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FEASIBILITY STUDIES OF RADIONUCLIDE REMOVAL FROM KAOLINITE BY ELECTROKINETIC SOIL PROCESSING

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirement for the degree of Doctor of Philosophy in The Department of Chemistry

by

Dionisio Alberto Ugaz
B.S., Catholic University of Peru, 1989
December 1994
A mis Padres
A Liliana, Patty, Carlos, Jorge y Susy
A la Muffin
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ABSTRACT

Electrokinetic soil processing is an emerging remediation technique with the capability to decontaminate low permeability soils containing heavy metals and some organics. The process consists on applying small current densities between electrodes immersed in the soil mass; the electrochemistry developed across the system causes desorption and transport of the contaminants to the electrodes where, depending on their chemistry, they precipitate, electrodeposit, or elute with the electroosmotic flow. Its potential to remove selected radionuclides (uranium-238, thorium-232, and radium-226) is assessed in the present studies. The process removed 85 to 95% uranium-238 at 1000 pCi/g activity from kaolinite. Complicating features arise (i.e. precipitation of insoluble hydroxides, high electrical gradient profiles, high energy expenditure). The energy consumed during the process ranged between 81 to 315 kW-hr/m³ of processed soil. Due to precipitation of uranium hydroxide, the removal rate decreased close to the cathode, but enhanced tests (acetic acid depolarization, adipic acid-molded sections tests) showed it is possible to improve removal rates near the cathode at lower energy expenditure. Between 80 to 90% of thorium-232 at different activities was removed using an acid-molded enhancement technique. Thorium was strongly adsorbed onto the soil surface and also showed a strong tendency to precipitate as insoluble and gelatinous hydroxides, complicating its transport and increasing the energy expenditure during the process. Radium-226 at 1000 pCi/g precipitated as insoluble radium sulfate, preventing its transport. Use of complexing agents may be needed to achieve radium removal. The
efficiency of the process proved to be dependant on the chemistry of the specific radioactive contaminants, but its usefulness as a remediation technique was demonstrated in this work.
CHAPTER 1
GENERAL INTRODUCTION

1.1. INTRODUCTION

The growing concern about environmental issues in the last two decades has prompted an intensive research and development of remediation techniques for contaminated facilities. Radioactive contamination is a particularly serious problem, since radioactive materials cannot be chemically degraded, transformed, or destroyed by treatment technologies, and their natural decay proceeds for thousands or even millions of years.

The danger of radioactive contamination is further increased by the latent possibility of leaching from soils into groundwater resources, or inhalation of radioactive gases produced through decay and decomposition of radionuclides. The main public health threats from radionuclides are through inhalation of radon and radon progeny (decay products of uranium, thorium and radium), external whole body exposure to alpha, beta, and gamma radiation, and ingestion through food and water. These dangers will persist through the entire decay time if no remedial action is taken.

In 1980, the U.S. Congress enacted the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), or the so-called Superfund program. This program provides a mandate for the U.S. Environmental Protection Agency (EPA) to take actions in response to hazardous releases of pollutants and to require responsible parties to contribute to the remediation [1.1].
As of 1989, there were 33 radioactively contaminated sites listed or proposed for listing on a National Priorities List (NPL) [1.2-1.3] that require immediate remediation action. However, the list is significantly longer when considering other EPA remediation programs [1.4]. Contamination in most of these sites resulted from uranium milling and mining, the commercial radium industry, or the Department of Energy (DOE) weapons research, development, and production programs. The DOE has listed over 8500 waste sites needing remediation [1.5]. Mostly, these federal facilities contain soil contaminated with uranium, thorium, and/or radium, including their respective decay products. However, some other sites contain "mixed wastes", including heavy metals, organic hazardous chemicals, and transuranic wastes. This makes the remediation process a more complicated one.

From the above discussion, the need for remediation technologies that are better, cheaper, safer, and faster than those currently available is clear. In this scenario, the development of electrokinetic soil processing as an in situ remediation process represents an attractive alternative for soil remediation. The present work will assess the feasibility of utilizing this innovative technique for the removal of selected radionuclides.

1.2. TEXT ORGANIZATION

The rest of the present chapter will briefly describe current technologies used in soil remediation for radioactive sites. Chapter 2 presents a literature review of electrokinetic soil processing as well as a description of the main electroosmosis theories. Chapters 3, 4, and 5 present the results and discussion of some electrokinetic tests of
kaolinite clay contaminated with selected radionuclides (uranium-238, thorium-232, and radium-226, respectively). Enhanced experiments for uranium-238 and thorium-232 also are described in the corresponding chapters.

1.3. REMEDIATION TECHNIQUES FOR RADIOACTIVE SOILS

Several approaches have been taken in order to remediate radioactive soils [1.3-1.9]. Only excavation and land encapsulation have been used at field scale [1.4]. However, the rapid use of disposal space and rising cost of land disposal prompt the need to find new, innovative remediation technologies. Therefore, recent remediation techniques for radioactive materials have focused on separation/concentration of the radioactivity from the innocuous material and containment/stabilization of the radioactive matrix [1.10].

A program started by the EPA, Volume Reduction/Chemical Extraction (VORCE) [1.2], is aimed to reduce the volume of soil contaminated with radioactivity at Superfund sites. Although this volume reduction results in higher contaminant concentrations, final disposal by some type of containment and/or burial is simplified. The following is a brief review of the main techniques used for radioactive soil remediation listed in the literature.

1.3.1. Wet-Based Volume Reduction for Radioactive Soils

This technology is based on using the different physical properties of the soil constituents to separate contaminated soil particles from clean particles. These physical
properties include size, specific gravity, particle shape, magnetic properties, friability, solubility, wettability, and radioactivity. A different technology results depending on the physical property used for volume reduction (i.e. particle size-screening; settling velocity-classification; specific gravity-gravity separation; flotation-flotation; magnetic properties-magnetic separation) [1.2, 1.4, 1.9, 1.11].

Following particle separation, the next stage involves particle liberation, where contaminated soil particles are released from clean particles, resulting in a mixture of unattached contaminated and clean particles. Several particle liberation techniques have been reported [1.8] (i.e. washing, scrubbing, attrition, crushing and grinding, surface de-bonding). An approach considered is chemical extraction following physical separation. Chemical extraction can be accomplished by using water, inorganic salts, mineral acids, or complexing agents [1.4]. The last step includes dewatering of the contaminated portion prior to final disposal.

These methods have proven their potential for low-level radioactive soils. An actual remediation of the Montclair site (New Jersey) has been reported [1.9]. Main advantages are simplicity and low cost. However, it requires excavation and may involve excessive exposure of workers to contaminated soils.

1.3.2. Dry-Based Volume Reduction for Radioactive Soils

This technology is specially designed for sites that are not distributed uniformly, a condition most commonly found in contaminated soils. Since excavating only the contaminated spots is extremely difficult, large volumes of clean soil are usually
excavated along with contaminated soil. Volume reduction procedures, which separates clean and contaminated soils, reduce the volume of soil requiring wet, corrective action.

The first stage involves separating large rocks, which are typically cleaner, from sand and fine clays. Crushing these rocks reduces their size and allows radionuclides on their surfaces to be detected more easily. A series of devices sort soils based on their radioactivity content. Contaminated portions are diverted to a drum, washed, and separated in a settling pond. This system separates the very finest, highly contaminated, soils from the larger, less-contaminated, fines [1.9].

This process has been used successfully in cleaning-up a plutonium based site [1.8]. The advantages of this technology are the elimination of the cost of conducting a detailed site characterization and inexpensive operating costs. However, it also requires excavation and workers contact with the contaminated medium.

1.3.3. Disposal of Radioactive Contaminated Soils

Disposal can be subdivided into two categories: on-site disposal and off-site disposal [1.4]. Applicability of each of these depends upon site characteristics.

1.3.3.1. On-Site Disposal

Two approaches are reported for on-site disposal: *capping* and *vertical barriers*. Capping involves covering the contaminated site with a thick layer of low-permeability soil. This layer acts as a barrier to gamma radiation, prevents release of radon gas from the decaying radionuclides into the atmosphere, and protects the ground water. The
advantages are low cost and ease of application. However, it does not eliminate the
source of contamination, limits further use of the site, and does not prevent horizontal
migration of contaminants. Capping has been used in actual remediation of
contaminated sites [1.4].

Vertical barriers are used to prevent horizontal migration of radionuclides or
contaminated ground waters. These are easy to install but not always compatible with
waste chemicals. Also, they require the use of very low permeability materials.

1.3.3.2. Off-Site Disposal

This mode involves removing contaminated soils for off-site disposal to prevent
exposure of people and the environment to the radionuclides. This is usually the last
stage for materials that have been modified through volume reduction processes, but can
also be used for untreated soils. Four off-site methods are reported [1.4]: land
encapsulation, land spreading, underground mine disposal, and ocean disposal.

Land encapsulation involves excavating the contaminated soil and securing it in a
site designed to contain the wastes. It is advantageous since it removes the source of
contamination and it is relatively simple. However, it requires handling and transporting
the waste, and it is not always easy to find an existing site that will accept the waste.

Land spreading consists on transporting the contaminated soil to a suitable site,
and spreading it on unused land, assuring that radioactivity levels approach the natural
radiation background levels. It is not appropriate for soils containing mixed wastes.
Underground mine disposal secures the radioactive wastes in new or existing underground mines. It can be used in conjunction with volume reduction and solidification / stabilization. However, it could result costly, and possible migration into ground waters must be considered.

Although subjected to stringent regulation, ocean disposal is an alternative to land disposal options. However, it is limited to low radiation levels only.

1.3.4. On-Site Treatment

Under these classification, up to three approaches have been reported for radionuclide contaminated soils: vitrification, stabilization or solidification, and electrokinetic soil processing [1.4, 1.7, 1.9].

1.3.4.1. Vitrification

Vitrification is the process of converting materials into glass or glass-like substances at high temperatures [1.9]. Vitrification is an attractive option to stabilize soil contaminants since it immobilizes radioactive contaminants in an impervious matrix. Also, the technique is flexible in treating a wide variety of waste streams and contaminants, i.e. mixtures of organic and inorganic wastes, since it pyrolyses organics and immobilizes inorganics. It is the preferred technique for high-level radioactive waste around the world [1.7].

Vitrification can be done in situ (in situ vitrification or ISV) or ex situ. The in situ process melts the waste materials between two or more electrodes by applying a
high-voltage to heat soils (joule heating) [1.4]. Other types of vitrification technologies include plasma heating, microwave heating, and thermal process heating [1.7]. Since some of the volatile components may be vaporized radionuclides, volatilization of waste substances must be controlled by emission reduction or off-gas treatment. Another approach is the use of additives in the soil to reduce the level of volatile constituents and adding oxygen to enhance secondary combustion of organics and products of incomplete combustion [1.9].

1.3.4.2. Stabilization or Solidification

This technology also immobilizes radionuclides (and could attenuate radon emanation) by trapping them in an impervious matrix [1.3, 1.4, 1.8]. The solidification agent (Portland cement, silica grout, or chemical grout) can be injected directly into the soil mass or mixed with excavated soil.

In recent developments, the use of thermoplastic materials (e.g. polyethylene, PE) over conventional cement has been reported [1.9]. The use of PE produces a more durable waste form that minimizes the release of toxic contaminants to the environment, maintaining these characteristics under long-term storage or disposal conditions.

In solidification using PE, the waste is mixed with PE, heated, and extruded into a waste drum. Since PE melts at 120°C, high temperatures are not required. This diminishes the risk of volatilization of contaminants. Once the material cools, the contaminants are immobilized in a stable homogeneous, monolithic waste form. This form of containment has proven resistant to different weather conditions, ionizing
radiation, chemical attack of typical radioactive wastes, and even biodegradation. Thermoplastic materials also solidify in a matter of hours, compared to Portland cement that takes days to fully cure.

Advantages of using PE encapsulation are the immobilization of the radionuclides at relatively low cost. The final result is a durable and stabilized waste form.

The solidification agent can also be applied in situ (in situ grout injection). In situ grout injection contains material in a solid monolith by mixing it with cement grout producing a solid waste that has a similar nature to the one described in PE encapsulation. The mechanisms by which grouts contain hazardous wastes are not fully understood. It is believed that some of the mechanisms are precipitation, especially of metals as hydroxides in cements with pHs between 9.5 and 11; encapsulation, where wastes are physically coated and surrounded by cement; adsorption, particularly of organics and gamma pellet clays; etc. [1.9]. The ability to resist leaching, low cost, and equipment simplicity are among the major advantages. However, it is difficult to verify that the grout actually contained the waste.

1.3.4.3. Electrokinetic Soil Processing

Electrokinetic soil processing uses an electric current applied through inert electrodes immersed in the soil mass to decontaminate soils and slurries. This innovative technique has been proven to successfully decontaminate heavy metals [1.12-1.14] and certain organics [1.15-1.17]. However, prior to the beginning of the present work, only one paper was found on the applicability of the process for radioactively contaminated
soil [1.18]. Electrical fields were used to control the migration of strontium-90 in soils. However, the study was largely inconclusive and did not provide an insight of the real potential of the technique to remediate radionuclides. The feasibility of using electrokinetics to remove radionuclides (uranium-238, thorium-232, and radium-226) is studied in this work. Chapter 2 includes a literature review of the state-of-the-art in electrokinetic soil processing.
1.4. REFERENCES


CHAPTER 2
ELECTROKINETIC SOIL PROCESSING:
PRINCIPLES AND APPLICATIONS

2.1. INTRODUCTION

Early actions for remediation of hazardous waste sites consisted primarily in excavating and removing the contaminated soil from the site and disposal at a landfill. A series of technologies ensure waste volume reduction (VORCE) prior to final disposal. However, these techniques imply exposure of workers to the hazardous and/or radioactive materials, in addition to their subsequent handling and transportation, adding a safety factor to the cost.

Some \textit{in situ} techniques have proven partially successful (i.e. capping and vitrification), although the source of contamination is not removed, and the cost could reach prohibitive levels (vitrification). Other techniques, the so-called "pump-and-treat", rely on pressure-driven flow for soil decontamination. However, their success is limited in soils with low permeability (clays) since the flow will preferentially go through regions of high permeability (sands).

\textit{Electrokinetic Soil Processing}, also known as electrochemical decontamination, electrokinetic remediation, or electroeclamtion, is an emerging and promising technology for waste management. Its capability as an \textit{in situ} technique for low permeability soils and slurries has been demonstrated in the removal of several heavy metals and selected organics. The process encompasses different disciplines, namely basic electrochemistry, soil/colloid chemistry, and geotechnical/environmental
engineering. It has been considered by the EPA as a potential technology in the VORCE program for radionuclides at Superfund sites [2.1-2.3]. The technique, if effective, would be very attractive from several standpoints: cost savings, worker safety and reduced exposure to hazardous or radioactive substances, minimal disruption to the soil and surrounding environment, and substantial reduction of waste volume [2.4].

This chapter presents an overview of the principles of the process, the most commonly accepted theories for electroosmosis, and some applications of the technique in bench- and field- scale experiments.

2.2. BACKGROUND

Electrokinetic soil processing consists of the application of direct-current electric fields in contaminated soils [2.4-2.7]. The contaminants may be either adsorbed onto the soil surface or dissolved/precipitated in the pore fluid. The electrolysis of water at the electrodes generates an acid front at the anode and a basic front at the cathode. The transport of this acid front from the anode to the cathode by electroosmosis is responsible for the desorption/solubilization of contaminants present in the soil mass. However, the importance of migration in the transport of the acid front and other charged contaminants under an applied electric field has been emphasized [2.5, 2.6, 2.8, 2.9]. The contaminants are also transported towards the cathode where, depending on their chemistry, they are electrodeposited, precipitated, or eluted with the effluent.
2.2.1. Electrokinetic Phenomena in Soils

Electrokinetic processing derives its name from one of the four major electrokinetic phenomena, which are electroosmosis, streaming potential, electrophoresis, and migration or sedimentation potentials [2.10, 2.11] (Figure 2.1). Electroosmosis and electrophoresis are the movement of pore water and charged particles, respectively, due to the application of an electrical field. Streaming potential and sedimentation potential are the generation of an electrical field due to the movement of an electrolyte under hydraulic potential and the motion of charged particles in a gravitational field, respectively. These phenomena arise from the coupling between electrical and hydraulic flows and gradients in suspensions and porous (soil) media.

Of the four electrokinetic effects, electroosmosis has been given more attention in geotechnical engineering, because of its practical value for transport of water in fine grained soils. Electroosmosis in soils consists of passing low direct currents through electrodes immersed in a soil mass. As an electrical potential is applied, cations are attracted to the cathode and anions to the anode. There is an excess of cations in the system to neutralize the net negative charge on the soil particles. These cations form the double layer of the soil particles. As cations in the double layer migrate, they drag water with them inducing the bulk fluid to flow by viscous drag. The final result is a net water flow towards the cathode with a profile that resembles a plug flow (Figure 2.2).
Figure 2.1. Electrokinetic Phenomena in Soils
Figure 2.2. Electroosmotic Flow Profile in a Porous Media (adapted from Shapiro [2.27]).
The electroosmotic flow, $q_e$ (cm$^3$/sec), is defined with the empirical relationship,

$$q_e = k_e i_e A = \frac{k_e I}{\sigma} \tag{2.1}$$

where $k_e =$ coefficient of electroosmotic permeability ((cm/sec)/(V/cm) or cm$^2$/sec.V), $I =$ current (Amp), $s =$ conductivity (siemens/cm), $i_e =$ electrical potential gradient (V/cm), and $A =$ cross sectional area (cm$^2$). The coefficient of electroosmotic permeability is the volume rate of water flowing through a unit cross sectional area due to a unit electrical gradient. It is analogous to the hydraulic conductivity, $k_h$ (cm/sec), which defines the hydraulic flow velocity, $q_h$ (cm$^3$/sec), under a unity hydraulic gradient, $i_h$ (cm/cm)$^1$. $k_e$ is independent of the size and distribution of pores (fabric) in the soil mass (typical values range between $1 \times 10^{-5}$ to $1 \times 10^{-4}$ (cm/sec)/(V/cm)). However, $k_h$ is greatly affected by the fabric and decreases by five to six orders of magnitude ($1 \times 10^{-3}$ to $1 \times 10^{-8}$ cm/sec) from fine sands to clays. Therefore, electroosmosis induced flow can be considered to be an efficient pumping mechanism in low permeability, fine-grained soils.

### 2.2.2. Electroosmosis Theories

#### 2.2.2.1 Helmholtz-Smoluchowski Theory

Also known as Large Pore Theory, this theory is one of the earliest and most accepted explanations for electroosmosis. It was introduced by Helmholtz (1879) and later refined by Smoluchowski (1914) [2.11-2.13]. For simplicity, the flow through

---

1 Hydraulic flow is defined as $q_h = k_h i_h A$ (Darcy's law)
porous media was likened to the flow through a liquid-filled capillary. The capillary/liquid interface is treated as an electrical condenser with charges of one sign on the capillary walls and an equivalent amount of countercharges concentrated in a layer in the liquid a small distance from the wall (double layer). The charges on the capillary walls (or clay particles), usually negative, are present due to isomorphous substitutions, functional groups, preferential sorption, or preferential distribution of surfactants in solution. The mobile shell of counterions is assumed to drag water through the capillary by plug flow (Figure 2.2).

For a negatively charged surface, the double layer will be formed by an excess of positive charges. The excess ions nearest to the interface remain stationary while the excess ions away from the surface are mobile. The boundary between the mobile and the stationary ions is characterized by a surface of shear or slip surface (Figure 2.3). The theoretical potential at this surface is defined as the electrokinetic zeta potential, $\xi$. The fluid velocity at the slip surface is zero, but the velocity in the bulk fluid (farthest extent of the double layer) is the slip velocity, $v_0$.

Smoluchowski's model (1921) was based on the movement of the liquid adjacent to a flat, charged surface under the influence of an electric field applied parallel to the interface (Figure 2.4). Most of the following derivation is based on Hunter [2.14]. An electrical force, $F_e$, acting on the ions will be counterbalanced by a drag force, $F_d$, opposite to the direction of motion. These forces are represented in Figure 2.4, where:

$$F_e = E_zQ = E_z \rho A dx$$

(2.2)
Figure 2.3. Velocity Distribution and the Notion of a Slip Velocity (adapted from Eykholt [2.13]).
Figure 2.4. Smoluchowski Force Balance on Fluid Element Near a Uniformly Charged Plate (adapted from Eykholt [2.13]).
and,

\[ F_d = \eta A \left( \frac{dv_z}{dx} \right)_x - \eta A \left( \frac{dv_z}{dx} \right)_{x=a} = -\eta \frac{d^2 v_z}{dx^2} dx \]  \hspace{1cm} (2.3)

where \( Q \) is the total excess charge within the fluid element of area \( A \), \( r \) is the excess charge density, \( \eta \) the viscosity of the medium, and \( v_z \) velocity of the fluid element in the \( z \) direction. Using the Poisson equation\(^2\) in the \( x \) direction, equation 2.2 can be written as

\[ F_x = -\varepsilon E_x A \left( \frac{d^2 \psi}{dx^2} \right) dx \]  \hspace{1cm} (2.4)

where \( \psi \) is the potential across the double layer, and \( \varepsilon \) the permittivity. At equilibrium,

\[ -\varepsilon E_x A \left( \frac{d^2 \psi}{dx^2} \right) dx + \eta A \left( \frac{d^2 v_z}{dx^2} \right) dx = 0 \]  \hspace{1cm} (2.5)

Equation 2.5 can be integrated twice considering the boundary conditions: (1) \( x = \infty \) : \( \psi = 0 \) and \( v_z = v_e \), and (2) \( x = 0 \) : \( \psi = \xi \) and \( v_z = 0 \). The solution for equation 2.5 is

\[ v_z = - \frac{\varepsilon E_x}{\eta} \]  \hspace{1cm} (2.6)

which is known as the Helmholtz-Smoluchowski equation. In the derivation of this equation, it is assumed that both \( \eta \) and \( \varepsilon \) retain their normal bulk values. The negative sign in equation 2.6 indicates that when \( \xi \) is negative the space charge is positive and the

\(^2\) Poisson equation: \( \nabla^2 \psi = \delta^2 \psi / \delta x^2 = -\rho / \varepsilon \)
liquid flow is towards the negative electrode. The electroosmotic flow, $q_e$, can be expressed as

$$q_e = -\frac{\varepsilon \xi}{\eta}AE_z$$

(2.7)

and comparison with equation 2.1 provides an expression for the coefficient of electroosmotic permeability in terms of properties of the medium,

$$k_e = -\frac{\varepsilon \xi}{\eta}$$

(2.8)

However, for porous media (soils), the effective porosity, $n$, should be taken into account.

The Helmholtz-Smoluchowski equation is also valid for capillaries and curved surfaces, provided that the radius of curvature, $a$, is much larger than the extent of the diffuse layer. This condition is usually represented by stating that

$$\kappa a > 100$$

(2.9)

where $\kappa$ is the inverse Debye length\(^3\).

The assumption that the double layers at clay surfaces do not overlap does not hold in all cases. Therefore, the theory is applicable for pores of the order of one micron or greater in soils. Implicitly, the assumptions made to derive equation 2.6 are (1) very thin double layer, and (2) moderate interfacial (zeta) potential [2.16]. When these

\(^3\) The thickness of the double layer is approximated to the reciprocal of the Debye length, $1/\kappa$
assumptions are not met, the $\xi$ appears to vary as a function of particle size or pore radius [2.17]. A modified solution has been reported by Rice et al. [2.15] for uniform capillaries with small values of $\kappa a$ (overlapping double layers) and $\xi$ values. The electroosmotic velocity is given by

$$v_e = -\frac{e \xi}{\eta} E_z F(\kappa a) \quad (2.10)$$

where $F(\kappa a)$ is called an electroosmotic correction factor, and

$$F(\kappa a) = \left[1 + \frac{2}{\kappa a} \frac{I_0(\kappa a)}{I_1(\kappa a)}\right] \quad (2.11)$$

where $I_0$ and $I_1$ are modified Bessel functions of zero and first order, respectively. For large values of $\kappa a$, $F(\kappa a)$ approaches unity, and equation 2.11 approaches the Helmholtz-Smoluchowski expression. In general, electroosmotic flow rates are predicted to be reduced when the double layer occupies a significant fraction of the pore.

The theoretical approaches developed in the colloid science literature assume constant electrostatic and chemical potential conditions, and are for steady-state electrokinetic phenomena. The movement of ions in an electrokinetic process causes alterations in the local environment in the soil, changing the zeta potential, double layer thickness, solution conductivity, sorption conditions, solubilities, and redox conditions as a function of both time and space [2.16]. Some recent models have just started considering the importance of this temporal and spatial dependance of the zeta potential [2.18].
2.2.2.2. Spiegler Friction Theory

Spiegler (1958) presented a completely different model for electroosmotic flow in porous media [2.7, 2.11, 2.19]. This theory considers the interactions of the mobile components of soil (water and ions) on each other and the frictional interactions of these components with the pore walls. However, its assumption that the medium for electroosmosis is a perfect permselective membrane (admitting ions of only one sign, i.e. friction coefficients between cations and anions are neglected) is not valid for soils, where the pore fluid comprises dilute electrolyte [2.7]. Spiegler derived the following equation for the true electroosmotic transport of water, \( Q \) (moles/Faraday), across an ion exchange membrane,

\[
Q = \frac{C_3}{(C_1 + C_3 X_3/X_{13})}
\]  

(2.12)

where the true electroosmotic flow is expressed as the difference between the measured water transport and the ion hydration in moles per Faraday. \( C_3 \) (mole/cm\(^3\)) is the total water concentration in the membrane, \( C_1 \) (mole/cm\(^3\)) in the concentration of mobile counter ions in the membrane, and \( X_{ij} \) is the friction coefficient between components \( i \) and \( j \) (W.s\(^2\)/cm\(^2\).mole). Subscripts 1, 3, and 4 refer to the cations, the water molecules, and the solid ionic matrix (wall), respectively. This theory enables isolation of parameters to quantify specific ion/water frictional drag. Incorporation of this model with the classical one for electroosmosis could provide quantitative testing of the slip boundary condition [2.7].
2.3. ELECTROKINETIC SOIL PROCESSING

Electrokinetic soil processing involves applying low direct current through a wet soil mass by immersion of two or more electrodes. The principal mechanisms by which contaminant transport takes place under the action of an electric field are electroosmosis, electrophoresis, electrolytic migration (frequently called electromigration in the geotechnical literature) of ionic and polar species [2.6, 2.20-2.23], and ionic diffusion.

As discussed previously, electroosmosis is the convective liquid flow in the pores by drag interaction of the double layer and the bulk liquid. From the Helmholtz-Smoluchowski expression (equation 2.6), the electroosmotic velocity, \( v_e \), is proportional to the zeta potential, \( \xi \), and the applied electric field strength, \( E \). Electroosmosis is only effective in fine-grained soils with micrometer-size or smaller pores (i.e. clays).

Electrophoresis is the migration of charged colloids in soil-liquid system. This kind of transport is of limited importance in compacted soil systems since colloidal particles are restrained from movement.

Electromigration is the transport of charged ions in the pore liquid. This migration is responsible for conducting the current in a soil-water system. The ion velocity, \( v_m \), is proportional to the electric field, \( E \), and the ionic charge number, \( z \), or

\[
            v_m = uzFE
\]

where \( u \) is the ion mobility and \( F \) is the Faraday's constant. Electromigration is not dependent on pore size and is equally effective in coarse and fine-grained soils. Unlike electroosmosis, electromigration does not depend on the soil charge nature, or the zeta potential.
Another transport mechanism is ionic diffusion [2.5], which is a function of the effective diffusion coefficient of the specie in the porous medium and the specie's concentration gradient (Fick's law). This transport mode is slower and thus it is not as important as electroosmosis and electromigration, but should be taken into account in accurate modeling of the process.

