), Technomic Publishing Company, Inc., Lancaster, Pennsylvania, pp. 814- 823.
- Morel, F.M.M., Hering, J.G. (1993) *Principles and Applications of Aquatic Chemistry*, Wiley, New York.
- Ouki, S.K., Neufeld, R.D. (1989) Interactions of Hexavalent and Trivalent Chromium with Activated Carbon, in *Hazardous and Industrial Wastes*, Proceedings of the Twenty-First Mid-Atlantic Industrial Waste Conference, Cole, C.D., Long, D.A. (Eds.), Technomic Publishing Company, Inc., Lancaster, Pennsylvania, pp. 146-156.
- Pamukcu, S., and Wittle, J.K. (1992) Electrokinetic Removal of Selected Heavy Metals from Soil, *Envir. Progress*, **11** (3), pp. 241-250.

- Peters, R.W., and Shem, L. (1995) Treatment of Soils Contaminated with Heavy Metals, in *Metal Speciation and Contamination of Soil*, Allen, H.E., Huang, C.P., Bailey, G.W., and Bowers, A.R. (Eds.), Lewis Publishers, Boca Raton, pp. 255-261.
- Probstein, R.F. (1994) *Physicochemical Hydrodynamics: An Introduction*, 2nd ed., Wiley, New York.
- Probstein, R.F., Hicks, R.E. (1993) Removal of Contaminants from Soils by Electric Fields, *Science*, **260**, pp. 498-503.
- Shapiro, A.P., Probstein, R.F. (1993) Removal of Contaminants from Saturated Clay by Electroosmosis, *Envir. Sci. & Technol.*, **27** (2), pp. 283-291.
- Shapiro, A.P., Renaud, P.C., Probstein, R.F. (1989) Preliminary Studies on the Removal of Chemical Species from Saturated Porous Media by Electroosmosis, *PhysicoChem. Hydrodyn.*, **11** (5/6), pp. 785-802.
- Shmakin, B.M. (1985) The Method of Partial Extraction of Metals in a Constant Current Electrical Field for Geochemical Exploration, *J. of Geochem. Explor.*, **23**, pp. 27-33.
- Smith, D.B., Hoover, D.B., Sanzolone, R.F. (1993) Preliminary Studies of the CHIM Electrogeochemical Method at the Kokomo Mine, Russell Gulch, Colorado, *J. of Geochem. Explor.* **46**, pp. 257-278.
- Talapatra, A.K., Talukdar, R.C., De, P.K. (1986) Electrochemical Technique for Exploration of Base Metal Sulphides, *J. of Geochem. Explor.* **25**, pp. 389-396.
- Taylor, O.C. (1997) In-Situ Reduction of Hexavalent Chromium by Electroremediation with Ferrous Iron, Master of Science Thesis, Massachusetts Institute of Technology, Mechanical Engineering Department.
- Vitale, R.J., Mussoline, G.R., Petura, J.C., James, B.R. (1994) Hexavalent Chromium Extraction from Soils: Evaluation of an Alkaline Digestion Method, *J. Environ. Qual.*, **23**, pp. 1249-1256.
- Weeks, A., Pamukcu, S. (1995) Utilization of Solubilizing and Stabilizing Agents in Electrokinetic Processing of Soils, in *Hazardous and Industrial Wastes*, Proceedings of the Twenty-Seventh Mid-Atlantic Industrial Waste Conference, Sengupta, A.K. (Ed.), Technomic Publishing Company, Inc., Lancaster, Pennsylvania, pp. 824-834.
- Wong, J.S.H. (1995) EDTA-Enhanced Metal Contaminant Removal from Soils by Electric Fields, Master of Science Thesis, Massachusetts Institute of Technology, Mechanical Engineering Department.

6485-49