To the Graduate Council:

I am submitting herewith a thesis written by Son H. Nguyen entitled "Impact of Hydrogen Peroxide treatment on the binding and mobility of Uranium in soils." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Dr. Kevin Robinson, Major Professor

We have read this thesis
and recommend its acceptance:

Dr. Mriganka M. Ghosh

Dr. Chris D. Cox

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

IMPACT OF HYDROGEN PEROXIDE TREATMENT ON THE BINDING AND MOBILIZATION OF URANIUM IN SOILS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Son H. Nguyen
December 1995

ACKNOWLEDGEMENTS

I am very grateful to my major professor, Dr. Kevin Robinson, for his advice and to my other committee members, Dr. Mriganka Ghosh and Dr. Chris Cox, for their comments.

There are a number of other people whose assistance should be recognized. I would like to thank Steven Cline, Oak Ridge National Laboratory, for DOE soil analysis; Sharon Hale, Civil and Environmental Engineering Department (CEE) at The University of Tennessee, for laboratory safety; Jane Taylor and Marion Dills, CEE, for ordering chemicals; and Ganesh R.,CEE, for MINTEQ software.

This research was made possible through funding by the DOE's Office of Technology Development and by the joint program between The University of Tennessee and Martin Marietta.

ABSTRACT

Hydrogen peroxide has been recently used to oxidize organic contaminants in soil as an in-situ environmental restoration technique by the Department of Energy (DOE). However, many organic-contaminated soils at DOE facilities also contain uranium (U) which may become mobile during oxidation of target organics thereby increasing the potential for groundwater contamination and human exposure. This research addressed the impact of hydrogen peroxide (H_2O_2) treatment on U binding and mobilization in soils.

Three different types of clay (Kaolinite, Illite and Ca-Montmorillonite), two metal oxides (Al_2O_3 and Fe_2O_3) and three DOE natural soils (Hanford (I), (II), and Portsmouth) were used in the research. All soils and soil materials were spiked with U which ranged from 0.157 to 5.98 mg U/g and treated with 0 to 30% H_2O_2 (v/v) for varying contact times (1-hour and 24-hour). During treatment, solution pH was monitored to assess its impact on U mobilization. In addition, soils and soil materials were pretreated with 30% H_2O_2 before U loading to evaluate the impact of peroxide on soil binding capacity.

Equilibrium binding to untreated soils, in general, increased with increasing solution pH. Based on the distribution coefficient (K_d), binding affinity increased in the order of Hanford (I)< Hanford (II)< Al oxide < Fe oxide < Portsmouth ≈ Ca-Montmorillonite < Illite < Kaolinite.

Binding affinity of U to pretreated soils was in the order of Kaolinite ≈ Illite ≈ Al oxide ≈ Hanford (I)& II << Ca-Montmorillonite ≈ Portsmouth << Fe oxide. Peroxide pretreated soils were capable of sorbing U, however, binding intensity varied with soil composition. The sorption capacity of U after H_2O_2 treatment increased for the sandy soils (Hanford I & II) and Fe oxide whereas it decreased for clays, Al oxide and the clay-like soil (Portsmouth). Enhanced U binding in Hanford soils may be due to an increase in sorption sites which resulted from stripping trace metals from the soil matrix.

Oxidation of organic carbon, dissolution of soil calcite, complexation of U with carbonate and precipitation of uranyl peroxide controlled U mobilization. Complexation and precipitation affected U mobility upon H_2O_2 treatment in different pH domains. Carbonate complexation favored U mobilization (pH > 5) whereas precipitation of uranyl peroxide complexes limited mobilization(2 < pH < 5).

Minimum U mobilization (< 6%) was observed in clays (Kaolinite and Ca-Montmorillonite), oxides and Portsmouth soil at H_2O_2 loadings ≥ 18% after three one-hour treatments due to precipitation of uranyl peroxide. Maximum U mobilization, however, was detected for Illite and Hanford soils during this treatment period. Enhanced mobilization from Illite was due to the oxidation of organic carbon associated with this clay whereas carbonate complexation was responsible for the increased U mobilization observed in Hanford soils.

Longer contact time (> 1) increased U mobilization from Ca-Montmorillonite and Illite, and decreased U mobilization from Hanford soils and had little impact on U mobilization from Kaolinite, oxides and Portsmouth soil. In general, most of the U mobilized occurred during the first treatment.

The mobilization experiments indicated that soil peroxidation had the potential to release sorbed U from soils and soil matrix materials. The degree of U mobilization depended on several factors such as soil type, oxidant concentration, contact time and number of treatments. However, soil composition (organic content, amount of calcite) and treatment solution pH appeared to be critical factors controlling U mobilization.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont.)

CHAPTER I

INTRODUCTION

Uranium (U) exits in both natural and contaminated environments. Uranium concentrations in uncontaminated soils are typically in the range of 0.05-5 mg/kg (Alloway, 1990). The impact of released U in the environment is a major concern for industries and the public. Typical concerns include contamination of ground and surface waters, and the risks associated with possible ingestion by animals and humans.

Uranium is an unstable atom which emits α (proton and neutron) and β (electron or positron) particles to obtain a more stable atomic configuration. Ejection of α and β particles result in radioactive characteristics which can be harmful to bilogical tissues. Radiation damages human tissue by ionizing atoms in the cell molecules. As a result of atomic ionization, cell molecules can not function normally. In addition, the products of the molecular disintegration can poison the cells (Davis, 1967). The half-life of U ranges from 2.47×10^5 year (U-234) to 4.51×10^9 year (U-238) (Weast, 1975). The presence

of radioactive U in the environment, therefore, represents a human health and safety threat.

Release of U to the soil has resulted from mining and milling processes, deposition of air-borne particles originating from stacks of U production facilities, and leaking and spilling of U rich solvents during extraction and treatment processes. The Nuclear Regulatory Commission (NRC) has established a level of 35 pCi/g (equivalent to 52 mg U/kg soil) for U mill tailings. However, up to 2,000,000 m^3 of soil containing unacceptable levels of U (up to 540 mg/kg) was detected at the Fernald (Ohio) Department of Energy (DOE) facility (Francis et al., 1992).

In the environment, Uranium is relatively mobile under oxidizing conditions and immobile under reducing conditions. Hydrogen peroxide recently has been chosen as an in-situ chemical oxidant to remediate organic contaminants such as Trichloroethylene (TCE) at DOE facilities. However, many organically contaminated soils at DOE sites contain metals such as U which may become mobile during oxidative treatment. The use of oxidants, such as H_2O_2, to convert immobilized U (tetravalent state) to mobilized U (hexavalent state) have been used to extract U from ore. Researchers (Bolle et al., 1988; Eligwe and Torma, 1984) have demonstrated that peroxide partially mobilized uraninite mineral (UO_2) by oxidizing

insoluble U(+4) to soluble U(+6). The nature and the concentration of peroxide affected U mobilization. Eligwe and Torma (1984) found that stabilized peroxide mobilized more U from ore than unstabilized peroxide. Other researchers (Amell and Langmuir, 1978; Torma and Eligwa, 1982) have reported that high peroxide concentrations decreased the yield and rate of U extraction from ore. The authors concluded that precipitation of dissolved U in the form of uranyl peroxide reduced U mobilization.

Mobilization of U is also influenced by solution pH in two ways. First, speciation of U is pH dependent. In the +6 oxidation state, U forms many soluble ions such as uranyl cation (UO_2^{2+}), uranyl dicarbonate ion ($UO_2(CO_3)_2^{2-}$), uranyl tricarbonate ion ($UO_2(CO_3)_3^{4-}$), and uranyl sulfate ion ($UO_2(SO_4)_2^{4-}$). Hosteler and Garrels (1962) have investigated the equilibria of U minerals with natural solutions and found that stable soluble ions existed over a wide pH range under oxidizing conditions. Second, U mobilizes at low pH due to H^+ ion competition with UO_2^{2+} for sorption sites. Eligwe and Torma (1984) found that U leached completely from 200 g of U ore at high acid concentration (pH approaching 1) but was virtually insoluble at low acid concentration (pH 9).

Past work has focused on extraction of U from ore but limited work has been performed on the mobility of U from chemical oxidation of contaminated soils. During in-situ treatment of organic contaminants, U may mobilize downward from the soil treatment zone under the force of gravity, thereby contaminating subsurface soil below the treatment zone. If the subsurface soil has been previously treated, recontamination could occur. No work on U resorption to H_2O_2 treated soil materials has been conducted to date.

The objective of this research was to investigate how soil parameters and H_2O_2 treatment conditions impact U binding and mobilization. Three different types of clays (Illite, Kaolinite and Ca-Montmorilonite), two metal oxides (Aluminum and Ferric), and three natural soils (two sandy and one clayey) were chosen for study. The clays were chosen because of differences in U sorption capacity and their common occurrence in soil. Metal oxides, especially ferric, are common accessory minerals associated with sandstone-type U deposits (Barton, 1956, Reed et al., 1993). Natural soils were obtained from DOE sites and were chosen to represent model contaminated soils at DOE facilities.

CHAPTER II

LITERATURE REVIEW

1. Uranium in the environment

Uranium exists in nature as a trace constituent of soil minerals due to isomorphous substitution into the structural lattice of minerals at the time of crystallization (Gittus, 1963). It consits mainly of three isotopes with mass numbers of 234, 235 and 238. U-235 is used in the nuclear power industry and in the fabrication of nuclear weapons. U-238 accounts for approximately 99.3% of the total while U-235 and U-234 only comprise 0.7% and 0.005% of natural U (Tatsch, 1976). Industrially exploited sources of U include the minerals urananite (UO_2) and coffinite ($USiO_4$) and in some instances rock phosphate or uraniferous-rich organic matter (Alloway, 1990).

Uranium ore undergoes a number of industrial processes to arrive at the final product. Chemical conversion, purification, enrichment of U-235, fabrication of the fuel into an appropriate form, and storing of the spent fuel are all possible sources for U release into the environment. Up to 2,000,000 m^3 of soil containing unacceptable levels of U (up to 540 mg/kg) has been

found at the Fernald (Ohio) U-processing facility (Francis et al., 1992). It was reported that U-contamination resulted from leaking and spilling of U rich solvents during extraction and treatment processes and from the deposition of air-borne U particles originating from the stacks of the facility.

Coal combustion is another route in which U can be released into the environment and subsequently retained by soils. High concentrations of U in coal may give rise to atmospheric releases via fly-ash which impact soil through wet and dry deposition. Additionally, the application of U containing phosphate fertilizer to agricultural land may lead to U-contamination of soil. Alloway (1990) reported that phosphate rocks contain as much as 120 mg U/kg. The utilization of phosphate fertilizer in agricultural applications over a period of many years, therefore, likely results in an increase in the U content of soils.

2. Uranium chemistry

The most common mineral forms of U are reduced and mixed oxides (uraninite and pitchblende), silicates (coffinite and uranophane) and various phosphate and vanadate minerals. These forms of U were created in the nearly oxygen-free reducing conditions which existed during mineral formation (Tatsch,

1976). In soils, U exists in the forms of oxides, carbonates, phosphates or organically-bound constituents.

In general, the oxidation state of U directly impacts its solubility. Uranium in the tetravalent state is usually less soluble than that in the hexavalent state. The aqueous solubility of uraninite (+4) is less than 10^{-4} µg/L compared to 660 g/L for uranyl nitrate (+6). The relative insolubility of uraninite (UO_2) in aqueous solution leads to precipitation under reducing conditions such as those created by the decomposition of carbonaceous matter (Gittus, 1963). Under oxidizing conditions, the formation of uranyl ions (UO_2^{2+}) is believed responsible for the solubility of U over a wide pH range. Its solubility, however, may be limited by the formation of slightly soluble precipitates (i.e. phosphates and oxides) and sorption to clays and organic matter (Alloway, 1990). Dominant aqueous species include UO_2^{2+}, $UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$, and $UO_2(HPO_4)_2^{2-}$.

The speciation of U depends on pH and redox potential. Langmuir (1978) evaluated the Gibbs free energies, enthalpies and entropies of 42 dissolved U species and 30 U-bearing solid phases at 25°C. Langmuir showed that U in natural waters complexed with a variety of ligands such as hydroxide, phosphate, fluoride, sulfate and carbonate. These complexes

greatly enhanced the solubility of U minerals and the mobility of U in surface and ground waters. The author reported that uranous (U^{4+}) fluoride complexes dominated in reduced waters below pH 3-4 at the typical concentrations of chloride, fluoride, phosphate and sulfate found in most natural waters (Figure II-1). In oxidized water, uranyl ion (UO_2^{2+}) dominated speciation at pH < 5, $UO_2(HPO_4)_2^{2-}$ was the main species between pH 4 to 7.5 and at higher pHs, the domain belonged to mono-, di-, and tri-uranyl carbonate complexes. In the absence of other ligands, uranyl carbonate complexes were the major species at pH > 5 under oxidizing conditions whereas uranyl hydroxy complexes dominated in reduced waters at pH < 10 (Figure II-2). Even under reducing condition (Eh < 0 V), tri-uranyl carbonate complexes formed which indicated that binding within these complexes was very strong. Hsi (1981) used a computer program, WATEQF, to calculate the percent distribution of U as a function of pH in a 0.1M $NaNO_3$ solution containing carbonate. The author found that uranyl di- and tri-carbonate complexes and uranyl hydroxyl complexes dominated the solution chemistry. In the absence or insignificant carbonate, uranyl hydroxy is a dominant species at pH > 5 (Figure II-3). These results suggest that complex ion formation may greatly enhance the solubility of U, thereby impacting mobilization.

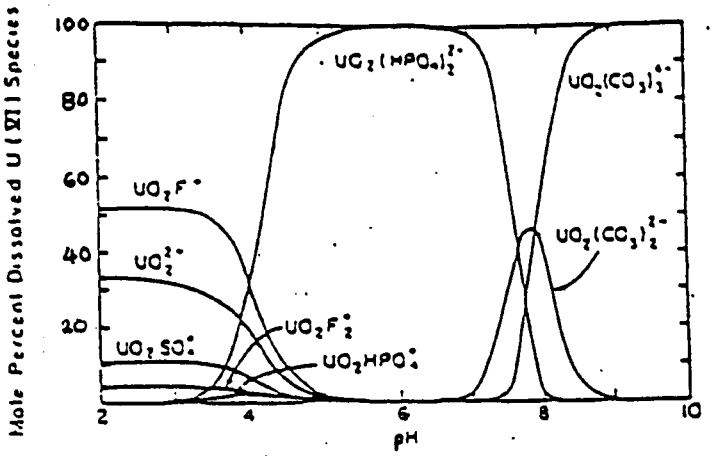


Figure II-1: Distribution of uranyl complexes vs pH for some typical ligand concentrations in ground waters at 25°C. P_{CO2} = $10^{-2.5}$ atm, ΣF = 0.3 ppm, ΣCl = 10 ppm, ΣSO_4 = 100 ppm, ΣPO_4 = 0.1 ppm, ΣSiO_2 = 30 ppm. Source: Langmuir D., 1978.

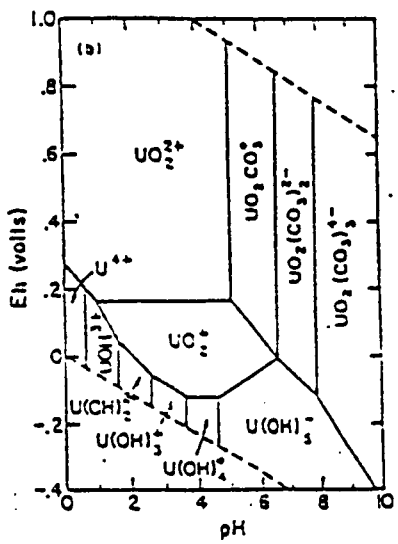


Figure II-2: Eh-pH diagrams of U species at a typical ground water. P_{CO2} = 10^{-2} atm, temp. = 25°C. Source: Langmuir D., 1978.

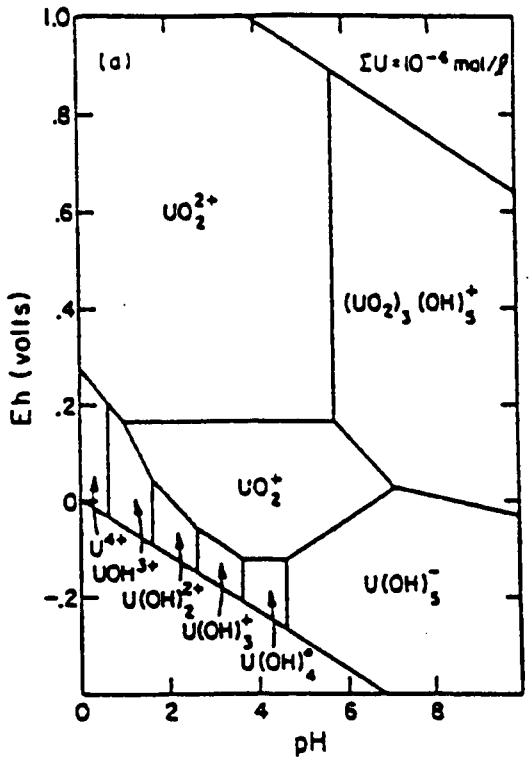


Figure II-3: Eh-pH diagrams showing the relative importance of +4, +5 (as UO_2^+) and +6 valent U species at 25°C for $\Sigma U = 10^{-6}$ M. Source: Langmuir D., 1978.

3. Uranium interaction with soils

Knowledge of the binding behavior of U in natural systems is of great importance for predicting mobility. Uranium can sorb and permeate into soils, often irreversibly, due to diffusion into the lattice of mineral phases and soil interstices. The binding of U is determined by the fixed charge surfaces of clay minerals and by the variable charged surfaces of metal oxides and organic matter. Soil chemisty, therefore, has a direct bearing on the behavior of U in soil.

3.1 Soil chemistry

Soil contains solid, liquid and gaseous components. Mineral (inorganic) and organic matter make up 50% by volume of soil; however, the mineral fraction accounts for 95% of the solid phase (Bolt and Bruggenwert, 1976). The mineral fraction of the soil includes oxides/hydroxides of Fe and Al, clay, carbonate, sulphates, phosphates, nitrates, sulphides, and halides (Bolt and Bruggenwert, 1976). The typical organic phase contains fats (2-20%), carbohydrates (5-25%), proteins (15-45%) and humified organic matter (33-75%). Surface soil contains 1-8% organic carbon (OC) whereas subsoil has less than 0.1% OC (Dragun and Willard Murray, 1986).

The formation of new soil minerals such as insoluble soil oxides, oxyhydroxides and phosphates occurs as a result of metal precipitation (Dragun and Willard Murray, 1986). For most metals, new mineral formation is the primary reaction controlling metal migration in soil-groundwater systems. In addition to precipitation, diffusion into the lattice of mineral phases or the formation of covalent bonds with mineral surfaces (chemisorption) leads to metal immobilization (fixation). Although it is unclear how uraniferous deposits originated, it is believed that U initially leached from volcanic glass associated within or above the host rock or from granitic terraces exposed along the margins of sedimentary basins (Tatsch, 1976). Uranium was then transported with the ground water in the hexavalent state until precipitation occurred under reducing conditions. Possible reducing agents include carbonaceous matter, $H_2S_{(g)}$ and sulfite.

3.2 U-binding

Important chemical processes affecting the behaviour of metals in soils are those related to sorption of metals from the liquid phase to the solid phase. Several different mechanisms can be involved in the sorption of metal ions, including cation exchange (or non-specific sorption), specific sorption, organic

complexation and co-precipitation. However, although the extent of sorption can be measured, it is frequently difficult to be precise about which particular process is responsible for the sorption of metals in any given soil (Alloway, 1990).

Cation exchange: Sorption of metals such as U by cation exchange processes depends upon the density of negative charge on the soil surface. Since U exists mainly as a cation in solution, electrostatic interactions with negatively charged surfaces occur. To achieve electroneutrality, the surface negative charge is balanced by an equal quantity of oppositely charged counter-ions. There are two types of surface negative charges. The first one is permanent (independent of pH) which is due to isomorphous substitution of major element ions within 2:1 clay minerals and edge effects on clay minerals. The second type is variable (dependent on pH) which is due to the dissociation of protons from carboxyl and phenolic hydroxyl groups on humic polymers and O^{-2} and OH^{-} groups on the surface of hydrous oxides and the edges of kaolinite crystals (Bolt, 1979). The cation exchange process is generally reversible, diffusion controlled, stochiometric and selective. Sorption by cation exchange can also be described as the formation of outer-sphere complexes with the surface functional groups to which they are bound electrostatically. The amount of exchangeable cations in

solution to neutralize negative charges on the soil surface is defined as the cation exchange capacity (CEC) of soil (usually expressed in meq/100 g of soil). Alloway (1990) reported CEC of oxides, clays and humic matter as followed: Hydrous oxides of Fe and Al at pH 8 (0.5-1.0 meq/100 g), Kaolinite (3-20 meq/100 g), Illite (10-40 meq/100 g), Smectites (60-120 meq/100 g) and humic matter (150-300 meq/100 g).

Specific sorption: Specific sorption involves the exchange of metal cations with surface ligands to form partial covalent bonds. It results in metal ions being sorbed to a far greater extent than would be expected from the CEC of a soil. Specific sorption is strongly pH dependent and is related to the hydrolysis of metal ions. The hydrous oxides of Al, Fe and Mn are thought to be the main soil constituents involved in specific sorption reactions.

Organic complexation: In addition to the above sorption processes, humic substances on the soil surface also sorb metals by forming chelate complexes. Humic compounds with funtional groups such as hydroxyl, phenoxyl and carboxyl form coordination complexes with metal ions. Low-molecular weight organic ligands can form soluble complexes with metals and prevent them from being sorbed or precipitated.

Co-precipitation: This process is defined as the simultaneous precipitation of a chemical agent in conjuntion with other elements by any mechanism and at any rate (Sposito, 1983). The types of mixed solid commonly formed include clay minerals, hydrous Fe and Mn oxides and calcite in which isomorphous substitution has occurred.

3.2.1 U binding to clay

Clay minerals, in addition to iron oxides and oxyhydroxides are the major components of particulate matter and sediments (Beckett, 1986; Bolt and Van Riemsdijk, 1987). Clay minerals consit of aluminum or magnesium silicates in a layered structure. This orientation results in a permanent negative charge on the minerals which is compensated by exchangeable hydrated inorganic cations (Bailey and White, 1970).

The most common types of clay minerals include Kaolinite, Illite, and Smectite (also called Montmorillonite). The Kaolinites consist of one silica sheet (Si-O tetrahedra) and one gibbsite sheet (Al-OH octahedra) with a Si:Al ratio of 1:1. The Illites and Smectites comprise two silica sheets and one gibbsite sheet with a Si:Al ratio of 2:1. With the exception of Kaolinite, isomorphous substitution within the mineral lattice results in a net negative charge on the surface of the mineral.

Little variable charge exists for these minerals. In Kaolinite, the 1:1 units are tightly bonded together by hydrogen bonds between hydrogen and oxygen atoms of adjacent lamellae. Due to the presence of exposed hydroxyl groups in the structure, Kaolinite has a variable negative charge. The specific surface area (5-100 m^2/g) and the cation exchange capacity (3-20 meq/100 g) of this mineral are low because of little isomorphous substitution. Illite (non-expanding clay) has the 2:1 units bonded by K ions. Because of the interlayer potassium, the unit layers are bonded more strongly than Montmorillonite. The specific surface area (100-200 m^2/g) and CEC (10-40 meq/100 g) of Illite are larger than those of Kaolinite. Smectite (expanding clay) has the largest specific surface area (700-800 m^2/g) owing to relatively weak interlayer bonding. This weak bonding allows the intermicellar spaces to expand upon penetration of water molecules. The CEC is also quite high (80-120 meq/100 g) as a result of the large specific surface area.

Tsunashima et al. (1981) investigated U sorption to Wyoming Na-Montmorillonite from nitrate solution and found that sorption could be directly correlated to the exchange capacity of the clay. Goldsztaub and Wey (1955) reported similar results for U binding to Na-Montmorillonite from uranyl nitrate and uranyl acetate solutions. These authors concluded that U

sorption to clay was mainly due to the exchange capacity of the clay minerals. However, Davey and Scott (1956) obtained approximately 1/2 CEC from a uranyl nitrate solution and 1/10 CEC from a sulfate solution. The difference was due to different U concentrations and clay-liquor ratios from those used by Goldsztaub and Wey (1955). Low exchange in sulfate media was due to the strong uranyl sulfate complex which formed in solution thereby reducing sorption. Uranium sorption, therefore, was affected by the solution medium. Not only the anions affected U sorption but also the exchange cation in the clay structure. Borovec (1981) found that U had the highest sorption affinity when Na^{+} was the exchange cation and the lowest when Ca^{2+} or Mg^{2+} were exchanged. The author concluded that U sorption was influenced by the type of the exchange cation which compensated for the charge deficiency of the clay lattice.

Surface area also impacts U binding. Borovec (1981) reported that U binding was in the order of Kaolinite < Illite < Montmorillonite at U concentrations below 10^{-4} mol/L. The author found that: 1) U was sorbed to both outer and inner surfaces of Montmorillonite whereas U was bound only to the outer surface of Kaolinite and 2) the ratio of the amount of negative to the positive charges was found to be higher on Montmorillonite (~7)

than Illite (~2.5) and Kaolinite (~0.5). The difference in binding affinity of U to various clay, therefore, was due to differences in surface area, charge density on the surface and/or source of the charges (positive or negative). This shows that U binds preferentially to Montmorillonite as a result of charge attraction (CEC) and high surface area. Charlet et al. (1987) also found that minerals with high specific surface areas such as Illite and Lepidocrocite sorbed more U than minerals with low specific surface areas such as Kaolinite.

These finding, therefore, suggest that U binding to clay depends on the exchange capacity, surface area and the solution media.