The relative magnitude of the contributions of electroosmosis and electromigration in the transport of contaminants is not clear. Acar et al. [2.5] defined a mass transport number, $\lambda$, as the ratio of the contributions of electromigration and electroosmotic transport$^4$. In experiments performed at Louisiana State University, the mass transport number $\lambda$ showed a time dependence changing from 10 to 300 for later stages of the process. Also, other experiments [2.9] showed that at high concentrations of ionic species, electromigration will play an increasingly significant role in transporting the contaminants.

Some attempts to model the transport mechanism of contaminants in soils under an applied electric field have been reported [2.5, 2.18], and will be briefly discussed in a later section.

\begin{subsubsection}{2.3.1. Electrolysis in Electrokinetic Soil Processing}
Electrolysis reactions dominate the chemistry at the boundaries. Upon application of the electric field, the current flow requires faradaic reduction and oxidation at the cathode and anode, respectively. When water is available at inert

\begin{footnote}{Mass transport number, $\lambda = J^*/J^\circ$, where $J^\circ$ is the electromigration mass flux, and $J^*$ is the electroosmotic mass flux.}
electrodes, the electrolysis of water produces \( H^+ \) ions at the anode and \( OH^- \) ions at the cathode,

\[
\text{Anode: } 2 \text{H}_2\text{O} - 4 e^- \rightarrow \text{O}_2 + 4 \text{H}^+ \quad (2.14)
\]

\[
\text{Cathode: } 2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad (2.15)
\]

If the proton and hydroxyl ions are not removed or neutralized, these reactions will lower the pH at the anode and raise it at the cathode. Subsequent transport by electroosmosis, electromigration, and diffusion of these fronts into the porous system will determine the occurrence of pH gradients [2.24-2.26] within the soil. At the anode, the pH will drop to below 2 while at the cathode it will increase to above 12, depending on the current density. Eventually, the acid front will reach the base front at a region close to the cathode (i.e. ionic the mobility of \( H^+ \) ions is 1.8 times that of the \( OH^- \) [2.5]), and both fronts will be neutralized. Attempts to model the acid-base distributions are reported in the literature [2.20, 2.26].

The presence of other electroactive species in the system will alter the faradaic efficiency of these primary reactions. For example, organic compounds might be oxidized at the anode. Metal ions, hydrogen ions and dissolved oxygen might be reduced at the cathode [2.5, 2.7]. The contaminant of interest may or may not be electrolyzable.

Hydrogen ions will exchange with metal ions adsorbed on the clay surfaces [2.7], i.e.

\[
2 \text{H}^+ + \text{Pb}^{2+} (\text{clay})^{2-} \rightarrow 2 \text{H}^+ (\text{clay})^{2-} + \text{Pb}^{2+} \quad (2.16)
\]

Additionally, a low pH condition is favorable for the dissolution of basic metal complexes and precipitates. Other positively charged ions introduced at the anode are also reported as possible exchangeable species [2.7] (e.g. \( NH_4^+ \), \( Na^+ \), \( Ca^{2+} \), etc.), although they might not be environmentally acceptable. Further complications of the pH
gradient throughout the porous medium are the different speciation and solubility of the contaminants at different pHs. For example, lead has been reported to be removed from sections close to the anode (low pH), only to be found precipitated in sections close to the cathode (high pH), where its limited solubility prevented further removal [2.25]. These complicating aspects of electrokinetic processing will be addressed in a later section.

The transient and spatial migration of the acid front is also responsible for changes in the soil surface properties like the double layer thickness and the zeta potential. These local changes affect the overall electroosmotic flow, exerting some effect on the transport mechanism of the contaminants as a function of time and space.

2.3.2. Transport Models

Significant contributions to modeling the transport processes in electrokinetic soil processing have been reported in the literature [2.18, 2.20, 2.26, 2.27]. The approaches by Acar et al. [2.26], Alshawabkeh et al. [2.20] and Shapiro et al. [2.27] are based on the Nernst-Planck flux equations. The total mass flux of a specie $i$, $J_i$, due to diffusion, electromigration, and electroosmotic convection (usually referred as advection in the geotechnical literature) are given by the following expression (Nernst-Planck eq.),

$$J_i = J_i^d + J_i^m + J_i^e$$

(2.17)

where $J_i^d$, $J_i^m$, $J_i^e$ represent the mass flux due to diffusion, electromigration, and electroosmosis, respectively. The diffusion term is given by Fick's law:

$$J_i^d = D_i^e \nabla (-C_i)$$

(2.18)
where $C_i$ is the molar concentration of specie $i$, and $D_i^*$ is the effective diffusion coefficient of specie $i$ in the porous medium\textsuperscript{5}. The electromigration term is given by:

$$J_i^m = u_i^* C_i \nabla (-E) \tag{2.19}$$

where $u_i^*$ is the effective ionic mobility of specie $i$ in the porous medium\textsuperscript{6}. Each ion will have a different electromigration flux, depending on the electric field and its mobility.

The electroosmotic mass flux is given by:

$$J_i^e = C_i k_e \nabla (-E) \tag{2.20}$$

where $k_e$ is the coefficient of electroosmosis defined by equation 2.8. Note that the electroosmotic flux is the same for each specie of a particular charge. Shapiro \textit{et al.} [2.18] and Anderson \textit{et al.} [2.28], recognized the importance of the local electrical environment by including an expression of the electroosmotic flux as a function of local values for the zeta potential and electric field,

$$J_i^e = \overline{C_i \langle \xi \overline{E} \rangle} \tag{2.21}$$

where the expression between $\langle \rangle$ denotes the volume average of the scalar product of the local $x$ and the change in electric field. The overbars indicate average values of the variables over the cross section of the pore. However, the time dependence of the zeta potential is not considered in this model.

\textsuperscript{5} $D_i^* = D_i \tau n$, where $D_i$ diffusion coefficient in free solution at infinite dilution, $\tau$ tortuosity factor, and $n$ porosity [2.5].

\textsuperscript{6} $u_i^* = u_i n = D_i^* z_i F/RT$, where $u_i$ ionic mobility in free solution, $z_i$ valence, $F$ Faraday constant, $R$ universal gas constant, $T$ absolute temperature [2.5].
Equation 2.17 may also include a hydraulic component (described by Darcy's law). However, this term can be suppressed by proper experimental design (i.e. no hydraulic gradient).

The overall equation governing the concentration distribution for each specie \( i \) is \[ 2.18, 2.20 \]

\[
\frac{\partial C_i}{\partial t} = -\nabla C_i + R_i \tag{2.22}
\]

where the inclusion of a retardation factor, \( R_i \), has been considered to account for chemical and physical changes such as sorption, precipitation-dissolution, oxidation / reduction, and aqueous phase reactions. This term is difficult to characterize since it is dependent on pH (acid-base chemical reactions), ionic strength, mechanism of adsorption and kinetics, competitive adsorption, etc. Their nature are discussed in \[2.20\] and \[2.27\].

The expanded form of equation 2.22 represents a system of coupled nonlinear differential / algebraic equations. A numerical approach, finite element method (FEM) \[2.7\], has been used to provide a solution to this system of equations. The model requires adequate definitions for the boundary conditions (nature of electrolyses, flow behavior). Two types of boundary conditions specified for the solution are \[2.20\] (1) constant potential (hydraulic, electrical, and chemical potentials), and (2) constant flux. A detailed description of the numerical solutions is provided in \[2.20\], \[2.25\], and \[2.28\].

There have been no attempts at incorporating the effects of double layer thickness and time changing zeta potential in these models. However, it is recognized that these variables will affect only the electroosmotic transport, while electromigration depends mainly on local electric field strength. Under circumstances where electroosmosis is negligible (high ionic strength of the pore fluid or zero zeta potential),
it is expected that electromigration will be the main transport mechanism of contaminants in the pore liquid.

2.3.3. Effect of Zeta Potential on the Electroosmotic Transport

Considerable understanding has been developed of the zeta potentials, $\xi$, at soil particles-water interfaces being a prime variable affecting electroosmotic flow (equation 2.16). The extent of the zeta potential will determine the amount of electroosmosis flow in the system. A typical negative value signifies negatively charged soil surface and electroosmotic flow towards the cathode.

The zeta potentials of clays are known to have a strong dependance on the local pH of the saturating solution [2.29]. Depending on the pH, typical $\xi$ values range between 0 to -100 mV, with more negative values at high pHs. For silica particles, the point of zero charge (PZC) is reported to be at a pH of two [2.30]. Below pH two, silica surface will be positively charged and $\xi$ will be positive. Therefore, electroosmotic flow will be stopped or reversed. In electrokinetic soil processing, the effect of the H$^+$ ions on the soil surface is translated in a decrease of electroosmotic flow with time, associated with the time dependance of $\xi$.

The zeta potential is also reported to change linearly with the logarithm of concentration described by, [2.31]

$$\xi = A - B \log C$$  \hspace{1cm} (2.23)

where A and B are two constants that are evaluated experimentally, and C is the total concentration of the electrolyte. The kind of ion adsorbed will also exert an effect on zeta potential changes. James and Healy [2.30] studied the effect of hydrolyzable species on $\xi$ of silica particles as a function of pH, type of ions and ionic strength (Figure 2.5). It is noted the existence of three charge reversals (CR) of the $\xi$ value, depending on the
Figure 2.5. Schematic Illustration of Zeta Potential Changes of Colloid Systems in the Presence and Absence of Hydrolyzable Metal Ions (adapted from James and Healy [2.30]).
pH. James and Healy attributed CR.1 (approximate pH=2) to the PZC of colloidal silica; CR.2 as the point where metal hydroxides start precipitating under the local environment surrounding the colloidal particles; and, CR.3 at the pH point where the colloidal particles are coated by metal hydroxide, referred to as the PZC of the metal hydroxide.


2.3.4. Complicated Features of Electrokinetic Soil Processing

2.3.4.1. Adsorption-Desorption

The clay minerals are hydrous aluminosilicates formed by sequential stacking of sheets with an octahedral lattice (Al$^{3+}$ cations in sixfold coordination with OH$^{-}$ anions) and sheets with a tetrahedral lattice (Si$^{4+}$ cations in fourfold coordination with O$^{2-}$ anions). Most clays have a negative surface charge due to nonstoichiometric isomorphous substitution of cations within the structure, i.e. $\text{Al}^{3+}$ for $\text{Si}^{4+}$ in tetrahedral sheets, and $\text{Mg}^{2+}$ for $\text{Al}^{3+}$ in octahedral sheets. The extent of substitution controls the surface charge and the amount of cation adsorption [2.32].

Cations are highly attracted to this soil surface negative charge. The mechanism of sorption depends on the nature of the ions (i.e. size and oxidation state) and the soil (i.e. surface charge density). In general, cations of higher valence tend to replace those of lower valence, and are more difficult to replace when already adsorbed [2.32]. For cations of the same valence, the ion with the smaller hydrated radius is more strongly adsorbed. The presence of organic matter in most soils, i.e. humic and fulvic acids, represent another factor in the adsorption of cations in porous media. Humic and fulvic acids are polyelectrolytic weak acids that form complexes with metal ions. Usually, humates form negatively charged colloids that coagulate and precipitate in the presence of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ [2.33], strongly adsorbing and immobilizing other metal ions.
Sorption mechanisms include surface complexation (adsorption) or ion exchange [2.5]. It is expected that H⁺ ions generated at the anode and transported into the soil system will exchange with adsorbed contaminants (equation 2.16). Species in a higher oxidation state (e.g. Th⁴⁺) are more retained to the soil surface, and require four charge equivalents to be desorbed. Therefore, the different sorption nature of the species will affect the time and efficiency of the processing.

2.3.4.2. Dissolution and Precipitation

The success of the technique in removing contaminants from soils is highly influenced by the dissolution of any precipitates and formation of new ones. Unless the base front generated at the cathode (equation 2.15) is more than neutralized by the acid front generated at the anode (equation 2.14) or by other means, it will cause the precipitation of heavy metals as hydroxides at the point where they reach their solubility product. This accumulation of metal has been likened to *isoelectric focusing* by Gray and Schlocker [2.34]. The precipitation limits further removal of contaminants, since its posterior dissolution will be dependent on the respective thermodynamic and kinetic characteristics of the precipitate.

It has been reported that lead [2.25], copper [2.13], zinc [2.36], uranium and thorium [2.36] precipitated as their respective hydroxides in regions close to the cathode. However, lead and zinc are amphoteric species, and higher pHs are expected to dissolve the hydroxides and form plumbites and zincates, respectively. These negatively charged species are then transported towards the anode. On the other hand, thorium hydroxide is highly insoluble and subsequent dissolution by either acid or base is prevented.
Thus, the extent of the precipitation will differ from one specie to another and it will be highly dependent on the resulting soil and pore fluid pH and the concentration of the species.

2.3.4.3. Current Efficiency

It is expected that the generation of the acid front and its consequent transport towards the cathode will cause dissolution or desorption of contaminants present in the soil. However, the transport and action of this acid front are limited by the buffer capacity of the soil. Availability of organic species and salts (such as CaCO$_3$ [2.5]) that may react with the acid would increase the buffering capacity of the soil. Also, in transporting the current through the porous media, calcium ions would migrate together with the contaminant specie in a competitive manner, decreasing the efficiency of the process.

In field studies, Lageman et al. [2.23, 2.37] found that the existence of metallic objects in the soil interfered with the electric current, since these provide preferential pathways to the current conduction within the soils. Also, any insulating material would interfere in the process.

2.3.4.4. Unenhanced vs Enhanced Electrokinetic Processing

From the above discussion, it is clear that the electrochemistry (i.e. electrolysis of water) at the electrodes is responsible for both the removal and subsequent complication of the process. Recently, Acar et al. [2.5] referred to unenhanced electrokinetic remediation as the case when the electrochemistry at the electrodes is that depicted by equations 2.14 and 2.15. In order to prevent precipitation of hydroxides, a series of modifications have been proposed [2.9, 2.38, 2.39], and have been referred to as enhanced electrokinetic remediation. The proposed enhancements are based on
(1) depolarizing the cathodic reaction, which prevents the formation of the base front that causes precipitation; (2) neutralization of the base front; (3) solubilize hydroxide precipitates by use of complexing agents; or, (4) use of ion exchange membranes. Some of these approaches are used to enhance removal of radionuclides and are explained in the following chapters.

2.3.5. Selected Examples of Bench and Field Scale Tests

The feasibility and cost effectiveness of the technique in removal of contaminants from soils have been demonstrated through bench-scale laboratory studies and pilot-scale studies [2.40].

Runnels and Larson [2.41] studied the removal of Cu$^{2+}$ ion from quartz silty sand, reporting removals ranging between 7 to 53% of a 0.01M CuSO$_4$ solution in the sand by using 15 V/m electric fields. Eykholt [2.13] also reported removal studies of Cu$^{2+}$ ion from kaolinite by electrokinetics. Electric fields in the range of 15 to 40 V/m and copper concentrations between 0 to 320 ppm were studied. Most of the copper was found precipitated in regions closer to the cathode. Power consumption was typically 7 kW-hr/m$^3$.

Pamukcu et al. [2.35] studied the removal of Zn$^{2+}$ ion from kaolinite. Concentrations of 20,000 ppm zinc in clay were studied. High electric fields (400 V/m) were applied for short periods of time to study the effect of electroosmosis and diffusion. Due to its amphoteric nature, zinc was found to increase at the anode chamber. Some precipitate (zinc hydroxide) in regions closer to the cathode was also reported. Jacobs et al. [2.41] reported the formation of zincates (HZnO$_2$) in regions close to the anode, with subsequent transport towards the anode. Zinc was found to precipitate where the zinc hydroxide solubility product was reached.
Pamukcu et al. [2.21] also studied the electrokinetic removal of cadmium, cobalt, nickel, and strontium from kaolinite, kaolinite mixed with humic acid, montmorillonite, and sand mixed with montmorillonite clay. Concentrations above 500 ppm and high electric field (400 V/m) were used for 24 to 50 hr time periods. Removal was between 85 to 95% for sections close to the anode. At the end of the test, most of the metals were accumulated close to the cathode. It is reported that the development of a pH gradient caused precipitation and formation of complex species that hindered the removal process.

Hamed et al. [2.24] reported a comprehensive treatise on removal of lead from kaolinite by electroosmosis. Current densities between 0.012 to 0.037 mA/cm² for time periods ranging from 100 to 1300 hr were studied. The process removed 75 to 95% of lead concentrations of up to 1500 ppm in kaolinite, at an energy consumption of 29 to 60 kW-hr/m³. Hamed [2.43] also studied the removal of cadmium and chromium ions from kaolinite. Removal efficiencies higher than 92% were reported for Cd²⁺ ion at 120 ppm. However, Cr³⁺ ions loaded at 120 ppm of dry soil indicated only 60-70% removal efficiencies, which may reflect both difficulties in desorbing this trivalent species due to redox interactions (Cr(III) - Cr(VI) equilibria). Lindgran et al. [2.44] reported the removal of 100 ppm CrO₄²⁻ ion from unsaturated sands. The anion was transported towards the anode.

The feasibility of electrokinetic soil processing for removal of organic contaminants has been established by Bruell et al. [2.45]. Bruell reported the removal of some gasoline hydrocarbons (benzene, toluene, ethylene, and m-xylene, or BTEX at their water solubility level, and trichloroethylene) from kaolinite. Removals ranging from 10 to 25% for 3 to 25 days processing at 40 V/m were reported. Shapiro et al. and Renaud [2.18, 2.27, 2.46] demonstrated up to 90% removal of 0.5M acetic acid and 450 ppm phenol in kaolinite. Acar et al. [2.47] removed 85 to 95% of 500 ppm phenol in
kaolinite at an energy expenditure of 19 to 39 kW-hr/m³. Some studies [2.48] showed that non-polar organics could also be removed by electrokinetics using micelle additives.

The use of electrokinetic soil processing for remediation of radionuclides is presented in this work. Case and Cutshall [2.49] reported the only previous application of electrokinetics for removing radionuclides from soils. This study attempted to control the migration of radionuclides, specifically strontium-90 from alluvial deposits by application of electrical currents. The study showed a slight accumulation of ⁹⁰Sr near the cathode, but it was largely inconclusive and did not permit an assessment of the potential of using electrical gradients in remediating radionuclides since a comprehensive analytical survey of contaminant transport was not attempted.

Field studies of the process are limited. Lageman [2.22, 2.23, 2.37] reported the removal of 73% of lead at a concentration of 9000 ppm from fine argillaceous sand, 90% removal of As at 300 ppm from clay, and varying removal rates ranging between 50 to 90% of Cr, Ni, Pb, Hg, Cu, and Zn from fine argillaceous sand. Cd, Cu, Pb, Ni, Zn, Cr, Hg, and As at concentrations of 10 to 173 ppm were also removed from a river sludge at efficiencies of 50 to 71%. The energy expenditure ranged between 60 to 220 kW-hr/m³ of soil processed. Figure 2.6 shows a schematic view of the use of electrokinetics in a field application.

In view of all the bench-scale studies and reported field tests, electrokinetic soil processing has proved to be a promising technology with the capability to remediate heavy metals, selected organics, and, potentially, radionuclides.
Figure 2.6. Schematic View of Electrokinetic Soil Processing in Field Application (adapted from Acar [2.5]).
2.4. REFERENCES


CHAPTER 3
FEASIBILITY STUDIES OF URANIUM REMOVAL FROM KAOLINITE
BY ELECTROKINETIC SOIL PROCESSING

3.1. INTRODUCTION

Most of the radioactively contaminated sites in the United States are the result of uranium ore mining and milling operations that have produced hazardous wastes (tailings) [3.1]. Uranium-238 is the major isotope in naturally occurring uranium. It has relatively low specific activity. Table 3.1 presents the naturally occurring uranium isotopes, half-lives, and decay modes [3.2]. Uranium is of great importance as a nuclear fuel. Natural uranium, slightly enriched with $^{235}$U by a small percentage, is used in nuclear power reactors for the generation of electricity.

During uranium extraction, many of the short-lived decay products of uranium disappear, whereas the long-lived nuclides remain. The most hazardous of these long-lived nuclides is radium-226 and gaseous radon-222. Figure 3.1 shows the decay chain for uranium-238. Due to the different chemistries, most of the daughter products of uranium-238 are not extracted by the typical leaching procedures, rendering tailings with non-usable and hazardous nuclides [3.4, 3.5]. Also, the extremely long half-life of uranium-238 precludes appreciable buildup of radium-226 in uranium tailings.

Most of the uranium mill-waste environmental studies have placed emphasis on radium-226 because of its hazard to human health; information about uranium-238 has been secondary. This is perhaps because of the general feeling that uranium is an
Table 3.1. Naturally Occurring Uranium Isotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (%)</th>
<th>Half-Life (years)</th>
<th>Decay Type</th>
<th>Specific Activity (pCi/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U}$</td>
<td>99.275</td>
<td>$4.468 \times 10^9$</td>
<td>Alpha, Gamma</td>
<td>$3.33 \times 10^5$</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>0.720</td>
<td>$7.038 \times 10^8$</td>
<td>Alpha, Gamma</td>
<td>---</td>
</tr>
<tr>
<td>$^{234}\text{U}$</td>
<td>0.005</td>
<td>$2.446 \times 10^5$</td>
<td>Alpha, Gamma</td>
<td>$2.14 \times 10^6$</td>
</tr>
</tbody>
</table>
Figure 3.1. Uranium-238 Decay Scheme
integral part of the environment. However, uranium and its compounds are highly toxic, both from a chemical and radiological standpoint. The finely divided metal is pyrophoric and presents a fire hazard. Also, the national presence of uranium in many soils has become a subject of concern because of the generation of radon and its daughters.

A typical radiation level for uranium-238 in soils is 1 pCi/g. The Superfund program reports uranium contaminated soils with activities ranging from 30 to 20,000 pCi/g [3.6]. Removal of uranium from contaminated sites has been conducted by acid leaching, carbonate and citric acid extractions, and the use of chelating agents like 1,2-diaminocyclohexanetetraacetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA) [3.7]. However, cost and exposure of workers to radiation are the major disadvantages.

The objective of this section is to assess the feasibility of removal of uranium-238 from Georgia kaolinite by using electrokinetic soil processing in bench-scale laboratory studies and to determine the efficiency of removal. Air-dried Georgia kaolinite (purchased from Thiele Kaolinite Co. in Wrens, GA) was used through all these studies. This mineral was selected because of its low activity and low permeability [3.8]. Typical physical properties and chemical composition are given in Table 3.2 [3.9].

3.2. ADSORPTION ISOTHERM AND CATION EXCHANGE CAPACITY

Prior to removal studies, the cation exchange capacity (CEC) of Georgia kaolinite was determined. Uranium-238 adsorption tests were conducted to determine

---

1 Cation Exchange Capacity (CEC): quantity of exchangeable cation require to balance the charge deficiency of a clay (meq/100 g clay).
Table 3.2. Typical Physical and Chemical Properties of Kaolinite (Thiele Kaolin Company)

<table>
<thead>
<tr>
<th>Typical Physical Properties</th>
<th>Typical Chemical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>Ignition Loss (%)</td>
</tr>
<tr>
<td>2.63</td>
<td>13.4 - 14.2</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>Silica (SiO₂) (%)</td>
</tr>
<tr>
<td>0.5 - 1.5</td>
<td>43.5 - 44.5</td>
</tr>
<tr>
<td>Particle Size</td>
<td>Alumina (Al₂O₃) (%)</td>
</tr>
<tr>
<td>% Less than 2 μm</td>
<td>38.0 - 40.5</td>
</tr>
<tr>
<td>89</td>
<td>IronOxide (Fe₂O₃) (%)</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>0.9 - 1.3</td>
</tr>
<tr>
<td>20 - 26</td>
<td>Titanium Dioxide (TiO₂) (%)</td>
</tr>
<tr>
<td>Mineralogical Composition (wt %)</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>--</td>
</tr>
<tr>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Na-Montmorillonite</td>
<td></td>
</tr>
<tr>
<td>Initial pH of Soil</td>
<td></td>
</tr>
<tr>
<td>4.7 - 5.0</td>
<td></td>
</tr>
<tr>
<td>(measured at 50% water content)</td>
<td></td>
</tr>
<tr>
<td>Initial Water Content (%)</td>
<td></td>
</tr>
<tr>
<td>1.75</td>
<td></td>
</tr>
</tbody>
</table>
the adsorption of ionic uranium species by this mineral. Uranyl nitrate 
\[(UO_2)(NO_3)_2\cdot6H_2O\] salt was used. The range of solutions prepared for the adsorption 
studies was 1 ppm to 10,000 ppm. Duplicate samples of 3.00 g of dry kaolinite clay 
were mixed with 30 mL of uranium solution in polyethylene jars with screw caps. The 
samples were shaken for three days in order to achieve equilibrium. The supernatant 
solution was filtered and analyzed by Inductively Coupled Plasma (ICP) for uranium 
content. The amounts of ions present adsorbed onto the clay were calculated from the 
differences in ion concentrations between the original solutions and those obtained in the 
filtered supernatants.

Figure 3.2. presents the uranium adsorption test results. The maximum amount 
of ions adsorbed was found to be 1700 µg/g of dry kaolinite or 1.43 meq UO_2^{2+}/100 g 
kaolinite, assuming UO_2^{2+} as the predominant uranium ionic species in solution. This 
value is comparable to 1.06 meq/100 g kaolinite reported by Hamed et al. for Pb^{2+} ion 
[3.10]. The difference can be attributed to surface charge density changes between the 
different batches of the Georgia kaolinite, or different adsorption kinetics of lead and 
uranyl ions. Also, no attempt was made to control hydrolysis of the uranyl ions, and it is 
possible that other ionic species were present (e.g. UO_2(UO_3)_n^{2+}, U_5O_8^{2+}, etc) as reported 
by Grindler [3.11].

The uranium exchange capacity of 1700 µg U/g (or 570 pCi ^{238}U/g)^2 implies that 
when the concentration exceeds this amount, the excess ions will be largely present in the 
pore fluid. The laboratory tests were conducted at 3000 µg U/g soil (approximately

\[^2\text{Specific activity of }^{238}\text{U} = 3.33 \times 10^5 \text{ pCi/g }^{238}\text{U}\]
Figure 3.2. Uranium Adsorption Isotherm for Kaolinite
1000 pCi $^{238}$U/g). This value corresponds to a concentration of 1.8 times the CEC of kaolinite. Therefore, approximately equivalent amounts of $\text{UO}_2^{2+}$ ions will be present both in the diffuse double layer and in the free pore fluid of the specimens prepared.

3.3. EXPERIMENTAL

3.3.1. Sample Preparation

Air-dry kaolinite was mixed with uranyl nitrate solutions to obtain an activity of about 1000 pCi $^{238}$U/g soil. The activity selected was based on mean levels of $^{238}$U contamination levels found in Superfund sites, which range from 30 pCi/g to 20,000 pCi/g. A typical radiation background level for uranium-238 is 1 pCi/g [3.6].

Previous electrokinetic tests at Louisiana State University [3.10, 3.12] were performed at 100% degree of saturation. However, the effects of saturation on electroosmotic efficiency were studied and reported by Acar et al. [3.13, 3.14] and a 42% water content$^3$ was selected for the present studies. The soil was then slowly mixed with enough deionized water to obtain 42% water content, which corresponds to 90 to 100% degree of saturation. Lindgren et al. [3.15] have reported the removal of chromate ions by electrokinetics under unsaturated conditions also.

After mixing the sample with deionized water and uranyl solution, the mixture was left overnight to allow for equilibration. Triplicate samples were taken to determine initial uranium concentration$^4$, initial water content, and initial pH.

$^3$ Water content is defined as the ratio of water/soil (wt/wt).

$^4$ See Section 3.3.2 for Analytical Procedure.
The sample was then compacted using the Standard Proctor Effort Method (ASTM D1557-78) into polyacrylite sleeves (10 cm length and 10 cm outside diameter). These sleeves were removed from the compaction mold and used as the cell to perform the electrokinetic tests.

Samples mixed and compacted as described above showed uniform distribution (± 2%) of uranium across the specimen, as depicted in Figure 3.3. The mean activity was 925 pCi/g, or approximately 2780 μg U/g soil.

3.3.2. Test Apparatus

Figure 3.4 presents the test setup. Inert graphite electrodes (0.3 cm thickness and 10 cm diameter) were used to prevent introduction of extraneous products due to electrolytic reaction of the electrodes themselves. One sheet of paper filter was placed at both ends of the specimen. Uniform flow conditions across the electrodes are ensured by drilling thirty-five to fifty 0.3 cm holed into the electrodes. The electrodes were held in place by polyacrylite end caps connected with threaded rods. A liquid reservoir of 150 mL capacity was available at each end. Holes were drilled on top of each end cap above these reservoirs to allow venting of gaseous electrolysis products. After compaction, the sample was placed in between the end caps, as depicted in Figure 3.4.

A constant current density of 0.13 mA/cm² was applied to the system. Constant current rather than constant potential was selected based on previous work at Louisiana State University [3.8, 3.10, 3.16]. Constant current facilitates mathematical modeling by establishing initial constant flux boundary conditions for electrogenerated products at the
Figure 3.3. Typical Uranium Initial Distribution (average 925 ± 19 pCi/g soil or 2%)
Figure 3.4 Schematic Diagram of Test Apparatus for Laboratory-Scale Electrokinetic Studies
anode. The electrode reactions at the cathode are usually more complex and may change appreciably over extended periods of electrolysis.

The total duration of the tests ranged between 85 to 500 hrs. Parameters monitored during the test were the potential across the specimen, the electroosmotic flow, pH of effluent, and current.

After completion of a test, the sample was sliced into ten or six fractions. Each fraction was analyzed for uranium concentration, water content, and in situ pH. Any effluent due to electroosmosis was measured, collected and analyzed for uranium content. Also, the electrodes were extracted with HNO₃ (1 M) in order to desorb any uranium deposited or adsorbed. For some tests, the coefficient of electroosmotic permeability, $k_e$, and the energy consumption were calculated. The removal efficiency was determined by comparison with the initial uranium concentration. A total mass balance was conducted for total uranium loaded and extracted, and served as a guide to validate an experiment.

3.3.3. ICP Analytical Method for Uranium

3.3.3.1. Scope and Application

This Inductively Coupled Plasma (ICP) method was developed for elemental uranium analyses in solution for spiked laboratory soil tests, based on reference [3.17].
3.3.3.2. Sample Preparation

A portion of each soil section from a test was weighed, oven dried at 110°C for 18 hr minimum, cooled in a desiccator, and reweighed to determine its water content. Dried sections were labeled and stored in polyethylene bags.

From these samples, triplicate portions of 3.00 g were extracted for 24 hr minimum with 30.0 mL of 1 M nitric acid, under constant shaking. The samples were then filtered, diluted to a concentration range within 100 ppm solution, and sealed in polyethylene containers for ICP analyses. For reproducibility, a standard deviation of less than 5.0% was taken as acceptance criterion. Samples showing higher dispersion than 5.0% were reextracted and analyzed again. Similarly, a blank sample of kaolinite (no uranium) was also extracted for comparison. Samples extracted using this procedure showed a recovery of 95±6 % for kaolinite loaded with 1000 pCi/g (or approximately 3000 μg U/g soil).

The electrodes were extracted by immersing them in 1 M HNO₃ for 24 hr, filtering the extract, and diluting to a typical volume of 1.0 L. The extracts were then properly diluted to within 100 ppm concentration range. Also, any effluent or liquid sample was filtered, and diluted to within 100 ppm range using 1 M nitric acid. Similarly, these samples were sealed in polyethylene containers for ICP analyses.

3.3.3.3. Procedure

Uranium was analyzed using the 409.07 nm emission wavelength in an ARL Model 34000 ICP Spectrometer (Department of Agronomy, Louisiana State University).
Other lines were available for uranium analysis, but this particular line was recommended by the manufacturer under the instrument settings. The reported sensitivity limit for uranium was 0.02 ppm. However, only a sensitivity of 1 ppm could be achieved. Typical reproducibility within 2% was accomplished for each reading. This sensitivity limit was quite ample for the electrokinetic studies, was fast, and devoid from matrix effects.

Before each batch of samples was analyzed, the instrument was checked for calibration with a commercial AA standard uranium solution (Aldrich Chemicals, 980 ppm). Calibration curves using 0, 10, 50, and 100 ppm in 1 M HNO₃ solutions were obtained. A typical calibration curve is shown in Figure 3.5.

Each set of samples had a proper set of blank extractions, and standards included within the set of samples to double check for accuracy of analysis.

3.3.3.4. Interferences

The ICP minimizes matrix effects and chemical interferences. However, the efficient excitation of sample constituents at high temperature results in the possibility of spectral overlap interferences. Since the electrokinetic tests were made with extracts from kaolinite spiked with uranium, no spectral overlap was observed. Blank extractions were conducted to subtract from sample readings. No interferences were listed in the manufacturer's manual for the 409.07 nm line.
Figure 3.5. Typical ICP Calibration Curve for Uranium
3.3.3.5. Calculations

(i) Soil Samples

A linear calibration curve within a 100 ppm range was obtained prior to each analysis of a set of sample. Assuming a linear relation of \( S = mC + b \), where \( S \) is the signal given by the ICP, \( C \) the uranium concentration of the nitric acid extract in ppm (\( \mu g \) U/g solution), \( m \) and \( b \) the slope and intercept of the calibration curve (typically \( b = 0 \)), the concentration of uranium in the nitric soil sample and the corresponding activity were calculated as follows:

\[
\mu g \text{ U/g soil} = \frac{(S - b)}{m} \times F \times \left[ \frac{30.0 \text{ mL extract}}{3.00 \text{ g soil}} \right] \quad (3.1)
\]

\[
pCi^{238}U/\text{g soil} = \left[ \mu g \text{ U/g soil} \right] \times \left[ 3.33 \times 10^5 \text{ pCi}^{238}U/\mu g \right] \times \left[ 10^{-6} \text{ g/} \mu g \right] \quad (3.2)
\]

where \( F \) is the dilution factor. The fraction of uranium left in each section after the process was calculated by calculating the ratio:

\[
\text{Fraction left} = \frac{[pCi^{238}U/g soil]_{\text{section}}}{[pCi^{238}U/g soil]_{\text{initial}}} \quad (3.3)
\]

For mass balance purposes, the total uranium content in each section was calculated by multiplying the \( \mu g \) U/g soil obtained for each section times the total dried weight of each section. The total uranium initially loaded in the specimen and the total uranium left in the soil processing were calculated as follows:

\[
\text{Total initial U in soil (g)} = \left[ \mu g \text{ U/g soil} \right]_T \times W_T \times \left[ 10^{-6} \text{ g/} \mu g \right] \quad (3.4)
\]

\[
\text{Total U left in soil (g)} = \sum_i \left[ \mu g \text{ U/g soil} \right]_i \times w_i \times \left[ 10^{-6} \text{ g/} \mu g \right] \quad (3.5)
\]

where \( W_T \) represents the total dried weigh of kaolinite (g) used in the experiment, \( [\mu g \text{ U/g soil}]_T \) is the concentration of U in the original mix, \( w_i \) is the dried weigh of soil (g) in
each section after slicing the specimen, and \([\mu g \text{ U/g soil}]_i\) is the corresponding uranium concentration for each section.

(ii) Liquid Samples and Extracts

For liquid samples and extracts, the total uranium content in g was calculated as follows:

\[
\text{Total U in effluent (g)} = \left[\mu g \text{ U/mL solution}\right] \times F \times V (mL) \times 10^6 (g/\mu g) \tag{3.6}
\]

where \([\mu g \text{ U/mL solution}]\) is the concentration obtained using the calibration curve, \(F\) is the dilution factor, and \(V \text{ (mL)}\) is the total volume of liquid sample or extract.

(iii) Mass Balance

For a mass balance, (3.5) and (3.6) for each liquid sample were added and compared to (3.4). A mass balance of 75\% minimum was adopted as a criterion to validate an experiment.

3.4. URANIUM REMOVAL STUDIES

Table 3.3 summarizes the initial conditions and parameters for uranium tests. The cells were labeled as U42XX, where XX represents the experiment number.

3.4.1. Final and Initial pH Across the Specimen

Figure 3.6 represents the final in situ pH distribution across the specimens. The pH determined by in situ insertion of a glass electrode into the soil results in a
Table 3.3. Uranium Removal Test Program and Initial Parameters for Electrokinetic Tests

<table>
<thead>
<tr>
<th>Uranium Test</th>
<th>Water Content (%)</th>
<th>Saturation S (%)</th>
<th>Porosity e</th>
<th>Initial Activity (pCi/g)</th>
<th>Current Density (mA/cm²)</th>
<th>Duration (hr)</th>
<th>Effluent Volume (cm³)</th>
<th>Pore Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>U4201</td>
<td>39.2</td>
<td>87.7</td>
<td>1.17</td>
<td>917.5</td>
<td>0.13</td>
<td>424</td>
<td>443</td>
<td>1.00</td>
</tr>
<tr>
<td>U4202</td>
<td>41.9</td>
<td>86.7</td>
<td>1.27</td>
<td>1004.7</td>
<td>0.13</td>
<td>498</td>
<td>370</td>
<td>0.80</td>
</tr>
<tr>
<td>U4203</td>
<td>38.0</td>
<td>92.3</td>
<td>1.08</td>
<td>1021.0</td>
<td>0.13</td>
<td>500</td>
<td>305</td>
<td>0.71</td>
</tr>
<tr>
<td>U4204</td>
<td>41.6</td>
<td>89.5</td>
<td>1.22</td>
<td>954.7</td>
<td>0.13</td>
<td>240</td>
<td>317</td>
<td>0.70</td>
</tr>
<tr>
<td>U4205</td>
<td>41.5</td>
<td>92.3</td>
<td>1.17</td>
<td>979.7</td>
<td>0.13</td>
<td>470</td>
<td>83</td>
<td>0.19</td>
</tr>
<tr>
<td>U4206</td>
<td>40.1</td>
<td>89.8</td>
<td>1.17</td>
<td>929.4</td>
<td>0.13</td>
<td>363</td>
<td>269</td>
<td>0.60</td>
</tr>
<tr>
<td>U4207</td>
<td>43.3</td>
<td>93.1</td>
<td>1.22</td>
<td>979.2</td>
<td>0.13</td>
<td>516</td>
<td>344</td>
<td>0.76</td>
</tr>
<tr>
<td>U4208</td>
<td>42.4</td>
<td>95.0</td>
<td>1.17</td>
<td>1005.7</td>
<td>0.13</td>
<td>85</td>
<td>219</td>
<td>0.50</td>
</tr>
</tbody>
</table>

1 Pore volume is defined as the total volume of the specimen multiplied by porosity (or e/1+e). All specimens had a total volume of 825 cm³.
Figure 3.6(a). Final in situ pH Profile for Uranium Tests
Figure 3.6(b). Final in situ pH Profile for Uranium Tests
quasi-thermodynamic determination of the H\(^+\) activity, since solution phase H\(^+\) ions, double layer and adsorbed H\(^+\) ions may all contribute to the measured activity [3.18].

The pH profile observed in Figure 3.6 followed the trend described in the literature [3.8, 3.10, 3.19] for an electrokinetic test, with lower pH values at regions closer to the anode and increasing towards the cathode. This is in agreement with the electrolytic reactions that take place at the electrodes, and the subsequent transport of the acid and base front generated at the anode and cathode, respectively.

Acar et al. [3.8] modeled the development of a pH gradient in electrokinetic soil processing as a function of time. At earlier stages of the process, the expected pH profile would follow those showed in Figure 3.6, with low pH in sections closer to the anode (pH=2.0), and larger as the cathode is approached, where a pH=10-12 is expected due to the upstream transport of the base generated in this electrode. The H\(^+\) ions transported from the anode to the cathode would eventually flush the cell specimen, neutralizing the base front where these two fronts meet. The result of this acid-base neutralization is a final uniform and acidic value for the in situ pH across the specimen. It should be noted that due to the faster transport of H\(^+\) ions over OH\(^-\) ions (the ion mobility of H\(^+\) ions is 3.63 x 10\(^{-3}\) cm\(^2\)/V.s compared to 2.06 x 10\(^{-3}\) cm\(^2\)/V.s for the OH\(^-\) ions), these two fronts are expected to meet each other in a section close to the cathode. Therefore, for sufficient processing time (which depends upon the test processing parameters, e.g. current density, water content, ionic strength), an acidic flat profile for the in situ pH measurements would be expected.
The lower initial pH values observed before processing (pH = 3.5 to 4.0) are due to the uranium ions in the pore fluid. The hydrolysis of these uranyl ions produced an acidic initial pH. This relatively low pH compared to blank specimens (same water content, no contaminant, pH = 4.0 to 5.0), implies higher H⁺ ion concentration (high ionic strength), which affects the zeta potential by making it less negative. In terms of electroosmotic flow, equation 2.6 predicts a decrease in flow for the lower pH uranyl samples compared to blank specimens, an effect that is discussed below.

3.4.2. Electroosmotic Flow and Electrical Gradient

Figure 3.7 depicts the electroosmotic flow for the uranium tests. For comparison, a blank test is plotted together with these data. The blank specimen was compacted at the same water content as the uranium samples. The blank test showed a steady flow, significantly larger than those observed for the uranium tests. After 500 hrs processing time, the blank specimen showed approximately 2000 mL of flow, or 4.4 pore volumes of flow. For the same average processing time, the uranium tests showed only between 0.2 to 1.0 pore volumes. This difference in flow rate was due to the initial high ionic strength (3000 µg U/g soil) of the pore fluid in the uranium samples.

The effect of high ionic strength on the zeta potential is provided by equation 2.23 [3.19],

\[ \xi = A - B \log C \]

---

5 Pore Volume = Total Flow/(Cell Volume x Porosity of Compacted Specimen)
Figure 3.7(a). Electroosmotic Flow for Uranium Tests. A blank test is shown for comparison.
Figure 3.7(b). Electroosmotic Flow for Uranium Tests
where $\xi$ is the zeta potential, $C$ is the ion concentration, and $A$ and $B$ are constants. The ion concentration is directly proportional to the ionic strength. A high ionic strength causes the zeta potential to become less negative, which affects directly the electroosmotic flow as shown by equation 2.7,

$$q_e = \frac{\varepsilon \xi A E_z}{\eta}$$

where $q_e$ is the electroosmotic flow, $\varepsilon$ is the dielectric constant of the medium, $\xi$ is the zeta potential, $\eta$ is the viscosity of the medium, $A$ the area of the specimen, and $E_z$ the electric field. Also, the low pH due to hydrolysis of the uranyl species [3.11] will cause a less negative value, similar to those reported by James and Healy [3.13] for silica (Figure 2.5) in the presence of hydrolyzable ions like Co$^{2+}$, La$^{3+}$, and Th$^{4+}$. James and Healy studied the electrophoretic mobility behavior of silica, supplemented by streaming potential data, in aqueous solutions of these ions, and found several charge reversals for the silica surface charge (hence, the zeta potential, $\xi$) as a function of pH and concentration of the ions. These charge reversals were not observed for silica in the absence of these hydrolyzable ions. A silica with reverse surface charge would imply that $\xi$ is positive, and therefore, the electroosmotic flow would be reversed (i.e. from cathode to anode). These two factors (high ionic strength and low pH) caused a decrease in electroosmotic flow in the uranyl samples compared to blank specimens.

Figure 3.8 presents a comparison of the electrical gradients in these tests. In general, uranium tests showed significantly higher electrical gradients compared to the blank test. In some instances, the potential required to maintain the set current density (0.13 mA/cm$^2$) exceeded the maximum capacity of the power supply (110 to 120 V or
Figure 3.8(a). Electrical Gradient for Uranium Tests. A blank test is shown for comparison.
Figure 3.8(b). Electrical Gradient for Uranium Tests. A blank test is shown for comparison.
11 to 12 V/cm electrical gradient for a 10 cm long cell) after 60 to 200 hrs processing time, compared to an average value of 50 V or 5 V/cm for the blank test. The latter showed an increase in electrical gradient for the first 80 hrs of the process, reaching an equilibrium electrical gradient value of 5 V/cm, which was maintained for the remaining time of the process. In those uranium tests where the maximum capacity of the regulator was exceeded, the current density could not be maintained constant. In these cases, the current drop was recorded.

The high electrical gradient (high resistivity) generated in some tests was attributed to the precipitation of the uranyl ions as hydroxides in regions close to the cathode and on the cathode itself, as observed in the form of a yellow precipitate (uranyl hydroxide has a bright yellow color [3.11]). This high electrical gradient due to precipitation of hydroxides has been reported in the literature [3.10, 3.20, 3.21]. Acar et al. [3.8] also predicted the formation of a region of high resistivity where the base front is neutralized by the acid front (i.e. water formation). To better understand this observation, the development of the electrical potential gradient across the cell was monitored for one test (U4207). The results shown in Figure 3.9 provided insights to the electrochemistry developed across the cell:

1. An electrical potential difference of 5 V is generated within 1.8 hr of processing. There is no significant change across the specimen except within the zone extending from a normalized distance of 0.85 to 1.00 from the anode. This implies that the electrical conductivity across the specimen is high enough to prevent any significant losses until the zone close to the cathode is reached.
Figure 3.9. Electrical Gradient Development for an Uranium Test (U4207)
2. The potential difference increased up to 58 V in 215 hr. There is no significant change in the potential difference across the specimen from 215 to 516 hr. The zone where the potential drop is observed extends from a normalized distance of 0.60 to 1.00 from the anode. This zone extends gradually towards the middle of the specimen with further processing.

These findings imply that the zone that generates the high resistance extends from very close to the cathode during the initial stages of testing to a normalized distance of 0.60 from the anode with further processing.

It is postulated that the low resistance in sections closer to the anode is due to both the initial high concentration of uranium in the soil and the acid front generated at the anode, which is transported towards the cathode. Precipitation of uranium hydroxide, formation of water by the advancing acid front, and anion depletion due to migration to the anode are reasons for the decrease in conductivity near the cathode. Uranium hydroxide (yellow precipitate, with probable composition \((\text{UO}_2)(\text{OH})_2\cdot\text{H}_2\text{O}\) [3.11]) was found precipitated on the filter paper and on the graphite electrode in the cathode compartment. This precipitate is likely to be nonconducting and its formation affected the total resistance across the cell increasing the electrical gradient. The random nature of the precipitation can explain the fact that the voltage increase was observed only in some, rather than in all, tests. The precipitate was observed to be randomly distributed on the cathode in each test.
3.4.3. Coefficient of Electroosmotic Permeability, \( k_e \)

Figure 3.10 presents the coefficient of electroosmotic permeability, \( k_e \), calculated using equation 2.1.

\[
q_e = k_e E_x A
\]

where \( q_e \) is the electroosmotic flow, \( E_x \) is the electrical gradient, and \( A \) is the area of the specimen. For comparison, \( k_e \) calculated for a blank test is also shown. Typical values for \( k_e \) range between \( 1 \times 10^{-5} \) to \( 1 \times 10^{-4} \) cm\(^2\)/V.s. Acar et al. [3.13] reported values ranging from \( 1 \times 10^{-6} \) to \( 3 \times 10^{-5} \) for kaolinite specimens compacted at different water content. Hamed et al. [3.11] also reported similar values for kaolinite loaded with lead at concentrations in the 100 \( \mu \)g/g soil. The general trend observed for \( k_e \) by Hamed et al. [3.11] was a rapid increase in \( k_e \) at earlier stages of processing, with subsequent decrease to an equilibrium value as the flow rate decreases at later stages. Acar et al. [3.13] did not observe a decreasing trend in \( k_e \) for blank specimens, but a direct increase in \( k_e \) to an equilibrium value.

Figure 3.10 shows a similar trend in \( k_e \) as reported by Acar et al. [3.13] for blank specimens and Hamed et al.[3.11] for lead contaminated kaolinite. The average equilibrium value observed for uranium tests was between \( 5 \times 10^{-7} \) and \( 1 \times 10^{-6} \), compared to \( 4 \times 10^{-6} \) cm\(^2\)/V.s for the blank specimen. This difference is a direct result from the lower electroosmotic flow observed in the uranium tests compared to the blank specimen. Therefore, the same reasons given to explain the lower electroosmotic flow and higher electrical gradient in the uranium tests (Section 3.3.3.2) can account for the low \( k_e \) values. The changes in \( k_e \) for the uranium tests are due to the time dependence
Figure 3.10. Coefficient of Electroosmotic Permeability ($k_e$) for Uranium Tests. A blank test is shown for comparison.
nature of the zeta potential, $\xi$ (equation 2.8), and the changing local conditions within the contaminated soil, as explained in Section 2.3.3.

3.4.4. Uranium Removal Efficiency

Figure 3.11 presents the uranium removal profiles for these tests. For long duration tests (U4201-U4203, U4205, and U4207), the process removed about 80 to 95% of the loaded uranium in regions close to the anode. There is a continuous increase in the remaining uranium concentration as the cathode compartment is approached. The increase in pH profile towards the cathode together with the decrease in electroosmotic flow in time hindered the transport of the acid front towards the cathode and resulted in lower removal rates in sections close to the cathode. For tests conducted for more than 240 hrs, most of the uranium was found precipitated on the cathode (71-97%). Different approaches were developed to increase removal rates close to the cathode, and are described in Section 3.5. For shorter tests (U4204, U4206, U4208), the uranium removal across the specimen was lesser, depending on the processing time.

Table 3.4 presents the mass balance for the uranium removal studies. Most of the removed uranium (71 to 97%) was precipitated on the cathode for tests conducted for more than 240 hrs. These tests displayed that uranium was significantly removed (80 to 95%) across the specimen in longer duration tests. Test U4208 ($t=85$ hrs) showed the least uranium removal from all tests. Table 3.4 shows that compared to longer duration tests (>240 hrs), only 52% of the initial uranium content was found precipitated on the
Figure 3.11(a). Final Uranium Distribution Profiles
Figure 3.11(b). Final Uranium Distribution Profiles
Table 3.4. Mass Balance for Uranium Electrokinetic Experiments

<table>
<thead>
<tr>
<th>Uranium Test Code</th>
<th>Initial Uranium Content pCi/g</th>
<th>Initial Uranium U(g)</th>
<th>Final Uranium Distribution Soil U(g) (%), Cathode U(g) (%), Effluent U(g) (%)</th>
<th>Mass Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U4201</td>
<td>917.5</td>
<td>2.753</td>
<td>0.160 5.8, 2.633 95.6, 0.073 2.7</td>
<td>104.1</td>
</tr>
<tr>
<td>U4202</td>
<td>1004.7</td>
<td>3.129</td>
<td>0.420 13.4, 2.340 74.8, 0.136 4.3</td>
<td>92.7</td>
</tr>
<tr>
<td>U4203</td>
<td>1021.0</td>
<td>3.180</td>
<td>0.486 15.3, 2.269 71.4, 0.093 2.9</td>
<td>89.6</td>
</tr>
<tr>
<td>U4204</td>
<td>954.7</td>
<td>2.778</td>
<td>0.379 13.6, 2.021 72.8, 0.101 3.6</td>
<td>90.0</td>
</tr>
<tr>
<td>U4205</td>
<td>979.7</td>
<td>2.921</td>
<td>0.283 9.7, 2.525 86.4, ---</td>
<td>96.1</td>
</tr>
<tr>
<td>U4206</td>
<td>929.4</td>
<td>2.766</td>
<td>0.496 17.9, 2.174 78.6, 0.079 2.9</td>
<td>99.4</td>
</tr>
<tr>
<td>U4207</td>
<td>979.2</td>
<td>2.887</td>
<td>0.175 6.1, 2.794 96.8, 0.056 1.9</td>
<td>104.8</td>
</tr>
<tr>
<td>U4208</td>
<td>1005.7</td>
<td>3.029</td>
<td>1.352 44.6, 1.563 51.6, 0.081 2.7</td>
<td>98.9</td>
</tr>
</tbody>
</table>
cathode after the process. The removal profile for U4208 (Figure 3.11(b)) showed the transport of uranyl ions towards the cathode. For this test, it was observed a 75 to 95% removal in the first half of the specimen (close to the anode). However, due to the short period of time for which this test was conducted (85 hrs), uranium was concentrated in the second half of the specimen, where the final/initial uranium concentration ratio was close to or greater than one. This observation demonstrated the importance of a minimum processing period in order to desorb and transport the contaminants to the cathode.

The tests conducted in this work were not conclusive in determining the minimum amount of hours required to significantly remove uranium from kaolinite (>95%) using this process and with the parameters described in Section 3.3 (0.13 mA/cm² current density, 42% water content, 1000 pCi²³⁸U/g kaolinite). However, based on the results shown in Figure 3.11 and Table 3.4, it was observed that a 500 hr-processing time under the conditions described above, accounted for a 90 to 95% uranium removal from kaolinite. This removal decreased in sections close to the cathode. A 240 to 363 hr-processing time (U4204 and U4206, respectively), also removed 90 to 95% of the initial uranium content, but only in the first two thirds of the specimen (close to the anode). The removal rate decreased to 60-80% in sections close to the cathode.

In general, the amount of uranium left on the soil was substantially below the CEC (570 pCi/g or 1710 μg U/g soil) determined for kaolinite. These amounts ranged between 5.8 to 17.9 % (or 58 to 179 pCi/g, considering an average 1000 pCi/g initially
loaded onto the kaolinite). Therefore, it could be stated that uranium was desorbed from the soil, transported towards the cathode and precipitated at regions of higher pH. Small amounts of uranium were found in the effluent (1.9 to 4.3% of total uranium initially loaded).

3.4.5. Energy Consumption

Figure 3.12 shows the energy expenditure for the uranium tests. The energy expenditure per unit volume of soil processed, $E_u$ (kW-hr/m$^3$), was calculated using the following equation:

$$E_u = \frac{E(t)}{V_s} = \int \frac{I \cdot V(t) \cdot dt}{V_s} \times F$$

where $E_u$ is the energy (kW-hr), $V_s$ is the volume of soil mass processed (m$^3$), $V(t)$ is the voltage (V) as function of time, $I$ is the current (A), $t$ is the processing time (s), and $F$ is a unit correction factor to express $E_u$ in kW-hr/m$^3$. In tests with the constant current condition, the energy expended is directly related to the voltage as a function of time. Therefore, the energy consumption was only calculated in those tests where the current could be maintained at a constant value.