3.2.2 Binding to oxides

Most secondary clay minerals have a surface coating of noncrystalline Fe, Mn, and Si oxyhydroxides. These elements are liberated during the weathering process of clay minerals and lead to the formation of both amorphous and crystalline insoluble compounds. Weathering refers to the disintegration and alteration of rocks and minerals by physical and chemical processes. Physical weathering is caused by physical stresses within the rock or mineral whereas chemical weathering is caused by chemical reactions. While physical processes only change the

material size, chemical processes alter the weathered products. In nature, both physical and chemical weathering may occur simultaneously.

Of the above oxides (Fe, Al, Mn and Si), noncrystalline ferric oxyhydroxide has the highest U binding affinity, above that of secondary clay minerals. Upon removal of excess Fe-oxides from secondary smectite, Ames et al. (1982) found that U sorption decreased. High potential U sorption by iron oxide was also shown in the work of Rodden and Warf (1951). They found that colloidal iron oxide adsorbed all of the uranyl ions initially in the text solution (Σ U = 10^{-5} mol/L).

Hsi (1981) examined sorption of UO_2^{2+} (10^{-6}-10^{-8} mol/L) on synthetic goethite, amorphous ferric oxyhydroxide, hematite and natural hematite and found that uranyl ions were strongly sorbed by each material despite the fact that both the uranyl ions and the oxides or oxyhydroxides had net positive charges. In addition, the author found that for a given surface area, amorphous ferric oxyhydroxide had the highest U sorption potential while hematite had the lowest. Barton (1956) also reported a similar finding. The author investigated U binding to oxidized base metal ores and found that Limonite (hydrous ferric oxide) sorbed uranyl carbonate, uranyl hydroxide and uranyl ions. However, depending on the composition of Limonite,

the degree of sorption varied. The results showed that Limonite with only goethite (α-FeOOH) present sorbed 0.25 meq/10 gram ores whereas Limonite with hematite (α-Fe_2O_3), goethite and quartz sorbed only 0.08 meq/10 g. Hsi (1981) concluded that surface area and surface charge were important factors but not the only factors determining U sorption. This leads to the conclusion that surface functional groups (i.e. O^{2-} and OH^-) could be responsible for the differences in U sorption for the above oxides.

3.2.3 Binding to organics

Organic material is commonly subdivided into humic and nonhumic substances. The humic fraction is the major organic constituent of most soils. Davis and Leckie (1979) noted that metal binding to soil particles coated with humic compounds was greatly enhanced over soil particles consisting mainly of simple oxides. Gueniot et al. (1988a) investigated the geochemical behavior of U in soils and found that oxyhydroxides and humified organic matter were responsible for U retention and accummulation. Clays alone, the authors concluded, were not efficient U sorbers.

Sheppard et al. (1989) reported a large amount of U was recovered in the humic acid fraction of soils. Upon combining

with fulvic acid extracts, U recovery from soil reached 89%. The authors concluded that organic matter was the sink for U sorption.

Berthelin et al. (1987) found that organic decomposition resulted in enhanced U binding. They noticed that the consumption of cellulose due to microbial activity increased U sorption. The authors found that U sorption increased approximately 10 fold (i.e. from 2-4 μg U/g cellulose to 20-25 μg U/g cellulose) with increasing microbial population. They concluded that the transformation of cellulose during microbial activity enhanced U sorption due to the creation of functional groups which facilitated U binding. The same idea was reported by Landais et al. (1987). The authors noted that surface oxidation of organic matter resulted in an increase in oxygen content, hydroxylic (OH) and carboxylic (COOH) functional groups, the destruction of aliphatic chains, the relative increase in aromaticity and the formation of oxygen bridges. They found that the regeneration of carboxylic groups and the formation of humic-like oxygen rich macromolecules from oxidation of kerogen enhanced U binding.

Gueniot et al. (1988b) investigated the distribution of U in hydromorphic soils and soil sequences. They identified two main processes for U binding: 1) complexation with organic

compounds in reduced layers and 2) retention on amorphous oxyhydroxides in oxidized layers. They also observed that the amount of U bound varied with the accumulation of organic matter. The greatest U concentration was found in the humic layer of hydromorphic soils (reduced and organic rich horizons topsoil). The authors concluded that soil topography influenced U distribution. Organic matter, especially humic acids, was identified as the main component impacting U accumulation from organic-rich, reduced soil horizons (Scharpenseel et al., 1975), peats (Lopatkina, 1967; Coker and Dilabio, 1979) and humic acids (Brookins and Olsen, 1984).

Szalay (1964) showed that lignite, peat and other decayed fossil plant debris sorbed U from aqueous solution in the pH range of 3 to 7. The author found that peat bound up to 10% of the initial U in solution and that binding was reversible. Furthermore, after dilute NaOH extraction to remove the humic acid fraction, the peat's sorption capacity for U was reduced. The author concluded that humic acid was primarily responsibe for U binding.

Breger et al. (1955) investigated La^{+3} exchange with U in a fossil uraniferous lignite from Dakota and found that only a small fraction of the U was exchangeable. They concluded that U was sorbed in the form of an organic complex. Szalay (1969)

also noted that U binding in coals was irreversible. However, the author reported that ion-exchange of uranyl ion was only the primary process, and would be followed by secondary mineralization over the course of geological time.

Based on the CEC values, humic matter appears to bind more U than oxides and clays. Accumulation is due to complexation of U with the functional groups associated with humic substances such as COOH and OH. These groups can coordinate with the uranyl ion to form stable complexes.

3.3 Impact of pH on U binding

According to Giblin et al. (1981), Kaolinite surfaces exhibited two distinct interfacial activity types. The first one was due to negative charges on the flat faces which resulted from isomorphous substitution. The second one derived from charges on the edges of the flake which were controlled by the solution concentrations of Al^{3+} and OH^-. The magnitude of edge effect was thus pH dependent. The authors found that the degree of U sorption by Kaolinite was pH dependent: Kaolinite did not significantly immobilize U below pH 5.5 whereas maximum immobility occurred at pH 6.5. The authors concluded that UO_2^{2+} was less readily sorbed by Kaolinite than its hydroxyl complexes at pH 6.5. The reason for this conclusion, according to James

and Healy (1972), was that sorption of hydrolyzed cations and other complexes occurred more readily than sorption of simple ions. The authors postulated that hydrolysis or complex formation decreased the sorption energy barrier which, in turn, provided a closer approaching of complexes to an interface. This resulted in a greater coulombic interaction, and consequently favored sorption.

A similar finding was report by Hsi (1981) and Ho and Doern (1985). Hsi (1981) examined sorption of UO_2^{2+} (10^{-6}-10^{-8} mol/L) on synthetic goethite, amorphous ferric oxyhydroxide, hematite and natural hematite at pH 4 to 10. The author found that all sorbents strongly bound uranyl ions at pHs above 5 to 6. Ho and Doern (1985) investigated sorption of uranyl ions on hematite as a function of solution pH and U concentration. Their results show that sorption of U increased with increasing U content in solution. In addition, significant uptake of U occurred as pH was raised from 5 to 6.2 which corresponded to an increase in the $(UO_2)_3(OH)_5^+$ concentration.

Szalay (1969) noted that humic acid contains phenol-hydroxyl and carboxyl groups. The carboxyl functional group dissociates at a pH 5 or greater and participates in cation exchange. The phenol-hydroxyl group, on the other hand,

dissociates at pH 9 and cation exchange interactions would be minimal at naturally occurring pH values (5-7).

Solution pH impacts not only U speciation but also the surface charge of soils and soil materials. Sorption of uranyl ion to amorphous silica, Ti and Zr oxyhydroxydes (Maya, 1982a), amorphous ferric oxyhydroxides, goethite, hematite (Hsi, 1981; Hsi and Langmuir, 1980; Van Der Weijden et al, 1976), clays and organic matter (Borovec, 1981; Langmuir, 1978) have been studied. Regardless of soil composition, maximum uranyl sorption occurred in the pH range from 5 to 8.5. This was despite the fact that some soil materials, such as ferric oxyhydroxides, had a net positive surface charge within this pH range. The finding indicated that charge attraction (CEC) on the ferric oxide surface was not the main sorption mechanism. Van der Weijden et al. (1976) suggested that the strong chemical bonding of uranyl ion to the oxide surface through surface oxygen and/or hydroxyl group interaction resulted in enhanced sorption in the pH range 5-8.5.

The above results indicated that U binding increased with increasing solution pH due to the enhanced negative surface charge. In addition, the strength of bonding as a function of solution pH between U and surface functional groups on soils also enhanced U binding.

3.4 Impact of other ions on U binding

Competition for sorption sites may limit sorption of individual metals. Work of Tsunashima et al. (1981) indicated that uranyl ions sorbed to a greater extent to monocation-clays (i.e.Na^+or K^+-clay) than to divalent cations clays (i.e.Mg^{2+}, Ca^{2+}or Ba^{2+}-clay). The authors found that Na-clay sorbed up to its CEC whereas Ca-clay only sorbed to 50% CEC at pH 4.0-4.5. The result suggests that sorption is a selective process.

Hsi (1981) investigated the effect of Na^+/ K^+ and Ca^{2+}/ Mg^{2+} systems on the sorption of U to ferric oxyhydroxides at which the concentration of individual cations was 10^{-3} mol/L. The author found that uranyl sorption was relatively the same regardless of solution pH (4-10) and concluded that sorption of U to ferric oxyhydroxides was independent of cation concentrations.

Anion complexation can alter the binding characteristic of U to soil. Uranyl ions are stable at pH < 5 and can combine with ligands such as Cl^-, NO_3^-, SO_4^{2-} , HPO_4^{2-}, and CO_3^{2-} to form stable complexes in solution. Uranyl carbonate complexes inhibited uranyl sorption especially in alkaline solutions (Hsi, 1981). Sorption inhibition was proportional to the total dissolved carbonate content. Uranyl di- and tri-carbonate complexes were weakly sorbed, if at all, whereas hydroxyl

complexes (UO_2OH^+, $(UO_2)(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$) were strongly sorbed. Increasing the total carbonate concentration from 0 to 10^{-2} mol/L reduced uranyl sorption to goethite by 2 to 3 orders of magnitude. Berthelin et al. (1987) found that phosphorite (rock phosphate) enhanced U sorption in acidic solutions (pH 3-4).

It appears that in the presence of low ionic strength solutions, uranyl ion concentrations were regulated partially by exchange processes. The uranyl ion sorbed to clays, oxides and organics. However, as the ionic strength of the solution increased, other ions such as Ca^{2+}, Mg^{2+} and K^+, displaced the uranyl ion thereby reducing U sorption. In addition, anions (i.e. carbonate and phosphate) form strong soluble complexes with uranyl ion, further lowering sorption activity.

4. Equilibrium

A variety of empirical and theoretical models have been used to explain and/or fit laboratory metal adsorption data. Among them are surface ionization and complexation, simple Langmuir, Freundlich, and Linear isotherms.

The surface ionization and complexation model (Davis and Leckie, 1978) has been used to describe uranyl sorption data in

simple electrolyte systems. However, in more complex solutions, modeling procedures become more difficult and uncertain.

The Langmuir and Freundlich models have been used to successfully represent uranyl sorption to soil under constant pH conditions. For variable pH conditions, their applications have been less successful (Hsi, 1981). The Langmuir model (1918) is based on the assumption that maximum sorption occurs upon saturation of a monolayer, sorption energy remains unchanged and bound metals do not migrate from the soil surface. The Freundlich model (1909), on the other hand, assumes that sorption energy decreases as metals migrate to soil.

Since Freundlich and Langmuir models have been widely used to describe U sorption, the following discussion will emphasize these two modelling techniques.

4.1 Freundlich isotherm

The general and linearized forms of Freundlich model are represented in equations 1 and 2:

$$q_e = KC^{1/n} \qquad \text{(EQ 1)}$$

$$\ln q_e = \ln K + (1/n) \ln C \qquad \text{(EQ 2)}$$

where:

q_e is the amount of solute sorbed per unit weight of sorbent (mg/kg) at equilibrium,

K is the Freundlich constant $[(L/kg)^{1/n}]$ and is related to the capacity or affinity of the sorbent, and

C is the measured solute concentration in solution (mg/L) at equilibrium

The n term is a measure of nonlinearity (dimensionless) and an indicator of the intensity of sorption or how the capacity of the sorbent varies with the equilibrium solute concentration. When $n > 1$, the isotherm is concave toward the X-axis. This situation occurs when specific binding sites are filled or remaining sites become less attractive to the solute molecules. When $n < 1$, sorption is significant only at high solute concentrations. This results from modification of the surface by previously sorbed molecules. In the case of $n = 1$, the attractiveness of soils to solute remains the same for all solute concentrations. The above equations, however, have the disadvantage of not indicating a sorption maximum.

A Linear sorption equation (special form of Freundlich equation when $n = 1$) is presented in equation 3:

$$q_e = K_d\ C \quad (n = 1) \qquad (EQ\ 3)$$

where K_d is the distribution coefficient corresponding to the slope of the isotherm and C is the equilibrium concentration of solute. The distribution coefficient (K_d) describes the partitioning of solute between the solid and liquid phases and

is a useful parameter for comparing the sorptive capacities of different soils or materials for any particular ion (when measured under the same experimental conditions). The distribution coefficient is defined as the ratio of the amount sorbed per unit weight of soil to the amount in solution per unit volume of liquid. Thus, K_d has the dimension of volume per weight (i.e. ml/g). The K_d value is affected by the pH and the CEC. Soils with high pH and CEC sorb large amounts of metal compared to soil with low pH and CEC. From the above definition, high K_d indicates that soil has a high affinity for a particular solute.

4.2 Langmuir isotherm

The general and linearized forms of the Langmuir model are represented in equations 4 and 5:

$$q_e = (Q^\circ bC) / (1 + bC) \qquad \text{(EQ 4)}$$

$$(1/q_e) = (1/Q^\circ) + [1/(bQ^\circ)] \; (1/C) \qquad \text{(EQ 5)}$$

where:

Q° is the amount of solute sorbed per unit weight of soil in forming a complete monolayer coverage on the soil surface (mg/kg), and

b is a constant related to the net enthalpy of sorption or bonding energy of solute with soil,

The terms q_e and C are the same as those discribed in the Freundlich equation.

The Langmuir model differs from the Freundlich model in that at very high solute concentrations, the factor 1 can be neglected from the denominator of equation 4. The equation then simplifies to $q_e = Q^0$ which indicates that q_e becomes constant at high concentration. That is, at high solute concentration, the soil surface becomes saturated and sorption reaches a maximum.

Borovec (1981) studied the sorption of uranyl species to Kaolinite, Illite and Montmorillonite at pH 6.0. The author found that the sorption profile fit the Langmuir equation for $U(+6) > 10^{-4}$ mol/L, whereas the Freundlich equation applied at lower concentrations. Tsunaskima et al. (1981) also found that U sorption to Montmorillonite followed a Langmuir-type curve for $U > 1.11 \times 10^{-3}$ mol/L. These findings, therefore, suggest that the Freundlich model should be used at low U concentration in which sorption continually increases. On the other hand, the Langmuir model should be used at high U concentration in which soil binding may reach saturation ($q_e = Q^0$).

Ames et al. (1983), from their study of U sorption to secondary minerals, pointed out that the Freundlich isotherm is generally useful up to about 5% of the capacity of the sorbent. In a study of U sorption to Biotite, Muscovite and Phlogopite,

Ames et al. (1983) reasonned that the Freundlich equation was appropriate only within specific conditions of temperature, pH, solution-composition, and U concentration. For modeling a complex natural geohydrologic system, according to the authors, the Freundlich model was not useful because the range of variables was too large.

A major assumption in the Langmuir model is that the distribution of sorption sites on the sorbent are uniform. According to Ames et al. (1982), the practical aspect of the Langmuir model was limited because most rock and mineral sorption sites were energetically heterogeneous. Also, the authors found that upon removal of excess Fe-oxides from the secondary smectite, U sorption was better described by the Freundlich model.

Giblin et al. (1981) studied U binding to Kaolinite from a simulated water containing 100 µg U/L and found the maximum distribution coefficient (K_d) was 35,000 ml/g. However, Langmuir (1978) calculated a K_d of 2 ml/g for U using same sorbent. The reason for the large difference in K_d values was unknown. It appears that K_d varies with experimental condition (i.e. pH, U concentration) which could partially explained the discrepancy in K_d from the works of Giblin et al. (1981) and Langmuir (1978). Borovec (1981) found K_d increased in the order

of Kaolinite < Illite < Montmorillonite at U concentrations below 10^{-4} mol/L. The K_d values obtained ranged from 50 to 1000 ml/g.

The distribution K_ds for U sorption to oxides have also been reported. Hsi (1981) calculated the distribution coefficient for U sorption to goethite and found that K_d varied by several orders of magnitude (10^2 to 10^6 L/kg). It was noted that K_d varied inversely with total U concentration which could be due to the availability of sorption sites at low U levels. Ames et al. (1983) reported that a distribution coefficient in excess of $2x10^6$ ml/g was obtained for ferric oxyhydroxide.

The above reports indicate that the Freundlich model is useful when describing U sorption at low concentrations. However, the distribution coefficient depends on both pH and U concentration and is very specific for each system. Therefore, any attempt to predict and model the sorptive behavior of U in natural systems based on a single measure of K_d is not appropriate.

5. Uranium mobilization

Uranium is a relatively mobile metal in the environment owing to its tendency to form stable complexes with a number of aqueous anions. In general, U mobilization in soil depends on

several factors such as system pH, the concentration and type of inorganic and organic complexing agents, and the redox state of the uranium species and environment.

Using solubility and sorption data, Langmuir (1978) showed that uranyl ion was least mobile in the pH range 5-8.5. Giblin et al. (1981) investigated U mobility in three simulated natural water systems and found that hydrous ferric oxide and Kaolinite affected U mobility in different pH-Eh domains. In addition, the authors found that aqueous carbonate enhanced mobility of U. Zielinski et al. (1988), from their calculations based on chemical compositions of the waters and thermodynamic data, concluded that uranyl-carbonate and uranyl-phosphate were the major dissolved U species. A similar finding was reported by Bondietti and Tamura (1980). They found that U sorbed to soil at pHs below 7.5 whereas uranyl carbonate complexes enhanced U solubility above pH 7.5.

The type of U-bearing mineral present in the subsurface also affects U mobilization. Berthelin et al. (1987) investigated the solubility of U from rock phosphate, syenite and natural uranium oxide and reported greater U mobilization under acidic soil conditions (pH 3.6-4.3). The authors believed that acid degraded the mineral surface or supplied H^+ ions which

competed with U for sorption sites. The degree of mobility increased as follows: phosphorite < uranium oxide < syenite.

The chemical form of U in soil also impacts mobilization. Bolle et al. (1988) studied extraction procedures for U minerals such as autunite ($Ca(UO_2)_2(PO_4)_2.4H_2O$), curite ($Pb_2U_5O_{17}.4H_2O$), torbernite ($Cu(UO_2)_2(PO_4)_2.8H_2O$), tyuyamunite ($Ca(UO_2)_2(VO_4)_2.2H_2O$) and uraninite (UO_2). They found that: 1) NH_4-acetate completely dissolved autunite and curite but only partially dissolved tyuyamunite, torbernite and uraninite, and 2) H_2O_2 dissolved uraninite partially.

Read et al. (1993) investigated the migration of U from uraniferous sedimentary rocks into peat-rich soils. They observed that weathering processes decalcified sandstone which, in turn, mobilized U. They also noted that natural organic matter competed successfully with carbonate for U below pH 6.

Eligwe and Torma (1984) investigated the influence of hydrogen peroxide on the extraction efficiency of U from a New-Mexico ore. They reported that over 82% U was released from the ore using sulfuric acid (3 g/L) at 30°C and complete removal occurred at 50°C. The presence of H_2O_2 improved the yield by 5 to 6% in the temperature range of 30-50°C. The yield improvement, according to the authors, was due to the oxidation of insoluble U(+4) to soluble U(+5) and U(+6). However, U(+5)

ion was unstable and experienced valency disproportionation to yield U(+4) and U(+6). The chemistry of U oxidation in acidic H_2O_2 solutions (Eligwe and Torma, 1984) is as follows:

$$H_2O_2 \rightarrow H^+ + HO_2^-$$

$$UO_2 + HO_2^- + 3H^+ \rightarrow UO_2^{2+} + 2H_2O$$

$$HO_2^- + H^+ \rightarrow 0.5O_2 + H_2O$$

$$UO_2 + 0.5O_2 + 2H^+ \rightarrow UO_2^{2+} + H_2O$$

The stability of H_2O_2 also affects U mobility. H_2O_2 is commercially sold in stabilized and unstabilized forms. The effectiveness of the stabilizer depends on pH and its concentration in the solution. From experiments, Eligwe and Torma (1984) found that stabilized H_2O_2 extracted more U from ore than unstablized H_2O_2. The difference was believed due to the faster decomposition of the unstabilized product than the stabilized one.

Amell and Langmuir (1978) studied factors influencing the solubilization rate of $UO_{2(s)}$ under conditions applicable to in-situ leaching. They found that U extraction was faster at 0.1% H_2O_2 than 1.0% H_2O_2 and concluded that this was due to partitial precipitation of dissolved U in the form of uranyl peroxide. Lawes (1978) reported that uranyl peroxide did not precipitate above pH 6-7. Torma and Eligwa (1982) found that an optimum H_2O_2 concentration for the extraction of U from ore was 13.1 mmol/L.

Further increases in H_2O_2 dosage decreased the yield and rate of U extraction. Similar findings were also reported by Eligwa and Torma (1984). Together these findings suggest that precipitation of uranyl peroxide could occur at high H_2O_2 concentrations when the pH is less than 6.

In the presence of hydrogen peroxide, the solubilization of $UO_{2(s)}$ can be expressed as:

$$UO_2(s) + H_2O_2 \rightarrow UO_2^{2+} + H_2O + O^{2-}$$

Extraction of U from a low grade ore with hydrogen peroxide was studied by Eligwe et al. (1981a). They found that extraction efficiency increased with H_2O_2 concentration and maximum removal occurred when a 4.64 molar ratio of H_2O_2 to U was utilized. In addition, these researchers observed that the rate of extraction (zero order with respect to H_2O_2) was fastest during the first 1.5 hour contact time (over 90% U removal). This suggests that U mobilization depends on both H_2O_2 concentration and treatment time.

Galichon et al. (1977) investigated the chemical factors influencing in-situ U leaching. They reported that the dissolution of reduced U(+4) was mass transfer controlled at high H_2O_2 concentrations. From their results, it appeared that U mobility was affected not only by the oxidizing potential of

peroxide but also by the accessibility of U to the oxidizer. The presence of clays appeared to inhibit U accessibility.

The oxidation reaction mechanism which involved sulfated Fe^{3+} and H_2O_2 was the main cause of dissolution of U(+4) (Torma and Eligwe, 1982; Merritt, 1971). This dissolution process, as suggested, was an electrochemical reaction: cathodic reduction of the oxidant and anodic oxidation of U(+4).

In general, immobilized U in the reduced state is oxidized to the U(+6) form at mineral-solution interfaces as a result of oxidative weathering. Uranium mobilization then depends on a number of factors including the amount of U, the composition of the solution (i.e. pH, Eh, carbonate content) and the composition of soils.

6. Effect of H_2O_2 treatment on soil property

During peroxidation, soil properties (chemical and physical) may be altered. This alteration, in turn, could affect subsequent metal binding and release. Bartlett et al. (1936) have shown that the total exchange capacity (organic and inorganic) of soil varied with peroxidation (6% H_2O_2) treatment of soil. The authors reported that the exchange capacity of sandy soils (low organic) was reduced significantly. They also found that hydrogen peroxide treatment increased the inorganic

exchange capacity in some soils. These results suggested that organic matter was a main cause for the reduced CEC. Peroxidation may have stripped bound cations such as Fe and Mn from the inorganic fraction, which, in turn, increased the CEC in soil. Bartlett et al. (1936) indicated that the total exchange capacity of Portsmouth loam soil was reduced 76% upon soil peroxidation: from 21.36 meq (5.29% organic matter) to 5.14 meq (1.45 % organic matter). However, under the same oxidation condition, the exchange capacity of Portsmouth fine sandy loam was reduced by up to 90%: from 11.43 meq (3.11% organic matter) to 1.15 meq (0.59 % organic matter). The authors correlated the loss in exchange capacity of the soil with the loss in organic matter due to peroxide treatment.

Douglas and Fiessinger (1971) used X-ray diffraction to investigate the degradation of clay minerals after H_2O_2 treatment and found that H_2O_2 caused only a small change in diffraction patterns of 2:1 clays (i.e. vermiculite and bentonite). However, the addition of H_2O_2 to clay with sucrose significantly altered the clay. They also reported a reduction in pH of the clay-H_2O-sucrose-H_2O_2 system. The finding indicates that organic matter was more affected by the H_2O_2 than was the clay mineral.

Tessier et al. (1979) reported a partial alteration of silicate and mica upon soil peroxidation. A similar result was

found by Burford et al. (1964) in which oxidation of soil resulted in exfoliation of mica edges as well as an increase in the external surface area, especially for fine materials. The reason for an increase in external surface area was due to the removal of organic coatings on soil which blocked sorption sites. An increase in surface area, therefore, may result from soil peroxidation.

The extent of soil organic matter oxidation is a function of H_2O_2 concentration. McLean (1930) reported that 86% of the total carbon and 89% of the total nitrogen were removed from organic soil using 60 ml of 6% H_2O_2 for 20 min. Further treatment at this peroxide level using a larger volume of peroxide (260 ml), resulted in maximum oxidation of the carbon (95%) but no increase for nitrogen. The author determined that 60 ml of 6% H_2O_2 was sufficient to decompose the organic compounds in soils containing both carbon and nitrogen. Also, according to McLean (1930), the oxidation of organic compounds using 3% H_2O_2 was sufficient for most non-carbonate soils with a pH $\leq$ 7 whereas 5% H_2O_2 was required for soils containing calcium carbonate.

Summary

The degree and mechanism of U binding to soils are influenced by a number of factors. Uranium speciation impacts

binding due to the fact that uranyl-hydroxy complexes sorb more readily than simple uranyl ions. Complexation with inorganic ligands (i.e. CO_3^{2-} , F^-, SO_4^{2-} and PO_4^{3-}) inhibites U binding. Uranium binding to soil varies with soil materials. Binding to clay surfaces occurres primarily by the exchange capacity mechanism. Clays with higher CECs, such as Montmorillonite, bind more U than clays with low CECs, such as Kaolinite. In addition, surface area and solution media also impact U sorption to clay. Oxyhydroxides have a higher affinity for U than oxides and differences in surface area and functional groups (O^{2-} and OH^-) are believed to be the reason for the variations observed. Uranium binds extensively to the humic fraction of soil through complexation mechanisms with humic functional groups (COOH, OH^-). It can be deduced from the above observations that: 1) U sorption to soil follows the order oxides < clay < oxyhydroxides < organic, 2) if soil has a high CEC then this parameter plays a dominant role in the sorption process; otherwise, surface area becomes an important factor for U binding and 3) the presence of functional groups on the soil surface enhances U sorption relative to CEC and surface area.

Uranium mobility is a function of soil pH, H_2O_2 concentration and U speciation. pH directly impacts U speciation and complexation. An increase in solution pH

increases U binding. Peroxide concentration may facilitate precipitation of uranyl peroxide at high concentration thereby reducing U mobility. Uranium in the tetravalent state is insoluble and requires oxidation to the hexavalent state before significant mobilization occurs.

CHAPTER III

MATERIALS AND METHODS

1. Overview of research

Experiments were initially conducted to obtain U(+6) binding rates and equilibrium sorption capacities for different soil components and whole soils. This information was used to define initial equilibrium conditions in subsequent U mobilization experiments. After synthetically contaminating each soil, U mobilization was evaluated for different H_2O_2 loadings (0 to 30% v/v), contact times, and number of treatments (using fixed peroxide loadings and contact times). Additionally, mobilization of reduced uranium (U^{+4}) upon peroxide treatment was determined.

The treatments tested were chosen to simulate, using a laboratory contaminated soil, those at a field demonstration of in-situ peroxidation at a DOE site in Portsmouth, OH. Batch systems were used to simulate activities at the field site and identify governing parameters impacting U mobilization. During field testing of the in-situ process, peroxide was to be pumped into a contaminated zone in the soil and mixed using 4 ft

diameter duel augers. The duel augers would then be moved to a contaminated zone above the previously treated zone for further soil treatment. In this treatment scenario, any U mobilized would move under the force of gravity to a soil zone below the treated area, thereby recontaminating the previously treated subsurface soil. Hence, additional experiments were performed to determine the extent of U resorption to peroxide treated soils. The data obtained provided information concerning the impact of peroxidation treatment on soil binding capacities.

2. Soil characterization

Three clay minerals, Kaolinite (Kga-2), Ca-Montmorillonite (Stx-1) and Illite (Imt-1), were obtained from the Source Clay Minerals Repository (Columbia, MO). Two metal oxides (Al_2O_3-gibbsite and Fe_2O_3-hematite) were obtained from Aldrich Chemical Company. Two uncontaminated whole soils were obtained near or within a Department of Energy (DOE) facility located in Hanford, WA (Hanford I and II) and one uncontaminated whole soil was obtained from the DOE Portsmouth Gaseous Diffusion Plant in Piketon, OH. Hanford (I) soil was collected from the Richland sanitary landfill which is located outside of the boundaries of the Hanford DOE site. The soil was collected to a depth of 20 ft. Hanford (II) soil originated from within the DOE Hanford

site in the 200 East and 200 West areas of the plant. The collected soil consisted of a subsample from a stockpile that was formed from excess soils exhumed during soil boring/coring investigations. The stockpile was a composite of soil collected from depths of 0-200 ft. The Portsmouth soil was obtained from one of the plant's borrow pit areas used for construction fills. This soil was collected from depths less than 20 ft.

Clays and metal oxides were used as received from the suppliers without further treatment. Hanford and Portsmouth soils were passed through a # 40 screen (0.0164 inch opening) before washing with deionized (DI) water. The screening process was employed to obtain a more uniform soil size. After washing, the soils were centrifuged at 10,000 rpm for 10 minutes, decanted to remove unsettled particles, and air-dried for approximately one week. Soils were washed to remove fines which would have been lost during subsequent soil contamination procedures thereby impacting U sorption capacity evaluation.

To evaluate U sorption capacity for peroxide treated soils, each soil material was pretreated by adding 150 ml of 30% H_2O_2 to 100 g of sorbent in a 500 ml uncovered glass beaker. The slurry was stirred every 20 minute for one-hour with a glass rod and then air-dried.

Subsequently, the dried soil materials (original and pretreated) were ground with a mortise and pestle, then screened again (# 40) to obtain a more homogenous mixture before use.

3. U standard preparation and preservation

All glassware was acid washed to prevent possible sample contamination. The glassware was first soaked in Baxter SP Micro Laboratory Cleaning solution for a minimum of one day, rinsed with tap water and then placed in a 6N HNO_3 bath for an additional one day. The glassware was then triple rinsed with distilled water, followed by another triple rinse with deionized water.

Aqueous U (+6) standards were prepared by dillution of a stock solution (Baxter Laboratory Supply Co.) containing 1000 mg/ L of uranyl nitrate ($UO_2(NO_3)_2.*6H_2O$) with DI water. A second, more concentrated standard (>3000 mg U/kg), was prepared by dissolving crystaline uranyl nitrate (Baxter Laboratory Supply Co.) with DI water. Uraninite $(UO_2)_s$ was used as the source of U(+4) in experiments performed to evaluate mobilization of reduced U. This material was used as supplied (Johnson Mattey Co.).

Standards and all samples after treatment were preserved by the addition of double distilled HNO_3 to a pH<2

(approximately one drop 10 N HNO_3 / 20 ml solution). Solutions were then stored at 4°C to prevent volume loss (EPA-3005 method) prior to analyses.

4. Kinetic experiments

Binding rate tests were conducted to determine the required time for equilibrium to be achieved between sorbed and aqueous U phases. The speed at which U sorbed to soil materials could be an important factor during peroxidation of contaminated soils. U released during peroxidation may resorb rapidly to the soil zone below the treated area.

Rate experiments were conducted using a soil to U stock solution ratio of 1:15 to minimize any U mass transfer limitations. Fifteen mls of diluted uranyl nitrate (pH ≈ 5.5) stock solution were added to 1.0 g of air-dried sorbent in a 50 ml polyethylene (PET) centrifuge tube. The initial U concentration added to each soil material was as follows: clay (33.3 mg U/L), oxides (115 mg U/L), Hanford I (35 mg U/L), Hanford II and Portsmouth (105 mg U/L). Varying U concentrations were used due to the difference in sorption capacity of each soil material. For peroxide pretreated soils, the initial U concentrations were: Kaolinite, Al oxide, Hanford (I & II) and Portsmouth (28.2 mg/L), Montmorillonite, Illite and

Fe oxide (86 mg/L). Each slurry was placed on a Wheaton rotary mixer (Baxter Laboratory Co.) at 60 rpm. Samples were removed from the mixer at different time intervals and centrifuged at 10,000 rpm for 10 minutes. The supernatant was decanted and then analyzed for U content. All samples were run in duplicate.

The amount of U sorbed was determined by subtracting the mass of U in solution from the initial U mass added to each soil. A blank solution, which contained 15 ml of 100 mg U/L solution and no soil, was also analyzed to determine U losses due to sorption on the test container walls.

5. Isotherm experiments

Isotherm experiments were conducted to determine the equilibrium binding capacity of each sorbent for U. By definition, equilibrium exists when the U concentration in the aqueous and sorbed phases no longer changes over time. Equilibrium times were established from the kinetic tests.

Each soil material in this study had different physical and chemical characteristics which could influence its sorption capacity. Information from the isotherm tests was used to assess the relative affinity of each soil material for U and to determine U loadings of uncontaminated soil materials to achieve desired contamination levels in subsequent mobilization studies.

Fifteen mls of uranyl nitrate solution were added to 1.0 g of sorbent in 50 ml PET centrifuge tubes. The range of initial U concentrations varied with each soil material as follows: Clay (0.1-40 mg/L), oxides (10-110 mg/L), Hanford I (10-80 mg/L), Hanford II (10-100 mg/L) and Portsmouth (50-250 mg/L). The U solution was adjusted to three pH levels (5, 7 and 9) to determine the impact of pH on U binding. The pHs were chosen to model various soil conditions present in the environment. Uranium solutions were adjusted to the desired pHs using either 0.1N NaOH or 0.1N HCl before mixing with each soil material. Mixtures were rotated at 60 rpm until equilibrium was reached (as determined from kinetic tests). The equilibrated solutions were centrifuged at 10,000 rpm for 10 minutes. Supernatant samples and controls, containing no soil, were analyzed for U content. A similar procedure was followed for the H_2O_2 pretreated soil materials. Initial U concentration ranges were: Clay (10 - 90 mg U/L), oxides (10-50 mg U/L), soils (10 -60 mg U/L). The amount of sorbed U was determined by subtracting the mass of U in solution at equilibrium from the initial (control) mass of U added.

6. Batch soil contamination for mobilization studies

Uranium contaminated soils were prepared by adding stock U (+6) solution to air-dried soil materials in a 250 ml centrifuge bottle with a screw cap. Uranium concentration and mass of sorbent added varied for each test material (table 1). The slurry was mixed on a rotary mixer at 60 rpm until equilibrium was achieved (1-2 days). The mixture was then centrifuged at 10,000 rpm for 10 minutes and the supernatant decanted and analyzed for U. The contaminated soil was washed with DI water to remove unbound U contained in the soil pore water and U loosely associated with the soil. The wash step was conducted by rotating the slurry mixture at 60 rpm for 10 minutes, centrifuging at 10,000 rpm for another 10 minutes, and decanting the supernatant for U analysis. Each washing was conducted in triplicate. The washing procedure was used to simulate field conditions in which percolating rainwater washes the soil. Loading on the soil was determined by subtracting the combined U mass in solution at equilibrium and in the wash waters from the initial mass added. The washed U contaminated soils were then air-dried in the same (open) container (approximately one week). The soil containers were placed in a hood with an upward air flow for drying. The small opening size of the 250 ml centrifuged bottle and the upward air flow minimized the

Table 1: Initial U concentration and mass of soil materials used in batch contamination process.

Soil materials	Initial U conc. (mg/L)	Initial U vol. (ml)	Mass of soil material (g)
Kaolinite	3015	180	90
Ca-Mont.	3015	200	100
Illite	1110	100	50
Al_2O_3	1110	200	100
Fe_2O_3	1110	200	100
Hanford(I)	154	200	100
Hanford(II)	210	200	110
Portsmouth	210	200	110

possibility of external contamination during the drying procedure. The dried soil materials were ground with a mortise and pestle, and then screened to obtain homogeneous subsamples. One gram of dry contaminated soil was placed in a screw-capped 50 ml PET centrifuge tube for peroxide treatment.

7. U mobilization upon H_2O_2 treatment

Batch experiments were conducted to evaluate U mobilization from the contaminated sorbents upon H_2O_2 addition. The following variables were evaluated: 1) soil type (clays, oxides, soils), 2) H_2O_2 loading (0-30% v/v), 3) contact time (1-hour and 24-hour), 4) number of treatments (single and triple), and 5) U oxidation state (+4 and +6).

The effect of peroxide treatment at different loadings was examined to determine levels at which minimum and/or maximum U mobilization occur. A soil to peroxide ratio of 1 to 15 (with mixing) was chosen to minimize the impact of mass transfer on U mobilization. The reaction time, defined as the actual contact time between the peroxide and the contaminated sorbent, was varied from one hour to several days. The variation in contact time helped to determine the flux of U into solution. Also, it was postulated that longer contact times would result in reduced U mobilization due to the creation of additional soil sorption

sites upon longer peroxide treatments. Oxidation state and U form (insoluble vs soluble) were also taken into account. The impact of multiple treatments on U mobilization was also investigated.

7.1 Mobilization of U(+6)

The following procedure illustrates the multiple treatment scenario at a one-hour contact time using 30% H_2O_2. Other contact times and H_2O_2 concentrations were performed similarly.

Fifteen mls of peroxide at 30% H_2O_2 (v/v) were added to 1.0 g of contaminated soil in a 50 ml PET screw-capped centrifuge tube. Additionally, 15 mls of 3% H_2O_2 (v/v) were added to 1.0 g of uncontaminated soil to evaluate background U mobility from each soil. The 3% H_2O_2 was used to avoid the possibility of uranyl peroxide precipitation due to high peroxide concentration. Samples and controls were evaluated in duplicate.

Centrifuge tubes were rotated at 100 rpm. Francis et al. (1992) have reported that U mobilization was enhanced by scrubbing as compared to stirring. Therefore, high speed rotating was used to represent a worst case scenario for U movement (i.e. maximum mobilization). After a one-hour contact time, the tubes were centrifuged at 10,000 rpm for 10 minutes.

The supernatant was decanted and filtered through a Whatman filter paper (# 2) to remove particles suspended in solution due to H_2O_2 off-gassing. The filtration step was omitted when 0% H_2O_2 (DI water) was used as the treatment agent. The pH of the supernatant was then measured (Appendix C1-C16). To evaluate the possibility that U sorbed to the filter, two stock U(+6) solutions (0.27 and 1.0 mg U/L) were filtered. The difference between filtered and non-filtered U concentration was due to filter sorption. The results showed that the filter sorbed approximately 5% of the stock U solutions and this information was incorporated in the data analysis. Five mls of the filtered supernatant were placed in a 20 ml glass vial and heated (approximately 70°C) to dryness to remove all residual peroxide. To this vial, five mls of 0.5 N HNO_3 were added to resolubilize U. The solution was then analyzed for U from this single treatment. The control, containing only the U stock solution, was treated similarly to determine if any U losses occurred during sample processing. The results showed that no U losses were detected during the sample drying and resolubilization procedure.

After the first treatment, any visible soil particles on the filter were scraped back into the original sample vial and an additional 15 mls of 30% H_2O_2 were added to the treated soil.

The sample was then mixed for an additional one-hour on the rotary mixer (100 rpm). The procedure was repeated as above to determine U mobilization from this second treatment. The third treatment was performed similarly.

Sorption of U to sample tube surfaces was also evaluated. Fifteen mls of 20 mg U/L were placed in a 50 ml PET centrifuge tube, rotated for one hour, and then analyzed for uranium. Sorption was determined by subtracting the U concentration after the one-hour contact time from the initial U concentration. Results showed that U sorption to the tube surfaces was negligible.

For longer treatment times (> 1 hr), soil particles loss occurred due to pressure build-up in centrifuge tube. A slightly different procedure was followed to avoid sorbent loss during the 24-hour contact time experiments. Contaminated soil and H_2O_2 were allowed to contact without mixing during the first 23-hour. The mixture was then rotated at 100 rpm for the last hour.

7.2 Mobilization of U(+6 and +4)

Uranium in contaminated soil can exist in the reduced (+4) or oxidized (+6) form. Peroxidation has the potential of oxidizing U from the tetravalent to the hexavalent state thereby

enhancing mobilization. Experiments were conducted in which both U(+4) and U(+6) were added to Hanford (I & II) soils.

The procedure below describes multiple peroxide treatment of soils containing both U(+4) and U(+6) utilizing a one-hour treatment time and 30% H_2O_2 concentration. Other treatment times and peroxide concentrations for the U(+4)/U(+6) contaminated soils were performed similarly.

Uranium dioxide solid (UO_2) was used as the source of U(+4). To one gram of U (+6) contaminated soil in a 50 mls PET centrifuge tube was added 4.0 ± 2.0 mg UO_2 (because of analytical balance limitations, this was the smallest amount of $UO_{2(s)}$ which could be reliability measured). Fifteen mls of 30% H_2O_2 were added to this mixture. The slurry was rotated at 100 rpm for one hour, decanted, filtered, heated and analyzed for uranium as in the U(+6) mobilization procedure. Another 15 mls of 30% H_2O_2 was added to 5.0 mg UO_2 crystals (no soil) to evaluate the amount of U(+4) which was oxidized to U(+6).

7.3 Effect of pH on U mobilization

As indicated in the literature review, the addition of peroxide can alter the soil pH which, in turn, impacts U mobilization. The following experiments were performed on Hanford (I & II) and Portsmouth soils to evaluate pH changes on

U mobilization. The DI water was adjusted to pH 2,3, 7 and 8 with 0.1 N HCl or 0.1 N NaOH. Fifteen mls of the pH adjusted water were added to 1.0 g U(+6) contaminated soil. The mixture was rotated at 100 rpm for 24 hours, then centrifuged at 10,000 rpm for 10 minutes. The supernatant was decanted and pH was measured (Appendix C17).

8. Analytical analyses

Physical and surface properties of the sorbents were carefully examined. Soil pH was measured using ASTM method # 04972. CEC was measured using EPA method 9081. Specific surface area was obtained on freeze-dried samples using the Brunauer, Emmett and Teller (BET) nitrogen adsorption method. Free Fe oxide concentration (Dithionite method: Mehra and Jackson (1960)), amorphous Fe oxide concentration (Oxalate method: McKeague and Day (1966)), and particle size distribution (EPA 600/2-78-054 or ASTM 422 method) were measured for Hanford and Portsmouth soils. Calcite was determined by gravimetric method for loss of CO_2 (Allison and Moodie, 1965b). Total organic carbon (TOC) for Hanford and Portsmouth soils was determined as followed: Samples were acidified to $2 < pH < 3$ with 50% v/v HCl, heated at 100°C to dryness and analyzed using a Model 183 TOC Boat Sampler with DC-180 TOC analyzer (Rosemount

Dohrmann). TOC for clays and oxides was determined by loss-on-ignition (Allison, 1965b).

The U concentration in each sample was determined by Kinetic Fluorescence using a model KPA-10 Kinetic Phosphorescene Analyser (Chem Chek Instrument, Richland, WA). The KPA-10 measures the phosphorescent intensity of U(+6). For H_2O_2 treatments, a 5 ml subsample was used for analysis while the remainder of the sample was discarded. However, residual peroxide in the subsample reduced the fluorescence intensity of U. Since peroxide interferred with U analysis, the 5 ml subsample was heated at 70°C to complete dryness using a plate heater. The drying process was employed to remove all residual H_2O_2 from each subsample. The residue was brought back into solution using 5 ml DI water containing 0.5 N HNO_3 before U analysis.

CHAPTER IV

RESULTS AND DISCUSSION

1. Soil collection and treatment

The amount of free and amorphous Fe oxide in Hanford (II) soil were 1937 and 1620 mg/kg, respectively whereas the levels measured in the Portsmouth soil were 23,311 and 1353 mg/kg. Surface areas of Hanford (II) and Portsmouth soil were 3.38 and 42.21 m^2/g, respectively. Table 2 presents properties of clays, oxides and DOE soils before and after H_2O_2 treatment. It was noted that CEC values between those which were obtained from Source Clay Society and Laboratory analysis were different. This was due to the difference in CEC measurement techniques (Methods of soil analysis, part 2). Peroxide treatment did not significantly alter the CEC in Kaolinite, Illite, Al or Fe oxide whereas a significant CEC reduction was observed in Ca-Montmorillonite. This decreasing is believed due to the swelling structure of Ca-Montmorillonite in which it was susceptible to the attack of hydrogen peroxide compared to the other minerals studied. Results of this peroxidation led to the

Table 2 : Physical/chemical properties of soil material.

Soil material	Soil composition (%)	CEC (meq/100g) (before)	CEC (meq/100g) (after)	%TOC (before)	%TOC (after)	$\%CaCO_3$ (before)
Kaolinite	SiO_2 (43.9), Al_2O_3 (38.5), Fe_2O_3 (0.98), FeO (0.15).	3.3* 14.7**	14.9**	BDL	BDL	BDL
Illite	SiO_2 (54.58), Al_2O_3 (21.93), Fe_2O_3 (7.41).	26.6* 21.74**	24.7**	4.67	n/a	2.64
Ca-Mont.	SiO_2 (70.1), Al_2O_3 (16.0), Fe_2O_3 (0.65), FeO (0.15).	84.4* 73**	27.3**	BDL	BDL	BDL
Al_2O_3	Al_2O_3 (100)	0.18**	0.15**	BDL	BDL	BDL
Fe_2O_3	Fe_2O_3 (100)	17.4**	15.6**	BDL	BDL	BDL
Hanford (I)	n/a	3.2	7.92	0.025	0.02	5.28
Hanford (II)	91% sand, 9% silt and clay	2.8	6.18	0.031	0.02	2.32
Portsmouth	63% sand, 37% silt and clay	17.47	22.25	0.093	0.045	BDL

* Source clay society
** Laboratory analysis (EPA method 9081)
BDL = below detection limit
n/a = not available

dissolution of Al and Fe compounds in clay thereby altered clay properties (Farmer and Mitchell, 1963). The CEC for the DOE soils increased after the treatment. Stripping of trace metals from soil surfaces and/or an increase in total soil surface area can increase soil CEC. Researchers (Bartlett et al., 1936) found that peroxidation stripped bound cations (i.e. Fe and Mn) from the soil inorganic fraction which increased soil CEC. Others (Burford et al., 1964) reported an increase in soil external surface area upon peroxidation. The enhancement in CEC upon peroxidation for the whole soils tested may be a result of one or both of these processes. The TOC data for DOE soils indicates that hydrogen peroxide treatment did not completely oxidize all of the organic matter initially present. However, very low levels were measured both before and after treatment.

2. Kinetics

Kinetic experiments were conducted to determine the relative rates of U binding and the amount of time required for establishment of equilibrium between the sorbed and aqueous phases

Uranium sorption to the three clays (Kaolinite, Illite and Ca-Montmorillonite) as a function of contact time is presented in Figure IV-1. The initial U concentration (33.3 mg U/L) added

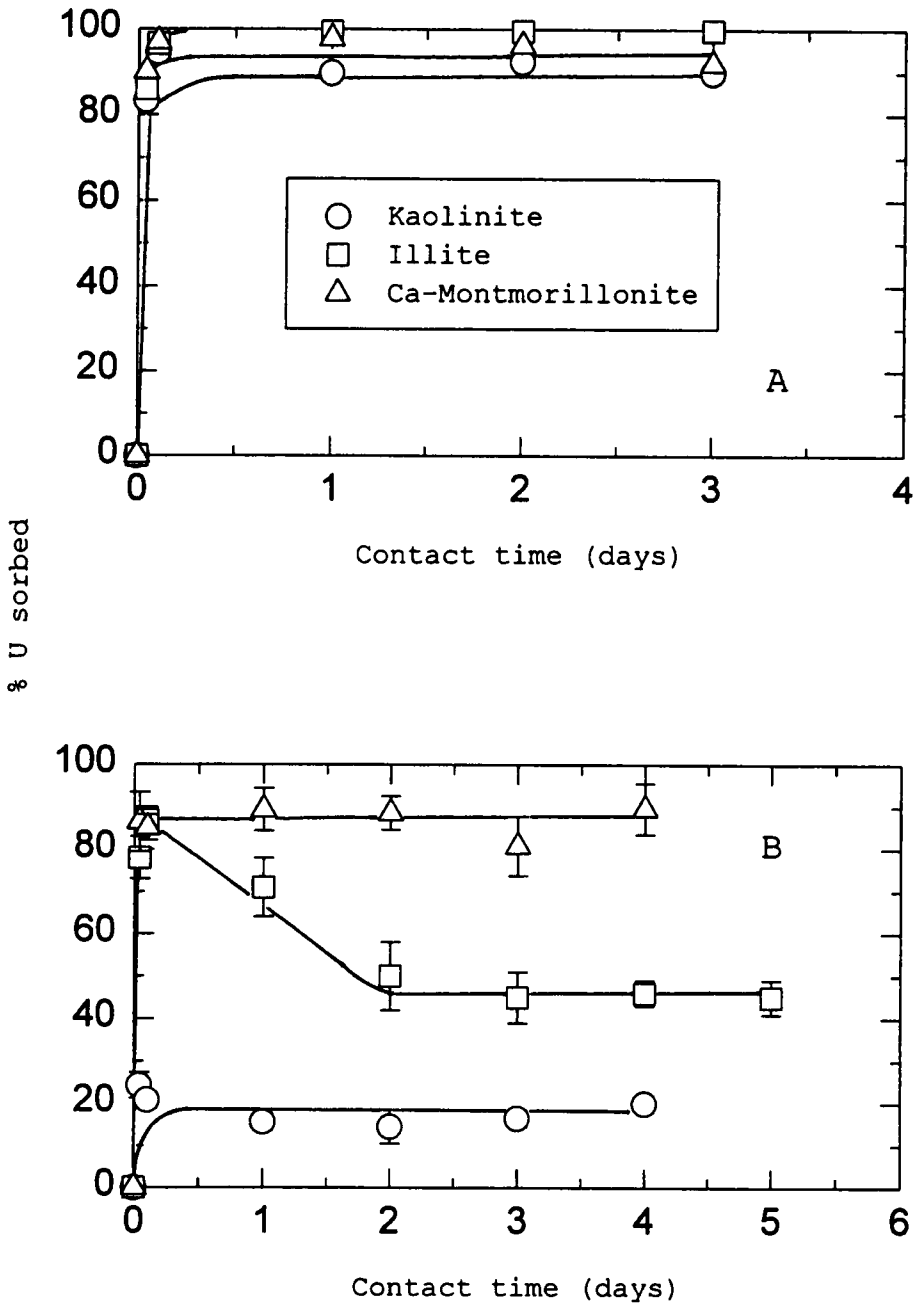


Figure IV-1: U sorption to clays over time (A = Untreated: Initial U = 30 mg/L; B = Pretreated: Kaolinite = 28 mg U/L, Illite & Ca-Montmorillonite = 86 mg U/L).

to untreated clays (Figure IV-1A) corresponded to initial mass loading of 500 mg U/kg clay. Uranium binding was rapid. After 24-hours, U sorption to clays remained unchanged over time indicating equilibrium had been achieved.