In previous electrokinetic processing tests with kaolinite clay, Hamed et al. [3.11] and Acar et al. [3.16] reported an energy consumption of 29 to 60 kW-hr/m$^3$ for lead removal and 13 to 28 kW-hr/m$^3$ for phenol removal, respectively. Figure 3.12 shows that the energy expenditure to remove uranium (80 to 95% of approximately 3000 μg U/g soil) using electrokinetics ranged between 81 to 315 kW-hr/m$^3$. These relatively high values
Figure 3.12. Energy Consumption for Uranium Tests
compared to those reported were due to the low electroosmotic flow and the high electrical
gradient developed. Any modification that results in lowering the increase in electrical
gradient (e.g. prevent uranyl ion precipitation or increase its transport efficiency) would
decrease the energy expenditure for the process.

3.5. ENHANCED ELECTROKINETIC REMOVAL OF URANIUM

A series of electrokinetic tests were designed in order to enhance uranium
removal efficiency at regions adjacent to the cathode. The complicating features
originated by the OH⁻ ions produced at the cathode have also been reported in the
literature, as described in Section 2.3.4. Most of the approaches considered were aimed
to prevent the formation of this base front at the cathode, or to neutralize it. Therefore,
it was envisioned that preventing the precipitation of hydroxide would allow the uranyl
ions to elute with the effluent or to freely migrate towards the cathodic compartment,
where they could be collected for disposal.

Table 3.5 presents a summary of the enhanced tests conducted for uranium
removal studies. The following sections describe the different procedures followed to
improve removal efficiency.

3.5.1. Acid-Molded Cathode Section Test

In an attempt to depolarize the cathodic reaction, an acidic soil section adjacent
to the cathode was included in the specimen system (Figure 3.13). A cell was filled up to
9/10 of its total volume with uranium spiked kaolinite (1000 pCi/g activity and 42 %
Table 3.5. Enhancement Experiments for Uranium Removal Studies.

<table>
<thead>
<tr>
<th>Uranium Test Code</th>
<th>Enhancement Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>U4209</td>
<td>Acid-Molded Cathode Section</td>
<td>Section adjacent to cathode molded with $1 \text{ M } \text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>U4210</td>
<td>Acetic Acid Depolarization</td>
<td>Cathode compartment filled with acetic acid</td>
</tr>
<tr>
<td>U4211</td>
<td>Acetic Acid Depolarization</td>
<td>Same as above</td>
</tr>
<tr>
<td>U4212</td>
<td>Acetic Acid Depolarization</td>
<td>Same as above</td>
</tr>
<tr>
<td>U4213</td>
<td>Buffer Depolarization</td>
<td>Buffer acetic acid/sodium acetate pumped around cathode, current density $= 0.065 \text{ mA/cm}^2$</td>
</tr>
<tr>
<td>U4214</td>
<td>Buffer Depolarization</td>
<td>Same as above</td>
</tr>
<tr>
<td>U4215</td>
<td>Regular Test</td>
<td>Current density $= 0.065 \text{ mA/cm}^2$</td>
</tr>
<tr>
<td>U4216</td>
<td>Buffer Depolarization</td>
<td>Same as U4214 &amp; U4215</td>
</tr>
<tr>
<td>U4217</td>
<td>Acid-Pumped</td>
<td>Acid from anode pumped to cathode</td>
</tr>
<tr>
<td>U4218</td>
<td>Pumped-Acid</td>
<td>Same as above</td>
</tr>
<tr>
<td>U4219</td>
<td>Adipic Acid Depolarization</td>
<td>Adipic acid paste in section adjacent to cathode</td>
</tr>
</tbody>
</table>
Figure 3.13. Schematic Diagram of Acid-Molded Cathode Section Test
water content). The mix was compacted as described in Section 3.3.1. The last 1/10 volume of the cell (section adjacent to the cathode) was filled with kaolinite molded with 1 M H$_2$SO$_4$, so as to obtain 42% water content. It should be noted that under these conditions, the clay CEC was largely exceeded (1.47 meq/100 g soil for 100 g soil and 42 mL 1 M H$_2$SO$_4$, representing 84 meq H$^+$ ions, or approximately 60 times the CEC of kaolinite). Therefore, most of the H$^+$ ions were present in the pore fluid.

The major expectation in this experiment was to prevent hydroxide precipitation by changing the cathodic reaction to the reduction of H$^+$ ions instead of water as the UO$_2^{2+}$ ions displaced adsorbed H$^+$ ions, i.e.

$$\text{UO}_2^{2+} + 2\text{clay-H}^+ \rightarrow \text{clay}_2\text{UO}_2^{2+} + 2\text{H}^+ \quad (3.7a)$$

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (3.7b)$$

instead of,

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (3.8)$$

In addition to the loaded H$^+$ ion reduction at the cathode, this last section was considered to serve as an ion exchange resin, where the uranyl ions, UO$_2^{2+}$, would be trapped by displacing the protons that would migrate, in turn, to the cathode. Therefore, it was envisioned that the uranyl ion would be easily removed by removing this last section of the cell.

The setup and experimental parameters were the same as those described in Section 3.3. This cell was coded U4209, and it was conducted for 550 hr duration time. Table 3.6 shows relevant parameters for test U4209.
Table 3.6(a). Uranium Removal Test Program and Initial Parameters for Enhanced Electrokinetic Tests

<table>
<thead>
<tr>
<th>Uranium Test</th>
<th>Water Content (%)</th>
<th>Saturation S (%)</th>
<th>Porosity e</th>
<th>Initial Activity (pCi/g)</th>
<th>Current Density (mA/cm²)</th>
<th>Duration (hr)</th>
<th>Effluent Volume (cm³)</th>
<th>Pore¹ Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>U4209</td>
<td>42.3</td>
<td>95.1</td>
<td>1.17</td>
<td>947</td>
<td>0.13</td>
<td>550</td>
<td>20</td>
<td>0.04</td>
</tr>
<tr>
<td>U4210</td>
<td>42.3</td>
<td>92.7</td>
<td>1.20</td>
<td>898</td>
<td>0.13</td>
<td>630</td>
<td>715</td>
<td>1.59</td>
</tr>
<tr>
<td>U4211</td>
<td>41.7</td>
<td>93.7</td>
<td>1.17</td>
<td>993</td>
<td>0.13</td>
<td>497</td>
<td>444</td>
<td>0.61</td>
</tr>
<tr>
<td>U4212</td>
<td>41.6</td>
<td>89.7</td>
<td>1.22</td>
<td>985</td>
<td>0.13</td>
<td>479</td>
<td>377</td>
<td>0.83</td>
</tr>
</tbody>
</table>

¹ Pore volume is defined as the total volume of the specimen multiplied by porosity (or e/(l+e)). All specimens had a total volume of 825 cm³.

² N.A. = Not Analyzed
Table 3.6(b). Uranium Removal Test Program and Initial Parameters for Enhanced Electrokinetic Tests

<table>
<thead>
<tr>
<th>Uranium Test</th>
<th>Water Content (%)</th>
<th>Saturation S (%)</th>
<th>Porosity e</th>
<th>Initial Activity (pCi/g)</th>
<th>Current Density (mA/cm²)</th>
<th>Duration (hr)</th>
<th>Effluent Volume (cm³)</th>
<th>Pore Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>U4213</td>
<td>42.1</td>
<td>93.2</td>
<td>1.17</td>
<td>1082</td>
<td>0.065</td>
<td>302</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>U4214</td>
<td>42.0</td>
<td>94.4</td>
<td>1.17</td>
<td>1117</td>
<td>0.065</td>
<td>302</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>U4215</td>
<td>42.4</td>
<td>95.3</td>
<td>1.17</td>
<td>1104</td>
<td>0.065</td>
<td>344</td>
<td>75</td>
<td>0.16</td>
</tr>
<tr>
<td>U4216</td>
<td>42.4</td>
<td>91.4</td>
<td>1.22</td>
<td>938</td>
<td>0.065</td>
<td>311</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>U4217</td>
<td>42.3</td>
<td>95.1</td>
<td>1.17</td>
<td>980</td>
<td>0.065</td>
<td>197</td>
<td>976</td>
<td>2.19</td>
</tr>
<tr>
<td>U4218</td>
<td>42.6</td>
<td>95.8</td>
<td>1.17</td>
<td>1011</td>
<td>0.065</td>
<td>192</td>
<td>835</td>
<td>1.87</td>
</tr>
<tr>
<td>U4219</td>
<td>42.3</td>
<td>83.9</td>
<td>1.33</td>
<td>935</td>
<td>0.13</td>
<td>318</td>
<td>56</td>
<td>0.12</td>
</tr>
</tbody>
</table>

1 Pore volume is defined as the total volume of the specimen multiplied by porosity (or e/(1+e)). All specimens had a total volume of 825 cm³.

2 N.A. = Not Analyzed
3.5.1.1. Electroosmotic Flow, Electrical Field, pH Profile

No appreciable electroosmotic flow was observed (20 mL total for 550 hr processing time). Considering the H\(^+\) ion concentration greatly exceeded the CEC (approximately 60 times) of the kaolinite in acid-molded section, a detrimental effect on the electroosmotic flow was expected, since high ionic strength (or low pH) cause a decrease in zeta potential and electroosmotic efficiency [3.19, 3.21-3.23]. Migration of H\(^+\) ions from the acid-molded section towards the anode could have caused a decrease in local zeta potential values throughout the specimen, decreasing \(k_e\), and hence, the overall electroosmotic transport. Under these conditions, it was expected that electromigration and diffusion would be the major transport mechanisms of the acid front generated at the anode and the uranyl ions.

Figure 3.14 shows the electrical gradient for tests U4209 and U4207, the latter used for comparison. Significant lower gradients (0.2 to 1.2 V/cm) were observed when compared to tests U4201 to U4208 (6 to 11 V/cm, Figure 3.7). Unlike test U4207, the acid-molded test showed no precipitate on the cathode, providing an indication that, at least partially, the reduction of water was suppressed or the base front produced was neutralized by the H\(^+\) ions in the pore fluid.

Figure 3.15 presents the initial and final pH profile for test U4209. The observed trend is somewhat similar to those obtained for tests U4201 to U4208 (Figure 3.6). However, in U4209, the acid front seemed to have swept completely across the cell (average in situ pH 1.5 to 2.0 across the specimen). This observation is in accordance
Figure 3.14. Electrical Gradient for Acid-Molded Cathode Section Test
Figure 3.15. Final in situ pH Profile for Acid-Molded Cathode Section Test
with both possibilities, the suppression of the electrolysis of water at the cathode, or the neutralization of the base front by the H\(^+\) ions in the acid-molded section.

3.5.1.2. Uranium Removal

Although negligible electroosmotic flow was observed, the final uranium profile shows that uranyl ions have been transported toward cathodic sections (Figure 3.16). This transport must be mainly due to electromigration and diffusion since little electroosmosis occurred. For comparison, Figure 3.16 also depicts the final uranium profile for tests U4207 (processing time 516 hr) and U4208 (processing time 85 hr), both with similar initial uranium concentration as U4209. Test U4207 showed removal uranium removal between 90 to 95% across the specimen. Only 6.1% of the initial uranium loaded onto kaolinite for test U4207 was found in the soil, while 97% was found precipitated on the cathode. On the other hand, although the processing time for U4208 was shorter, a better removal efficiency than for U4209 was observed. Figure 3.16 shows more uranium transport towards the cathode for test U4208 when compared to U4209. In test U4208, 45% of the uranium loaded onto the kaolinite was found in the soil, compared to 96% for test U4209. Table 3.7 presents a mass balance for this test.

As noted in Section 2.3, Acar et al. [3.19] reported that for a specific charged specie, electromigration can be at least one order of magnitude larger than electroosmotic transport. The ratio between the two transport mechanisms, given by \(\lambda^6\),

\[
\lambda = \frac{u^*}{k_e}
\]

where \(u^*\) is the effective ion mobility (electromigration) and \(k_e\) is the coefficient of electroosmotic permeability (electroosmosis).
Figure 3.16. Final Uranium Distribution for Acid-Molded Cathode Section Test
Table 3.7(a). Mass Balance in Enhanced Electrokinetic Tests for Uranium Removal Studies

<table>
<thead>
<tr>
<th>Uranium Test Code</th>
<th>Initial Uranium Content</th>
<th>Final Uranium Distribution</th>
<th>Mass Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pCi/g</td>
<td>U(g)</td>
<td>U(g) (%)</td>
</tr>
<tr>
<td>U4209</td>
<td>947</td>
<td>2.488</td>
<td>2.475</td>
</tr>
<tr>
<td>U4210</td>
<td>898</td>
<td>2.661</td>
<td>0.031</td>
</tr>
<tr>
<td>U4211</td>
<td>993</td>
<td>2.980</td>
<td>0.153</td>
</tr>
<tr>
<td>U4212</td>
<td>985</td>
<td>2.868</td>
<td>0.128</td>
</tr>
</tbody>
</table>
Table 3.7(b). Mass Balance in Enhanced Electrokinetic Tests for Uranium Removal Studies

<table>
<thead>
<tr>
<th>Uranium Test Code</th>
<th>Initial Uranium Content</th>
<th>Final Uranium Distribution</th>
<th>Mass Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pCi/g</td>
<td>U(g)</td>
<td>Soil</td>
</tr>
<tr>
<td>U4213</td>
<td>1082</td>
<td>3.224</td>
<td>0.430</td>
</tr>
<tr>
<td>U4214</td>
<td>1117</td>
<td>3.341</td>
<td>0.610</td>
</tr>
<tr>
<td>U4215</td>
<td>1104</td>
<td>3.279</td>
<td>0.584</td>
</tr>
<tr>
<td>U4216</td>
<td>938</td>
<td>2.776</td>
<td>0.518</td>
</tr>
<tr>
<td>U4217</td>
<td>980</td>
<td>2.934</td>
<td>0.937</td>
</tr>
<tr>
<td>U4218</td>
<td>1011</td>
<td>3.008</td>
<td>1.392</td>
</tr>
<tr>
<td>U4219</td>
<td>935</td>
<td>2.377</td>
<td>1.562</td>
</tr>
</tbody>
</table>
was found to be time dependent [3.19], increasing at later stages of the process due to the decrease in $k_e$. However, the presence of other charged species that might preferentially carry the current through the porous medium will affect this ratio. It was not possible to quantify the amount of ions transported by either transport mechanism, since we have not determined all of the mobile ionic species in the pore fluid. Nevertheless, the absence of electroosmotic flow and the final uranium profile in test U4209, showed that electromigration was the main transport mechanism.

Test U4209 (processing time 550 hrs, no electroosmotic flow) showed less uranium removal than test U4207 (processing time 516 hrs, 0.76 pore volumes flow) and test U4208 (processing time 85 hrs, 0.50 pore volumes flow). It is thought that in U4209, the high ionic strength in the acid-molded section had two effects that caused this difference in removal: (1) preferential transport of the current through the clay system by the $H^+$, $HSO_4^-$, and $SO_4^{2-}$ ions, in competition with the $UO_2^{2+}$ ions, and (2) the high conductivity in the acid-molded section prevented precipitation of uranyl hydroxide and neutralized the base front; as a result, low electric gradients were developed across specimen U4209 compared to U4207 (Figure 3.14). The effect of electrical gradient on the electromigration rate is given by equation 2.13,

$$v_m = u z F E$$

where $v_m$ is the migration rate, $u$ is the ion mobility, $z$ is the ion charge, $F$ the Faraday constant, and $E$ is the electrical gradient. Therefore, low electrical gradients will result in slow migration rates.
From the electrical gradients for tests U4207 and U4209 (Figure 3.14), it can be calculated that the electric field strength was approximately 30 times larger for test U4207 than U4209. In addition, U4207 produced 0.76 pore volumes of effluent compared to only 0.04 for U4209 in approximately the same period (520 hr). Therefore, the transport of uranyl ions in test U4209 was mainly due to electromigration. On the other hand, this transport was enhanced by both electroosmosis and electromigration for test U4207.

As a conclusion, it is stated that although electromigration generally is at least one order of magnitude larger than electroosmosis transport, the importance of the latter mechanism should not be disregarded, especially in porous media with low ionic strength. As described in Section 2.3.4.3, the addition of extraneous ions will lower the current efficiency of the process, increasing processing time and cost.

### 3.5.2. Effect of the Acid-Molded Cathode Section on the Electroosmotic Flow

As described in Section 3.5.1, the use of 1 M H$_2$SO$_4$ at a 42% water content in the acid-molded section greatly exceeded the CEC of kaolinite, causing a deleterious effect on the electroosmotic flow. In order to study the effect of this acid-molded section on the flow, an acid-molded blank test was conducted. Based on the previous experience, the acid-molded section was loaded with 0.01 M H$_2$SO$_4$ at a 42% water content. Under these conditions, assuming a CEC of 1.47 meq/100 g kaolinite (determined from the uranium adsorption isotherm), the molded section was loaded at 0.6 times its CEC. Therefore, all the H$^+$ ions loaded would be adsorbed onto the soil
surface. The initial in situ pH measured was 4.12 for the blank test, and 4.22 for the acid-molded blank test. The initial in situ pH of the acid-molded section itself was 3.23.

Figure 3.17 shows the electroosmotic flow for this acid-molded blank test. For comparison, a blank test is also shown. Both tests showed a similar flow rate, which was uniform throughout the processing time. Figure 3.18 and 3.19 present the electrical gradient and the coefficient of electroosmotic permeability for these tests. In both cases, the observed profiles are similar.

Although the acid-molded section had a lower initial in situ pH (3.23) compared to regular compacted samples (4.22), the electroosmotic flow was not affected. This was expected since the CEC of the specimen did not exceed unity. However, if most of the H\(^+\) ions are adsorbed onto the soil surface, they would not be available to neutralize the base front or to depolarize the cathodic reaction. Therefore, it would be necessary to use conditions where part of the H\(^+\) ions are present in the pore fluid, although not in a large excess. Section 4.4.1 compares the effect of thorium removal for different acid concentrations used in the molded section.

3.5.3. Acetic Acid Depolarization Tests

In order to prevent the electrolysis of water at the cathode, the cathodic compartment was filled with acetic acid, HOAc. It was expected that introducing a weak acid (HOAc, \(K_a = 1.76 \times 10^{-5}\) at 20°C) would not tend to significantly increase the ionic strength in the system, thus, not affect the electroosmotic flow as much as the
Figure 3.17. Electroosmotic Flow for a Blank Test and an Acid-Molded Blank Test
Figure 3.18. Electrical Gradient for a Blank Test and an Acid-Molded Blank Test
Figure 3.19. Coefficient of Electroosmotic Permeability for a Blank Test and an Acid-Molded Blank Test.
addition of an equivalent amount of strong acid. In addition, the acetate ions would migrate towards the anode and would not precipitate with the uranyl ions, since uranyl acetate is a soluble salt. This approach would ensure that the uranyl ions would elute with the effluent.

In order to optimize the conditions for this enhanced test, the amount of $H^+$ ions that are generated by the dissociation of HOAc was calculated, and the amount of $H^+$ ions that are consumed by the expected reaction,

$$2H^+ + 2e^- \rightarrow H_2$$

These calculations would ensure that enough HOAc of a proper concentration is added to the cathode compartment, and therefore, effectively depolarize the reduction of water.

Based on the following chart, an overview of the calculations are presented,

<table>
<thead>
<tr>
<th>HOAc</th>
<th>$H^+$</th>
<th>OAc$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>$M - x$</td>
<td>$x$</td>
</tr>
<tr>
<td>Electrolysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New Equilibrium</td>
<td>$M - x - x'$</td>
<td>$x - \frac{it}{FV} + x'$</td>
</tr>
</tbody>
</table>

where $M$ is the molar concentration of HOAc; the product $\frac{it}{FV}$ is the molar concentration of $H^+$ ions that are consumed by electrolysis (current $i$ (A), time $t$ (s), $F$ Faraday constant equal to 96,490 Coul/eq, and $V$ cathode compartment volume (L)); $x$ is the molar concentration of $H^+$ ions due to dissociation from HOAc; and, $x'$ is the new amount of $H^+$ generated due to dissociation from HOAc and consumption of $H^+$ by
electrolysis. Equating these expressions, the following equation for the dependence of $H^+$ concentration as a function of time $(\lbrack H^+ \rbrack(t))$ is derived,

$$[H^+](t) = \frac{1}{2} \left\{ \sqrt{\left(\frac{it}{FV} - K_a\right)^2 + 4K_aM} \right\} - \frac{1}{2} \left\{ K_a + \frac{it}{FV} \right\}$$

where $K_a$ is the dissociation constant ($1.76 \times 10^{-5}$ at 20°C). Figure 3.20 shows a plot for the pH as a function of time, considering different applied currents $(i)$ and initial HOAc molar concentrations $(M)$. A cathode compartment volume $(V)$ of 0.5 L was used in the calculations. As shown in Figure 3.20, the use of low current (3 mA) and relatively high initial HOAc concentration (0.05 M) would ensure that the pH would be maintained below 5 for at least 100 hrs processing time. Low pH values in the cathode compartment would favor reduction of $H^+$ ions at the cathode, preventing the formation of base due to water electrolysis and subsequent precipitation of uranium hydroxide. However, high HOAc concentration may introduce unnecessary ions that increase the ionic strength within the soil specimen, and negatively affect the electroosmotic flow. Also, the use of low current, could slow down the transport of the uranyl ions. Since the HOAc was added batchwise on a daily basis, it was decided to use $i=10$ mA and HOAc 0.01 M. Therefore, the HOAc could be replaced every 15 hrs and the pH should still be below 7. In addition, the use of 0.01 M HOAc was not expected to increase the ionic strength significantly.
Figure 3.20. pH Changes as a Function of Time in Acetic Acid Depolarization Tests. Different applied currents and acetic acid concentrations are considered.
The test setup was the same as shown in Figure 3.4. The experimental parameters were the same as those used in previous uranium tests (i.e. current density 0.13 mA/cm², processing time 500 hr, uranium activity 1000 pCi/g). HOAc 0.01 M was selected based on the applied current density and the volume of the cathodic compartment. The acid was added batchwise into the cathodic compartment and replaced daily with fresh acid. The replaced fractions were collected and the pH was measured. These measurements provided an idea of the amount of H⁺ ions consumed during the 24-hr period. A significant increase in pH would indicate the consumption of the HOAc, or the neutralization of the base produced by electrolysis of water. The HOAc fractions were then filtered, properly diluted, and analyzed for uranium content. In addition, any effluent was collected and filtered for analysis. These tests were labeled U4210, U4211, and U4212; relevant parameters are shown in Table 3.5.

3.5.3.1. Electroosmotic Flow, Electrical Gradient, pH Profile

Figure 3.21 shows the final in situ pH profiles for the acetic acid depolarization test. For comparison, the data obtained for test U4201 are also shown. The results of test U4201 (i.e. pH profile, electroosmotic flow, uranium final distribution) represented an average for uranium tests conducted at approximately the same conditions (i.e. uranium concentration, processing time). Figure 3.21 shows the same profile type for the final in situ pH in acetic acid depolarization tests compared to U4201 and those obtained previously (Figure 3.6). It was expected that the pH would not increase near the cathode if the base front was neutralized by the HOAc, or if the cathodic reaction
Figure 3.21. Final in situ pH Profile in Acetic Acid Depolarization Tests for Uranium. Test U4201 is shown for comparison.
was depolarized. However, these tests showed an increase in in situ pH from the anode to the cathode, which implied that the cathodic reaction was not completely depolarized or the base produced was not completely neutralized. The pH readings for the HOAc used to fill the cathodic compartment changed from 3.5 to 4.5-6.0 for 15 to 24 hr period (1 to 2 orders of magnitude change in H⁺ ion concentration). This also indicated that at some point the H⁺ ion was nearly all consumed by electrolysis, or neutralized by base formed at the cathode. It should be noted that uranium can be quantitatively precipitated by the addition of ammonium hydroxide at pH of 4 or greater [3.11]. However, at the low uranium concentrations of the soil samples (3000 μg/g dry soil, which for a 1000 g soil sample at 42% water content corresponds to approximately 7100 μg U/mL solution, assuming the uranyl ions to be in the pore fluid), precipitation was observed to occur at a pH of 5 (Ksp of uranyl hydroxide was not found reported in the literature). Therefore, it was desirable to keep the pH at the cathode compartment below 4 to prevent precipitation of uranyl hydroxide. However, under the conditions reported for these tests, base was still free to migrate upstream, complicating the removal process.

Figure 3.22 presents the electroosmotic flow profiles for these tests. Similarly to test U4201, tests U4211 and U4212 showed an increase in flow rate in the first 200 hr of processing time, when the flow decreased or ceased. However, the latter showed lesser flow (0.61-0.83 pore volumes) compared to the regular test U4201 (1.00 pore volume). On the other hand, test U4210, conducted for longer period of time, showed a steady flow rate and a total of 1.59 pore volumes flow. No explanation was available for the
Figure 3.22. Electroosmotic Flow in Acetic Acid Depolarization Tests for Uranium. Test U4201 is shown for comparison.
difference, but it has been suggested [3.11] that differences in compaction or purity may affect the flow behavior in these systems.

Figure 3.23 depicts the electrical gradient as a function of time for these tests. The irregular pattern could be explained by the constant precipitation and dissolution of uranyl hydroxide formed at the cathode. Although HOAc was used in the cathodic compartment, a yellow precipitate was still observed on the cathode, an indication that the cathodic reaction was not completely depolarized and some water reduction was taking place. At later stage of the process (>300 hrs processing time, Figure 3.23), the tendency was observed for an equilibrium electrical gradient value in the acetic acid depolarization tests. This value (approximately 5 V/cm), is slightly lower than those observed in Figure 3.8 for regular uranium tests, where many of the tests exceeded the capacity of the power supply (i.e. electrical gradients > 11-12 V/cm) and others showed an average of 6 V/cm at late stages of the process. Partial depolarization of the cathodic reaction (i.e. H+ ion reduction) could account for these lower values at later stages of the process in the enhanced tests and less nonconducting uranyl hydroxide precipitate. It should be noted that in none of these tests was the power supply capacity exceeded. The energy expenditure was not calculated, but based on the electrical gradient profiles, the energy values are similar to those obtained in Section 3.4.5.

3.5.3.2. Uranium Removal

Figure 3.24 shows the final uranium distribution for the enhanced tests. Test U4201 is also shown for comparison, since its final distribution profile represents an
Figure 3.23. Electrical Gradient in Acetic Acid Depolarization Tests for Uranium. Test U4201 is shown for comparison.
Figure 3.24. Final Uranium Distribution in Acetic Acid Depolarization Tests for Uranium. Test U4201 is shown for comparison.
average of regular uranium tests conducted for about 500 hr period. The removal efficiency was similar except in the section closest to the cathode. An average removal rate between 90 to 95% was observed across the specimen. However, in the section adjacent to the cathode, test U4201 showed a removal rate of only 63%, compared to 85 to 95% removal in the enhanced tests. This increase in removal close to the cathode was attributed to the effect of acetate ions forming a soluble salt with the uranyl ions, or the dissolution of the hydroxide by direct action of the HOAc. However, between 60 to 76% of the initial uranium loaded into the system was still found precipitated on the cathode (Table 3.7). This range is lower than the average percentage of 82%7 found on the cathode for regular uranium tests. In addition, the effluent contained around 8 to 15% of the initial uranium loaded (Table 3.7), compared to only 2 - 4% found in regular tests (Table 3.4). This is an indication that more uranyl hydroxide was solubilized by the introduction of the acetic acid.

To summarize, the introduction of 0.01 M HOAc batchwise in the cathodic compartment increases the uranium removal close to the cathode by 22 to 32%. The flow and pH profiles were similar to those obtained in regular uranium removal tests, indicating that the cathodic reaction was only partially depolarized. The electrical gradient fluctuated between high and low values, presumably due to transient precipitation and dissolution of uranyl hydroxide. However, on the average the energy consumption would be similar to regular tests. The downside of using HOAc is introducing an additional cost to the process.

---

7 This value corresponds to the average amount of uranium found precipitated on the cathode (Table 3.4) after culmination of removal tests with processing time higher than 240 hrs.
3.5.4. Buffer Depolarization Tests

In order to counteract the effect of any base produced at the cathode, a 0.01 N acetic acid/sodium acetate (HOAc/NaOAc) buffer was pumped around the cathode (Figure 3.25). It was expected that constantly pumping buffer would neutralize the base more effectively. Similarly to the HOAc depolarization experiments, a concentration of 0.01 N was selected for the buffer based on applied current density and processing time. This relatively low concentration was expected not to effect the electroosmotic flow appreciably, although this was not recorded since the system was closed in the cathode section and under constant circulation (Figure 3.25). The amount of dissolved uranium present in the cathodic Mariotte bottle would indicate the amount of uranium that did not precipitate.

For these tests, a current density of 0.065 mA/cm² was selected. Previous uranium experiments (Table 3.3) showed that the usage of 0.13 mA/cm² current density removed between 85 to 95% of uranium across the specimen when the tests were conducted for at least 360 hr (e.g. test U4206). Based on the calculations shown in Figure 3.20, it was intended to study the effect of the current density in the uranium removal process. Figure 3.21 showed that the pH in the cathodic compartment would be maintained below 6 when using 5 mA density and 0.01 M HOAc concentration, Therefore, these buffer depolarization tests were conducted at lower current density, and for processing times ranging from 300 to 350 hr. For comparison, a uranium loaded specimen was also conducted at the same conditions. It was expected that the transport of uranium ions within the soil would be slowed down by the usage of lower current density. However, this lower current density was also expected to decrease the energy requirement for the removal process.
Figure 3.25. Schematic Diagram of Buffer Depolarization Test Apparatus
The buffer depolarization tests were labeled U4213, U4214, and U4216. Test U4215 was a regular test conducted at 0.065 mA/cm². Other relevant parameters for these tests are shown in Table 3.6.

3.5.4.1. Electroosmotic Flow, Electrical Gradient, pH Profile

Figure 3.26 presents the final in situ pH profiles for the buffer depolarization tests. The observed trend in all tests matches that described for all previous uranium tests. The increase in pH in sections close to the cathode indicated that base was still generated and migrating up stream. The reference test, U4215, showed a remarkably similar profile. It is evident from these profiles that the buffer pumped around the cathode did not appreciably modify the cathodic reaction or completely neutralize the base.

No electroosmotic flow was recorded for these tests. However, test U4215 (regular test) produced only 75 mL (0.16 pore volumes) for 344 hr processing time. This flow rate is significantly lower than the average of 0.76 pore volumes⁸ observed in regular tests conducted at 0.13 mA/cm² (Figure 3.7).

Figure 3.27 shows the electrical gradient profiles for these tests. Since a lower current density was used, lower voltage requirements were anticipated. Tests U4213 and U4215 showed the expected behavior, with an equilibrium electrical gradient of 3.0 to 3.2 V/cm, much lower than those for tests conducted at 0.13 mA/cm² (approximate average electrical gradient of 8 V/cm). Tests U4214 and U4216 showed an irregular pattern, similar

---

⁸ This value correspond to the average pore volume obtained for regular uranium tests (processing time > 240 hrs) reported in Table 3.4. Test U4205 was not included in the average.
Figure 3.26. Final in situ pH Profile in Buffer Depolarization Tests for Uranium. Test U4215 is a regular test shown for comparison.
Figure 3.27. Electrical Gradient in Buffer Depolarization Tests for Uranium. Test U4205 is a regular test shown for comparison.
to those observed for HOAc depolarization tests. It is possible that the precipitation/dissolution of uranyl hydroxide could have caused this behavior. In all of these tests, a yellow precipitate was observed on the cathode while the tests were conducted. This observation, together with the pH profile, provided an indication that the buffer did not fully depolarize the cathodic reaction.

3.5.4.2. Uranium Removal

Figure 3.28 presents the final uranium distribution profiles for the buffer depolarization tests. The profiles are similar for the four tests showed. In general, a removal rate ranging from 70 to 90% across the specimens was observed. Most of the uranium (69 to 81%) was still found precipitated on the cathode, while very little was found in the buffer itself (1 to 3%). Table 3.7 shows the mass balance for these tests.

The removal rate for these tests was in general lower than those obtained for regular tests and the previous depolarization tests. Several reasons can be given to explain this observation. Due to the lower current density, lower electrical gradient were generated across the specimen. Therefore, the transport of uranyl ions by migration would be affected. In addition, the use of a buffer introduced ions that competed with the uranyl ions in transporting the current within the specimen, lowering the transference efficiency of the contaminant cation.

To summarize, the use of a lower current density slowed down the transport of uranyl ions towards the cathode. The 0.01 N HOAc/NaOAc buffer circulated around the cathode did not fully neutralize the base front, nor did it prevent precipitation of uranyl
Figure 3.28. Final Uranium Distribution in Buffer Depolarization Tests for Uranium. Test U4215 is a regular test shown for comparison.
hydroxide. Most of the uranium was still found precipitated on the cathode and very little dissolved in the buffer.

3.5.5. Acid-Pumped Enhanced Test

In order to neutralize the base produced at the cathode, a setup was designed in which a fraction of the anodic liquid is bypassed directly into the cathodic chamber. It was expected that the acidic nature of the anodic liquid would partially neutralize the base, or depolarize the reaction, and the effluent flow remove any excess of base. In addition, bypassing some of the H⁺ ion produced at the anode to the cathode would prevent the saturation of the kaolinite in sections close to the anode, lowering the pH, and affecting the electroosmotic flow. Therefore, these tests were designed with a two-fold purpose, to neutralize/depolarize the cathodic reaction and to prevent overloading of the soil with H⁺ ions. Figure 3.29 shows the schematic diagram for these tests. As described in the previous section, a 0.065 mA/cm² current density was selected. The processing time was 200 hr. These tests were labeled U4217 and U4218. Test U4215 (0.065 mA/cm², 350 hr) was used for comparison.

Assuming a 1000 pCi/g uranium activity loaded onto the kaolinite sample, the amount of UCV² moles loaded would be,

\[
\text{moles UCV}^2 = \frac{1000 \text{ pCi U/g soil} \times 1000 \text{ g soil} \times (3.33 \times 10^5 \text{ pCi U/g U})}{(238 \text{ g U/mol})^4}
\]

\[= 1.26 \times 10^2 \text{ moles (or } 2.52 \times 10^2 \text{ equivalents)}
\]

To desorb this quantity of uranyl ions would require twice as much H⁺ ions (2.52 x 10² moles); therefore, the time required to produce this amount of H⁺ ions at the anode would be,
Figure 3.29. Schematic Diagram for Acid-Pumped Tests
\[ t = \frac{(2.52 \times 10^{-2} \text{ eq})(96,490 \text{ Coul/eq})}{(5 \times 10^{-3} \text{ A})(3600 \text{ s/hr})} = 135 \text{ hrs} \]

where a current of 5 mA was applied. However, if the CEC of kaolinite is taken into consideration (CEC = 1.4 meq/100 g soil), the amount of uranyl ions that would be adsorbed is given by the following calculation,

\[
\text{moles UO}_2^{+2} \text{ adsorbed} = (1.4 \text{ meq UO}_2^{+2}/100 \text{ g soil})(1000 \text{ g soil})(10^{-3} \text{ meq/eq})(1 \text{ mol/2 eq}) = 7.00 \times 10^{-3} \text{ moles (or 55.6\% of total loaded)}
\]

which would require only 135 hr (0.556) = 75 hrs. It should be noted that these calculations were made under the assumptions of 100 % water oxidation efficiency and only the amounts of time necessary to produce the required H\(^+\) ions, without taken into consideration the required time for transport of the desorbed species. It should also be noted that a small fraction of this H\(^+\) produced at the anode was bypassed to the cathode (assuming a pump rate of 2 mL/hr, this represents approximately 1\% of the total generated in one hour). Therefore, the calculated time may not represent the actual need for these tests. Nevertheless, it was expected that 200 hrs would be long enough to ensure the desorption and transport of the uranyl ions towards the cathode.

The pump used was able to deliver 2 mL/hr of acidic liquid to the cathode. Taking into account the amount of H\(^+\) generated at the anode (moles H\(^+\) produced = \(i F\), where \(i = 5\) mA, \(t\) time, and \(F\) the Faraday constant), the pumping rate, and the anode compartment volume (200 mL), it was expected that the amount of H\(^+\) pumped to the cathode would not be enough to completely neutralize the base formed (only 1 % of the acid produced in one
hour was bypassed to the cathode). However, it was anticipated that the base at the cathode would also be flushed away with the forced effluent due to the pumping action.

### 3.5.5.1. Electroosmotic Flow, Electrical Gradient, pH Profile

Figure 3.30 presents the final in situ pH profile for these tests. For comparison, test U4215 is also shown (0.065 mA/cm², 344 hr processing time). It is interesting to note that although tests U4217 and U4218 were conducted for only 200 hr, the final in situ pH profile across the specimen was below the initial pH. Test U4215 showed a typical final pH profile with increasing pH while approaching the cathode. These profiles for the acid-pumped experiments provided an indication that the cathodic reaction was effectively depolarized, or that the base generated at the cathode was either neutralized or flushed away together with the effluent.

Since part of the anodic liquid was pumped to the cathode, it was not possible to determine the electroosmotic flow. However, it was suspected that due to the lower amount of H⁺ ions entering the soil, the electroosmotic flow should not decrease as fast as shown for regular uranium tests (Figure 3.7). The total effluent was filtered and analyzed for uranium content. At the end of the tests, a yellow precipitate was observed in the cathodic liquid (final pH=10.12), which dissolved upon addition of 1M HNO₃.

Figure 3.31 presents the electrical gradients for these tests. The average equilibrium gradient for the acid-pumped tests (1.5 V/cm) was somewhat lower than the one showed for U4205 (2.0 to 2.5 V/cm). This was a further indication that the cathodic reaction was depolarized. These low electrical gradients were due to the use of a low current density
Figure 3.30. Final in situ pH in Acid-Pumped Tests for Uranium. Test U4215 is shown for comparison.
Figure 3.31. Electrical Gradient in Acid-Pumped Tests for Uranium. Test U4215 is shown for comparison.
(0.065 mA/cm²) and the depolarization/neutralization of the cathode reaction. This would imply lower energy expenditure in a practical application with this approach.

3.5.5.2. Uranium Removal

Figure 3.32 depicts the final uranium distribution in these tests. Results for U4215 are also shown for comparison. In general, it is observed that uranium was transported toward the cathode. However, the removal rates range between 30 to 80%, compared to an average removal of 80% for test U4215. Table 3.7 shows the mass balance for U4217 and U4218. Most of the uranium was found in the soil (32 - 44 %) and precipitated adjacent to the cathode (25 - 39 %). These lower removal rates within the soil were attributed to the lower current density used and the shorter processing time compared to U4215. However, the effluent held a 14.5-15.0% of dissolved uranium compared to 2 to 4 % found in regular uranium tests (Table 3.4). This observation indicates that the uranyl ions were transported past the cathode into the cathodic compartment, where they precipitated due to the high pH (pH=10.12). This high pH was also an indication that base was still produced at the cathode, but was not transported up stream so significantly into the specimen.

To summarize, the acid- pumped tests showed that they have potential to partially neutralize the base front generated at the cathode. However, the removal efficiency was lower (30 to 80%) than regular tests conducted at the same current density, where the average removal rate was 80% (test U4215). Different processing times and lower current density could account for this observation. The pH profiles proved that most of the base produced at the cathode was prevented from entering the specimen, reducing precipitation,
Figure 3.32. Final Uranium Distribution in Acid-Pumped Tests for Uranium. Test U4215 is shown for comparison.
and therefore, permitting lower electrical gradient profiles (hence, lower energy consumption). Some uranium was still precipitated at the cathode and in the cathodic liquid, where the pH was high (10-12). It is possible that the use of a faster bypass pumping rate and longer processing duration time might permit the complete removal of uranium.

3.5.6. Adipic Acid Depolarization Test

A different approach was conducted by using an adipic acid (1,4-hexanedicarboxylic acid) molded section adjacent to the cathode. Adipic acid is a dicarboxylic acid \((K_1 = 3.90 \times 10^{-5}, K_2 = 5.29 \times 10^{-6}\) at 25°C), slightly soluble in water (solubility 1.44 g/100 mL cold water, 160 g/100 mL boiling water), and non-toxic. It was envisioned that a slightly soluble acid next to the cathode would prevent any base from entering the soil system, and possibly trap the uranyl ions by complexation or precipitation. However, laboratory tests showed that uranyl ions did not form a precipitate when added to saturated solutions of adipic acid.

The test apparatus was similar to that described for the acid-molded section (Figure 3.13). An adipic acid paste was prepared (42% water content) and loaded in the last 1/10 of the cell volume (section adjacent to the cathode). The amount of adipic acid compacted in the system was calculated based on the current density and processing time. The amount of base generated at the cathode using a current density of 0.13 mA/cm\(^2\) (or a current of 10 mA for a 76.9 cm\(^2\) surface electrode) and 300 hrs processing time would be,

\[
\text{moles OH}^- = \frac{(5 \times 10^{-3} \text{ A})(300 \text{ hrs} \times 3600 \text{ s/hr})}{(96,490 \text{ Coul/eq})(1 \text{ eq/mol})} = 5.60 \times 10^{-2} \text{ moles}
\]

and given the following neutralization adipic acid-base,
\[
\text{HOOC-(CH}_2\text{)}_6\text{-COOH} + 2 \text{OH}^- \rightarrow \text{OOC-(CH}_2\text{)}_6\text{-COO}^- + 2 \text{H}_2\text{O}
\]

the amount of adipic acid required to neutralize the base produced under the given conditions would be \(2(5.60 \times 10^{-2}) = 1.12 \times 10^1\) moles adipic acid, or \((1.12 \times 10^1\) moles)(146.14 g/mol) = 16.4 g of adipic acid. In order to fill the last 1/10 of the cell volume, the prepared paste consisted of 70 g adipic acid, and 39.8 \% water content. These conditions were anticipated to effectively neutralize the base generated at the cathode during the processing time, and, therefore, prevent its migration up stream, and formation of uranyl hydroxide.

Paper filters separated the adipic acid paste section from the soil matrix. The soil specimen was prepared as described in Section 3.3. This test was labeled U4219. Relevant parameters are shown in Table 3.6.

3.5.6.1. Electroosmotic Flow, Electrical Gradient, pH Profile

Figure 3.33 shows the final in situ pH profile for test U4219. Test U4206 (0.13 mA/cm², 344 hr) is also shown for comparison. Test U4206 showed a slight increase in in situ pH close to the cathode. Test U4219 showed a flat pH profile below the initial pH measurement. Similarly to the acid-pumped tests in Section 3.5.5, this indicated that base was largely prevented from migrating up stream, i.e. it was neutralized by the adipic acid section.

Figure 3.34 depicts the electroosmotic flow observed for this test. For test U4219, the flow ceased after 90 hr processing time. After this time period, reverse flow was observed (i.e. from cathode to anode) judging by the increase in water level in the Mariotte bottle. However, due to experimental design this flow could not be quantified. It was
Figure 3.33. Final in situ pH in Adipic Acid-Molded Section Test for Uranium. Test U4206 is shown for comparison.
Figure 3.34. Electroosmotic Flow in Adipic Acid-Molded Section Test for Uranium. Test U4206 is shown for comparison.
speculated that the adipic acid entering the soil system was causing some kind of change on the zeta potential conditions within the soil, resulting in a reverse electroosmotic flow. The sign of the zeta potential could be reversed by adsorption of species to the soil surface, or at pH sufficiently low (pH<2). The anions produced by dissociation of adipic acid are unlikely to be adsorbed appreciably on the soil surface due to its negative charge. The possibility of some complexation of adipic anion with the uranyl ions and subsequent adsorption of metal complexes also must be considered. Saturated solutions of adipic acid showed a pH of 2.70. Interestingly, this value was the average final in situ pH measured across the specimen.

Figure 3.35 presents the electrical gradient observed for test U4219. Possibly due to the neutralization of the base by the adipic acid section or depolarization of the cathode reaction, a low profile was obtained. The electrical gradient showed a steady but slow increase during the process, with final values in the order of 2.5 to 3.0 V/cm. Test U4206 showed that the capacity of the power supply was exceeded after 65 hrs, reaching an electrical gradient of 12 V/cm. The average electrical gradient in these regular tests was approximately 8 V/cm (Figure 3.8). The lower values means that the energy expenditure will be significantly lower compared to those obtained in Section 3.4.5 if this approach is used to enhance the process.

3.5.6.2. Uranium Removal

Figure 3.36 depicts the final uranium profile for this test. Uranium was essentially removed (>90%) in sections close to the anode, and it accumulated in sections close to the cathode. None was found in the adipic acid section. Table 3.7 shows the final mass balance
Figure 3.35. Electrical Gradient in Adipic Acid-Molded Section Test for Uranium. Test U4206 is shown for comparison.
Figure 3.36. Final Uranium Distribution in Adipic Acid-Molded Section Test for Uranium. Test U4206 is shown for comparison.
for U4219. Most of the uranium (66 %) loaded into the kaolinite was found close to the cathode, and a significant amount (34 %) eluted with the effluent. A yellow precipitate was observed in the cathode compartment, but very little precipitated on the cathode (1.5 %). Based on the little electroosmotic flow observed for this test, it was concluded that the major transport mechanism was electromigration. As discussed in Section 3.5.1 for the acid-molded section, the lower electrical gradient developed across the specimen could account for slower migration rates. A major finding in this experiment is the increased amount of uranium found in the effluent. Again, this implied that more uranyl ions were transported without precipitating on the cathode and this avoids high electrical gradient profiles due to resistive films.

To summarize, the adipic acid section prevented the base from migrating into the soil system, preventing the precipitation of uranium on the cathode. Due to the adipic acid section, reverse flow (cathode to anode) was observed. The exact effect of the adipic acid on the zeta potential could not be determined. The lower electrical gradient causes a slower migration rate for the uranyl ions, but would also imply less energy expenditure. Tests with longer processing time should remove uranium more efficiently without the complicating features of the regular tests, i.e., increase in electrical gradient due to precipitation.

3.6. CONCLUSIONS AND RECOMMENDATIONS

1. Uranium at an activity of 1000 pCi/g clay (approximately 3000 μg/g) was efficiently removed (85 to 95% ) from kaolinite by electrokinetic processing. The removal decreased as the cathode compartment was reached, due to the increase in pH and
precipitation of uranium as a hydroxide (presumably UO$_2$(OH)$_2$.H$_2$O). Most of the uranium initially loaded (>85%) was found precipitated on the cathode.

2. Hydroxide precipitation increased the resistance and the electrical gradient across the specimens. This also means an increase in energy expenditure. The increase in electrical gradient caused the electroosmotic flow to drop as the capacity of the power supply was exceeded. Although it is reported that net transport by electromigration is an order of magnitude larger than electroosmotic flow, it was found that the latter played an important role in the removal of uranium.

3. The acid-molded cathode section test showed a partial depolarization of the cathodic reaction. This resulted in a lower electrical gradient which reduced energy expenditure, but also slowed down the transport of uranyl ions. Due to overloading the section with H$^+$ ions (60 times CEC of kaolinite) when 1 M H$_2$SO$_4$ was used in the molded section, no electroosmotic flow was observed. The final uranium distribution showed transport of uranyl ions towards the cathode, mainly due to electromigration since no electroosmotic flow was observed. However, removal rates did not exceed 70% in any section of the specimen tending to accumulate in the second half of the sample; most of the uranium (99.5%) was left in the soil. Due to the lower electrical gradient observed in this approach, it is recommended to continue studies by using lower acid concentrations in the molded section.

4. The acetic acid depolarization experiments showed an increase in uranium removal (22 to 32%) in the section adjacent to the cathode compared to regular tests. The cathodic reaction was only partially depolarized based on the final in situ pH profiles.
The transient precipitation/dissolution of uranyl hydroxide possibly caused notorious fluctuations in the electrical gradient.

5. The buffer depolarization tests did not show an increase in uranium removal. The buffer used did not fully neutralize the base produced at the cathode nor prevent the precipitation of uranyl hydroxide. Most of the uranium initially loaded into the clay (69 to 81 %) was still found precipitated on the cathode. The use of a lower current density (0.065 mA/cm²) resulted in a lower electrical profile (3.0 to 3.2 V/cm) when compared to regular uranium removal tests (0.13 mA/cm², 8 V/cm average). The lower electrical gradients caused a slow transport rate for the uranyl ions, and therefore, only 70 to 90% removal rates along the sample.

6. Acid-pumped tests showed potential to neutralize the base generated at the cathode. The pH profiles showed that excessive base was prevented from entering the soil system. Electrical gradients were significantly low (1.5 to 2.0 V/cm) due to prevention of uranium precipitation and the use of a lower current density (0.065 mA/cm²). Removal efficiency was lower (30 to 80%) compared to regular tests conducted at the same current density, where the average removal rate across the specimen was 80%. This can be explained by the low electrical gradients observed for the acid-pumped tests. Longer duration tests (>300 hrs), faster pumping rates (>2 mL/hr), and the use of higher current density (e.g. 0.13 mA/cm²) are recommended to improve uranium removal. This approach is promising since it offers an alternative to depolarize/neutralize the cathode reaction without introducing other chemicals into the system.
The use of adipic acid in an enhanced electrokinetic test neutralized the base and prevented its transport into the soil system. The final in situ pH profile showed a uniform value below the initial measurement for the specimen. A lower electrical gradient resulted in slower migration rates for the uranyl ions compared to regular tests conducted at similar conditions (300 hrs processing time, 0.13 mA/cm² current density, 1000 pCi/g soil activity). This slower transport resulted in removal rates of 90 to 95% close to the anode, but accumulation close to the cathode to levels between 150 to 260% of the initial uranium concentrations. Reverse electroosmotic flow was observed for this experiment. The reasons for this reversed flow are unclear and further studies are required. Since the major mechanism of transport would be electromigration, it is recommended to conduct further studies at longer processing times.

These tests demonstrated that the application of the technique is highly dependent on the acid-base chemistry of the contaminants. The ultimate decision on an enhancement alternative for electrokinetic processing would be dictated by the decision on whether the contaminant should be concentrated within the soil, or extracted with the effluent. However, the potential of the process to remove uranium with low energy expenditure has been demonstrated in these uranium removal studies.
3.7. REFERENCES


3.22. R. James and Healy. J. Colloid Interface Sci. 40, 1, 53 (1972)

CHAPTER 4
FEASIBILITY STUDIES OF THORIUM REMOVAL FROM KAOLINITE
BY ELECTROKINETIC SOIL PROCESSING

4.1. INTRODUCTION

Thorium is the second member of the actinide series of elements. There are twenty-five known isotopes of thorium with atomic masses ranging from 212 to 236, all of them unstable [4.1]. The most common isotope is thorium-232, which occurs naturally and has a half-life of $1.4 \times 10^{10}$ years. Figure 4.1 shows the decay scheme of the thorium series. Due to the dazzling light it produces, thorium was used primarily in the preparation of gas mantles. Because of the high refractive index and low dispersion of glass containing thorium oxide, it has found application in high quality lenses for cameras and scientific instruments.

Thorium-232 disintegrates with the production of radon-220 gas, which is an alpha emitter and presents a radiation hazard. Therefore, good ventilation areas are essential where thorium is stored or handled. Another isotope of interest is thorium-230, which is a daughter of uranium-238 (Figure 3.1). Thorium-230, with a half-life of $8 \times 10^4$ years, is the precursor of radium-226, a major environmental concern from a health standpoint. Most of the studies on thorium contaminated soils have been on this isotope [4.2, 4.3]. These two radionuclides are naturally occurring elements that are found in trace quantities in all soils, rocks, and water, producing very low-level background
Thorium-232
$1.4 \times 10^{10}$ years

$\alpha$

Radium-228
5.7 years

$\beta$

Actinium-228
6.13 hours

$\alpha$

Thorium-228
1.9 years

$\beta$

Radium-224
3.64 days

$\alpha$

Radon-220
55.6 seconds

$\alpha$

Polonium-212
$0.3 \times 10^{-6}$ seconds

$\beta$

Bismuth-212
60.6 minutes

$\alpha$

Polonium-216
0.15 seconds

$\alpha$

Thallium-216
3.1 minutes

$\alpha$

Lead-208
stable

$\beta$

Figure 4.1. Thorium-232 Decay Scheme
radioactivity. However, the level of contamination in uranium mill tailings represents a much higher concentration of these radionuclides [4.4].

Radium-226 is the most hazardous radionuclide because its short-lived, gaseous daughter, radon-222, grows rapidly, posing a significant health threat. However, the removal of radium-226 can only be accomplished together with the removal of thorium-230. Therefore, the importance of remediating thorium is evident.

Thorium has been reported to be the least mobile radionuclide among uranium, thorium, and radium [4]. The factors most prevalent in the sorption process of thorium are (1) ion exchange with clays and organic matter, and (2) precipitation as thorium hydroxide and hydrated thorium oxide. It was also reported [4.4] that strong humic and fulvic acid complexes with thorium in the neutral to acidic pH range are noncationic and mobile. The migration of thorium in the natural environment is reported to be mainly in the colloidal form (adsorbed on clay minerals).

The objective of this section is to assess the feasibility of removal of thorium-232 from Georgia kaolinite by using electrokinetic soil processing in bench-scale laboratory studies and to determine the efficiency of removal. Physical properties and chemical composition of the mineral clay used were described in section 3.1.

4.2. ADSORPTION ISOTHERM AND CATION EXCHANGE CAPACITY

Similarly to uranium studies, the cation exchange capacity of the kaolinite batch used for these experiments was determined by thorium-232 adsorption tests. A series of thorium solutions with concentrations ranging from 1 to 10,000 ppm were prepared by
dissolving proper amounts of thorium nitrate [Th(OH)₄·4H₂O] in deionized water. No attempt was made to adjust the solutions pH. Duplicate samples of 3.00 g of dry kaolinite were mixed with 30 mL of the thorium solutions in polyethylene jars with screw caps. The samples were shaken for three days in order to achieve equilibrium. The supernatant solution was filtered and analyzed for thorium content by ICP⁴. The amount of ions adsorbed onto the clay was calculated from the differences in ion concentrations between the original solution and those obtained in filtered supernatants.

Figure 4.2 depicts the adsorption isotherm of thorium onto kaolinite. The maximum amount of thorium adsorbed was approximately 4000 μg Th/g of soil. The CEC could not be calculated in its usual units (meq/100 g soil), since the chemical nature of thorium is not known due to extensive hydrolysis [4.4]. Therefore, it was not possible to compare the CEC for the batch of kaolinite used in these experiments with those used in previous uranium tests, and those reported in the literature [4.5-4.6].

The CEC of 4000 μg ²³²Th/g soil is equivalent to an approximate activity of 440 pCi ²³²Th/g soil ². The difference between the amounts of thorium and uranium adsorbed by kaolinite (1700 μg U/g soil) may reflect the tendency of thorium ions to hydrolyze and form more soluble polynuclear species.

---

¹ See Section 4.3.3 for Analytical Method.