The binding profiles for the H_2O_2 pretreated clays are shown in Figure IV-1B. The uptake rate was rapid during the first hour for all clays and, with the exception of Illite, equilibrium was established after 24-hours contact time. The kinetic profile of Illite differs from the other pretreated clays in that initially sorbed U was released back into solution over time. This could be due to the release of organic carbon into solution. Researchers (Griffith and Schnitzer, 1977) found that hydrogen peroxide oxidation of soils produced water-soluble organic compounds. These soluble organic compounds may compete with binding sites on the soil for U in the system. Therefore, it may be that differences in characteristics of the treated and untreated organic materials led to the sorption behavior of Illite over time.

Uranium binding to oxides is shown in Figure IV-2. The plot indicates a fast uptake during the initial contact time (< 1 hour) for untreated oxides (Figure IV-2A). Both Fe and Al oxides reached equilibrium within 24-hours. Hsi (1981) also

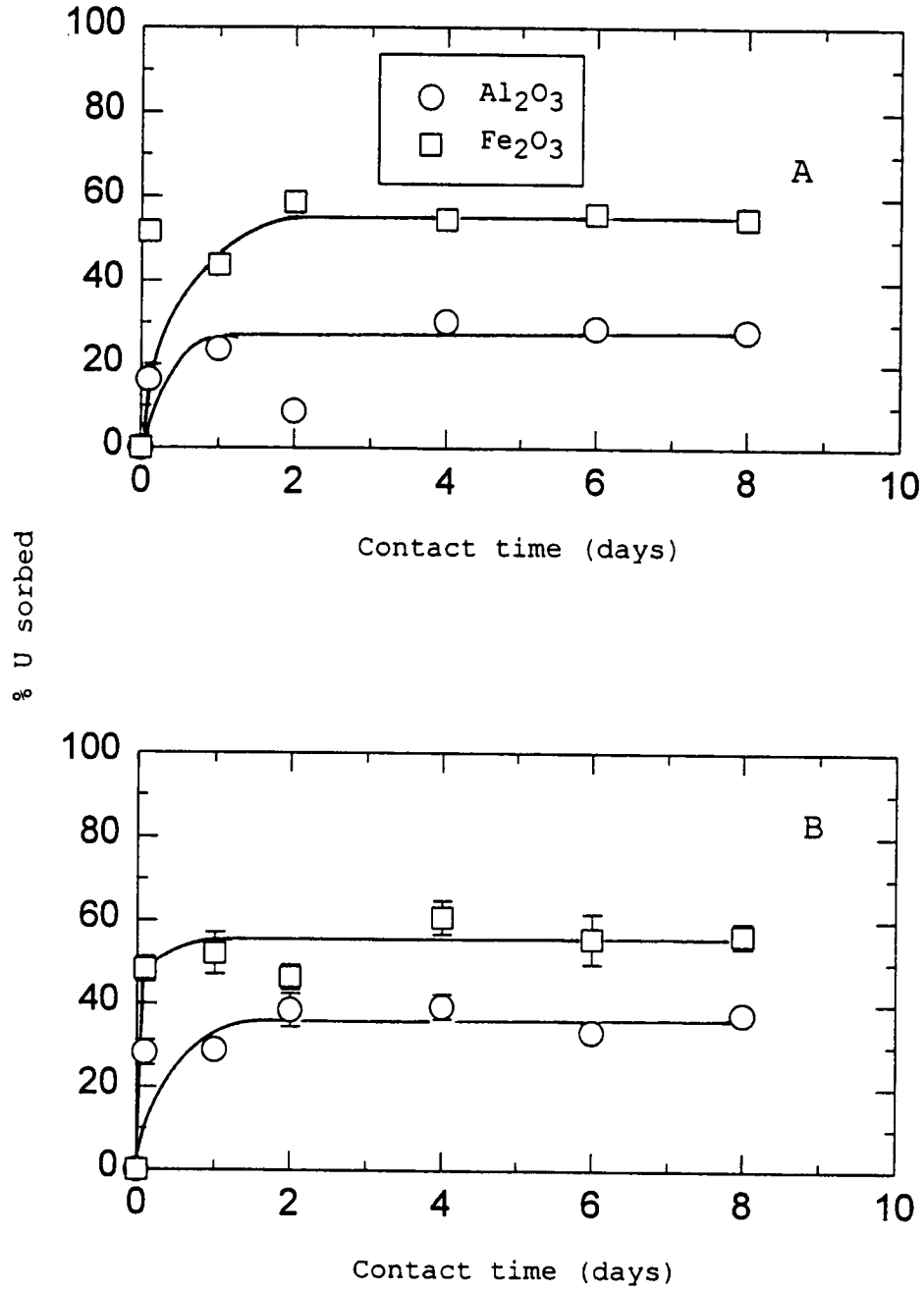


Figure IV-2: U sorption to oxides over time (A = Untreated: Initial U = 115 mg/L; B = Pretreated: Al_2O_3 = 28 mg U/L, Fe_2O_3 = 86 mg U/L).

found that U sorption to Fe oxide (and oxyhydroxides) was very fast during the first few minutes. Similar binding profiles for the pretreated oxides was observed in Figure IV-2B. The oxides sorbed U very quickly and equilibrium was achieved within 24-hours.

The binding profiles for Hanford (I & II) and Portsmouth soils are shown in Figure IV-3. Uranium binding to untreated Hanford (II) and Portsmouth soil was very rapid and equilibrium was reached after one day of contact (Figure IV-3A). Sorption of U to Hanford (I) differed from other soils in that U was slowly released back into solution after initial binding. Sorption appeared to stabilize after 2 days indicating equilibrium was achieved. The binding trend of Hanford (I) was similar to the binding profile of pretreated Illite. The analysis of soil composition (Table 2) indicated that Hanford (I) soil contained 5.28% equivalent $CaCO_3$. Dissolution of $CaCO_3$ (Appendix A-1) yields Ca^{2+} ion which may compete with U for soil sorption sites and CO_3^{2-} ion which can complex U. Uranyl-carbonate complexes have high stability constants indicating U preference in solution.

Figure IV-3B shows the kinetic curves for U sorption to the H_2O_2 pretreated soils. Equilibrium seemed to be reached after one day.

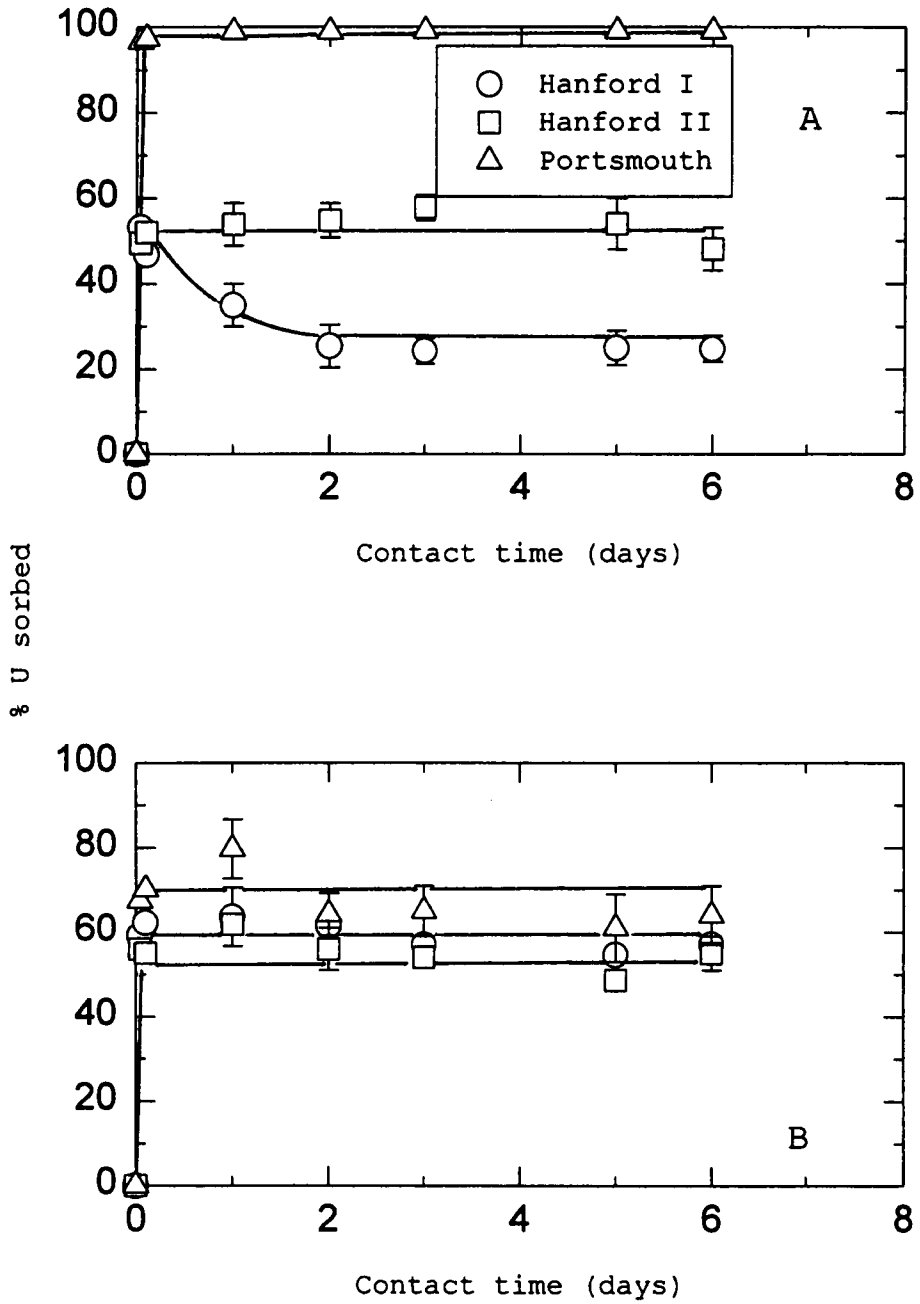


Figure IV-3: U sorption over time to soils obtained from DOE sites (A = Untreated: Hanford I = 35 mg U/L, Hanford II & Portsmouth = 105 mg/L; B = Pretreated: Initial U = 28 mg U/L).

3. Sorption isotherms

Sorbent physical and chemical properties impact overall binding capacity. The following study utilized sorbents (untreated and H_2O_2 pretreated), U concentrations and initial solution pHs to investigate the relative affinity of each sorbent for U. This information was used to determine final soil U loading levels for subsequent mobilization studies.

Since U sorption was determined to be pH dependent (Giblin et al., 1981; Tsunashima et al., 1981; Hsi, 1981; Chisholm-Brause and Morris, 1992), three initial solution pH levels (5, 7, and 9) were utilized to examine the effect of pH on sorbent binding capacity.

3.1 Uranium sorption to clays

Figure IV-4 depicts sorption isotherms of U on both untreated and pretreated Kaolinite. The plots indicate sorption increased with pH and varied linearly (at pH 7 and 9) within the U concentration range studied for untreated Kaolinite (Figure IV-4A). It should be noted that the CEC of Kaolinite varies with pH because the charge on this clay is pH dependent. Researchers (Giblin et al.,1981; Tschapeck et al., 1974) found that the overall net charge on Kaolinite particles was always

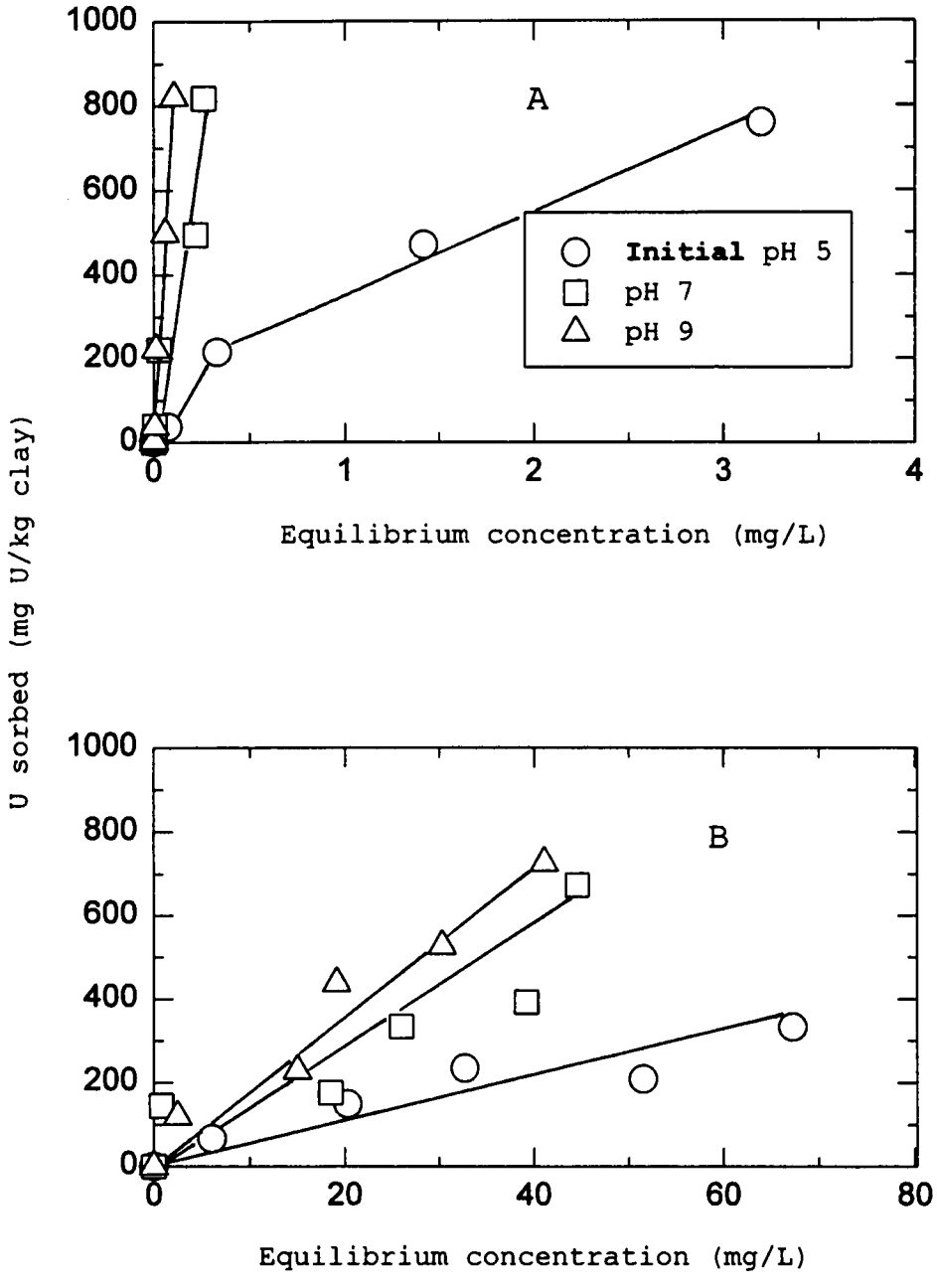


Figure IV-4: Binding isotherms of U for Kaolinite at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

negative above pH 3. Hence a higher pH enhanced the net negative surface charge, which, in turn, attracted more uranyl cations by a Coulombic electrostatic force (CEC). At pH 5, U binding varied linearly at low U concentration but approached saturation beyond a loading of 200 mg U/kg. This could be due to the fact that uranyl ion (UO_2^{2+}), the dominant species at this pH, was less favored by Kaolinite relative to the polymeric uranyl hydroxyl complexes which form at pHs 7 and 9 (Giblin et al., 1981) or that the alteration of Kaolinite surface at this pH inhibited U binding. Chisholm-Brause and Morris (1992) used emission spectroscopy to investigate the nature of U(+6) sorbed to Montmorillonite in the pH range 3.7 to 7. They found that the clay surface sites varied as a function of pH and the spectra of sorbed U changed markedly as a function of surface activity. Thus, they concluded that the presence of multiple sorption species reflected sorption of U to distinct surface sites.

As discussed in the equilibrium model section, the distribution coefficient (K_d) can be used to compare the sorption capacities of different soils for any particular ion. K_d is the slope of the equilibrium sorption curve (in the linear range of sorption isotherm) and a large K_d indicates a high binding affinity. From the slopes of the sorption curves, K_ds

were found to be 2652 and 7570 L/kg at pH 7 and 9 respectively. Within the linear range of U sorption at pH 5 (up to 200 mg/kg), K_d was 643 L/kg. Giblin et al. (1981) reported a K_d of 35,000 L/kg at pH 6.5, Borovec (1981) recorded a K_d of 50 L/kg at pH 6 and Langmuir (1978) found K_d to be 2 L/kg for U binding to Kaolinite. An increase in pH from 7 to 9 resulted in an approximate 3 fold increase in U binding to this clay. Since U sorption to clay varies with pH (Giblin et al., 1981), K_d will also vary with pH. Giblin et al. (1981) found that U sorption increased with pH and UO_2^{2+} was less readily sorbed to Kaolinite compared to uranyl hydroxy and neutral complexes at pH > 5 (UO_2^{2+} is the dominant species up to pH 5 then uranyl hydroxy becomes the stable species). The difference in sorption affinity, therefore, could be attributed, in part, to the impact of pH on U speciation. Since uranium containing solutions were open to the atmosphere for only a short period of time, it was assummed that experiments were carried out in a closed system. Therefore, the present of carbonate in solution, which was due to the transfer of CO_2 from the atmosphere, was minimized. Uranium speciation calculations (Appendix B1-B3) also show that uranyl hydroxy complexes were the dominant species in solutions. The formation of uranyl carbonate which inhibited U sorption was

not significant compared to the formation of uranyl hydroxy complexes at the pH's tested.

Figure IV-4B represents the binding of U to pretreated Kaolinite clay. The data shows that sorption increased with increasing solution pH and varied linearly with U concentration. There was no indication of saturation binding at all pH levels. However, the slopes of the sorption lines revealed that the pretreated clay had a reduced binding affinity for U. The K_d values were found to be 4, 11 and 16 L/kg at pH 5, 7 and 9 respectively. The reason for increasing sorption with increasing solution pH was discussed in the untreated Kaolinite. The K_ds values indicate that U sorption to pretreated clay was less pH dependent compared to those in untreated clay. Table 2 shows that CEC was unchanged but pretreated Kaolinite lost most of its sorption capacity. The reason could be due to that cation exchange was not the only process involved. The reduction in binding affinity, therefore, was believed due to the alteration in clay properties upon peroxidation. Researchers (Farmer and Mitchell, 1963, Lavkulich and Wiens, 1970) found that peroxidation removed hydrous oxides of Si, Mn, Fe and Al from soils which led to significant alteration in clay properties. However, since there was no sorption work performed

on the peroxide pretreated soil up to date, hence there is no data for comparison.

Figure IV-5 illustrates the relationship between the amount of U sorbed to Illite and the amount of U remaining in the solution after reaching sorption equilibrium. Like Kaolinite, U binding to Illite increased with pH and varied linearly at pH 7 and 9 within the U concentration range studied (Figure IV-5A). Uranium sorption at pH 5 varied linearly up to a loading of 280 mg U/kg. Loading then proceeded linearly but at a reduced level.

The distribution K_ds within the linear range were found to be 972, 1829 and 2197 L/kg at pH 5, 7 and 9 respectively. These values indicate that U binding to Illite was less pH dependent compared to Kaolinite clay.

Figure IV-5B shows U sorption to pretreated Illite. The plot indicates that sorption varied linearly and was independent of solution pH. The distribution K_d was approximately 37 L/kg for all pHs in this study. When compared to the untreated Illite, the sorption capacity of pretreated Illite, based on K_d values, was reduced by a factor of 26 at pH 5 to 59 at pH 9. It was noted that Illite contained approximately 4.67% organic carbon (OC). Oxidation of the OC upon H_2O_2 pretreatment can explain, in part, the reduced sorption capacity.

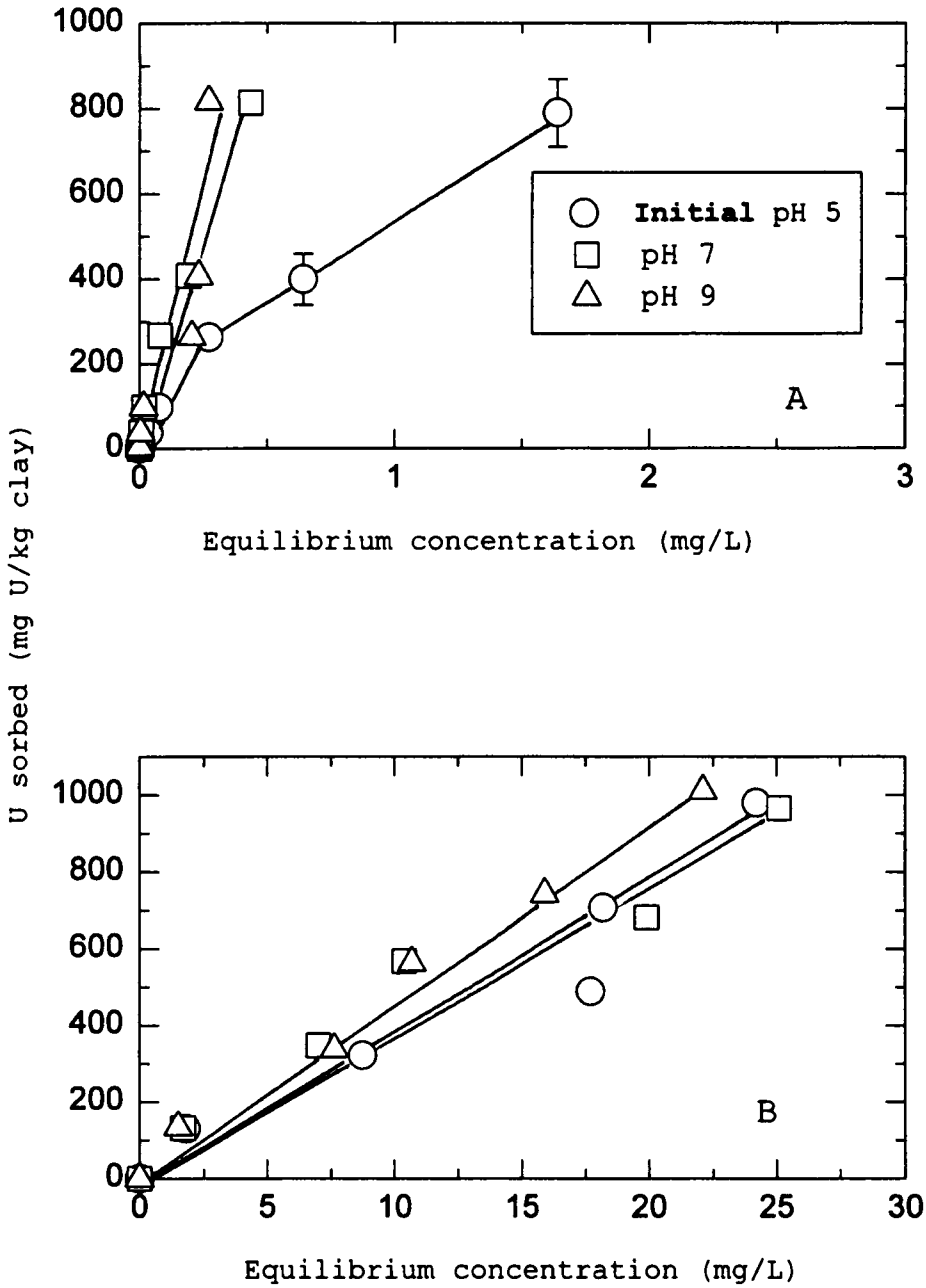


Figure IV-5: Binding isotherms of U for Illite at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

Sorption of U to Ca-Montmorillonite is shown in Figure IV-6. The plot shows that binding varied linearly with respect to U concentration for untreated clay (Figure IV-6A). Uranium sorption was greatest at pH 7 and decreased at both higher and lower pHs. Distribution coefficients were 1500, 2800 and 1100 L/kg at pH 5, 7 and 9 respectively. These values indicate that U affinity increased by approximately a factor of 2 at pH 7 compared to the lower and higher pHs. It remains unclear as to why U sorption was elevated at pH 7.

Figure IV-6B indicates the sorption behavior of U to pretreated Ca-Montmorillonite. Within the linear range (up to 945 mg/kg), U sorption was pH independent and the K_d was found to be 412 L/kg. Binding continued to increase linearly at pH 5 above a loading of 945 mg/kg while at higher pHs, binding approached saturation. The binding affinity of the pretreated clay was reduced by a factor of 3.6 (pH 5) to 6.8 (pH 7) compared to the untreated clay possibly due to the reduction in CEC observed.