² Specific activity ²³²Th = 1.09 x 10⁵ pCi/g.
Figure 4.2. Thorium Adsorption Isotherm for Kaolinite
4.3. EXPERIMENTAL

4.3.1. Sample Preparation

Similarly to uranium tests, thorium specimens were prepared by mixing air-dried Georgia kaolinite with thorium nitrate solutions to get the activity selected. Deionized water was added to the system in order to obtain a mix with 42% water content. The rationale for this value was explained in Section 3.3.1. The sample was left overnight to allow equilibration. Triplicate samples were taken to determine initial thorium concentration, initial water content, and initial in situ pH. The sample was then compacted using the Standard Proctor Effort Method (ASTM D1557-78) into polyacrylite sleeves (10 cm length and 10 cm outside diameter), as described in Section 3.3.1.

Figure 4.3 shows the thorium profile across the specimen for a sample mixed and compacted as described above. The average activity was 167 pCi/g soil (1500 μg Th/g soil), with a standard deviation of 4%.

The activity reported for thorium-232 in Superfund sites ranges between 4 to 16,000 pCi/g [4.7-4.8]. The initial activity selected for the electrokinetic studies was 1000 pCi \(^{232}\text{Th}/\text{g soil}\) (9200 μg Th/g soil), or approximately 2.3 times the CEC. It should be noted that a similar activity of uranium-238 is equivalent to only 3000 μg U/g soil.

Although a 1000 pCi \(^{232}\text{Th}/\text{g soil}\) activity (2.3 times CEC) is comparable to the one used for uranium tests (1.8 times CEC), due to problems encountered in removing

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3 See Section 4.3.3 for Analytical Procedure
Figure 4.3. Typical Initial Thorium Distribution in Cell (Average 167 ± 7 μgTh/g soil).
thorium (low mobility) and the negligible electroosmotic flow observed in the 1000 pCi $^{232}$Th/g soil tests (high ionic strength), it was decided to study lower concentrations (300, 150, 100, and 50 pCi/g corresponding to approximately 2800, 1400, 900, and 500 µg Th/g soil) for removal feasibility. These activity values are lower than the CEC for thorium. Therefore, all the thorium spiked into the kaolinite clay was adsorbed onto the soil surface.

4.3.2. Test Apparatus and Parameters

The apparatus and parameters used for the thorium experiments were identical to those described in Section 3.3.2. A constant current of 0.13 mA/cm$^2$ was applied to the system, and was selected based upon the results obtained by Hamed [4.5]. The total duration of the tests ranged from 150 to approximately 700 hr. Parameters monitored during the tests were the potential across the specimen, the electroosmotic flow, pH of effluent, and current density.

After completion of a test, the sample was sliced into ten fractions. Each fraction was analyzed for thorium concentration, water content, and in situ pH. Any effluent due to electroosmosis was measured, collected and analyzed for thorium content. Also, the electrodes were extracted with 1 M HNO$_3$ in order to desorb any thorium deposited or adsorbed. For some tests, the coefficient of electroosmotic permeability, $k_e$, and the energy consumption were calculated. The removal efficiency was determined by comparison with the initial thorium concentration. A total mass balance was conducted for total thorium loaded and extracted, and served as a guide to validate an experiment.
4.3.3. *ICP Analytical Method for Thorium*

4.3.3.1. Scope and Application

This Inductively Coupled Plasma (ICP) method was developed for elemental thorium analyses in solution for spiked laboratory soil tests, based on reference [4.7].

4.3.3.2. Sample Preparation

A portion of each soil section from a test was weighed, oven dried at 110°C for 18 hr minimum, cooled in a desiccator, and reweighed to determine its water content. Dried sections were labeled and stored in polyethylene bags.

From these samples, triplicate portions of 3.00 g were extracted for 24 hr minimum with 30.0 mL of 1 M nitric acid, under constant shaking. The samples were then filtered, diluted to a concentration range within 100 ppm solution, and sealed in polyethylene containers for ICP analyses. For reproducibility, a standard deviation of less than 5.0% was taken as acceptance criteria. Samples showing higher dispersion than 5.0% were reextracted and analyzed again. Similarly, a blank sample of kaolinite (no thorium) was also extracted for comparison. Samples extracted using this procedure showed a recovery of 97±1 % for kaolinite loaded with 1000 pCi/g (or approximately 9200 μg Th/g soil).

The electrodes were extracted by immersing them in 1 M HNO₃ for 24 hr, filtering the extract, and diluting to a typical volume of 1.0 L. The extracts were then properly diluted to within 100 ppm concentration range. Also, any effluent or liquid
sample was filtered, and diluted to within 100 ppm range using 1 M nitric acid. Similarly, these samples were sealed in polyethylene containers for ICP analyses.

4.3.3.3. Procedure

Thorium was analyzed using the 283.73 nm emission wavelength in an ARL Model 34000 ICP Spectrometer (Department of Agronomy, Louisiana State University). Other lines were available for thorium analysis, but this particular line was recommended by the manufacturer under the instrument settings. The reported sensitivity limit for thorium was 0.02 ppm. However, only a sensitivity of 1 ppm could be achieved. Typical reproducibility within 2% was accomplished for each reading. This sensitivity limit was quite ample for the electrokinetic studies, was fast, and devoid from matrix effects.

Before each batch of samples was analyzed, the instrument was checked for calibration with a commercial AA standard thorium solution (Aldrich Chemicals, 1000 ppm). Calibration curves using 0, 10, 50, and 100 ppm in 1 M HNO₃ solutions were obtained. A typical calibration curve is shown in Figure 4.4.

Each set of samples had a proper set of blank extractions, and standards included within the set of samples to double check for accuracy of analysis.

4.3.3.4. Interferences

The ICP minimizes matrix effects and chemical interferences. However, the efficient excitation of sample constituents at high temperature results in the possibility of
Figure 4.4. Typical ICP Calibration Curve for Thorium
spectral overlap interferences. Possible elemental spectral interferences are reported if Cr, Fe, Mg, Ni, or V are present in the extract. However, since the electrokinetic tests were made with extracts from synthetic kaolinite spiked with thorium, no spectral overlap was observed. Blank extractions were conducted for background checks and were subtracted from sample readings.

4.3.3.5. Calculations

(i) Soil Samples

A linear calibration curve within a 100 ppm range was obtained prior to each analysis of a set of sample. Assuming a linear relation of \( S = mC + b \), where \( S \) is the signal given by the ICP, \( C \) the thorium concentration of the nitric acid extract in ppm (\( \mu g \) Th/g solution), \( m \) and \( b \) the slope and intercept of the calibration curve (typically \( b=0 \)), the concentration of uranium in the nitric soil sample and the corresponding activity were calculated as follows:

\[
\begin{align*}
\mu g \text{ Th/g soil} &= [(S - b)/m] \times F \times \frac{30.0 \text{ mL extract}}{3.00 \text{ g soil}} \quad (4.1) \\
pCi^{232}\text{Th/g soil} &= [\mu g \text{ Th/g soil}] \times [1.09 \times 10^5 \text{ pCi}^{232}\text{Th/g Th}] \times [10^6 \text{ g/} \mu g] \quad (4.2)
\end{align*}
\]

where \( F \) is the dilution factor. The fraction of thorium left in each section after the process was calculated by calculating the ratio:

\[
\text{Fraction left} = \frac{[pCi^{232}\text{Th/g soil}]_{\text{section}}}{[pCi^{232}\text{Th/g soil}]_{\text{initial}}} \quad (4.3)
\]

For mass balance purposes, the total thorium content in each section was calculated by multiplying the \( \mu g \) Th/g soil obtained for each section times the total dried weight of
each section. The total thorium initially loaded in the specimen and the total thorium left in the soil processing were calculated as follows:

\[
\text{Total initial Th in soil (g)} = [\mu g \text{ Th/g soil}]_T \times W_T \times [10^{-6} \text{ g/\mu g}]
\]  

(4.4)

\[
\text{Total Th left in soil (g)} = \sum [\mu g \text{ Th/g soil}]_i \times w_i \times [10^{-6} \text{ g/\mu g}]
\]  

(4.5)

where \(W_T\) represents the total dried weigh of kaolinite (g) used in the experiment, \([\mu g \text{ Th/g soil}]_T\) is the concentration of Th in the original mix, \(w_i\) is the dried weight of soil (g) in each section after slicing the specimen, and \([\mu g \text{ Th/g soil}]_i\) is the corresponding Th concentration for each section.

(ii) Liquid Samples and Extracts

For liquid samples and extracts, the total thorium contents in g were calculated as follows:

\[
\text{Total Th in effluent (g)} = [\mu g \text{ Th/mL solution}] \times F \times V (mL) \times 10^{-6} \text{ (g/\mu g)}
\]  

(4.6)

where \(\mu g \text{ Th/mL solution}\) is the concentration obtained using the calibration curve, \(F\) is the dilution factor, and \(V (mL)\) is the total volume of liquid sample or extract.

(iii) Mass Balance

For a mass balance, (4.5) and (4.6) for each liquid sample were added and compared to (4.4). A mass balance of 75% minimum was adopted as a criterion to validate an experiment.
4.4. THORIUM REMOVAL STUDIES

Table 4.1 summarizes the initial conditions and parameters for thorium tests. The cells were labeled as Th42XX, where XX represents the experiment number.

4.4.1. Final and Initial pH Across the Specimen

Figure 4.5 presents the final *in situ* pH distribution across the specimens after completion of the tests. The observed trends are similar to those obtained for uranium tests (Section 3.4.1) and described in the literature [4.5, 4.6, 4.10]. Also, the initial *in situ* pH levels were relatively low (pH 3.5 to 4.0) compared to blank tests (pH 4.0 to 5.0). This was mainly due to hydrolysis of the thorium ions in the solution used to load the kaolinite. As described in Section 3.4.1., this lower pH and the high ionic strength due to the large amounts of thorium ions, caused a decrease in the zeta potential and affected the electroosmotic flow, as discussed in the next section.

Although most of the tests were conducted for more than 500 hr (Table 4.1), Figure 4.5 does not show appreciable transport of the acid front from the anode to the cathode. In addition, sections close to the cathode show an increase in pH. For comparison, the final *in situ* pH profiles for uranium tests (Figure 3.3) showed a more uniform pH distribution, with almost no significant rise of pH values close to the cathode which can be attributed to the advance of the acid front towards the cathode. The slower transport of the acid front for the thorium tests can be attributed to two factors: (1) the slower desorption kinetics of Th\(^{4+}\) ions from the clay surface compared to the UO\(_2\)\(^{2+}\) ions, requiring two times the equivalents of H\(^+\) ions for desorption, and (2) the
Table 4.1. Thorium Removal Test Program and Initial Parameters for Electrokinetic Tests

<table>
<thead>
<tr>
<th>Thorium Test</th>
<th>Water Content (%)</th>
<th>Saturation S (%)</th>
<th>Porosity e</th>
<th>Initial Activity (pCi/g)</th>
<th>Current Density (mA/cm²)</th>
<th>Duration (hr)</th>
<th>Effluent Volume (cm³)</th>
<th>Pore Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th 4201</td>
<td>42.4</td>
<td>87.6</td>
<td>1.27</td>
<td>312.9</td>
<td>0.13</td>
<td>144</td>
<td>18</td>
<td>0.04</td>
</tr>
<tr>
<td>Th 4202</td>
<td>42.9</td>
<td>96.1</td>
<td>1.17</td>
<td>277.5</td>
<td>0.13</td>
<td>621</td>
<td>67</td>
<td>0.15</td>
</tr>
<tr>
<td>Th 4203</td>
<td>42.5</td>
<td>99.1</td>
<td>1.13</td>
<td>145.6</td>
<td>0.13</td>
<td>571</td>
<td>82</td>
<td>0.19</td>
</tr>
<tr>
<td>Th 4204</td>
<td>44.2</td>
<td>99.0</td>
<td>1.17</td>
<td>176.9</td>
<td>0.13</td>
<td>677</td>
<td>32</td>
<td>0.07</td>
</tr>
<tr>
<td>Th 4205</td>
<td>43.0</td>
<td>92.5</td>
<td>1.22</td>
<td>94.7</td>
<td>0.13</td>
<td>668</td>
<td>288</td>
<td>0.64</td>
</tr>
<tr>
<td>Th 4206</td>
<td>41.8</td>
<td>100.0</td>
<td>1.08</td>
<td>45.2</td>
<td>0.13</td>
<td>664</td>
<td>129</td>
<td>0.30</td>
</tr>
</tbody>
</table>

1 Pore volume is defined as the total volume of the specimen multiplied by porosity (or e/(1+e)). All specimens had a total volume of 825 cm³.
Figure 4.5(a). Final in situ pH Profile for Thorium Tests
Figure 4.5(b). Final in situ pH Profile for Thorium Tests
low electroosmotic transport (low $k_e$), which, as discussed in the next section, was not significant.

4.4.2. Electroosmotic Flow and Electrical Gradient

Figure 4.6 depicts the electroosmotic flow for the thorium tests. The flow rates observed in these experiments were significantly lower (less than 0.2 pore volume) than those obtained for uranium tests (Figure 3.6) and blank tests.

The initial concentrations of thorium in the experiments ranged between 400 to 2900 µg/g soil (equivalent concentrations to activities of 45 to 312 pCi $^{232}$Th/g soil, respectively, Table 4.1). Compared to the initial concentrations of the uranium tests, 3000 µg/g soil, it was expected that the ionic strength would be less for the thorium specimens, or similar. Therefore, similar electroosmosis flow should have been observed during the earlier stages of the process, where the chemistry of the species does not play a significant role (e.g. precipitation of hydroxides).

On comparing Figure 4.6 with Figure 3.6, it is evident that the thorium ions ($\text{Th}^{4+}$) were exerting a bigger effect on the zeta potential than the uranyl ions ($\text{UO}_2^{2+}$), causing $\xi$ to be less negative. James and Healy [4.11] reported the effect of hydrolyzable ions on the zeta potential of silica as a function of the ions charge. For cations with higher charges, the net effect was described to be a charge reversal in zeta potential at lower pHs than the required pH for bulk precipitation. Therefore, it is expected that $\text{Th}^{4+}$ ions will cause a significant decrease in $\xi$ compared to the $\text{UO}_2^{2+}$ ions, in spite of the lower ionic strength of the thorium experiments.
Figure 4.6(a). Electroosmotic Flow for Thorium Tests
Figure 4.6(b). Electroosmotic Flow for Thorium Tests
The extent of the thorium ions hydrolysis compared to the uranyl ions should be considered also. A major tendency to hydrolyze by the thorium ions will produce lower pH that also exerts an effect on the zeta potential.

Figure 4.7 shows the electrical gradient developed in the thorium tests. In most of the tests, the voltage gradients reached high values, usually exceeding the maximum capacity of the power supply (110 to 120 V, or a gradient of 11 to 12 V/cm for a 10 cm long cell). The drop in current was monitored when the maximum voltage was exceeded. It was observed that the time at which the maximum capacity of the regulator was reached was inversely related to the initial thorium activity, i.e. the more the initial thorium concentration, the less time it took to reach the maximum voltage available. Due to these high voltage gradient profiles (current density was not maintained constant throughout the process) and the little electroosmotic flow observed, the energy expenditure and coefficient of electroosmotic permeability were not calculated.

The high electrical gradients observed were attributed to the precipitation of thorium hydroxide, which in addition to increasing the resistance in the medium, also clogged the soil pores due to its gelatinous nature [4.4], preventing electroosmotic flow. The development of the electrical gradient as a function of time was followed for one test and is described in Section 4.5.1.

4.4.3. Thorium Removal Efficiency

Figure 4.8 presents the thorium removal profiles for these tests. Although thorium experiments were conducted at different initial activities, they all displayed the
Figure 4.7(a). Electrical Gradient for Thorium Tests
Figure 4.7(b). Electrical Gradient for Thorium Tests
Figure 4.8(a). Final Thorium Distribution Profiles
Figure 4.8(b). Final Thorium Distribution Profiles
same trend for final distribution. These tests showed a removal between 20 to 70% for
the first half of the cell (closest to the anode), and an accumulation of thorium species in
the second half (closest to the cathode). The final thorium distribution profile is directly
related to the final pH profile (Figure 4.5).

The low transport of thorium was due to the high charge (+4) and comparatively
small radius of the thorium cations, resulting in an extensive adsorption on the soil
surface. Therefore, in order to desorb thorium, it is necessary to generate a higher
acidity level than that required for uranium (i.e. longer processing time). In addition to
difficult desorption, thorium ions show a strong tendency to interact with water (i.e.
usually 4 to 12 molecules associated per atom) and many anions present, forming
complexes that do not migrate easily. It is reported [4.4] that in general, thorium is the
less mobile radionuclide among uranium, thorium, and radium.

In addition, thorium hydroxide is a very insoluble and nonamphoteric gelatinous
precipitate, with a solubility constant of $1 \times 10^{-39}$ at 20°C [4.4]. When thorium ions
migrate within the cell to the cathode, they precipitated as hydroxide upon reaching the
base front migrating upstream. This is clear when comparing the final in situ pH with the
final thorium profile. This precipitation also was one of the factors responsible for the
increase in voltage requirements during the process. An increase in initial thorium
concentration resulted in faster voltage increases. This can be related to the amount of
thorium precipitating, causing the voltage to increase in a faster manner.

It should be noted that tests Th4201 to Th4206 had initial thorium concentrations
below their cation exchange capacity. Therefore, all the thorium spiked into the kaolinite
was adsorbed onto the clay surface. It has been reported [4.12-4.14] that less removal efficiency is obtained when the specie under investigation is present in the system below its CEC. No data for thorium concentration above the CEC were obtained. However, the fact that it is strongly adsorbed onto the clay surface and in amounts below the CEC for kaolinite further complicated the removal process.

Table 4.2 presents a mass balance for the thorium experiments. Most of the total initial thorium loaded (90 to 95%) remained in the soil, and small amounts were found on the cathode and in the effluent. However, the process removed 20 to 70% of the initial thorium present in sections close to the anode, and it was transported to sections closer to the cathode, where it precipitated as a hydroxide. Methodologies that improve the removal close to the cathode are needed.

### 4.5. ENHANCED ELECTROKINETIC REMOVAL OF THORIUM

The low removal of thorium (20 to 70% for the first half in sections close to the anode) in unenhanced electrokinetic tests, made thorium an attractive specie to study the efficiency and improvement of the enhanced electrokinetic approaches. Using the same approaches described in Section 3.5, the enhanced tests were aimed to neutralize base produced, or prevent the electrolysis of water at the cathode. Table 4.3 presents the enhanced tests conducted for thorium. The following is a description of the different procedures followed to improve the efficiency of the process in removing thorium.
Table 4.2. Mass Balance for Thorium Electrokinetic Experiments

<table>
<thead>
<tr>
<th>Thorium Test Code</th>
<th>Initial Thorium Content</th>
<th>Final Thorium Distribution</th>
<th>Mass Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pCi/g</td>
<td>Th (g)</td>
<td>%</td>
</tr>
<tr>
<td>Th 4201</td>
<td>312.9</td>
<td>2.764</td>
<td>2.648</td>
</tr>
<tr>
<td>Th 4202</td>
<td>277.5</td>
<td>2.547</td>
<td>2.567</td>
</tr>
<tr>
<td>Th 4203</td>
<td>145.6</td>
<td>1.479</td>
<td>1.562</td>
</tr>
<tr>
<td>Th 4204</td>
<td>176.9</td>
<td>1.608</td>
<td>1.586</td>
</tr>
<tr>
<td>Th 4205</td>
<td>94.7</td>
<td>0.851</td>
<td>0.742</td>
</tr>
<tr>
<td>Th 4206</td>
<td>45.2</td>
<td>0.427</td>
<td>0.373</td>
</tr>
</tbody>
</table>
Table 4.3. Enhancement Experiments for Thorium Removal Studies.

<table>
<thead>
<tr>
<th>Thorium Test Code</th>
<th>Enhancement Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th4207</td>
<td>Acid-Molded Cathode Section Test</td>
<td>Section adjacent to cathode molded with 1 M H₂SO₄</td>
</tr>
<tr>
<td>Th4208</td>
<td>Acid-Molded Cathode Section</td>
<td>Section adjacent to cathode molded with 0.1 M H₂SO₄</td>
</tr>
<tr>
<td>Th4209</td>
<td>Acid-Molded Cathode Section</td>
<td>Section adjacent to cathode molded with 0.01 M H₂SO₄</td>
</tr>
<tr>
<td>Th4210</td>
<td>Acid-Molded Cathode Section</td>
<td>Same as above</td>
</tr>
<tr>
<td>Th4211</td>
<td>Acetic Acid Depolarization</td>
<td>Cathode compartment filled with acetic acid</td>
</tr>
<tr>
<td>Th4212</td>
<td>Acetic Acid Depolarization</td>
<td>Same as above</td>
</tr>
<tr>
<td>Th4213</td>
<td>Adipic Acid Depolarization</td>
<td>Adipic acid paste in section adjacent to cathode</td>
</tr>
</tbody>
</table>
4.5.1. Acid-Molded Cathode Section Test

As described in Section 3.5.1, a cell was filled up to 9/10 of its total volume with thorium spiked kaolinite (45 pCi/g activity and 42% water content). The mix was compacted as described in Section 4.3.1. The last 1/10 volume of the cell (section adjacent to the cathode) was filled with kaolinite molded with $H_2SO_4$, so as to obtain 42% water content. Based on the experience obtained for the uranium test, 0.1 M and 0.01 M $H_2SO_4$ were used for the thorium experiments. Under these conditions, the clay CEC was not greatly exceeded. Assuming 1.47 meq/100 g soil for 100 g soil and 42mL $H_2SO_4$, it would represent about 6 times the CEC of kaolinite for 0.1 M $H_2SO_4$ and 0.6 times for 0.01 M $H_2SO_4$. Therefore, the ionic strength was kept at a low value so as to avoid deleterious effects on the electroosmotic flow. In addition, when using 0.01 M $H_2SO_4$, it was expected that all the $H^+$ ions would be adsorbed onto the soil surface. For comparison, an acid-molded test using 1 M $H_2SO_4$ was also conducted. Therefore, as explained in Section 3.5.1, the amount of $H^+$ loaded exceeded the CEC of kaolinite by approximately 60 times.

Similarly to the uranium experiments, it was expected that the acid-molded section would neutralize the base front generated by electrolysis of water at the cathode, or depolarize the reaction by reduction of $H^+$ ions present in the pore fluid of this last section. However, when using 0.01 M $H_2SO_4$ it was unlikely the depolarization of the cathodic reaction would occur since few $H^+$ ions would be available for reaction.

---

4 Determined from uranium adsorption experiments.
The test apparatus and experimental parameters were the same as those described in Section 4.3. These cells were coded Th4207 for 1 M H$_2$SO$_4$, Th4208 for 0.1 M H$_2$SO$_4$, and Th4209 and Th4210 for 0.01 M H$_2$SO$_4$. Table 4.4 shows relevant parameters for these tests.

4.5.1.1. Electroosmotic Flow, Electrical Field, pH Profile

Figure 4.9 depicts the electroosmotic flow observed for cells Th4207 to Th4209. For comparison, the electroosmotic flow for test Th4206 (same initial activity as Th4207-Th4210) is shown also. Acid-molded tests using 0.1 M and 0.01 M H$_2$SO$_4$ showed a dramatic increase in flow compared to a normal test. As expected, negligible flow was observed for 1 M H$_2$SO$_4$-molded cathode section. Table 4.4 presents the initial \textit{in situ} pH measurements and the electroosmotic flow after 500 hr of processing for the different systems. Cell Th4206 is also shown for comparison.

The difference in electroosmotic flow between these acid-molded tests can be explained in terms of the effect of the different conditions on the local zeta potential. As observed for uranium (Section 3.5.1), the use of 1 M H$_2$SO$_4$ in the molded section prevented any electroosmotic flow by increasing the ionic strength and lowering the pH. As reported in the literature [4.5, 4.8, 4.12], silica is positively charged at low pH. According to Shoesmith [4.15], the surface charge is positive at pH < 1, is zero between pH 1 and 3, and becomes progressively more negative above pH 3. James and Healy [4.11] stated that the PZC of silica is at pH 2, below which the surface charge becomes positive.
### Table 4.4. Thorium Removal Test Program and Initial Parameters for Enhanced Electrokinetic Tests

<table>
<thead>
<tr>
<th>Thorium Test</th>
<th>Water Content (%)</th>
<th>Saturation S (%)</th>
<th>Porosity e</th>
<th>Initial Activity (pCi/g)</th>
<th>Current Density (mA/cm²)</th>
<th>Duration (hr)</th>
<th>Effluent Volume (cm³)</th>
<th>Pore¹ Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th 4207</td>
<td>41.6</td>
<td>96.1</td>
<td>1.14</td>
<td>N.A.²</td>
<td>0.13</td>
<td>496</td>
<td>13</td>
<td>0.03</td>
</tr>
<tr>
<td>Th 4208</td>
<td>41.4</td>
<td>96.0</td>
<td>1.13</td>
<td>45.1</td>
<td>0.13</td>
<td>725</td>
<td>545</td>
<td>1.24</td>
</tr>
<tr>
<td>Th 4209</td>
<td>41.4</td>
<td>96.6</td>
<td>1.13</td>
<td>45.5</td>
<td>0.13</td>
<td>785</td>
<td>1131</td>
<td>2.59</td>
</tr>
<tr>
<td>Th 4210</td>
<td>42.0</td>
<td>90.4</td>
<td>1.22</td>
<td>41.8</td>
<td>0.13</td>
<td>647</td>
<td>836</td>
<td>1.85</td>
</tr>
<tr>
<td>Th 4211</td>
<td>41.6</td>
<td>93.5</td>
<td>1.17</td>
<td>93.7</td>
<td>0.13</td>
<td>462</td>
<td>120</td>
<td>0.27</td>
</tr>
<tr>
<td>Th 4212</td>
<td>41.4</td>
<td>92.1</td>
<td>1.18</td>
<td>97.0</td>
<td>0.13</td>
<td>509</td>
<td>112</td>
<td>0.25</td>
</tr>
<tr>
<td>Th 4213</td>
<td>41.6</td>
<td>76.5</td>
<td>1.43</td>
<td>97.7</td>
<td>0.13</td>
<td>320</td>
<td>---</td>
<td>0.11</td>
</tr>
</tbody>
</table>

¹ Pore volume is defined as the total volume of the specimen multiplied by porosity (or e/1+e). All specimens had a total volume of 825 cm³.

² N.A. = Not Analyzed
Figure 4.9. Electroosmotic Flow in Acid-Molded Cathode Section Tests for Thorium. Test Th4206 is shown for comparison.
Table 4.5 reflects an agreement with this surface charge dependence on the pH. The \textit{in situ} pH of the acid-molded section decreased with the higher acid concentration, causing a change in the surface charge. The net effect is that the electrokinetic zeta potential becomes less negative with decreasing pH, and may eventually become zero for pH < 1 or 2. As reflected by equation 2.6, the consequence is lower electroosmosis transport, $k_e$. The flow observed after 500 hr for each case was used as an indication of the magnitude of electroosmotic transport as a function of the initial \textit{in situ} pH of the molded section.

Also shown in Table 4.5 is the \textit{in situ} pH and electroosmotic flow measurements for a regular test (Th4206). Although the initial \textit{in situ} pH for the clay system was comparable to those observed for the enhanced tests, the lack of an acid-molded section prevented an efficient electroosmotic transport. As discussed in Section 4.4.2, the low \textit{in situ} pH was due to hydrolysis of the thorium. In addition, the effect of hydrolyzable ions on the soil surface charge was also described [4.11]. These two factors combined accounted for lower electroosmotic flow in regular tests. It is suggested that the absence of Th$^{4+}$ ions in the acid-molded section improved the electroosmosis flow in the enhanced studies where this section was not overly saturated with H$^+$ ions.