It appears that variation in U binding can be attributed to differences in CEC, surface area, and /or source of the charges (positive or negative). Cation exchange capacity is defined as the product of surface charge per unit area and surface area. Researchers (Borovec, 1981; Charlet et al., 1987)

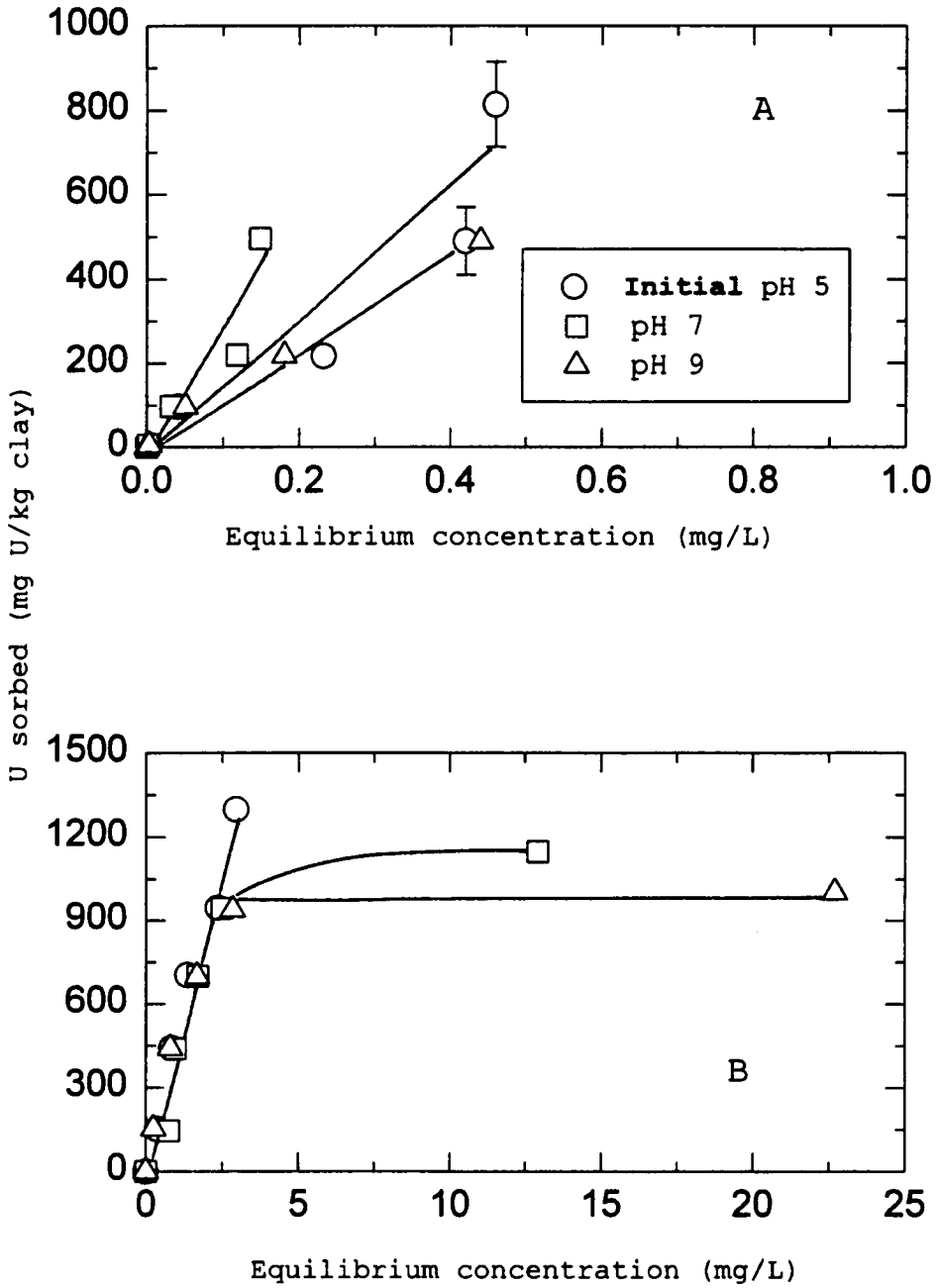


Figure IV-6: Binding isotherms of U for Ca-Montmorillonite at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

reported that clay minerals with high CEC and large surface area possessed a greater tendency for U sorption. Peroxide treatment reduced the sorption affinity of the clays tested at each pH. This decrease in affinity results from the fact that peroxide lowered the exchange capacity of the clay (Bartlett et al., 1936) or changed the surface clay structure (Douglas and Fiessinger, 1971; Tessier et al, 1979). In addition, as stated by Ames et al. (1982), surfaces of most secondary minerals are coated with amorphous Fe, Mn and Si oxyhydroxides. Upon removal of these oxides by peroxide, these researchers found that U sorption was reduced.

Variations in solution pH clearly affected U sorption to clays. pH alters both U speciation and the nature of sorption sites on clays. Borovec (1981) found that sorption of UO_2^{2+} and its hydroxo complexes increased in the order of Kaolinite < Illite < Ca-Montmorillonite at pH 6.0. The author noted that the above sorption order was due to the charge (positive or negative) on soil sufaces. Borovec (1981) also reported that the ratio of the amount of negative to the positive charge on the clay was approximately 7 (Montmorillonite), 2.5 (Illite) and 0.5 (Kaolinite) at pH 6. Hence, Ca-Montmorillonite had the highest U sorption up to this pH.

3.2 Uranium sorption to oxides

Figure IV-7 displays the sorption isotherm of U to Al oxide. The plot indicates that U binding to untreated Al oxide was similar up to a loading of 500 mg/kg with a K_d of 133 L/kg (Figure IV-7A). However, beyond this loading, binding continued to increase linearly at pH 7 while it approached saturation at pH 5 and 9. Reduced sorption at pH 9 could be due to its low CEC (Table 2). The point of zero charge (PZC) of Al oxide was reported to be 8.3 (Alloway, 1990). Uranium binding to this oxide at pH < pH_{zpc} is believed due to specific sorption. Aluminum oxide possessed more positive surface charge at pH 5 than at pH 7 which could lead to lower U binding at pH 5. Alloway (1990) stated that specific sorption resulted in metal ions being sorbed to a far greater extent than would be expected from the CEC of a soil. Van der Weijden (1976) also suggested that the strong chemical bonding of uranyl ions to the surface oxygen groups outweighed the repulsive coulombic and solvative forces. Brummer (1986) showed that the sorption capacities of amorphous Fe and Al oxides for Zn were 7 and 26 times greater than their CECs at pH 7.6. The hydrous oxides of Al, Fe and Mn are thought to be involved in the specific sorption process.

Uranium sorption to pretreated Al oxide is illustrated in Figure IV-7B. The data shows that sorption increased with

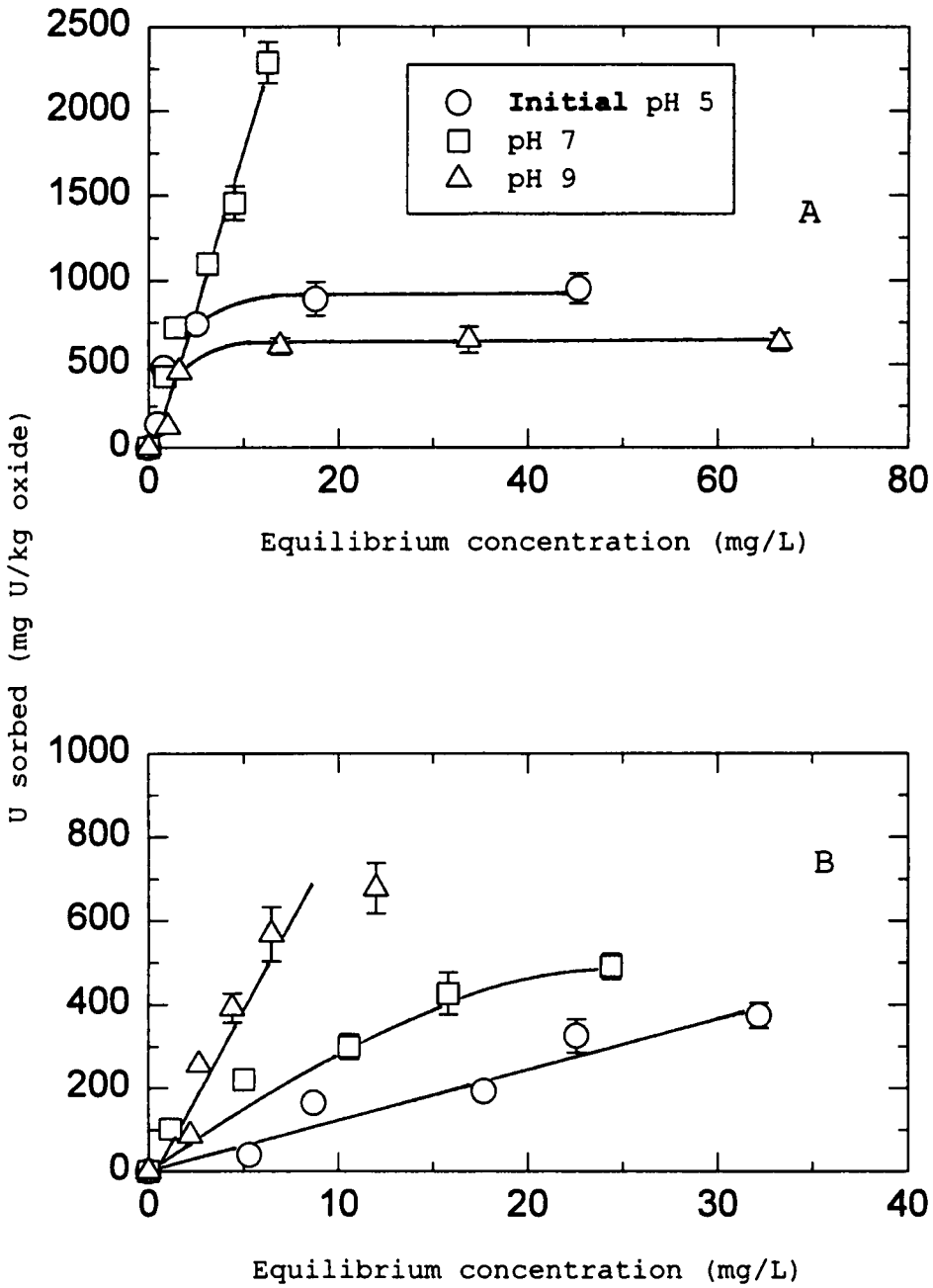


Figure IV-7: Binding isotherms of U for Al_2O_3 at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

increasing solution pH. Uranium binding varied linearly at pH 5 and 9. At pH 7, however, sorption was linear only upto a loading of 300 mg/kg. Beyond this level, binding shows saturation. The distribution coefficients (within the linear range) were 14, 174 and 92 L/kg at pH 5, 7 and 9 respectively. The binding affinity of this pretreated oxide was reduced compared to the original oxide.

Figure IV-8 illustrates the sorption behavior of U to Fe oxide. The data indicates that the sorption capacity of untreated Fe oxide decreased with decreasing pH (Figure IV-8A). Researchers (Hsi, 1981; Hsi and Langmuir, 1985) also found that uranyl ions were strongly sorbed to Fe oxides at pHs above 5. The authors noted that enhanced binding at high pH corresponded to an increase in the uranyl hydroxyl complexes. Therefore, sorption of these complexes was one reason presented for the increase in U binding capacity of Fe oxide with respect to the solution pH. In addition, the strong chemical bonding between uranyl ion and O^{2-}/OH^{-} on the oxide surface enhanced U sorption in the pH range of 5-8.5 (Van der Weijden et al., 1976). The plot also shows that sorption varied linearly at pH 9 in the U concentration range studied. However, at lower pHs, the data shows a diminishing sorption capacity above the loadings of 1150 (pH 7) and 500 mg U/kg oxide (pH 5) which is believed to be due

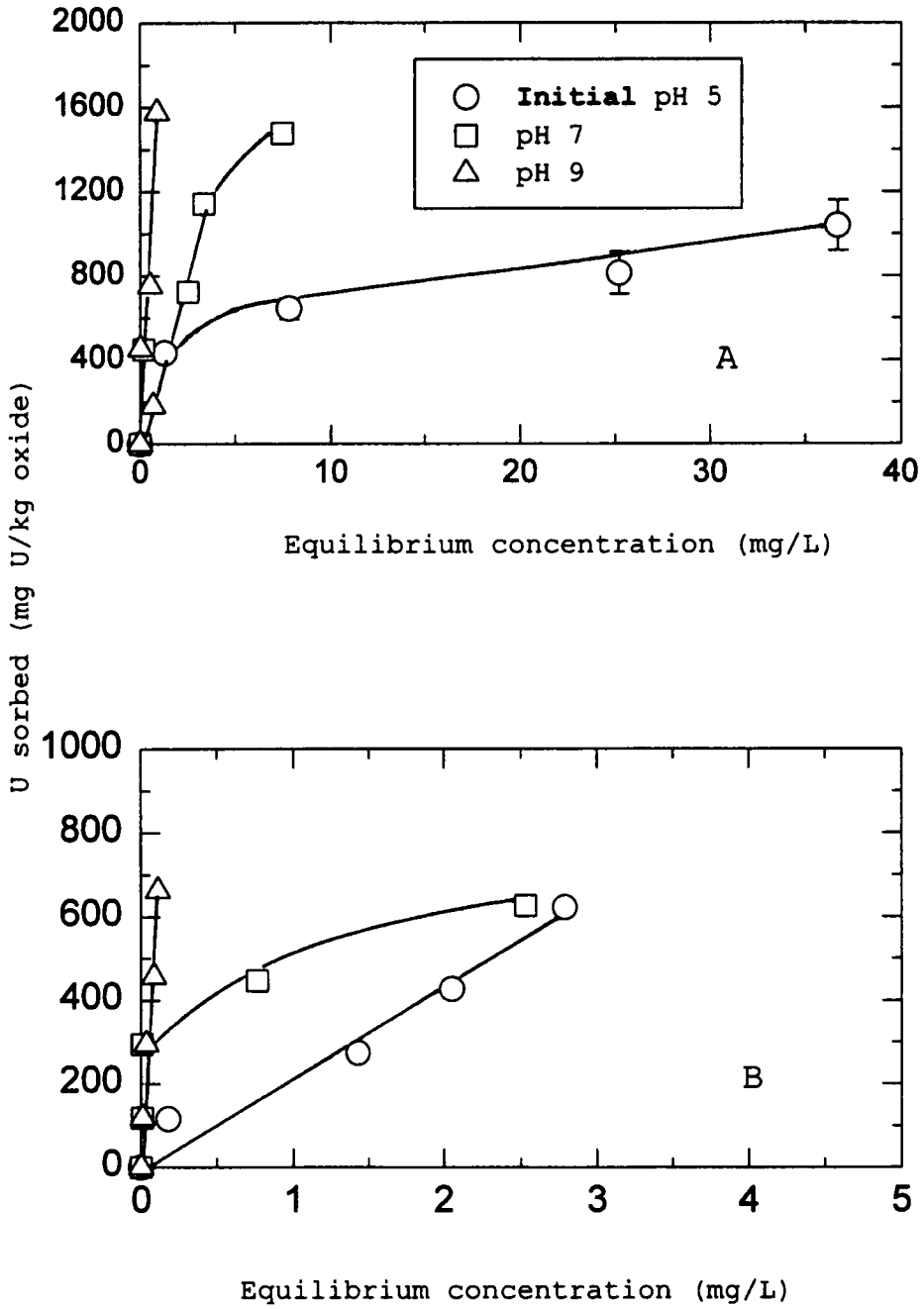


Figure IV-8: Binding isotherms of U for Fe_2O_3 at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

to changes in surface sorption sites (Hsi, 1981; Hsi and Langmuir, 1980; Van der Weijden et al., 1976). Up to a loading of 500 mg/kg (the linear range for all sorption data), the K_d was found to be 1252 L/kg at pH 9 and 336 L/kg at both pH 5 and 7.

Figure IV-8B depicts the sorption isotherms of U for pretreated Fe oxide. The data indicates that sorption decreased with decreasing solution pH. Sorption varied linearly with the initial U concentration studied at pH 5 and 9. At pH 7, the data shows a diminishing capacity beyond a loading of 300 mg/kg. Sorption curves also indicate that U binding was similar up to a 300 mg/kg level at pH 7 and 9. The distribution coefficient K_d in the linear range was 185 L/kg at pH 5 and 5624 L/kg at both pH 7 and 9.

In comparing the sorption capacity of oxides, U was preferentially bound to Fe compared to Al oxide at all pH levels. From the laboratory analysis, the CEC of Fe oxide was higher than that of Al oxide which could contribute to the sorption difference.

3.3 Uranium sorption to DOE soils

Figure IV-9 portrays sorption of U to Hanford (I) soil. Uranium binding to untreated Hanford (I) soil shows that

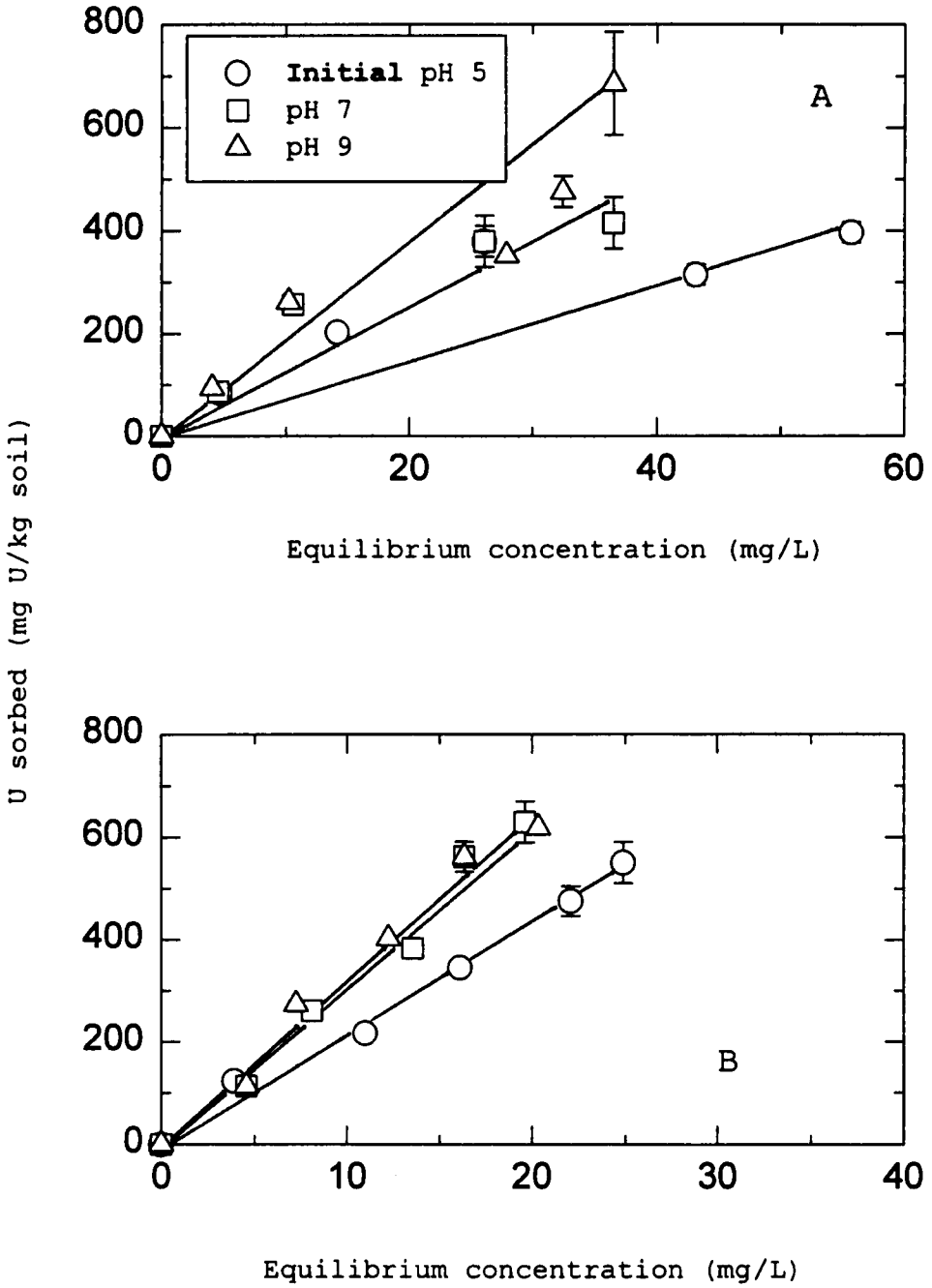


Figure IV-9: Binding isotherms of U for Hanford (I) at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

sorption increased with solution pH and varied linearly with U concentration (Figure IV-9A). The distribution coefficients were 7, 11 and 15 L/kg at pH 5, 7 and 9, respectively. These values indicate low U sorption affinity for the Hanford (I) soil compared to clays and oxides.

The binding of U to pretreated Hanford (I) soil is illustrated in Figure IV-9B. The plot shows that sorption varied linearly with pH and the binding capacity was lowest at pH 5. Uranium binding at pHs 7 and 9 appears to be approximately the same. The K_d values are 21 L/kg at pH 5 and 33 L/kg at pHs 7 and 9.

A comparison of the original and the pretreated Hanford (I) revealed that the affinity of pretreated soil for U increased at all pH levels studied. Based on the CEC data, additional surface sites were created upon soil peroxidation, which led, in part, to increase sorption. During peroxide treatment, the bound metals found in natural soil (i.e. Fe, Al and Mn) could be stripped off from the soil matrix which exposed new sorption sites. Burford et al. (1964) found that peroxidation partially altered silicate and mica minerals thereby increasing their external surface area. Sequi and Aringhieri (1977) discovered that the destruction of organic matter coatings on the soil created new binding sites. These

new sites, according to the authors, were blocked by organic matter prior to peroxidation. Charlet et al. (1987) reported that minerals with high specific surface area sorbed more U than those with low specific surface area.

Uranium sorption isotherms for both untreated and pretreated Hanford (II) soil are presented in Figure IV-10. The curves (Figure IV-10A) indicate that binding decreased with increasing pH and varied linearly within the U concentration studied. The distribution coefficients were 47, 26 and 13 L/kg at pH 5,7, and 9, respectively. These values indicate that ≈ 50% of the binding capacity was lost with each pH increase. Since Hanford (II) soil contains 9% silt and clay (mostly Montmorillonite) and the sorption capacity of this clay for U showed that U sorption decreased upon solution pH increase (from 7 to 9), it could be concluded that this clay partially influenced the Hanford (II) U sorption behavior. Overall, U binding to Hanford (II) soil was greater than Hanford (I) soil at pH ≤ 7.

Figure IV-10B represents the binding of U to pretreated Hanford (II) soil. Sorption varied linearly and was essentially the same up to a soil loading of 350 mg/kg at all pH levels which suggests that, at low U loading, this pretreated soil was independent of solution pH. The K_d was found to be 44 L/kg.

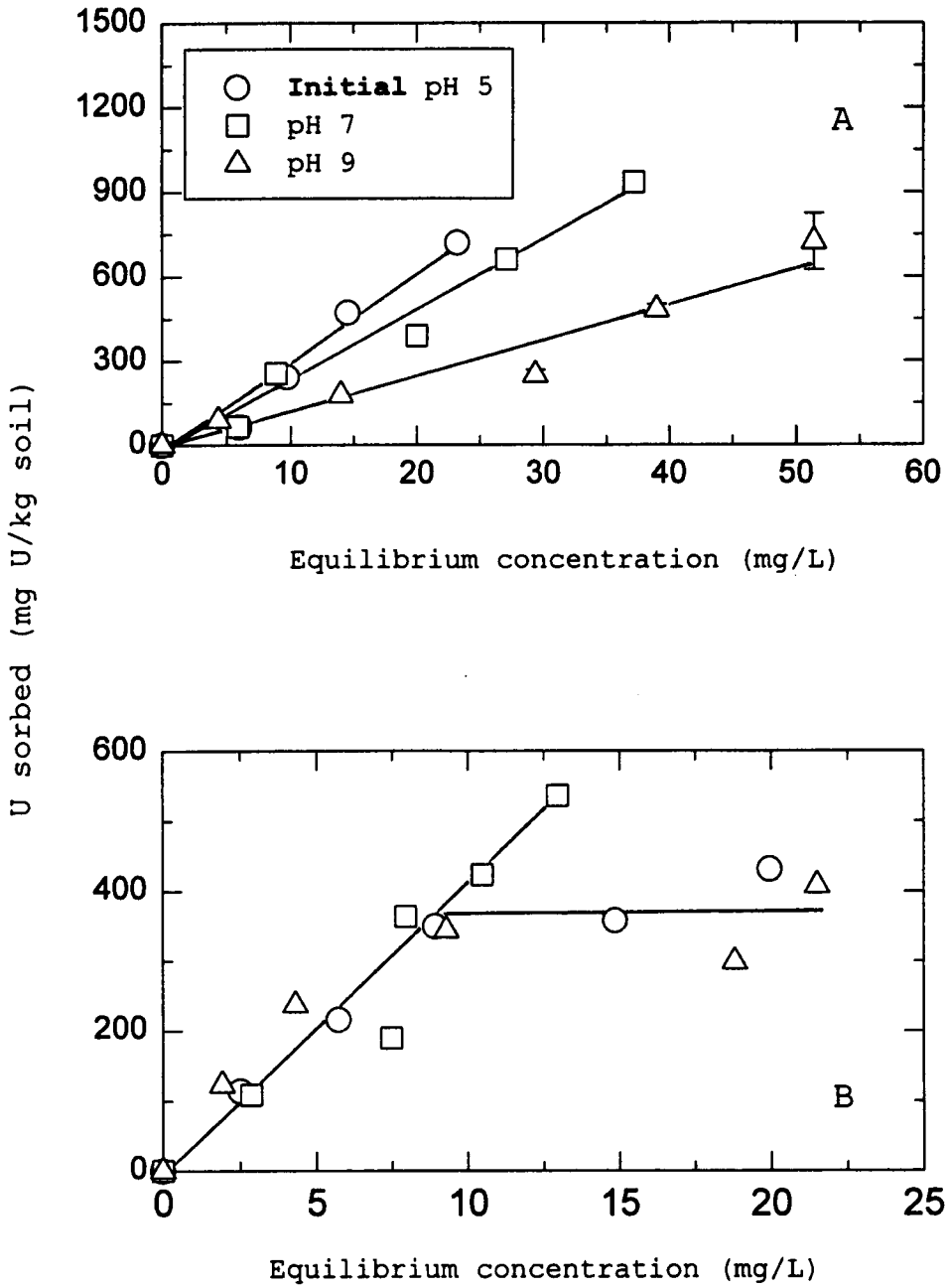


Figure IV-10: Binding isotherms of U for Hanford (II) soil at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

Sorption continued to increase linearly at pH 7 while it began to level-off at pHs 5 and 9, indicating the binding sites were reaching saturation. It was noted that this treated soil and untreated Al oxide had a similarly binding pattern. Hence, a plausible explaination for the continuing increase sorption at pH 7 was due to the impact of Al oxide.