Figure 4.10 depicts the electrical gradient of the acid-molded cathode section thorium tests. Test Th4206 is also shown for comparison. Significantly lower electrical gradients were developed with the molded section tests. The addition of H$^+$ ions in the porous media increased its conductivity and lower the energy requirements to sustain a constant current. For all the enhanced removal tests, a tendency to reach an equilibrium
Table 4.5. Initial in situ pH in Acid-Molded Cathode Section Tests for Thorium

<table>
<thead>
<tr>
<th>Test Code</th>
<th>Acid Conc. in Molded Section</th>
<th>Acid-Molded in situ pH</th>
<th>Initial Th Conc. (ug/g)</th>
<th>Initial Soil in situ pH</th>
<th>Flow after 500 hr (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th4206</td>
<td>---</td>
<td>-----</td>
<td>415</td>
<td>3.71</td>
<td>129</td>
</tr>
<tr>
<td>Th4207</td>
<td>1 M</td>
<td>0.81</td>
<td>N.A.</td>
<td>3.96</td>
<td>13</td>
</tr>
<tr>
<td>Th4208</td>
<td>0.1 M</td>
<td>2.88</td>
<td>414</td>
<td>3.87</td>
<td>381</td>
</tr>
<tr>
<td>Th4209</td>
<td>0.01 M</td>
<td>3.86</td>
<td>383</td>
<td>4.18</td>
<td>751</td>
</tr>
<tr>
<td>Th4210</td>
<td>0.01 M</td>
<td>4.10</td>
<td>417</td>
<td>3.75</td>
<td>648</td>
</tr>
</tbody>
</table>
Figure 4.10. Electrical Gradient in Acid-Molded Cathode Section Tests for Thorium. Test Th4206 is shown for comparison.
reading of 8 to 9 V/cm was observed. This value is still higher than those reported for blank specimens (4 to 6 V/cm) [4.16]; however, it is significantly lower than those observed for unenhanced thorium tests (Figure 4.6), where the voltage requirement exceeded the power supply capacity. The lower electrical gradients were related to an increase in conductivity closer to the cathode and by both the depolarization of the cathodic reaction and the neutralization of the base front generated at the cathode, the latter preventing extensive precipitation of thorium as hydroxide.

In order to study the transient development of the electrical gradient, a study similar to the one described in Section 3.4.2 was conducted. Figure 4.11 shows the development of the electrical gradient with time for test Th4209. The pattern observed is similar to the one described in Section 3.4.2 and in the literature [4.5, 4.6].

1. There was a significant change in the electrical gradient for the last sections of the cell within 11 hr of processing. Within the zone extending from a normalized distance from anode of 0.00 to 0.85, there was no significant electrical potential changes. This implies that the electrical conductivity across the specimen is high enough to prevent any significant losses until the zone close to the cathode is reached.

2. The potential difference reached a steady value of 73 V in 117 hr, remaining about the same until the end of the test (647 hr). However, the potential drop was extended from a normalized distance of 0.60 to 1.00 from the anode. It was observed that this zone extends gradually towards the middle of the system with further processing.
Figure 4.11. Development of Electrical Gradient for a Thorium Test
Both observations could be explained in terms of the advancing acid front and the precipitation of thorium hydroxide. However, unlike uranium, no thorium precipitate was observed on the cathode. This fact was explained in terms of the lower mobility and slower kinetics of desorption of the $\text{Th}^{4+}$ ions compared to the $\text{UO}_2^{2+}$ ions. As a consequence, most of the precipitate was found in middle portions of the specimen.

Figure 4.12 shows the final *in situ* pH obtained for the acid-molded cathode section tests. For comparison, the results of test Th4206 are presented. Compared to a regular test, the enhanced studies showed that the acid front was transported further into the inner sections of the system. The pH average value for the first half of the specimens was 1.8, compared to values of 1.6 to 4.6 for the same halves of regular thorium tests (Figure 4.3). This is in agreement with the significant increase in electroosmotic flow for the acid-molded tests, which aided the transport of the acid front. However, for regions closer to the cathode, an increase in pH was still observed. This indicates that the basic front was only partially neutralized by the acid-loaded kaolinite, and was still able to cause thorium precipitation within the specimen.

**4.5.1.2. Coefficient of Electroosmotic Permeability, $k_e$**

Figure 4.13 presents the coefficient of electroosmotic flow calculated using equation 2.1 for the acid-molded tests. Since test Th4207 did not show appreciable flow, only $k_e$ for tests Th4208 to Th4210 are presented. As discussed in Section 3.4.3, typical values for $k_e$ in clays range between $1 \times 10^{-5}$ to $1 \times 10^{-4} \text{ cm}^2/\text{V.s}$. A blank test shown in Figure 3.10 showed an average value of $4 \times 10^{-6} \text{ cm}^2/\text{V.s}$. Acid-molded
Figure 4.12. Final in situ pH Profile for Acid-Molded Cathode Section Tests for Thorium. Test Th4206 is shown for comparison.
Figure 4.13. Coefficient of Electroosmotic Permeability ($k_e$) in Acid-Molded Cathode Section Tests for Thorium
experiments for thorium showed an average equilibrium value of $0.5 \times 10^{-6}$ cm$^2$/V.s. This value is still below the one observed for blank specimens; however, it represented a significant increase over the regular thorium tests, where the electroosmotic flow was minimum and high electrical gradients were observed. It was evident that the acid-molded section in the enhanced tests was controlling the overall electroosmotic flow. The presence of a thorium-free section prevents the soil surface from acquiring a less negative zeta potential which, as described by James and Healy [4.10], lowers $\xi$ and, therefore, the electroosmotic flow rate.

4.5.1.3. Thorium Removal

Thorium removal for sections close to the anode was significantly enhanced in these experiments compared to the regular tests. Figure 4.14 shows that thorium ions were more efficiently transported than in regular tests. Table 4.6 presents the mass balance for these tests. A removal between 80 to 90% for the first half of the specimen was observed, compared to no removal to 80% in regular tests (Figure 4.8). Similarly, most of the thorium was concentrated in the second half of the cell. The enhancement in removal was attributed to the increased electroosmotic flow. It was evident that the enhanced flow facilitated the transport of the acid front and thorium ions. As described in Section 4.4.3, the comparison of the final distribution and the final in situ profiles provided an indication that thorium is precipitating as hydroxide.
Figure 4.14. Thorium Final Distribution in Acid-Molded Cathode Section Tests. Test Th4206 is shown for comparison.
Table 4.6. Mass Balance in Enhanced Electrokinetic Tests for Thorium Removal Studies

<table>
<thead>
<tr>
<th>Thorium Test Code</th>
<th>Initial Thorium Content (pCi/g)</th>
<th>Thorium Initial Th (g)</th>
<th>Thorium Final Th (g)</th>
<th>Thorium Final Th Distribution (%)</th>
<th>Mass Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th4207</td>
<td>N.A.¹</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Th4208</td>
<td>45.1</td>
<td>0.365</td>
<td>0.373</td>
<td>102.2</td>
<td>105.2</td>
</tr>
<tr>
<td>Th4209</td>
<td>45.5</td>
<td>0.382</td>
<td>0.385</td>
<td>100.8</td>
<td>102.1</td>
</tr>
<tr>
<td>Th4210</td>
<td>41.8</td>
<td>0.334</td>
<td>0.327</td>
<td>97.9</td>
<td>102.4</td>
</tr>
<tr>
<td>Th4211</td>
<td>93.7</td>
<td>0.860</td>
<td>0.809</td>
<td>94.1</td>
<td>93.9</td>
</tr>
<tr>
<td>Th4212</td>
<td>97.0</td>
<td>0.883</td>
<td>0.878</td>
<td>99.4</td>
<td>100.6</td>
</tr>
<tr>
<td>Th4213</td>
<td>97.7</td>
<td>0.798</td>
<td>0.716</td>
<td>89.7</td>
<td>94.6</td>
</tr>
</tbody>
</table>

¹ N.A. = Not Analyzed
With these observations, the following assertions can be made:

1. The acid-molded section improved the electroosmotic flow by (i) increasing the electrokinetic zeta potential, and (ii) decreasing power requirement by partially depolarizing the cathode reaction, or partially neutralizing the base front generated at the cathode and preventing extensive or premature precipitation of thorium hydroxide.

2. The difference in electroosmotic transport, $k_e$, for the different concentrations of $\text{H}_2\text{SO}_4$ used in the molded sections reflected the dependence of $k_e$ on the ionic strength and the zeta potential. Therefore, to optimize $k_e$, a compromise between acid concentration and optimum electroosmotic flow should be made.

4.5.1.4. Energy Expenditure

Figure 4.15 presents a plot of the energy expended per unit volume of soil (kW-hr/m$^3$) as a function of time. The energy expenditure per unit volume soil, $E_u$ (kW-hr/m$^3$), was calculated as follows:

$$ E_u = \frac{E(t)}{V_s} = \int \frac{I \cdot V(t) \cdot dt}{V_s} \times F $$

where $E_u$ is the energy (kW-hr), $V_s$ is the volume of soil mass processed (m$^3$), $V(t)$ is the voltage (V) as function of time, $I$ is the current (A), $t$ is the processing time (s), and $F$ is a unit correction factor to express $E_u$ in kW-hr/m$^3$. In tests with constant current condition, the energy expended is directly related to the voltage as a function of time.
Figure 4.15. Energy Consumption in Acid-Molded Cathode Section Tests for Thorium. Test Th4206 is shown for comparison.
In general, thorium tests showed a higher energy expenditure compared to uranium tests. Test Th4206 (regular thorium test) consumed 425 kW-hr/m³ for 350 hr processing time, compared to 81 to 315 kW-hr/m³ for 200 to 500 hr processing period for uranium tests (Figure 3.12). The energy expenditure was significantly decreased for the enhanced thorium tests, as can be by the lower slopes in Figure 4.14 for tests Th4208 to Th4210. For these tests, an energy consumption between 520 to 650 kW-hr/m³ for 650 to 800 hr processing time was measured. However, it should be emphasized that this range of energy only resulted in 80 to 90% thorium removal for the first half of the specimen.

4.5.2. Acetic Acid Depolarization Tests

As described in Section 3.5.3, this test was intended to hamper the electrolysis of water at the cathode. Therefore, the prevention of base formation will avoid precipitation of thorium hydroxide, which complicated the removal process. It was expected that introducing a weak acid (HOAc, Kₐ = 1.7 x 10⁻⁵) in the cathodic compartment would not significantly increase the ionic strength in the system, thus affecting the electroosmotic flow to a lesser extent. In addition, the acetate ions would migrate towards the anode and would not precipitate with the thorium ions, since thorium acetate is a soluble salt. This approach was expected to depolarize the cathode reaction and allow thorium ions to elute with the effluent.

The test setup was the same as shown in Figure 3.4. The experimental parameters were the same as those used for regular thorium tests (i.e. current density 0.13 mA/cm², processing time 500 hr, thorium activity 100 pCi/g). As described for
similar enhanced uranium tests, HOAc 0.01 M was selected based on the applied current density and the volume of the cathodic compartment. The acid was placed manually into the cathodic compartment and replaced daily with fresh acid. The replaced fractions were collected and the pH was measured. These measurements provided an idea of the amount of H⁺ ions consumed during the 24-hr period. A significant increase in pH would indicate the consumption of the HOAc, or the neutralization of the base produced by electrolysis of water. The HOAc fractions were then filtered, properly diluted, and analyzed for uranium content. In addition, any effluent was collected and filtered for analysis. These tests were labeled Th4211 and Th4210; relevant parameters are shown in Table 4.4.

4.5.2.1. Electroosmotic Flow, Electrical Gradient, pH Profile

Figure 4.16 shows the final in situ pH profiles for the acetic acid depolarization tests. For comparison, the data obtained for test Th4205 (0.13 mA/cm², thorium activity 95 pCi/g, 670 hr processing time) are also shown. Figure 4.16 shows the same profile type for the final in situ pH in acetic acid depolarization tests compared to Th4205 and those obtained previously (Figure 4.5). It was expected that the pH would not increase near the cathode if the base front was neutralized by the HOAc or the cathodic reaction was depolarized. However, these tests showed an increase in in situ pH from the anode to the cathode, which implied that the cathodic reaction was not completely depolarized, or the base produced was not completely neutralized. The pH readings for the HOAc used to fill up the cathodic compartment changed from 3.6 to
Figure 4.16. Final in situ pH Profile in Acetic Acid Depolarization Tests for Thorium. Test Th4205 is shown for comparison.
This also indicated that at some point the HOAc was nearly all consumed, or neutralized by base formed at the cathode. Under these circumstances, base could be free to migrate up-stream, complicating the removal process.

Figure 4.17 presents the electroosmotic flow profiles for these tests. Tests Th4211 and Th4212 showed reproducibility. Interestingly, the flow for these tests ceased after 200 hr, while flow in the regular test was maintained during the process. This observation was made at nearly the same time as the electrical gradient exceeded the maximum capacity of the power supply, and might have been caused by precipitation of thorium hydroxide within the pores of the specimen, which prevents further electroosmotic flow.

Figure 4.18 depicts the electrical gradient as a function of time for these tests. The enhanced tests showed a rapid increase during the first 200 hr, thereafter exceeding the capacity of the power supply. Consequently, a current drop was recorded (Figure 4.19). Normally, when the capacity of the power supply is exceeded, this causes a drop in current and electroosmotic flow. This was observed for the enhanced tests, where the flow ceased after the electrical gradient peaked the capacity of the regulator. However, for reasons that are not clear, this did not occur in test Th4205. It is possible that different compaction could have affected the electroosmotic permeability characteristics of the clay. The increase in electrical gradient might be an indication that the cathodic reaction was not completely depolarized and some water reduction was taking place, causing thorium hydroxide to precipitate.
Figure 4.17. Electroosmotic Flow in Acetic Acid Depolarization Tests for Thorium. Test Th4205 is shown for comparison.
Figure 4.18. Electrical Gradient in Acid Depolarization Tests for Thorium. Test Th4205 is shown for comparison.
Figure 4.19. Current Changes in Acetic Acid Depolarization Tests for Thorium. Test Th4205 is shown for comparison.
4.5.2.2. Thorium Removal

Figure 4.20 shows the final thorium distribution for the enhanced tests. Test Th4205 is shown for comparison. Table 4.5 presents the mass balance for these experiments. Most of the thorium initially loaded into the kaolinite (81 to 99%) was found in the soil. Compared to Test Th4205, less transport of the thorium ions towards the cathode was observed. Average removal rates were only 20 to 40% for the first half of the specimen. Thorium accumulated in the second half. Minor amounts of thorium were found in the effluent (0.2 to 0.6%) and on the cathode (1.0 to 1.2%). These results indicated that the cathodic reaction was not successfully depolarized, and that base was allowed to enter the soil system where it caused the precipitation of hydroxide.

To summarize, the introduction of HOAc at 0.01 M concentration in the cathodic compartment did not enhance thorium removal. The flow and pH profiles were similar to regular tests, indicating that the cathodic reaction was only partially depolarized. High electrical gradients were observed for these tests, which further indicated that base was entering into the soil system and precipitating the thorium ions as hydroxide.

4.5.3. Adipic Acid-Molded Section Depolarization Test

As described in Section 3.5.6, an adipic acid molded section test was conducted for thorium. Adipic acid is a dicarboxylic acid \( (K_1 = 3.90 \times 10^{-5}, \ K_2 = 5.29 \times 10^{-6} \text{ at } 25^\circ C) \), slightly soluble in water (solubility 1.4 g/100 mL cold water, 160 g/100 mL boiling water), and non-toxic. It was expected that a slightly soluble acid next to the cathode would prevent any base from entering the soil system, and possibly trap the thorium ions by complexation or
Figure 4.20. Final Thorium Distribution in Acetic Acid Depolarization Tests. Test Th4205 is shown for comparison.
precipitation. However, laboratory tests showed that thorium ions did not precipitate in saturated solutions of adipic acid.

The same calculations shown in Section 3.5.6 were used to prepare this test for thorium. The test apparatus is similar to that described for the acid-molded section (Figure 3.13). An adipic acid paste was prepared (42% water content) and loaded in the last 1/10 of the cell volume (section adjacent to the cathode). The amount of adipic acid compacted in the system was calculated based on the current density (0.13 mA/cm²) and processing time (anticipated 300 hr). Paper filters separated this section from the soil matrix. The soil specimen was prepared as described in Section 4.3.1. This test was labeled Th4213. Relevant parameters are shown in Table 4.6.

4.5.3.1. Electroosmotic Flow, Electrical Gradient, pH Profile

Figure 4.21 shows the final in situ pH profile for test Th4213 (0.13 mA/cm², 319 hr). Test Th4205 (0.13 mA/cm², 660 hr) is shown for comparison. Test Th4205 showed an increase in in situ pH close to the cathode. Although test Th4213 was conducted for only 319 hr, Figure 4.21 shows a flat pH profile below the initial in situ pH value. Consistent with the adipic acid tests for uranium (Section 3.5.6.1), this indicated that base was prevented from migrating upstream, i.e., it was neutralized by the adipic acid section.

Similarly to the adipic acid test for uranium (Section 3.5.6.1), test Th4213 presented reversed electroosmotic flow judging by the increase in water level in the Mariotte bottle. However, due to experimental design this flow could not be quantified. As stated earlier, it is possible that dissolved adipic acid entering the soil system was causing some kind of change
Figure 4.21. Final in situ pH Profile in Adipic Acid-Molded Section Test for Thorium (Th4213). Test Th4205 is shown for comparison.
on the zeta potential conditions within the soil, determining a reverse flow. The sign of the zeta potential could be reversed by adsorption of species to the soil surface, or at sufficiently low pH (pH<2). The exact reason for the possible reversal of the flow is not known. The anions produced by dissociation of adipic acid were unlikely to be adsorbed on the soil surface due to its negative charge. The possibility of complexation with the thorium ions and subsequent adsorption can be considered. Saturated solutions of adipic acid showed a pH of 2.70. Interestingly, this value was the average final in situ pH measured across the specimen similarly to that observed for the corresponding uranium test.

Figure 4.22 presents the electrical gradient observed for test Th4213. Test Th4205 is shown for comparison. Compared to test Th4205, Th4213 showed low values at earlier stages. However, after 250 hr, a rapid increase in electrical gradient was observed. Figure 4.23 shows the current drop after the maximum output of the power supply was exceeded. The reasons for this increase are not clear. Based on the amount of Th$^{4+}$ ions and the water content loaded into soil (2.90 g Th(NO$_3$)$_4$.4H$_2$O, F.W. =552 and 511 mL H$_2$O), the initial molar concentration of thorium ions in the pore fluid should be about 5.3 x 10$^{-3}$ M. The pH required to precipitate thorium hydroxide ($K_{sp}$=1 x 10$^{-39}$, 20°C) would be 4.74. This value was not reached across the specimen (Figure 4.21). It is possible that the pH increased to higher values in the pore fluid than those indicated by the in situ measurements. Speciation studies of thorium species across the specimen would provide further insights for the increase in the electrical gradient.
Figure 4.22. Electrical Gradient in Adipic Acid-Molded Section Test for Thorium (Th4213). Test Th4205 is shown for comparison.
Figure 4.23. Current Change in Adipic Acid-Molded Section Test for Thorium (Th4213). Test 4205 is shown for comparison.
4.5.3.2. Thorium Removal

Figure 4.24 depicts the final thorium profile for this test. In general, lower removal rates throughout the specimen was observed compared to Th4205. This could be explained by the lower electrical gradients in test Th4213 at earlier stages of the process. It is expected that longer processing time would increase thorium transport, since apparently base was prevented from entering into the soil system, and it is possible that hydroxide precipitation was also prevented. Table 4.6 presents the mass balance for this test. Some transport of thorium from the anode to the cathode was observed. Since reversed flow was observed, this transport was due to migration rather than electroosmosis. Most of the thorium initially loaded into the kaolinite (90%) was found within the soil, and minor amounts in the effluent (2%) and on the cathode (2%). These numbers are comparable to regular tests (Th4205, Table 4.2).

To summarize, based on the pH profiles, the adipic acid section prevented the base from migrating into the soil system, preventing the precipitation of thorium in the cathode compartment. Due to the adipic acid section, reverse flow (cathode to anode) was observed. The exact effect of the adipic acid on the zeta potential could not be determined. The lower electrical gradients than regular thorium tests at earlier stages of the process would mean a slower migration rate for the thorium ions. Tests with longer processing times ($t > 320$ hrs) might remove thorium more efficiently. Speciation studies are necessary to determine the chemical nature of thorium in the soil.
Figure 4.24. Final Thorium Distribution in Adipic Acid-Molded Section Test (Th4213). Test Th4205 is shown for comparison.
4.6. CONCLUSIONS AND RECOMMENDATIONS

1. Thorium removal tests at 50 to 300 pCi/g of activity showed that thorium is transported mainly by migration from the anode to the cathode. Due to its lower mobility compared to uranium, this transport was not as effective as that of uranyl ions. The mobility of thorium is greatly affected by its high ionic charge (+4), which causes stronger adsorption onto the clay surface and makes desorption by hydrogen ions more difficult. The tendency to hydrolyze of thorium ions also caused a decrease in electroosmotic flow. Thorium precipitated as insoluble hydroxide within the specimens, increasing the electrical gradient, and preventing further transport to the cathode.

2. The use of an acid-molded section (sulfuric acid tests) increased significantly the electroosmotic flow and the transport of thorium to the cathode, increasing the removal rate to 85 to 95%. The amount of increase in flow was found to be related to the acid concentration used to load the molded section: high acid concentration (1 M H$_2$SO$_4$) prevented electroosmotic flow due to a large excess over the CEC of kaolinite. Lower acid concentrations (0.01 M H$_2$SO$_4$) provided a larger increase in electroosmotic flow. However, based on the pH profiles, the acid-molded section did not neutralize the base; therefore, complete depolarization/neutralization of the cathodic reaction was not achieved. This approach demonstrated the technique's capabilities to enhance removal of low mobility species.
3. The acetic acid depolarization test did not adequately depolarize/neutralize the cathode reaction. Thorium removal was lower due to probable precipitation of hydroxide. High electrical gradients and little electroosmotic flow were observed.

4. The use of adipic acid in an enhanced electrokinetic test prevented the base from migrating into the soil system. The pH profile showed no base migration upstream. Reverse electroosmotic flow was observed for this experiment. The reasons for this reversed flow are unclear and further studies are required. Since the major mechanism of transport would be electromigration, it is recommended that further studies at longer processing times (t > 320 hrs) be conducted. However, high electrical gradients were still observed. It is recommended that speciation studies to determine the chemical nature of thorium within the soil would be helpful to understand these effects.

5. These tests demonstrated that the application of the technique is highly dependent on the chemistry of the contaminants. The precipitation of insoluble, non-amphoteric thorium hydroxide prevented any further removal. In addition, in view of its gelatinous and non-conducting nature, this hydroxide plugs the soil pores, increasing the resistance across the specimen, the voltage requirements, and the energy output. It is essential to use species that would solubilize this hydroxide, or to prevent its precipitation. However, the potential of the process was demonstrated in these thorium removal studies.
4.7. REFERENCES


CHAPTER 5

FEASIBILITY STUDIES OF RADIUM REMOVAL FROM KAOLINITE
BY ELECTROKINETIC SOIL PROCESSING

5.1. INTRODUCTION

Radium-226 contamination in Superfund sites has been produced by radioactive decay of uranium-238 from uranium ores and tailings (Figure 3.1). The total amount of uranium processed in the United States from 1948 to 1975 was $1.3 \times 10^8$ tons [5.1]. Assuming that uranium is in secular equilibrium with its decay products, the total amount of radium-226 associated with this amount of ore equals to approximately $7 \times 10^4$ Ci (or a ratio of only 0.6 mg of radium-226 in 1 ton of uranium ore averaging 0.25% $\text{U}_3\text{O}_8$).

Most of this uranium (>95%) is found in the tailing solids from the mills that have processed uranium ores during this period. Radium is also concentrated in deposits which collect on oil or gas drilling equipment.

There are 25 known isotopes of radium, all of them radioactive. From these, the most common is radium-226 with a half-life of 1600 years. Radium emits alpha, beta, and gamma rays. Its former industrial uses have been in self-luminous paint formulations due to its luminescence, as a neutron source, and in some medicinal applications. However, other radionuclides (i.e. $^{60}\text{Co}$) are preferred instead of radium due to its radiological hazards.

Although weakly penetrating alpha particles emitted by radium-226 and its decay products are not generally a hazardous source of external radiation, damaging internal
radiation may result when radium is ingested by drinking contaminated water, breathing radium-bearing dust, or breathing the daughters of gaseous radon-222 which pose a serious threat to the lungs [5.2, 5.3], causing cancer and other body disorders. In some instances, tailings have been used in building materials, posing a direct threat to the public.

Therefore, the environmental concern arises from the possibility of gradual release of these radionuclides into ground waters. In dry weather, there is the danger of blowing dust and the consequent spread of radioactive soils. At present, this is controlled by impounding of current wastes and by the development of techniques to stabilize wastes. However, there is no confidence that any mode of containment will be effective for a long time [5.4]. A better approach is to separate the radium and decay products from the wastes, concentrate and store them in such a way that they could not escape into the environment.

Historically, uranium has been removed from ores by the sulfuric acid or the alkaline carbonate leaching process. However, due to the dissimilarity of the chemistry of uranium and its decay products (e.g. radium-226, thorium-230), the latter are not removed with the leaching process, resulting in highly to moderately radioactive mill-tailings. Almost all radium-226 initially present in the ore ends up in the tailings as sulfate (or carbonate) coprecipitated with barium, calcium and lead [5.4, 5.5]. Radium-226 is adsorbed by finer particles (clays) and/or by organic matter (humic acid) [5.6-5.7].

Different approaches have been taken to remove radium-226 from these mill-tailings [5.8, 5.9]. The use of mineral acids like nitric acid, HNO₃, and hydrochloric
acid, HCl, removed between 95 to 97% of radium-226 from some tailings [5.1-5.3]. The use of dilute salts (i.e. NH₄Cl, NH₄NO₃, NaCl, NaHCO₃) has been reported to moderately desorb radium-226 [5.10-5.11]. Combined dilute acids with inorganic salts (e.g. NaCl and HCl, and CaCl₂ and HCl) mixtures proved to be also effective in facilitating removal [5.12]. Several successful radium extraction tests with complexing agents have been reported. Removal rates from 80 to 92% have been reported by using ethylenediaminetetraacetic (EDTA) acid and sodium diethylenetriaminepentaacetate (Na₅DTPA) [5.14-5.16]. The use of EDTA and other chelating agents in removing metals from contaminated soils has been also reported elsewhere [5.16, 5.17].

The major disadvantages of these processes are the increased operating and capital costs due to expensive reagents. In many cases, multistage processes are required, with further increased costs. Also, the introduction of anions like NO₃⁻ and Cl⁻ by these reagents are environmentally undesirable. The resulting chemically leached material may create a waste stream that is more harmful that the original tailing mixture. In addition, these procedures involve unnecessary exposure of workers to the source of radiation.

The high radium-226 activity found in mill-tailings prompted the search for new technologies to remove radium and its decay products. EPA has recommended a level of 15 pCi ²²⁶Ra/g for rehabilitated tailings and a 20 pCi ²²⁶Ra/g in the solids for building materials. A radium level of 30 pCi/g is considered environmentally safe for surface disposal of tailings [5.4]. Superfund sites listed in EPA reports [5.12, 5.18] showed that contaminated sites reached activities as high as 23,000 pCi/g, usually concentrated in the
finer particles (clays), or adsorbed on organic matter. Values as high as 80,000 pCi \(^{226}\text{Ra}/\text{g}\) have been reported for these fractions [5.5].