The U sorption affinity for both untreated and pretreated soil was approximately the same at pH 5. On the other hand, the affinity increased approximately 41% at pH 7 and 70% at pH 9 in the linear range. The additional surface sites and the increase in CEC may explain the increase in sorption capacity.

Figure IV-11 depicts the sorption isotherm of U to Portsmouth soil. Figure IV-11A shows that sorption appeared to be independent of the solution pH for untreated soil. The distribution coefficient, below a loading of 2300 mg/kg , was 1540 L/kg for all studied pHs. A further increase in U loadings beyond 2300 mg/kg resulted in a reduced uptake of U which indicated that most sorption sites were filled and diffusion was likely taking place.

In comparing Hanford soil with Portsmouth soil, a much higher binding affinity for U was measured at all pHs for Portsmouth soil. This could be due to the large amount of clay (37% vs 9% in Hanford (II)) as well as the free Fe oxides

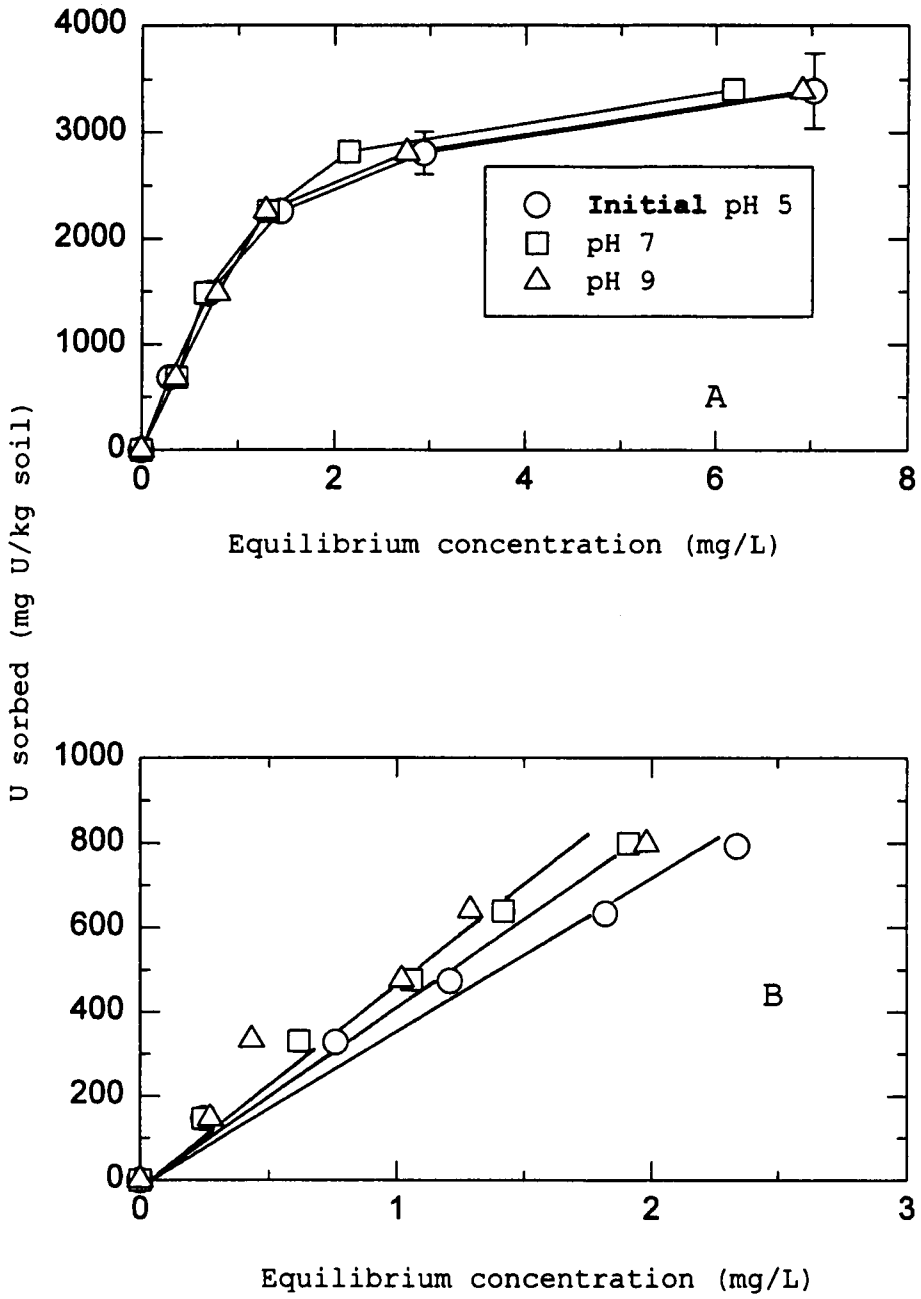


Figure IV-11: Binding isotherms of U for Portsmouth soil at different initial pHs. (A = Untreated, B = H_2O_2 Pretreated).

(23,311 vs 1937 mg/kg in Hanford (II)) present in this soil. Uranium sorption to clay (Kaolinite, Illite and Ca-Montmorillonite) was found high in this study. Ames et al. (1982) showed that the removal of Fe oxides reduced U sorption by a factor of 10 at the initial U concentration of 10^{-4} mol/L. Uranium binding to Fe oxide at pH $\geq$ 7 showed that U sorbed up to 1500 mg/kg from this study. Hence, it could be concluded that Fe oxide contributed up to 50% U sorption in the Portsmouth soil.

Figure IV-11B shows U sorption to pretreated Portsmouth soil. The plots indicate that binding varied linearly with U concentration and appear to be pH independent. The distribution coefficient was approximate 352 L/kg at all pH levels. This pretreated soil behaved similarly to the pretreated Ca-Montmorillonite below a loading of 900 mg/kg indicating that this clay influenced the sorption affinity of the Portsmouth soil.

Comparing the pretreated and untreated Portsmouth soils, the pretreated soil sorption affinity decreased by 75% over the untreated soil even though its CEC increased. The significant decrease in sorption capacity of the pretreated Portsmouth soil could be related to the pretreated clay data (Kaolinite, Illite and Ca-Montmorillonite) since this soil contained 37% silt and

clay. These clay also showed a reduction in sorption capacity after peroxide treatment. Hence, the increase in CEC of the pretreated Portsmouth soil is not the main mechanism of U sorption to this clay. From the works of Bartlett et al. (1936), Portsmouth loams lost 76% of their total exchange capacity upon soil peroxidation. Also, according to the authors, organic matter in the soil played a major role in exchange capacity. They found that Portsmouth fine sandy loams lost 90% of their capacity as the result of peroxide treatment.

The binding affinity of the test soils for U may influence metal mobilization upon soil peroxidation. From this study, binding appears to depend on soil type and solution pH. Overall, untreated clay and clay-like soil sorb more U than untreated oxide and sandy soil. In addition, these experiments indicated that mobilized U contacting peroxide treated soil could sorb to this material. However, the extent of resorption varies with soil composition. The sorption capacity of U increased for the peroxide treated sandy soil (Hanford) and Fe oxide and decreased for peroxide treated clays, Al oxide and clay-like soil (Portsmouth). Within the linear range of data, the extent of U binding to each sorbent (based on K_d values) is:

pH 5: Portsmouth > Ca-Montmorillonite > Illite > Kaolinite > pretreated Ca-Montmorillonite > pretreated

Portsmouth > Fe oxide > pretreated Fe oxide > Al oxide > Hanford (II) > pretreated Hanford (II) > pretreated Illite > pretreated Hanford (I) > pretreated Al oxide > Hanford (I) > pretreated Kaolinite.

pH 7: Pretreated Fe oxide > Ca-Montmorillonite > Kaolinite > Illite > Portsmouth > pretreated Ca-Montmorillonite > pretreated Portsmouth > Fe oxide > pretreated Al oxide > Al oxide > pretreated Hanford (II) > pretreated Illite > pretreated Hanford (I) > Hanford (II) > Hanford (I) = pretreated Kaolinite.

pH 9: Kaolinite > pretreated Fe oxide > Illite > Portsmouth > Fe oxide > Ca-Montmorillonite > pretreated Ca-Montmorillonite > pretreated Portsmouth > Al oxide > pretreated Al oxide > pretreated Hanford (II) > pretreated Illite > pretreated Hanford (I) > pretreated Kaolinite > Hanford (I) > Hanford (II).

Sorption parameters from Linear, Freundlich and Langmuir isotherm models for both untreated and pretreated soil materials were presented in Table 3 and 4.

4. Uranium mobilization upon H_2O_2 treatment

A range of U loadings was utilized based upon levels measured at contaminated DOE sites. For example, Francis et al.

Table 3: Linear (K_d), Freundlich (K,n) and Langmuir (Q°, b) isotherm parameters for untreated soil materials.

Soil materials	pH	K_d (L/kg)	K $(L/kg)^{1/n}$	n	Q° (mg/kg)	b (L/mg)
Kaolinite	5	643	358	0.9	-1667	-0.43
	7	2652	3422	1.0	41	71.2
	9	7570	6581	1.2	-4167	-0.92
Illite	5	972	720	1.0	-200	-5.0
	7	1829	2150	0.9	-455	-9.6
	9	2197	758	0.8	-83	-48.0
Ca-Mont.	5	1500	1339	1.0	-532	-2.41
	7	2800	2441	1.0	2500	1.33
	9	1100	1141	0.9	43478	0.04
Al_2O_3	5	133	262	0.4	2000	0.10
	7	133	321	0.7	3226	0.09
	9	133	176	0.4	1111	0.08
Fe_2O_3	5	336	400	0.2	877	0.74
	7	336	711	0.3	1111	3.60
	9	1252	1253	0.3	1099	45.5
Hanford (I)	5	7	37	0.6	500	0.04
	7	11	34	0.7	1667	0.01
	9	15	35	0.8	1000	0.03
Hanford (II)	5	47	3	1.8	-200	-0.05
	7	26	10	1.3	-500	-0.02
	9	13	25	0.8	500	0.05
Portsmouth	5	1539	1489	0.5	3704	0.82
	7	1539	1591	0.5	7692	0.29
	9	1539	1519	0.5	5882	0.39

Table 4 : Linear (K_d), Freundlich (K,n) and Langmuir (Q°, b) isotherm parameters for pretreated soil materials.

Soil materials	pH	K_d (L/kg)	K $(L/kg)^{1/n}$	n	Q° (mg/kg)	b (L/mg)
Kaoline	5	4	22	0.6	400	0.03
	7	11	136	0.3	323	1.00
	9	16	61	0.6	588	0.10
Illite	5	37	77	0.7	1000	0.08
	7	37	92	0.7	1250	0.07
	9	37	93	0.8	1111	0.09
Ca-Mont	5	412	459	1.0	-5000	-0.08
	7	412	358	0.6	-2500	-0.10
	9	412	420	0.4	1429	0.50
Al oxide	5	14	8	1.1	-303	-0.02
	7	174	99	0.5	455	0.25
	9	92	67	1.1	-588	-0.08
Fe oxide	5	185	284	0.6	526	1.58
	7	5624	503	0.2	588	56.7
	9	5624	2697	0.7	833	12.0
Hanford	5	21	38	0.8	909	0.04
(I)	7	33	21	1.2	-1250	-0.02
	9	33	25	1.1	-1111	-0.02
Hanford	5	44	69	0.6	769	0.07
(II)	7	44	33	1.1	5000	0.01
	9	44	110	0.4	500	0.18
Portsmouth	5	352	411	0.8	1250	0.53
	7	352	471	0.8	2000	0.31
	9	352	497	0.8	5000	0.12

(1992) reported soil U concentrations of 0.538 - 5.469 mg/g at the Fernald (Ohio) DOE facility. Uranium concentrations in soils at the DOE Y-12 site ranged from 0.15 to 0.20 mg/g. The following U loadings were utilized in mobilization experiments: Clay: Kaolinite = 2.35 mg U/g, Illite = 1.97 mg U/g, Ca-Montmorillonite = 5.98 mg U/g; Oxide: Al = 0.66 mg U/g, Fe = 1.25 mg U/g; DOE soils: Hanford (I) = 0.157 mg U/g, Hanford (II) = 0.30 mg U/g, Portsmouth = 0.383 mg U/g.

Background U which mobilized during soil peroxidation treatment was determined after treating uncontaminated soil (1.0 g) with 15 ml 3% H_2O_2 for 24 hours. This peroxide level was used to avoid the possibility of uranyl peroxide precipitation due to high peroxide concentration. Background U mobilizations of 0.059 µg (Kaolinite), 0.045 µg (Illite), 0.056 µg (Ca-Montmorillonite), 0.0 µg (Al oxide), 0.075 µg (Fe oxide), 0.172 µg (Hanford I), 0.009 µg (Hanford II) and 0.014 µg (Portsmouth) were measured. Uranium loadings were adjusted to include background levels. Analytical results were also adjusted for losses during filtration (5%) to more accurately determine mobilization.

4.1 Mobilization of U(+6) from clays

Figure IV-12 shows U mobilization from Kaolinite using varying peroxide loadings and number of treatments after 1-hour (Figure IV-12A) and 24-hour (Figure IV-12B) contact times. Approximately 13% U was mobilized using DI water alone (0% H_2O_2) after 3 one-hour treatments (Figure IV-12A). The large amount of U mobilized using DI water could be due to solution pH. The final solution pH (D-1) using DI water ranged from 5-6 in this study. Uranium binding to Kaolinite was greatly reduced at this pH level when compared to binding at higher pH levels as indicated from sorption isotherms. The data also shows that the extent of U removal was less than 1% for any H_2O_2 loading and was independent of concentration (H_2O_2 > 0%) during the treatment periods. Reduced mobilization due to H_2O_2 addition may be due to two factors. The first involves the instability of H_2O_2 in solution. Peroxide readily decomposed to oxygen and water. The presence of oxygen bubbles on the clay surface may limit fluid contact with the U containing clay surface. Francis et al. (1992) stated that U must be exposed to the extractant in order to be mobilized as a prerequisite condition. The second factor involves precipitation of U from solution as uranyl peroxide during treatment. The following reaction has been demonstrated during peroxide oxidation (Eligwe et al., 1982):

$$UO_2^{2+} + H_2O_2 + 2\ H_2O \rightarrow UO_4(H_2O)_2 \downarrow + 2\ H^+$$

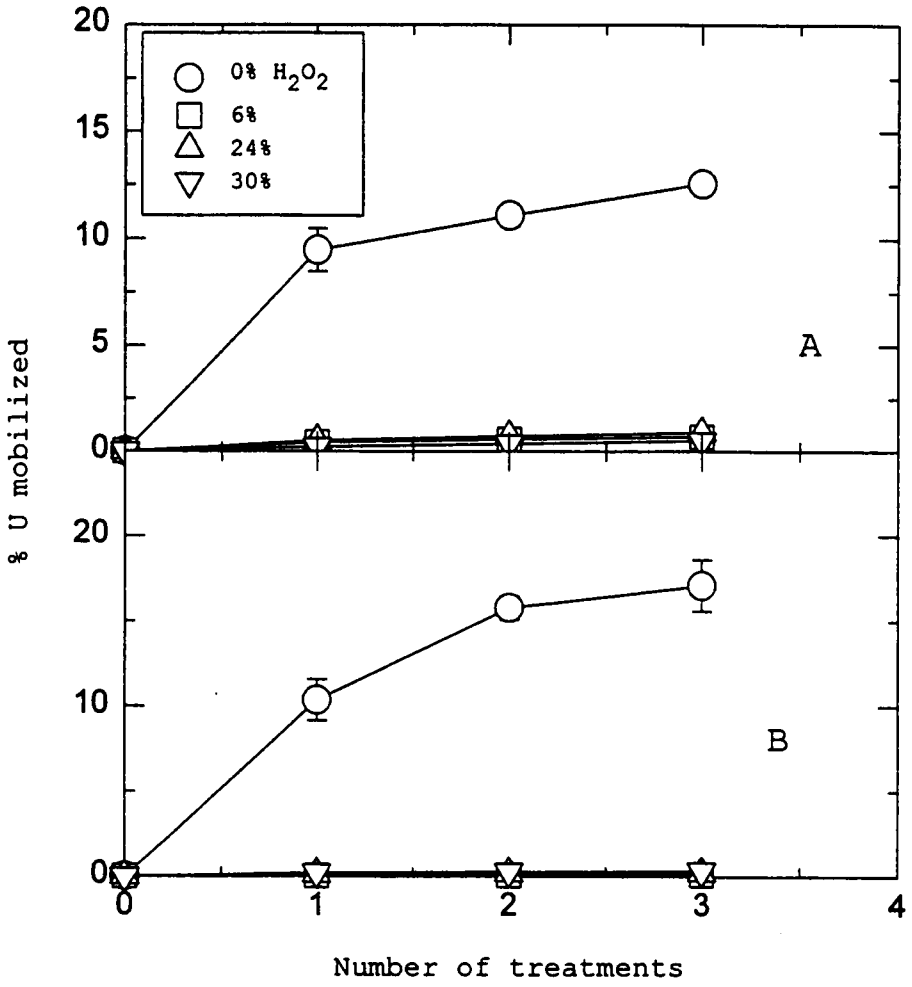


Figure IV-12: Mobilization of U from Kaolinite utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 2.35 mg/g. (A = 1-hour, B = 24-hours contact).

This reaction is a function of pH and peroxide loading. Elgwe and Torma (1982) found that uranyl ion mobilization decreased from 53% to 20% when pH was increased from 4.0 to 6.0 due to uranyl peroxide precipitation. Merritt (1971) reported that pH in the range of 1.0-2.0 was required to prevent precipitation of uranyl peroxide. In this work, final solution pH ranged from 3 to 5 when H_2O_2 was used as the extraction fluid. Therefore, precipitation of uranyl peroxide was anticipated.

Figure IV-12B shows the same treatment condition for Kaolinite using a longer treatment time (24-hour). The same U mobilization trend was observed. Data again shows that the highest U removal was observed when only water was utilized as the extraction fluid (16.6%) compared to peroxide treatments (<1%) and most removal occurred after the first treatment. The increase in U mobilization with time when using water indicated that equilibrium for the system was not achieved after 1-hour. The plot also reveals that U mobilization upon H_2O_2 treatment varied little with number of treatments and was independent of H_2O_2 concentration.

From the results of the two contact times (1 and 24-hour), it appears that the longer treatment time increased U mobilization somewhat using water but had little impact on U mobilization using H_2O_2. Eligwe et al., (1981b) also found that

an increase in contact time from one-hour to four-hours increased U mobilization by 2% (from 85% to 87%) when distilled water was used as the extraction fluid.

Overall, peroxidation of Kaolinite did not mobilize U to any significant degree and, in fact, retarded mobilization when compared to water extraction. Immobilization of U is believed due, in part, to the precipitation of uranyl peroxide.

Figure IV-13 illustrates mobilization of U from Illite. The results show that mobility increased with increasing peroxide concentration and at high peroxide concentration most removal occurred in the first one-hour wash (Figure IV-13A). Water removed only a trace amount of U (0.40%) whereas peroxide treatment mobilized a significant amount of U. Low mobilization of U when using water could be due to the strong sorption affinity of U to organic carbon associated with Illite. Laboratory analysis showed that Illite contained 4.67% organic carbon (Loss-on-Ignition method). Davis and Leckie (1979), Gueniot et al., (1988a) found that organic matter was responsible for U sorption. At low peroxide concentration (0.6% H_2O_2), U mobilization was linear with respect to number of treatments. However, at high peroxide concentration (18%), over 90% of the mobilized U was released during the first treatment. Uranium mobilization increased from 20.2% at 0.6% H_2O_2 to 83.3 %

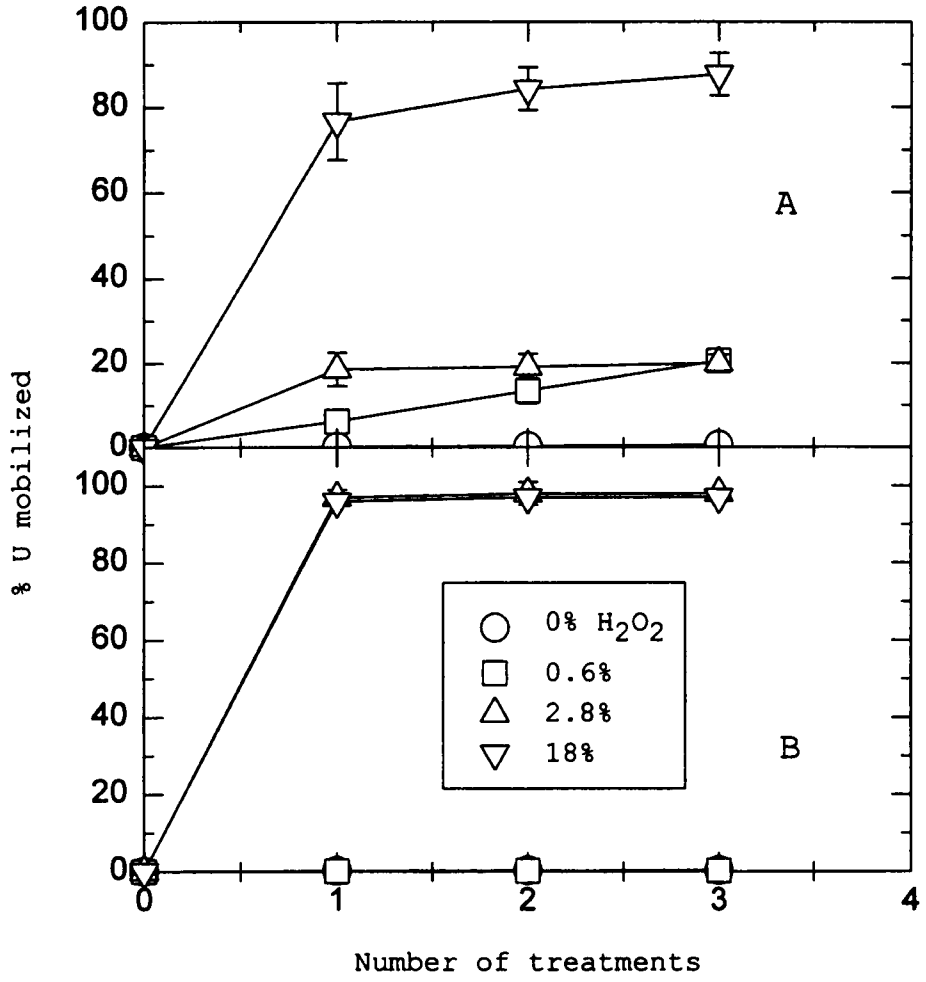


Figure IV-13: Mobilization of U from Illite utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 1.97 mg/g. (A = 1-hour, B = 24-hours contact).

at 18% H_2O_2 after 3 treatments. Enhanced mobilization during peroxide treatment could be due to two possible parameters: Organic carbon (OC) content and presence of calcite within the clay. Peroxide oxidizes OC thereby releasing U sorbed to this fraction. Berthelin et al., (1987) indicated that the destruction of organic matter enhanced U mobilization from U-bearing rocks and minerals. The oxidation of OC was evident from the increase in temperature (exothermic reaction) during the treatment. In this work, peroxidation of Illite resulted in a significant decrease in U binding (as indicated by the isotherm study) which also suggested oxidation of binding sites (OC) was occurring.

Laboratory analysis found that the Illite contained 2.64% $CaCO_3$. Birkeland (1974) found that dissolution of $CaCO_3$ was more pronounced at low pH (Appendix A-1). Solution pH ranged from 2.2 to 4.7 after H_2O_2 treatment. Read et al., (1993) have reported that weathering processes decalcified sandstone which enhanced U mobilization due to carbonate complex formation. The following reactions are involved in formation of soluble U/carbonate complexes:

$$UO_2^{2+} + CO_3^{2-} \rightarrow UO_2(CO_3)_2^{2-} \qquad K_s = 1.67 \times 10^{16}$$

$$UO_2(CO_3)_2^{2-} + CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-} \qquad K_s = 3.01 \times 10^{5}$$

$$UO_2^{2+} + 3\ CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-} \qquad K_s = 5.03 \times 10^{21}$$

where K_s is the representative equilibrium stability constant for each reaction. Precipitation of uranyl peroxide is prevented due to strong complex ion formation with carbonate. Additionally, uranyl carbonate may react with H_2O_2 to form a soluble uranyl-peroxide-carbonate complex as followes:

$$UO_2(CO_3)_3^{4-} + H_2O_2 \rightarrow UO_2(CO_3)_2HO_2^{3-} + HCO_3^- \quad K_s = 10^{2.2}$$

Since K_s of the uranyl-peroxide-carbonate complex is significantly lower than those of uranyl carbonate complexes, this complex will not dominate U speciation.

Figure IV-13B depicts U mobilization from Illite after 24-hour treatment times. Water and 0.6% H_2O_2 did not mobilize any U. On the other hand, essentially all of the bound U was mobilized for H_2O_2 levels > 0.6%. Hence, longer contact times released more U for H_2O_2 > 0.6% and lowered U mobilized for $0 \leq H_2O_2 \leq 0.6\%$. At low H_2O_2 loading ($\leq$ 0.6%), the peroxide concentration may not be sufficient to oxidize all of the organic matter associated with the clay. Uranium readsorption to the unoxidized organic carbon may occur over time. At 2.8% H_2O_2, almost all bound U was removed after the first 24-hour treatment. The mobilization increased by a factor of 5 compared to the same level of peroxide after the first 1-hour treatment. This led to the conclusion that oxidation of OC and dissolution of $CaCO_3$ continued over time. The bound U released complexed

with bicarbonate/carbonate to form uranyl-bicarbonate/uranyl-carbonate complexes. Precipitation of uranyl peroxide may not occur, even within the desired range of pH (3-5.5) for precipitation, because of the formation of the stable uranyl carbonate complexes in solution.

Figure IV-14 shows U mobilization from Ca-Montmorillonite after multiple treatments. The same U mobilization profiles were observed as those found for Kaolinite with the exception of H_2O washing. Less than 1% U was mobilized from Ca-Montmorillonite utilizing water (Figure IV-14A). Uranium mobilization dfferences using H_2O could be due to the very high affinity of this clay for U (high CEC and surface area) compared to the U affinity for Kaolinite. The distribution coefficient (K_d) for untreated clays shows that Ca-Montmorillonite has a higher K_d than that found for Kaolinite at pH $\leq$ 7 (pH of water was 5.5). Less U was expected in solution when Ca-Montmorillonite was utilized compared to Kaolinite for equal soil masses.

Mobilization of U after three 24-hour treatments is presented in Figure IV-14B. Removal appeared to be linear with respect to number of treatments for all wash fluids. The data indicates that water mobilized 2.4% U after three treatments. Uranium removal using H_2O_2 ranged from 1.6% at 24% H_2O_2 to 4.8%

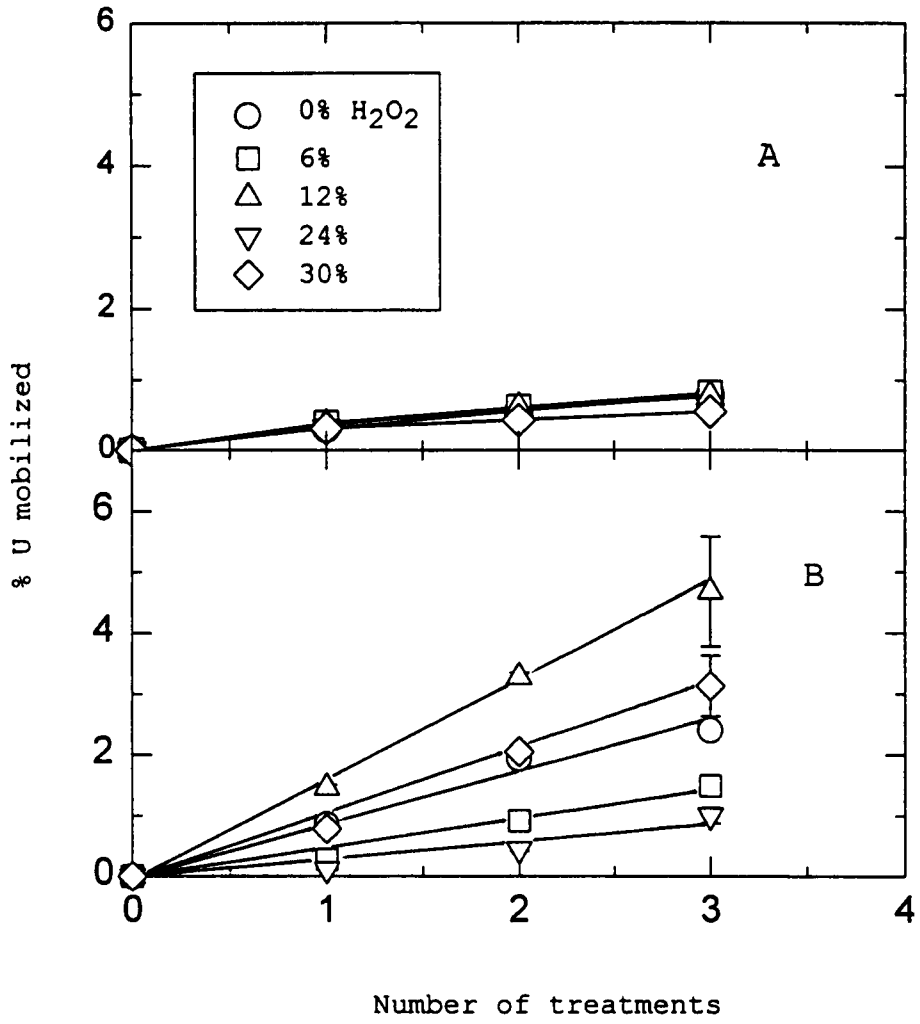


Figure IV-14: Mobilization of U from Ca-Montmorillonite utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 5.98 mg/g. (A = 1-hour, B = 24-hours contact).

at 12% H_2O_2. For other peroxide concentrations (i.e., 6 and 30%), the removal fell into the above range. The reason for mixed results were unclear and there was no data available for comparison from the literature. An increase in U mobilization over time was due to less peroxide in solution to precipitate U. During the treatment, Ca^{2+} was released from the clay matrix and formed calcium peroxide, $CaO_2.8H_2O$ (s), with treatment peroxide (Perry and Green, 1984). This process, in turn, decreased the peroxide concentration in the solution thereby reducing the available peroxide to precipitate U as uranyl peroxide.

4.2 Mobilization from oxides

Data plotted in Figure IV-15 represents the impact of peroxide treatment on U mobilization from Al oxide after multiple treatment times. A significant amount of U was mobilized (14.5%) using water alone after three one-hour treatments (Figure IV-15A). Less U mobilized when H_2O_2 was used as the extraction fluid. Data also shows that mobility of U varied with H_2O_2 concentration. Maximum mobilization (7.42%) occurred using a 2.8% H_2O_2 solution. Higher and lower H_2O_2 levels decreased U mobilization. In general, 50% of mobilized U occurred after first treatment. Comparing to U mobilization from Kaolinite, more U was mobilized from the oxide with respect

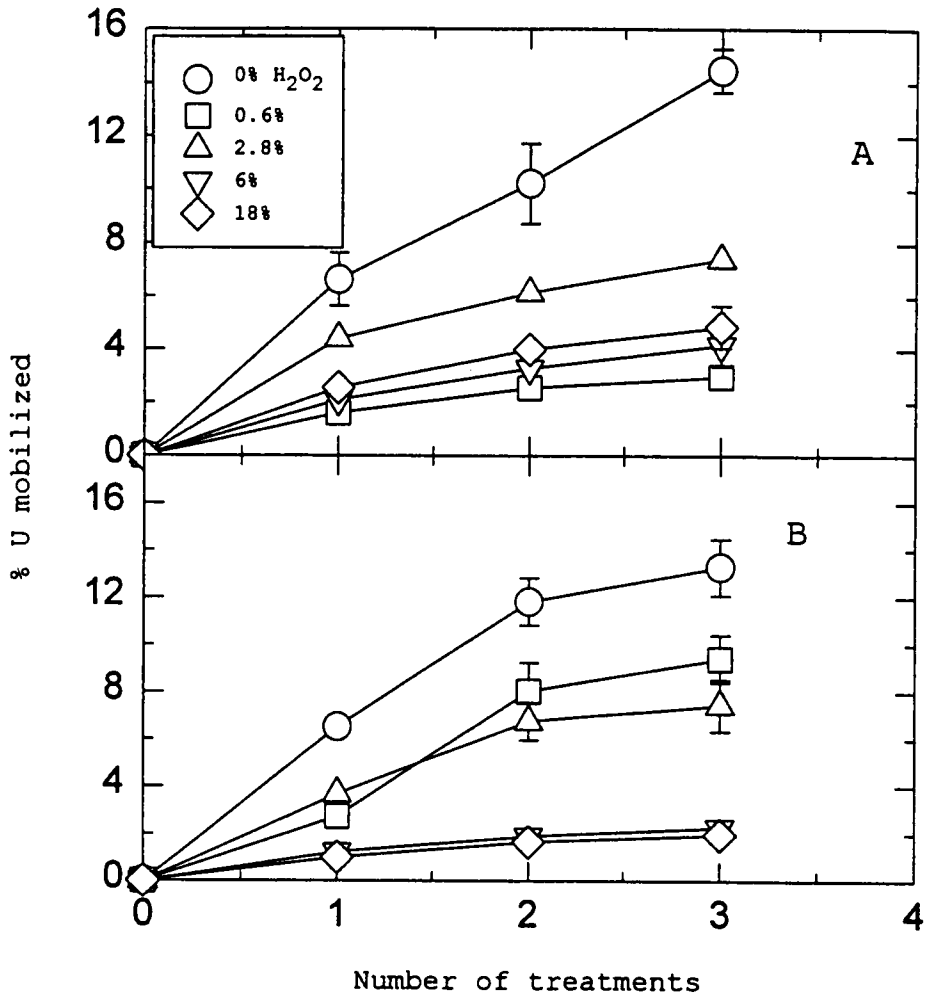


Figure IV-15: Mobilization of U from Al_2O_3 utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 0.66 mg/g. (A = 1-hour, B = 24-hours contact).

to H_2O_2 treatment. Theoretically, precipitation of uranyl peroxide should be expected because of the favorable pH range (Appendix C5-C6) to precipitate U. If precipitation occurred, less U was mobilized as those found from Kaolinite. However, at this point, it was unclear why more U was mobilized from Al oxide.

Data in Figure IV-15B depicts U mobilization after 24-hour H_2O_2 treatment times for Al oxide. It was observed that U mobilization varied with peroxide concentrations. The data also indicates that the percent U mobilized was high after the first two washes using $H_2O_2 \leq 2.8\%$. The highest mobility (13.3%) occurred utilizing water after three 24-hour treatment. When peroxide was used, U mobilization decreased from 9.4% at 0.6% H_2O_2 (pH 5.63) to 1.95% at 18% H_2O_2 (pH 3.0) which was believed due to precipitation of uranyl peroxide at high H_2O_2 treatments. An increase in the contact time from 1 to 24 hours increased U mobilization using 0.6% H_2O_2. Uranium mobilization did not change much over time for 0% (water) and 2.8% H_2O_2. At higher peroxide concentrations (> 2.8%), mobility decreased over time.

These results suggested that U removal was a function of peroxide concentration, contact time and number of treatments. Maximum U mobilization occurred when 2.8% H_2O_2 at 3 one-hour contact times (7.42% U mobility) or 0.6% H_2O_2 at 3 24-hour

treatment time (9.4% mobility) was utilized. For minimum U mobilization, the combination of 18% H_2O_2 and one 24 hour wash resulted in the lowest mobility (1.0%).

Figure IV-16 shows U mobilization from Fe oxide after multiple treatments. Water mobilized 7.7% U whereas less than 2% U mobilization was detected after 3 one-hour treatments at any peroxide concentration (Figure IV-16A). This is similar to the mobilization profile observed for Kaolinite. For peroxide treatment, precipitation of uranyl peroxide (solution pH ranged from 3-4) inhibited U mobilization. The data also shows that U mobilization appears to be independent of H_2O_2 loading for $H_2O_2 \geq$ 0.6%.

Figure IV-16B represents U mobilization after 24-hour treatment times. The longer contact time resulted in a 10 fold increase in U mobility (72%) using water alone (pH = 4) as the treatment fluid after three 24-hour treatments. On the other hand, U mobilization decreased with contact time when H_2O_2 was used as the treatment fluid. This could be due to continued precipitation of uranyl peroxide over time. The amount of mobilized U was less than 0.4%. It was noted that more U was mobilized from Al than Fe oxides. This could be due to differences in binding energy, as determined from isotherm

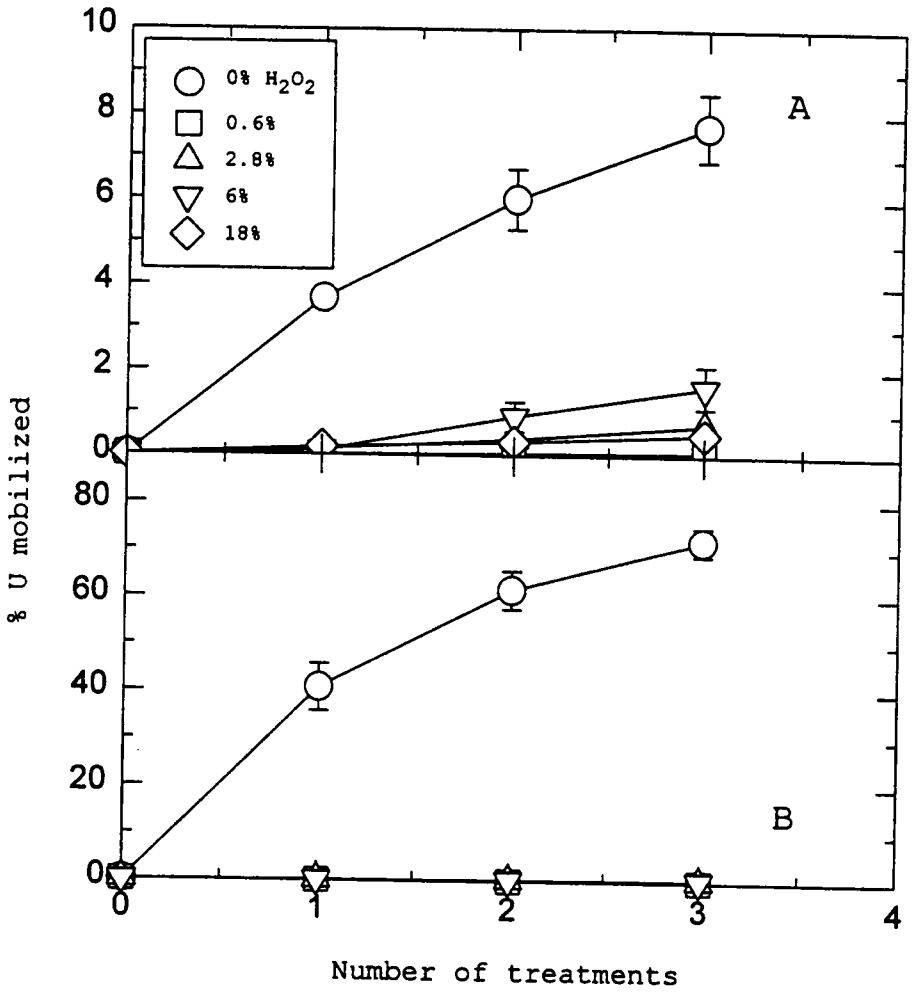


Figure IV-16: Mobilization of U from Fe_2O_3 utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 1.25 mg/g. (A = 1-hour, B = 24-hours contact).

experiments, which showed that Fe oxide has a stronger binding affinity than the Al oxide.

4.3 Mobilization of U(+6) from DOE soils

Figure IV-17 illustrates U mobilization from Hanford (I) soil after three treatments. Data indicates that mobility increased with the peroxide concentration and ranged from 11.4% at 0.6% H_2O_2 to 60.2% at 18% H_2O_2 after 3 one-hour successive treatment (Figure IV-17A). Water alone mobilized 13.4% during this treatment strategy. It was also noted that over 50% of the mobilized U was released during the first treatment. Enhanced mobilization was believed due, in part, to U complexation with CO_3^{2-}. Soil analysis showed that up to 5.28% equivalents of $CaCO_3$ (or 0.63% CO_3^{2-}-C) were present in the Hanford (I) material. Once uranyl ion was released into solution, it combined with CO_3^{2-} to form stable aqueous complexes thereby enhancing U mobilization. The final solution pH (6.1-7.1) favored formation of uranyl-carbonate complexes (Langmuir, 1978). Speciation calculations (Appendix B-4) showed that uranyl carbonate complexes were the dominant species in the treatment solution. Enhanced mobilization using H_2O_2 was also observed for Illite which contained $CaCO_3$ (2.64% equivalents).

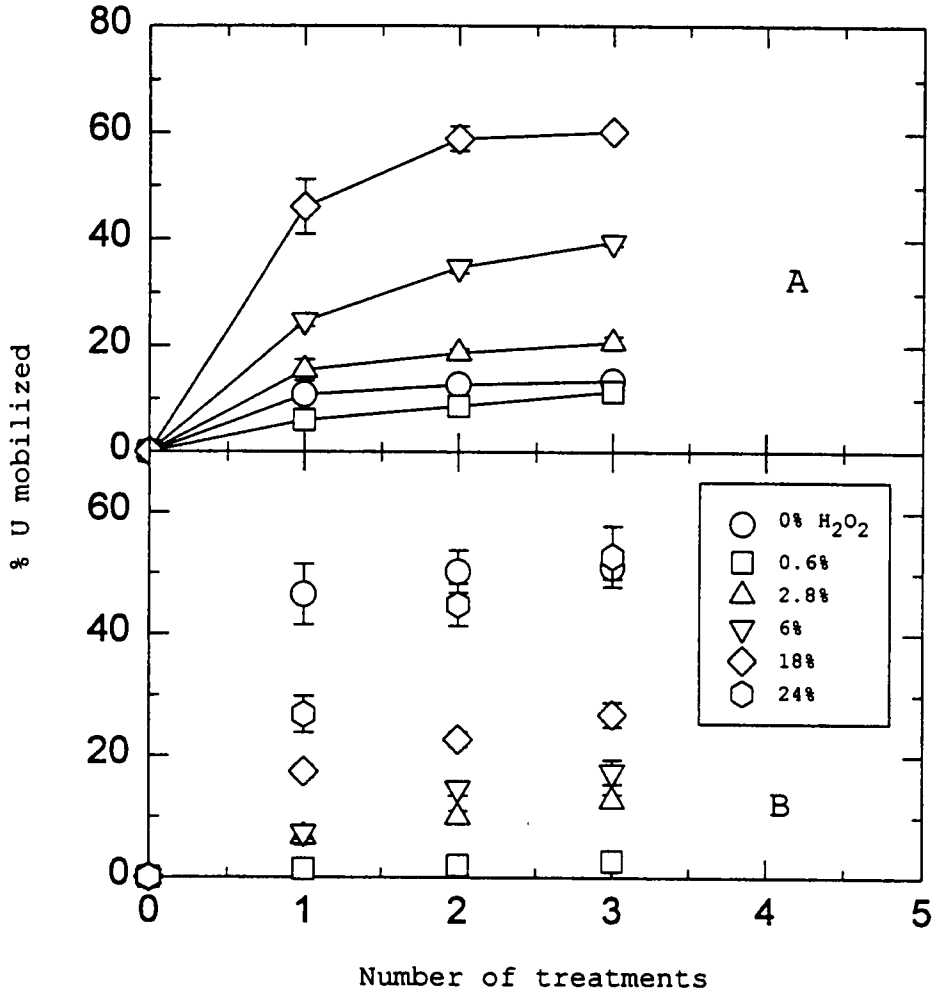


Figure IV-17: Mobilization of U from Hanford (I) soil utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 0.157 mg/g. (A = 1-hour, B = 24-hours contact).

Precipitation of uranyl peroxide was not likely to occur because of high solution pH.

Figure IV-17B represents repeated H_2O_2 treatment of the Hanford (I) soil after 24-hour treatment times. Again, U mobilization increased with peroxide concentration; however, levels mobilized were lower than those found in one-hour treatments. Approximately 2.7% U was mobilized at 0.6% H_2O_2 compared to 52.8% at 24% H_2O_2 after three 24-hour treatments. The longer contact time mobilized more U using water (from 13.4% after 3 one-hour treatments to 51% after three 24-hour treatments). The release of soil calcite over time due to soil dissolution coupled with the low affinity of this soil for U (as indicated from sorption isotherms) could be responsible for increase U mobilization over time using water. Additionally, the final solution pH increased after 24-hour treatment compared to 1-hour treatment (~ 7.6 vs 5.4) using water thereby enhancing the formation of uranyl-carbonate complexes. On the other hand, U mobility was reduced over time when H_2O_2 was used as the wash fluid. It was believed that resorption of uncomplexed uranyl ions to this soil over time resulted in the lower solution phase concentrations observed after 24-hour treatments. It was noted that the binding affinity increased approximately 50% for the pretreated Hanford (I) soil compared to the untreated soil which

suggested that peroxide treatment altered the soil structure. Since equilibrium required 24 hours for the pretreated Hanford (I) soil, one-hour treatments represent non-equilibrium conditions. Researchers (Tessier et al.,1979 and Burford et al.,1964) found that an increase in external surface area and a partial alteration of silicate and mica upon soil peroxidation impacted binding.

Figure IV-18 depicts the mobility of U from Hanford (II) soil after multiple treatment times. The results show that some U mobilization occurred for all peroxide concentrations (Figure IV-18A). Water alone mobilized 14% U after 3 one-hour treatments. Uranium sorption to this soil showed a low affinity in the pH range of 7-9 which corresponded to the final treatment pH using water. At the same time, the mobility of U using peroxide ranged from 7.4% at 15% H_2O_2 to 24% at 3% H_2O_2. Hanford (II) soil contained 2.32 % equivalent $CaCO_3$ (or 0.28% CO_3^{2-}-C) which impacted U mobilization. It also appeared that over 50% of the mobilized U occurred during the first one-hour treatment for all peroxide loadings.

The data plotted in Figure IV-18B illustrates U mobilization after 24-hour H_2O_2 treatment times. Again, some mobilization of U occurred at all peroxide concentrations. However, the percentage of U mobilized was somewhat lower in the

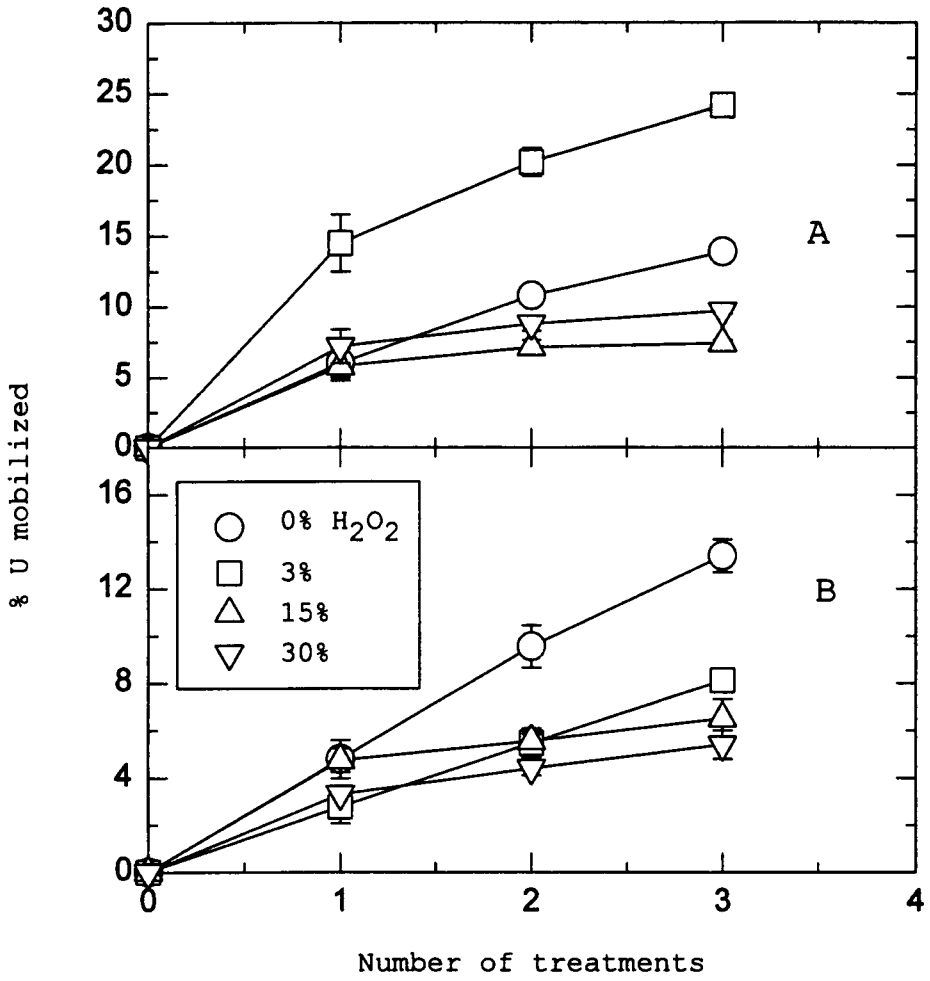


Figure IV-18: Mobilization of U from Hanford (II) soil utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 0.30 mg/g. (A = 1-hour, B = 24-hours contact).

24-hour treatments than the one-hour treatments. Uranium mobilization was maximized using water (13.4%) whereas 30% H_2O_2 mobilized the minimum amount of U (5.4%). It was also noted that over 60% of the mobilized U was removed from soil during the first 24-hour treatment time at $H_2O_2 \geq 15\%$. Reduced U mobilization with increasing treatment time and peroxide loading indicates that soil peroxidation created additional surface adsorption sites. The sorption capacity of the H_2O_2 pretreated soil (based on the isotherm data) which was increased 27% at pH 7 and 39% at pH 9 was likely the result of additional surface sorption sites. During treatment, pH was found to be greater than 7.0 for all peroxide concentrations. It was also noted that CEC increased from 2.8 (original soil) to 6.18 meq/100 g (pretreated soil). In addition, since this soil contained 1937 mg/kg Fe oxide and U mobilization was reduced in the presence of this oxide over time, it was believed that Fe oxide had a role in the mobilization reduction observed for this soil.