The need for an effective, inexpensive, and an \textit{in situ} technique is clear. This present chapter presents the laboratory scale electrokinetic tests for radium-226 removal from kaolinite clay. An average activity of 1000 pCi/g was studied. Unlike the tests for uranium and thorium, and adsorption isotherm was not obtain for radium due to the small amount of radium-226 chloride standard that was available.

5.2. EXPERIMENTAL

5.2.1. Sample Preparation

Due to the limited availability of radium standard, only two experiments were performed to assess radium removal feasibility by electrokinetics. The samples were prepared as described for uranium and thorium studies. Air-dried Georgia kaolinite was mixed with radium-226 chloride to obtain an activity of about 1000 pCi/g. The soil was then mixed with deionized water (42% water content). The mix was left overnight to allow equilibration. Triplicate samples were taken to determine initial radium concentration by gamma ray spectrometry\(^1\), water content, and initial \textit{in situ} pH. The specimens were compacted using the Standard Proctor method (ASTM D1557-78) into polyacrylate sleeves (10 cm length and 10 cm outside diameter). These sleeves were used as cells to perform the electrokinetic tests.

\(^1\) See Section 5.2.3 for Analytical Procedure
It should be noted that due to the high specific activity of radium-226 (0.988 Ci/g), an activity of 1000 Ci $^{226}$Ra/g is equivalent to a concentration of about 1 ng Ra/g soil (1 ppb). Therefore, it was anticipated that this low ionic strength will not affect the electroosmotic flow. Assuming Ra$^{2+}$ as the main ionic specie in solution (radium does not show a strong tendency to hydrolyze), the soil surface would be loaded with $9.0 \times 10^{-7}$ meq/100 g kaolinite. Therefore, it was expected that all the radium spiked into the kaolinite would be adsorbed onto the soil surface (CEC kaolinite = 1.43 meq/100 g (Section 3.2)). The transport of adsorbed species requires an initial desorption by the H$^+$ ions. Hence, it was anticipated that in spite of the low radium concentration, long processing time (>500 hrs) would be required for removal.

5.2.2. Test Apparatus

The test apparatus and parameters used for the radium studies were similar to those described in Section 3.3.2 and 4.3.2. A constant current of 0.13 mA/cm$^2$ was applied to the system based on studies by Hamed [5.19]. The total duration of the tests ranged from 550 to approximately 700 hrs. Parameters monitored during the tests were the potential across the specimen, the electroosmotic flow, pH of effluent, and current density.

After completion of a test, the sample was sliced into ten fractions. Each fraction was analyzed for radium concentration, water content, and in situ pH. Any effluent due to electroosmosis was measured, collected, and analyzed for radium content. Also, the electrodes were extracted with 1 M HNO$_3$ and the extract analyzed. The removal
efficiency was determined by comparison with the initial radium concentration. A total mass balance was conducted for total radium loaded and extracted.

5.2.3. Gamma Ray Spectrometry Test Method for Radium

5.2.3.1. Scope and Application

This Gamma Ray Spectrometry (GRS) method was developed for analysis of radium-226 in soils and effluent/liquid samples of electrokinetic experiments. The method is a modification of the traditional GRS methodology for radium-226 measurements in environmental samples [5.20-5.22].

5.2.3.2. Sample Preparation

(i) Solid Sample Standards and Calibration Curve

A calibration curve was prepared for radium-226 soil samples. The standards were prepared by spiking the proper amount of a $^{226}$Ra standard into previously washed kaolinite, oven dried for 24 hr at 110°C, and left in the shaker for 1 hr to ensure uniform distribution. The standard solution used was a 5 mL radium-226 chloride solution, with a total activity of 6.11 mCi, in a HCl matrix (Amersham International Inc.). Standards in the range 20 to 1000 pCi/g were prepared by weighing 70.00 g soil sample in a petri dish, sealed, and counted in the gamma ray spectrometer.

Electrokinetic processed soil samples were prepared in the same manner as the standards. These were oven dried for 24 hr at 110°C, cooled in a desiccator, ground, and a 70.00 g soil sample weighed in a petri dish, sealed, and counted in the gamma ray
spectrometer. In gamma ray counting, it is important that the matrices of samples and standards are as similar as possible.

(ii) Liquid Sample Standards and Calibration Curve

To analyze liquid samples, rather than obtaining a calibration curve, 250 mL of a standard solution was prepared and used to determine the counting efficiency of the gamma ray spectrometer. The standard and liquid samples were contained in 500 mL plastic jars with screw caps. Liquid samples were filtered prior to measurement. A calibration curve was not obtained for liquid samples due to the limitation of radium-226 standard.

5.2.3.3. Gamma Ray Spectrometry Procedure

The instrument used in the procedure was the following:

1. High Resolution HPGe System linked to a Canberra Series 35 Plus Multichannel Analyzer.
2. High efficiency 5 inch by 5 inch or 3 inch by 3 inch NaI (Tl) scintillator linked to a Nuclear Data Model 62 Multichannel Analyzer.
3. Zenith Z286 Microcomputer with gamma spectra analysis capability using the SPECTRAN program.

The instrument performance was periodically checked with $^{60}\text{Co}$ or $^{137}\text{Cs}$ standard sources, traceable to the National Institute of Standards and Technology (NIST).
The typical procedure for radium-226 analysis by gamma ray counting consists in sealing a radium-226 containing sample, and storing it for three weeks to allow the equilibrium with its daughters, bismuth-214 and lead-214. After this period, the sample is counted for bismuth-214 at its gamma emission of 609.4 keV (43% intensity), and its activity can be correlated to the initial amount of radium-226.

However, radium-226 has a low gamma emission at 185.6 keV (4% intensity). Since radium-226 is usually associated with uranium, a major disadvantage for the use of this emission energy is the interference of uranium-235, which has a gamma ray emission at 186 keV. However, provided that the sample has a relatively high activity in radium-226 (e.g. higher than 100 pCi/g) and that there is no uranium-235 present, the 185.6 keV radium-226 peak could be utilized to determine directly the radium activity. For the electrokinetic studies, synthetic kaolinite was spiked with radium-226 chloride standard. Therefore, no other radioisotopes were present in the soil sample. A background sample (pure kaolinite) was counted for background correction. This procedure makes it unnecessary to let the sample equilibrate for three weeks. It is noted that this methodology could not be used to measure radium-226 from natural sources.

(i) Solid Samples

A calibration curve was obtained by counting the standards prepared within a range from 20 to 1000 pCi $^{226}$Ra/g soil. The radium-226 gamma ray peak at 185.6 keV was selected for the measurements. Counting times ranged between 6000 sec (most activity) to 60,000 sec (least activity) in order to ensure a counting relative standard
deviation of less than 5 percent. In nuclear statistics, an approximate standard deviation for a certain counting rate is calculated as follows,

\[ s = \sqrt{\frac{x}{t}} \]  \hspace{1cm} (5.1)

where \( x \) = total number of counts and \( t \) = counting time. When a background is considered, the counts-per-minute (cpm) of background is subtracted from the sample counting rate, and the standard deviation was calculated as follows,

\[ s = \left( s_s^2 + s_b^2 \right)^{1/2} \]  \hspace{1cm} (5.2)

where \( s_s \) = standard deviation for sample's counting and \( s_b \) = standard deviation for background's counting. As the standard deviation is a function of counting time, the longer the counting time, the lower the standard deviation.

The calibration curve (soil activity vs cpm, blank corrected) is shown in Figure 5.1. Figure 5.2 shows the deviations of the standards (pCi/g) versus counts per minute (cpm, blank corrected) in a logarithmic plot in order to demonstrate deviation from linearity [5.23]. It was observed that for the range 70 to 1000 pCi/g, all data were within 10% from the linear fit.

Soil samples from electrokinetic tests were typically measured for enough time to ensure a relative standard deviation of 5 percent (typically 10,000 sec).

(ii) Liquid Samples

For liquid samples, the counting efficiency of the instrumentation was determined for a 250 mL radium-226 solution standard. The peak studied was the radium-226
Figure 5.1. Calibration Curve for Radium-226 Analyses by Gamma Ray Spectrometry
Figure 5.2. Deviations from Linearity Fit for Radium-226 Calibration Curve
gamma ray emission at 185.6 keV. The counting time was typically 60,000 sec for each time in order to ensure 5% relative standard deviation. Background corrections were also made.

5.2.3.4. Interferences

For typical radium-226 measurements in environmental samples, uranium-235 is usually reported as an interference. Therefore, it is preferred to allow secular equilibrium of the radium-226 with its daughters, and measure the activity of these. However, since synthetic kaolinite was spiked with radium-226 standard, no interferences were observed. Blank tests on pure kaolinite did not show any significant reading above background for the radium-226 peak at 185.6 keV.

5.2.3.5. Calculations

(i) Soil Samples

The activities in soil samples were determined directly from the calibration curve. Assuming a calibration curve given by \( cpm = mA + b \), where \( cpm \) is the measured counts-per-minute of a sample, \( A \) the calculated activity (pCi \(^{226}\)Ra/g soil), and \( m \) and \( b \) are the slope and intercept of the calibration curve, the total amount of radium in each section was calculated as follows,

\[ ^{226}\text{Ra in section (ng)} = [(cpm - b)/m] \times [0.988 \times 10^{12} \text{ pCi/g Ra}]^{-1} \times w_i \times [10^9 \text{ng/g}] \quad (5.3) \]
where \( w_i \) is the dry weight (g) of section \( i \). For the initial amount of radium-226 loaded into the soil sample, equation 5.3 was used where \( cpm \) was the measurement of the original mix, and \( w_i \) was replaced by \( W_T = \) total dry weigh of soil used in the study. Therefore, the fraction of radium remaining in a section \( i \) was calculated as,

\[
\text{Fraction left in section } i = \frac{A_i \, (\text{pCi/g})}{A_T \, (\text{pCi/g})}
\]  

(5.4)

where \( A_i \) and \( A_T \) are the measured activities per gram of soil of section \( i \) after completion of the test and the initial activity of the mix prior to the test, respectively. The total radium left in the soil was calculated by adding equation 5.3 for each section \( i \) of the specimen.

(ii) Liquid Samples

To calculate the total activity in liquid samples having the same geometry as the standard (total activity = 25,000 pCi), the following formula was used,

\[
\text{Total activity, } A \, (\text{pCi}) = \frac{\text{cpms}}{\text{Efficiency (cpm}_s/\text{pCi}_s)}
\]  

(5.5)

where \( \text{cpm}_s \) is the background corrected counts-per-minute for the sample, and the efficiency was calculated as the ratio between the standards counts-per-minute (cpm\(_s\)) and its activity (pCi). The total radium present in liquid samples was then calculated as,

\[
\text{Total radium (ng)} = A \, (\text{pCi}) \times 0.988 \times 10^{12} \, \text{pCi/g Ra}^{-1} \times 10^9 \, \text{ng/g}
\]  

(5.6)

The total radium found after completion of a test was calculating by adding the contribution of each section \( i \) in equation (5.3) plus equation (5.6), and compared with
equation (5.3) for the original mix. A mass balance higher than 75% was adopted as criterium to accept a test results.

5.3. RADIUM REMOVAL STUDIES

Table 5.1 summarizes the initial conditions and parameters for the radium tests. The cells were labeled Ra42XX, where XX represents the experiment number.

5.3.1. Final and Initial pH Across the Specimen

Figure 5.3 presents the final in situ pH distribution across the specimen after completion of the tests. The pH profile trends are similar to those reported in the literature [5.19, 5.24] and described in Sections 3.4.1 and 4.4.1. The ionic potential (charge/crystal radius) is particularly important to the properties of an ion in water since larger values indicate that the ion tends to hydrolyze in solution [5.9]. Due to the small ionic potential that alkaline earth cations (with the exception of beryllium) show, these do not show a tendency to hydrolyze in water. Table 5.2 shows the radii of the alkaline-earth cations. With a value of 1.32, radium has the smallest ionic potential of the alkaline-earth cations. Therefore, unlike UO$_2^{2+}$ and Th$^{4+}$ ions, Ra$^{2+}$ ions do not show a tendency to hydrolyze. This accounts for the comparable initial in situ pH observed in the radium specimens (4.1 and 4.2 for tests Ra4201 and Ra4202 respectively) and the blank specimens (pH 4.0 to 5.0) [5.25].

The tests were conducted for 550 and 675 hr. However, similarly to the pH profile reported for thorium specimens (Section 4.4.1), the profiles shown in Figure 5.3
Table 5.1. Radium Removal Test Program and Initial Parameters for Electrokinetic Tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>$t^1$ (kN/m$^3$)</th>
<th>$w^1$ (%)</th>
<th>$S^1$ (%)</th>
<th>$e^1$</th>
<th>Duration (h)</th>
<th>Effluent Volume (cm$^3$)</th>
<th>Pore$^2$ Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra4201</td>
<td>10.68</td>
<td>41.2</td>
<td>92.3</td>
<td>1.17</td>
<td>550</td>
<td>610</td>
<td>1.37</td>
</tr>
<tr>
<td>Ra4202</td>
<td>10.59</td>
<td>42.9</td>
<td>92.3</td>
<td>1.22</td>
<td>675</td>
<td>421</td>
<td>0.95</td>
</tr>
</tbody>
</table>

1 $t = \text{unit weight, } w = \text{water content, } S = \text{saturation, } e = \text{void ratio}$

2 Pore volume is defined as the total volume of the specimen multiplied by porosity (or $e/(1+e)$). All specimens had a total volume of 799 cm$^3$. 
Figure 5.3. Final in situ pH Profile for Radium Tests
Table 5.2. Radii of the Alkaline-Earth Cations (adapted from Richardson et al.[5.9])

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radii (A) Crystal</th>
<th>Hydrated Radii (A)</th>
<th>Ionic Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be$^{2+}$</td>
<td>0.31</td>
<td>4.59</td>
<td>6.45</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.65</td>
<td>4.28</td>
<td>3.01</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.99</td>
<td>4.12</td>
<td>2.02</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.13</td>
<td>4.12</td>
<td>1.77</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>1.35</td>
<td>4.04</td>
<td>1.48</td>
</tr>
<tr>
<td>Ra$^{2+}$</td>
<td>1.52</td>
<td>3.98</td>
<td>1.32</td>
</tr>
</tbody>
</table>
did not show a complete sweep of the acid front through the specimen. High pH readings were observed in regions closer to the cathode. As discussed in the next section, unlike thorium tests, the radium studies showed significant electroosmotic flow. When considering electroosmotic flow, electromigration, diffusion together with sufficient processing time, it was expected that the acid front would flush across the system, and that a uniform final in situ pH between 2.0 to 2.5 would be observed [5.25].

For the radium specimens, it was postulated that due to its low concentration when loaded into the system (1 ng Ra/g soil), the H⁺ ions generated at the anode and transported to the cathode were adsorbed by the clay surface to satisfy its CEC. An equilibrium state would be eventually reached; therefore, for sufficient processing time duration (>600 hr for radium specimens conducted at the conditions described in Section 5.2.3, i.e. 0.13 mA/cm² current density, 42% water content, 1000 pCi/g soil activity), a uniform acidic in situ pH is anticipated.

5.3.2. Electroosmotic Flow and Electrical Gradient

Figure 5.4 presents the electroosmotic flow observed in the radium experiments. Tests Ra4201 and 4202 showed 0.95 to 1.37 pore volumes of flow in 550 and 700 hrs processing time; these tests showed significantly more electroosmotic flow compared to those observed for regular uranium and thorium experiments (typical values ranged between 0.04 to 0.70 pore volumes for approximately 500 hrs processing time). However, the flow rates were still lower than those observed for blank specimen (Figure 3.17), where 4.4 pore volumes were obtained after 500 hrs processing time. For the
Figure 5.4. Electroosmotic Flow Profile for Radium Tests
radium tests, it was observed that the electroosmotic flow started decreasing after the maximum capacity of the regulator was surpassed (Figure 5.5) and the current dropped (Figure 5.6). This drop in current caused the decrease in flow rate, since less current was flowing within the soil specimen.

Figure 5.5 shows the electrical gradient developed in the radium tests. Both tests showed a steady increase in voltage gradient, reaching the maximum power supply capacity (equivalent to an electrical gradient of 11 V/cm) after 150 hr. When this occurred, the current level was automatically decreased by the voltage regulator to maintain the power input. This drop in current is presented in Figure 5.6. In general, test Ra4201 showed a steady drop in current (60% drop in 430 hrs). However, test Ra4202 showed a faster drop (70% in 80 hrs) in current, after which the current density was maintained for the rest of the process. The reason for this difference was not clear, but it could be attributed to different compaction characteristics of the two specimens.

The increase in resistance (i.e. increase in electrical gradient) was attributed to chemical effects of hydroxide at the cathode, impurities, or gas polarization at the electrodes. Very little radium species were present in these tests and removal tests showed no evidence for its mobility or extensive chemical change in time. The precipitation of radium sulfate (Section 5.3.3) is unlikely to have caused the observed high electrical gradients.

Due to the drop in current density, neither the coefficient of electroosmotic permeability nor the energy consumed in the process were calculated.
Figure 5.5. Electrical Gradient Profile for Radium Tests
Figure 5.6. Current Changes in Radium Tests
5.3.3. Radium Removal

Figure 5.7 depicts the final radium distribution across the specimens. Table 5.3 presents the corresponding mass balance. Most of the radium initially loaded onto the kaolinite specimen (77-98 %) was found in the soil. Between 3.6 to 7.5% was found in the effluent. Only test Ra4202 showed some radium (6.6%) on the cathode.

For test Ra4201, it was observed that apparently radium ions did not move appreciably during 550 hrs of processing. Most of the specimen fractions for this test showed a final/initial radium concentration ratio close to one. On the other hand, after 675 hrs, test Ra4202 showed a slight partial removal (20 to 30%) of radium towards the cathode, with a noticeable increase while approaching the cathode. The reason for this was not clear and might be attributed to the randomness of the experiments.

It was believed that radium precipitated as sulfate, with a reported solubility in water of $2.1 \times 10^{-8}$ g/mL at 25°C, or $K_{sp} = 4.25 \times 10^{15}$ [5.1, 5.9]. Sulfate (as sodium sulfate) is the reported predominant anion in soil washings of kaolinite, and has been reported at levels ranging from 3.7 to 14 mg/L in the pore fluid [5.26]. Radium sulfate is the least soluble of the alkaline earth sulfates and is the least soluble radium compound known. Although the reported concentration of sulfate anions is sufficient to precipitate all the radium loaded into the clay, James and Healey [5.27] reported that precipitation on the soil surface is influenced by the high electric field in the double layer. Also, Seeley [5.1] reported that the precipitation of radium was not related to its solubility product but was also affected by the presence of other metal ions like Ba$^{2+}$ (sometimes Pb$^{2+}$), with which radium coprecipitated. These two facts decrease the
Figure 5.7. Final Radium Distribution Profiles
Table 5.3. Mass Balance in Radium Removal Studies

<table>
<thead>
<tr>
<th>Test Code</th>
<th>Initial Activity (pCi/g)</th>
<th>Initial Weight (mg)</th>
<th>Final Soil (mg)</th>
<th>Final Cathode (mg)</th>
<th>Final Effluent (mg)</th>
<th>Mass Balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra4201</td>
<td>1029</td>
<td>1.028</td>
<td>1.002</td>
<td>---</td>
<td>0.037</td>
<td>101.1</td>
</tr>
<tr>
<td>Ra4202</td>
<td>1103</td>
<td>1.092</td>
<td>0.837</td>
<td>0.072</td>
<td>0.082</td>
<td>90.8</td>
</tr>
</tbody>
</table>
"effective solubility" of radium sulfate in porous media, and make radium movement more difficult.

In order to enhance radium removal, it is necessary to dissolve or prevent the precipitation of RaSO₄ that is formed in the porous medium. The dissolution of the sulfate could be accomplished by proper selection of a chelating agent. Most of the radium-226 present in mill tailings has been reported to be the insoluble sulfate, or coprecipitated with other metal ions [5.5, 5.9]. The use of complexing agents (e.g. EDTA and DTPA) have been reported to be effective in dissolving the Ba(Ra)SO₄ matrix [5.28], releasing the Ra²⁺ ions (the presence of other sulfates, e.g. CaSO₄ has been reported to interfere in this process [5.5]). However, these complexing agents usually act in a basic environment. The development of a pH gradient across the treated soil would determine different removal efficiencies depending upon the local pH environment. Since in a normal electrokinetic process the acid front tends to flush across the specimen, it is preferred that any chelating agent should complex the Ra²⁺ ions in an acidic pH. Alternatively, some additional process modifications could be made (e.g. flush anode compartment with base to neutralize acid generated at this electrode) so that typical complexing agents would be effective with electrokinetic processing.

Some potential complexing agents were tested in an attempt to obtain radium removal from kaolinite. The species used were sodium isethionate (sodium 2-hydroxyethanesulfonate, OHCH₂CH₃SO₃Na⁺) and o-phthalic acid (o-benzenedicarboxylic acid, HOOC-C₆H₄-COOH, pK₁=2.89 and pK₂=5.51 at 25°C), at concentrations between 0.01 and 0.001 M. The sulfonate specie was selected due to the strong acidity
that sulfonic acid shows, and the similarity to the sulfate group that forms the insoluble radium precipitate. It was expected that it would complex the radium ions at low pH. In addition, it was anticipated that the hydroxyl group would aid in the radium ions complexation, dissolving the radium sulfate, and making possible its removal from the kaolinite matrix. The o-phthalic acid was selected based on its high first dissociation constant (or low pKₐ). Therefore, it was expected that these species would complex radium at low pH values (i.e. favoring dissolution of RaSO₄ at the acidic conditions developed during electrokinetic soil processing), also aided by the bidentate nature (two hydroxyl groups) of the phthalate. None of these potential complexing agents were found reported in the literature.

For these tests, soil samples loaded with 1000 pCi/g activity of radium, in which radium was expected to be precipitated as sulfate, were extracted for 3 days with 0.01 and 0.001 M solutions of these potential complexing agents, and the soil sample analyzed by gamma ray spectrometry. The difference between the initial and final countings for the soil sample would provide the amount of radium extracted. However, no significant extraction of radium was observed for the species tested.

5.4. CONCLUSIONS AND RECOMMENDATIONS

1. Radium-226 at an activity of 1000 pCi/g (approximately 1 ng Ra/g soil) could not be removed from kaolinite by standard electrokinetic soil processing. It can be postulated that the precipitation of radium as sulfate prevented the transport of this radionuclide towards the cathode.
2. The acid front transport towards the cathode showed a trend similar to that of a blank specimen. It may be assumed that the low ionic strength in the porous medium would cause the soil surface to retain the $\text{H}^+$ ions to satisfy the soil CEC, delaying the advance of this front.

3. Due to the low ionic strength in the porous medium, radium tests showed relatively high electroosmotic flow (0.95 to 1.37 pore volumes) when compared with those observed for uranium and thorium tests (0.04 to 0.70 pore volumes) for comparable processing times. However, the electrical gradient increased with time exceeding the power supply capacity (11 V/cm). This increased caused a drop in current (60 to 70% in 80 to 400 hrs), and as a consequence, a drop in electroosmotic flow. The reasons for this increase in electrical gradient are unclear.

4. It is recommended that further studies are conducted by using complexing agents in order to dissolve the radium sulfate precipitate. Due to the acid-base nature of the electrokinetic soil process, it is preferred to use a complexing agent that complexes radium ions in an acidic environment. However, the testing apparatus could be modified in order to introduce chelating agents that complex radium in basic environments (i.e. EDTA and DTPA).

5. These tests further demonstrate that each specie represents a different problem. The different chemistry of the radionuclides requires different approaches to enhance the efficiency of the removal technique.
5.5. REFERENCES


Electrokinetic soil processing is an innovative remediation technique with the capability to treat soils contaminated with metal ions and selected organics. The technique involves the use of low direct current densities between electrodes immersed in the soil mass. The contaminants are desorbed and transported as a result of electrochemical and physical processes throughout the soil. The major advantages that electrokinetic soil processing offer are low cost, high removal efficiencies and minimum exposure of workers to the contaminated environment. Reported field applications to soils containing a variety of metal ions (e.g. lead, zinc, cadmium, copper, etc) showed its potential as an in situ remediation technique in low permeability soils. The capabilities of the process to remove selected radionuclides (i.e. uranium-238, thorium-232, radium-226) from kaolinite clay was assessed in these bench-scale studies.

The studies showed that the process removed 85 to 95% of uranium-238 of kaolinite specimens loaded at 1000 pCi/g activity. The removal rates decreased close to the cathode electrode (65% of initial concentration), where uranium-238 was found precipitated as uranyl hydroxide. The basic environment in this region was the cause of the complicating features of the process (i.e. high electrical gradient (11-12 V/cm), high energy expenditure, lower removal rates in sections close to the cathode). Typical energy consumption for the tests ranged between 81 to 315 kW-hr/m³ of processed clay. Enhanced tests were aimed to neutralize or suppress the formation of the basic environment developed near the cathode. The acetic acid depolarization tests and the
acid-molded section tests showed the possibility of increasing removal rates (up to 85-90%) close to the cathode at lower energy expenditure compared to regular tests. The adipic acid-molded section test showed that the base front was essentially neutralized, and it prevented precipitation of uranyl hydroxide. Low electrical gradients (2.5 V/cm) were developed in this test. However, uranyl ions were accumulated close to the cathode at levels between 150 to 260% the initial concentration. It is recommended to continue research with this enhanced test, since it offers the potential of removal at low energy expenditure.

Electrokinetic tests showed that thorium-232 was strongly adsorbed onto the clay surface. As reported in the literature, thorium-232 also proved to be the least mobile of the radionuclides tested. Between 80 to 90% of thorium-232 was removed using an acid-molded enhancement technique. Thorium showed a strong tendency to precipitate as insoluble and gelatinous hydroxide, complicating its transport and increasing the energy expenditure during the process (>600 kW-hr/m³ of soil for 500 hr processing time). The use of enhancement techniques increased removal rates of thorium-232 in regions close to the anode by 30% and decreased energy consumption of the process by 37%.

Studies performed with radium-226 in kaolinite at 1000 pCi/g activity showed that the precipitation of sulfates prevented the removal of radium. The use of complexing agents that solubilize this precipitate is recommended to achieve radium removal.
As a closing remark, it should be noted that in addition to any geotechnical characteristic of the soils, the efficiency of electrokinetic soil processing is highly dependent on the chemistry of the specific contaminants. Nevertheless, the usefulness of the process as a remediation technique for radioactive contaminated soils was demonstrated in these studies.
VITA

Dionisio Alberto Ugaz (Beto) was born on December 13, 1964 in Lima, Peru. He was born in a family of chemists. Therefore, his first lessons in chemistry were given at home. He completed his B.S. in Chemistry at the Catholic University of Peru in 1989, and the Ph.D. program at Louisiana State University in 1994. After graduation, he will be working in the Ink Division at Hewlett-Packard Co., in the San Diego area.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Dionisio Alberto Ugaz

Major Field: Chemistry

Title of Dissertation: Feasibility Studies of Radionuclide Removal from Kaolinite by Electrokinetic Soil Processing

Approved:

Robert J. Cole
Major Professor and Chairman

Dean of the Graduate School

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Date of Examination:

August 4, 1994