Figure IV-19 illustrates the mobility profile of U from the Portsmouth soil. Overall, less than 1% U was mobilized during 3 one-hour treatments using peroxide and mobilization was found to be independent of H_2O_2 loading (Figure IV-19A). Water (pH ~ 5.8) removed 1.7% of the initial bound U during this same treatment period. The low mobility of U from this soil was

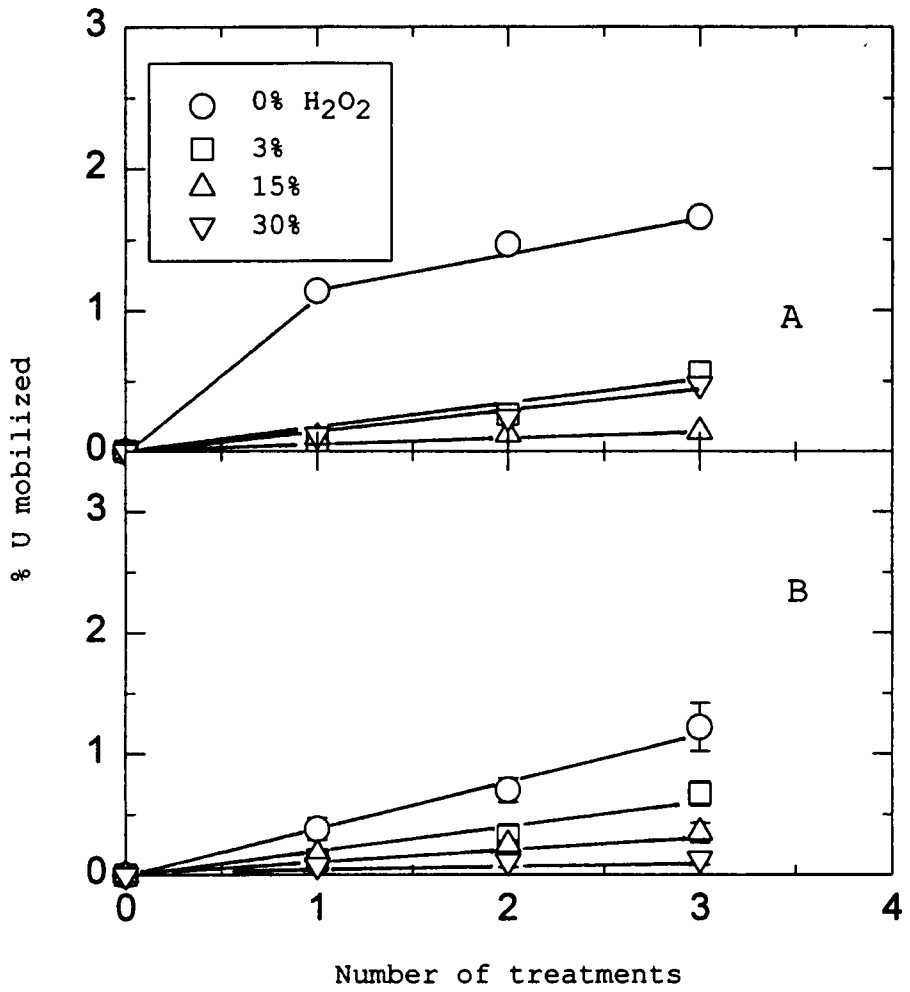


Figure IV-19: Mobilization of U from Portsmouth soil utilizing different H_2O_2 loadings and number of treatments. Initial U loading = 0.383 mg/g. (A = 1-hour, B = 24-hours contact).

believed due to a lack of $CaCO_3$ and the high percentage of clay which was associated with this soil. As indicated in the soil characterization data, the Portsmouth soil contained 37 % silt and clay. Merifield et al. (1980) found that silt sorbed 26 - 32 wt % U and clay sorbed 50-60 wt % while sand only contained 13-23 wt % U in sediment. The precipitation of uranyl peroxide was not likely occur because of high solution pH ($pH \geq 5.5$) when H_2O_2 was used. It was also noted that the Portsmouth soil, in addition to the clays (i.e. Kaolinite and Ca-Montmorillonite), had similiar U mobilization profiles in which less than 1% U was mobilized from 3 one-hour treatments. High binding affinity (K_d = 1539 L/kg) of Portsmouth soil was, partly, responsible for low U mobilization.

Data plotted in Figure IV-19B depicts U mobilization from Portsmount soil after 24-hour treatments. Water mobilized 1.3% U whereas less than 1% U mobilized using H_2O_2. Uranium mobilization appeared to be independent of H_2O_2 concentration and longer contact times had a little effect on U mobilization.

In general, the effect of H_2O_2 on mobility of U from Portsmouth soil was not as significant as that found for the Hanford soils. This was due, in part, to differences in soil composition (i.e. $CaCO_3$, % sand, silt and clay). Because of the high pH resulting from treatment, precipitation of uranyl

peroxide was not a mechanism controlling U mobilization from the DOE soils. Carbonate complexation reaction appeared to impact mobilization. Additionally, the binding energy was at least 90% higher in Portsmouth than in Hanford soils as determined by the isotherm study. This indicated that U was more strongly bound to the Portsmouth soil and hence less likely to desorbed.

4.4 Mobilization of U (+6 and +4) from Hanford soils

Uranium has been found in two different oxidation states at various DOE sites: U(+4) and U(+6). Therefore, an attempt was made to determine the impact of H_2O_2 on U mobility when present in both oxidized and reduced forms using the Hanford soils. Uranium in the tetravalent state (+4) can be oxidized to the hexavalent state (+6) which is a much more soluble form. Oxidation of $UO_{2\ (s)}$, according to Eligwe et al. (1981b), was as follows:

$$UO_{2\ (s)} + H_2O_2 \rightarrow UO_2^{2+} + H_2O + O^{-2}$$

When $UO_{2(s)}$ (4.0 +/- 1.0 mg) was treated (no soil) with 30% H_2O_2, an average of 0.27 mg U (5.7%) was solubilized. Results suggested that either precipitation of uranyl peroxide occurred or H_2O_2 was not an effective oxidizing agent for $UO_{2\ (s)}$. Eligwe and Torma (1984) also found that extracting U from a U-ore using peroxide improved the yield by only 5 to 6%.

Figure IV-20 shows the mobility profile of U from Hanford (I) soil after multiple treatments when both U forms were present. This soil was spiked with 0.272 mg U(+6) and 3.0 +/- 1.0 mg U(+4) per gram of soil. U(+6) as UO_2^{2+} was added to soils in the aqueous form whereas U(+4) as UO_2 was added to whole soils in the solid form. The results indicated that U mobilization increased with peroxide concentration during 1-hour treatments (Figure IV-20A). Water mobilized 0.12 mg U (3.5%) after 3-one hour treatment times. An average of 0.19 (5.1%), 0.26 (7.4%) and 0.29 mg U (8.6%) was removed from 3, 15 and 30% H_2O_2, respectively, during the treatment period. The same pattern of U mobilization (increasing with peroxide concentration) was also found from previous treatment of U(+6). From results of the U(+4) solubilization experiment using 30% H_2O_2, it suggestes that over 90% U mobilization from treatment of U(+4)/U(+6) in soil was due to U(+4) mobilization.

Figure IV-20B depicts U mobilization after 24-hour treatments. Uranium mobilization increased with peroxide concentration and ranged from 2.03% at 3% H_2O_2 to 3.8% at 30% H_2O_2 after three 24-hour treatments. The longer contact time reduced U mobilization which was also observed in the treatment of U(+6).

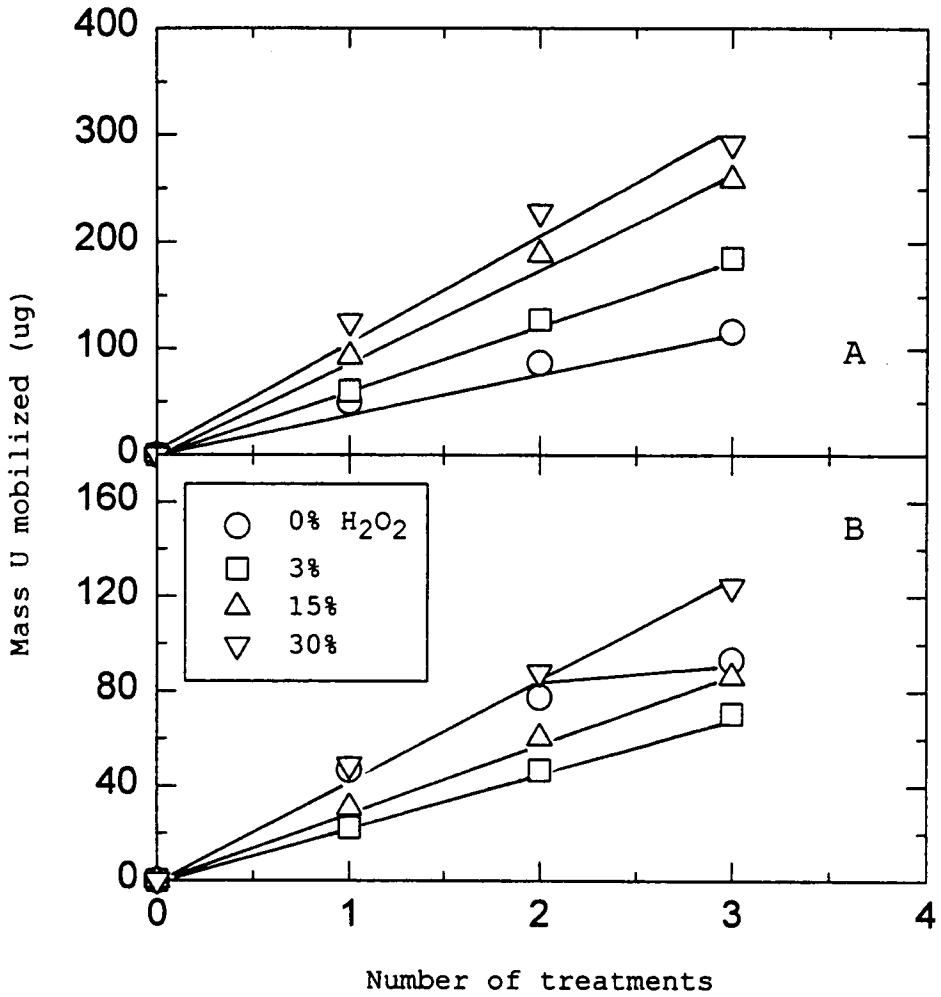


Figure IV-20: Mobilization of U(4+6) from Hanford (I) soil utilizing different H_2O_2 loadings and number of treatments. Initial U loading: U(6) = 0.272 mg/g, U(4) = 3.0 +/- 1.0 mg/g. (A = 1-hour, B = 24-hour contact).

Data plotted in Figure IV-21 shows the mobility of U from Hanford (II) soil. The curves show that U mobilization was approximately independent of peroxide concentration (Figure IV-21A). Data from previous treatment of the Hanford (II) soil showed that 3% and 15% H_2O_2 mobilized 0.073 (i.e. 24.2%) and 0.022 mg U (7.41%) after 3-one hour treatments. From this treatment, at the same H_2O_2 concentrations and contact times, U mobilization was 0.14 (4.31%) and 0.18 mg U (5.34%). The oxidized U(+4) was determined by subtracting the total mobilized U (+4 and +6) in this treatment from the mobilized U(+6) in the previous Hanford (II) study. The data showed that approximately 50% (using 3% H_2O_2) and 88% (using 15% H_2O_2) of the mobilized U was due to oxidation of U(+4). This result indicated that at low peroxide concentration, the oxidation of U(+4) was not effective. It appeared that U(+6) was readily mobilized at low H_2O_2 concentration (i.e. 3% H_2O_2) compared to U(+4). This is believed due to the low oxidizing potential of H_2O_2 at low concentration.

Figure IV-21B represents the 24-hour treatments of Hanford (II) soil. Water alone mobilized 0.123 mg U (3.74%). Since U(+4) is insoluble in water, the mobilized U was believed initially bound as U(+6) to the soil. The data also showed U was detected at all peroxide levels and U mobilization ranged from

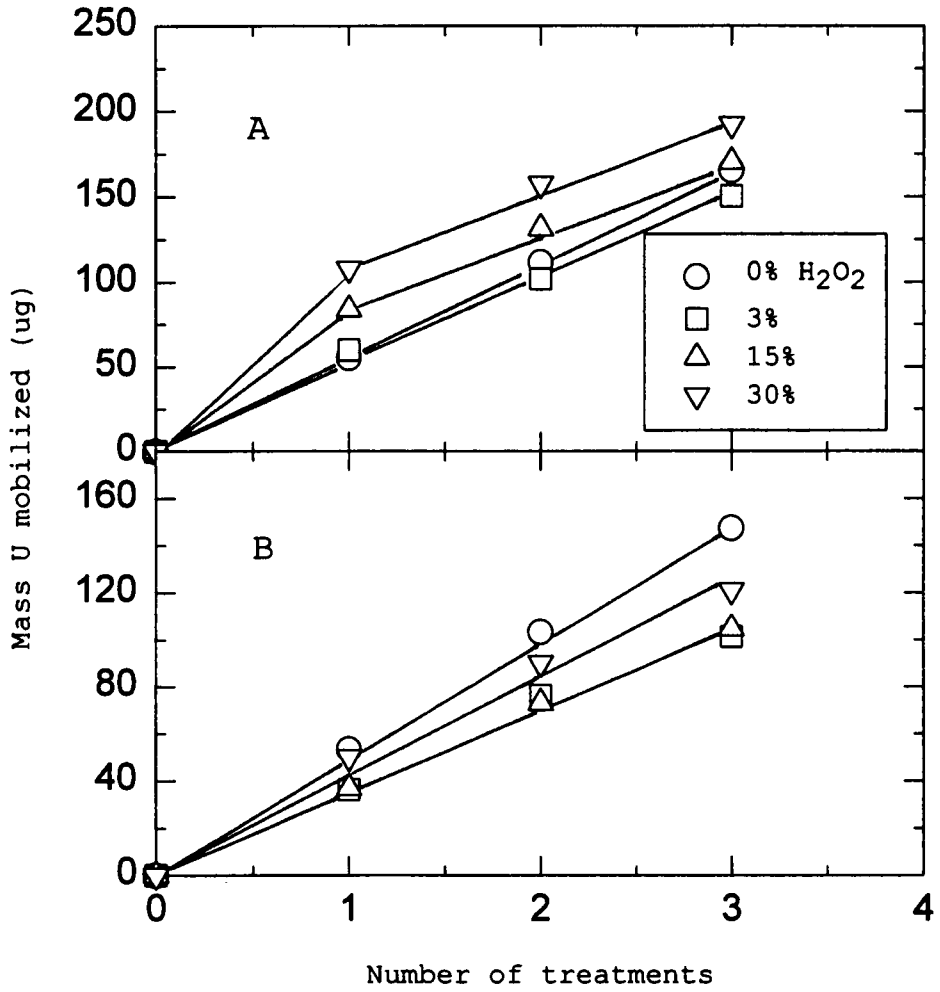


Figure IV-21: Mobilization of U(4+6) from Hanford (II) soil utilizing different H_2O_2 loadings and number of treatments. Initial U loading: U(6) = 0.29 mg/g, U(4) = 3.0 +/- 1.0 mg/g. (A = 1-hour, B = 24-hour contact).

0.10 mg U at 3% H_2O_2 to 0.12 mg U at 30% H_2O_2. The longer contact time decreased U mobilization as was observed in U(+6) mobilization from Hanford (II) soil.

IV-4.6 Effect of pH on U(+6) mobilization

Past researchers have indicated that pH impacts U mobilization. Berthelin et al. (1987) reported U mobilization was enhanced under acidic soil conditions (pH 3.6-4.3). Eligwe et al. (1981b) found that as much as 87% U was extracted from U ore containing 0.18% U_3O_8 at pH 1.5 utilizing H_2SO_4. The following experiment was performed for U(+6)-contaminated soils to differentiate U mobilization which was due to the effect of H^+ from the effect of H_2O_2. The final pH of the treatment solutions ranged from 2 to 5 for the clays and oxides and from 6 to 9 for the soils. In this experiment, DI water, was adjusted to four different pHs (2, 3, 7 and 8) with either 0.1N NaOH or 0.1N HCl before treatment.

Figure IV-22 illustrates single treatment of Hanford (I & II) and Portsmouth soils at 24-hour contact time. The data shows that U mobilization (6.4%) from Hanford (I) soil was independent of pH whereas mobilization of U from Hanford (II) soil decreased with increasing solution pH. The Portsmouth soil data indicates 4.7% U mobilization at pH 2 and ≈ 0% at higher

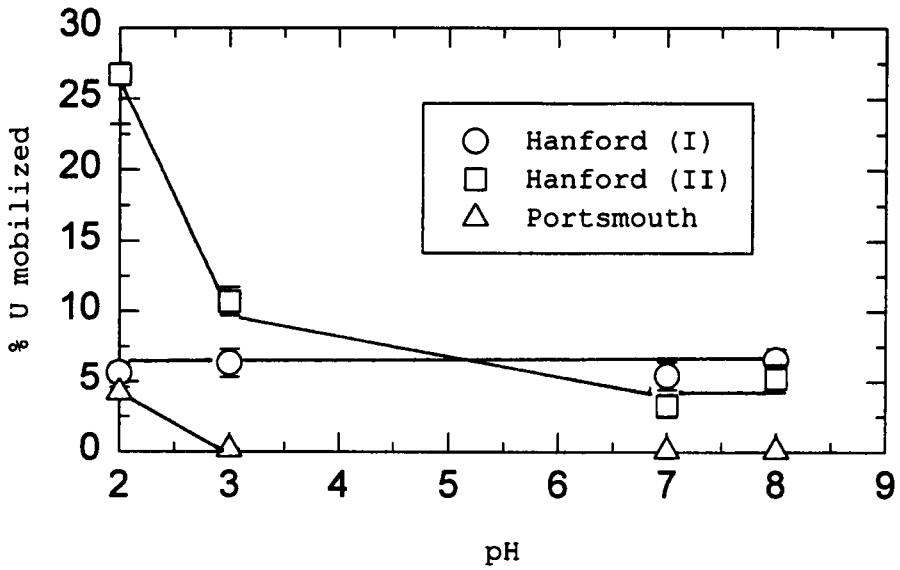


Figure IV-22: Mobilization of U(6) from DOE soils utilizing single treatment and different initial pHs. Contact time = 24-hours.

pHs. The decrease in U mobilization with increase in pH was due to the deficiency in H^+ ions to effect the dissolution of the sorbed U(+6) (Eligwe and Torma, 1982). In comparing with H_2O_2 treatment from these soils, the results suggest that U mobilization was due entirely to the effect of peroxide in the case of Hanford (I) and Portsmouth soils. Uranium mobilization from Hanford (II), however, was impacted by pH.

CHAPTER V

SUMMARY

Uranium binding varied with soil type and solution pH. The results showed that clays and clay-like soil had the highest affinity for U, followed by the oxides. Hanford soils had the lowest U sorption capacity. In general, an increase in solution pH resulted in an increase in U binding.

Hydrogen peroxide pretreated soils sorbed U, however, sorption varied with soil type. The sorption affinity of U increased in the Hanford soils and Fe oxide whereas it decreased for clays, Al oxide and the Portsmouth soils after peroxide treatment. In general, solution pH had less of an impact on U binding to the pretreated soils compared to the untreated soils.

Uranium mobilization from Kaolinite was not detected at H_2O_2 loadings > 0%. Additionally, longer contact times and repeated treatments did not improve the yield. Precipitation of uranyl peroxide was believed the cause for limited mobilization.

Peroxide concentration directly impacted U mobilization from Illite. An average of 20% U was mobilized using 0.6% H_2O_2 and increased to over 80% using 18% H_2O_2 after three 1-hour

treatments. Essentially all of the bound U was removed at H_2O_2 > 0.6% after one 24-hour treatment time. Oxidation of organic carbon coupled with dissolution of $CaCO_3$ and carbonate complexation appeared to govern mobilization.

Short contact times (three 1-hour) and varying peroxide concentrations did not mobilize U from Ca-Montmorillonite. However, longer contact times (three 24-hours) removed 1-5% U. Repeated treatment also mobilized additional U. The competition of the released Ca^{2+} and UO_2^{2+} for peroxide limited uranyl peroxide precipitation thereby enhanced U mobilization over time.

Mobilization of U from Al oxide varied with peroxide concentration. Less than 8% U mobilization was detected in Al oxide after three 1-hour treatments using 2.8% H_2O_2. More U was mobilized at low peroxide concentration (< 2.8%H_2O_2) when the contact time was increased.

Uranium mobilization from Fe oxide was independent of peroxide concentration (H_2O_2 > 0%) and number of treatments. Overall, less than 2% U was mobilized after three 1-hour treatments and essentially no U was mobilized after three 24-hour treatments. Precipitation of uranyl peroxide was the cause for the reduction in U mobilization over time

Peroxide concentration had a direct impact on U mobilization from Hanford (I) soil. Uranium mobilization ranged from 10% to 60% after three 1-hour contact times when 0.6% and 18% H_2O_2 concentrations were used. Dissolution of calcite and complexation with CO_3^{2-} to form aqueous uranyl carbonate complexes resulted in high soluble U levels. Longer contact time, however, reduced U mobilization. This was attributed to the resorption of uncomplex U to soil over time.

Uranium mobilization ranged from 7.5% using $H_2O_2 \geq 15\%$ to 25% using 3% H_2O_2 after three 1-hour treatment times from Hanford (II) soil. Complexation with carbonate enhanced U mobilization. Higher peroxide concentrations and longer treatment times, however, reduced mobilization. The varying amount of additional surface sorption sites with peroxide concentration could be the main mechanism for the reducing in mobility.

Peroxide treatment did not significantly mobilize U (<1%) from the Portsmouth soil. The large percentage of clay and its high binding affinity were believed to impact this mobilization behavior.

The oxidation of U(+4) to U(+6) using 30% H_2O_2 improved U mobilization by less than 6%.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Batch experiments have indicated that soil peroxidation does have the potential to release sorbed U from soils and soil materials. The degree of U mobilization depends on several factors such as soil type, oxidant concentration, contact time, and number of treatments. In addition, the strength of U binding to soils could affect the magnitude of mobilization upon soil peroxidation. However, soil composition (i.e. organic carbon, amount of calcite) and treatment solution pH were identified as critical factors controlling U mobilization.

The pH of soil-peroxide system clearly impacted U mobilization in which it favored the formation of soluble uranyl carbonate complexes (pH > 5) or the precipitation of uranyl peroxide (2 < pH < 5).

Based on the findings of the present study, the following recommendations for the oxidation of U-contaminated soils are offered:

Hanford (I): Minimum U mobilization would be achieved utilizing low peroxide concentration (≤ 0.6% H_2O_2) and longer treatment times.

Hanford (II): Longer treatment time (24 hours) and high peroxide loading would minimize U mobilization.

Portsmouth: H_2O_2 have little impact on U mobilization from this soil.

These recommendations further implied that DOE shoud use low peroxide concentration and short contact time to treat U contaminated clay or clay-like soil (Portsmouth). For sandy soil or for soil contains calcite, longer contact time should be employed to minimize U mobilization.

LITERATURE CITED

LITERATURE CITED

Allison L.E., 1965, Methods of soil analysis, Agronomy, v. 2, n. 9, p. 1367-1378.

Allison L.E. and Moodie C.D., 1965, Methods of soil analysis, Agronomy, v.2, n. 9., p. 1379-1396.

Alloway B.J., 1990, Heavy metals in soil, Bkackie Halsted Press Publisher.

Amell P. J. and Langmuir D., 1978, Factors influencing solution rate of uranium dioxide under conditions applicable to in-situ leaching, Final report, U.S. Dept. of Interior, Contract Grant # H0272019, p. 1-124.

Ames L. L, McGarrah J.E., Walker B.A. and Salter P.F., 1982, Sorption of U and Cs by Hanford Basalts and associated secondary smectite, Chemical Geology, v. 35, p. 205-225.

Ames L.L, McGarrah J.E. and Walker B.A., 1983, Sorption of trace constituents from aqueous solutions onto secondary minerals. 1.Uranium, Clays and Clay Minerals, v. 31, n. 5, p. 321-334.

Barton P.B., 1956, Fixation of U in the oxidized base metal ores of the Goodsprings district, Clark Co., Nevada, Econ. Geol., v. 51, p. 178-191.

Bartlett J.B., Ruble R.W. and Thomas R.P., 1937, The influences of hydrogen peroxide treatments on the exchange capacity of Maryland soils, Soil Sci., v. 44, n. 2, p. 123-138.

Beckett R., 1986, The role of particulate matter in the transport of pollutants, Water Quality Management, Hart B.H., Ed., p. 113-142.

Berthelin J., Gueniot B. and Munier-Lamy C., 1987, An in-situ experimental bag method to study the influence of environmental factors on uranium mobilization and preconcentration in soils, Uranium, v.3, p. 343-352.

Birkeland P.W., 1974, Pedogogy, Weathering and Geomorphological Research, Oxford University Press Publisher.

Bolt G.H. and Van Riemsdijk W.H., 1987, Aquatic surface chemistry, Wiley and Sons Publisher.

Bolle J.N., Martin H., Sondag F. and Cardoso Fonseca E., 1988, Selective chemical extraction of uranium from mineral, soil and stream sediment samples at Horta da Vilarica, Northeastern Portugal, Uranium, v.4, p. 327-340.

Bolt G.H. and Bruggenwert M.G.N., 1976, Soil Chemistry, Elsevier Scientific Publishing Co.

Bondietti E.A. and Tamura T., 1980, Transuranic elements in the environment-Physicochemical associations of plutonium and other actinides in soil, DOE report, DOE/TOC-22800, p. 145-165.

Borovec Z., 1981, The adsorption of uranyl species by fine clay, Chemical Geology, v. 32, p. 45-58.

Breger I. A., Duel M. and Rubinstein S., 1955, Geochemistry and mineralogy of a uraniferous lignite, Econ. Geology, v. 50, p. 206-225.

Brookins D.G. and Olsen C.E., 1984, Investigations in uranium geochemistry: Distribution of uranium as a function of sediment particle size, Uranium, v. 1, p. 227-247.

Burford J.R., Deshpande T.L., Greenland D.J. and Quirk J.P., 1964, Influence of organic materials on the determination of the specific surface areas of soils, J. of Soil Sci., v. 15, p. 192-201.

Charlet J.M., Doremus P. and Quinif Y., 1987, Concentration mechanisms of uranium in the nineralized fractures of the lower devonian of the Belgian Ardennes-The case of the Oizy area, Uranium, v. 3, p. 387-405.

Coker W. B. and Dilabio R.N.W., 1979, Initial geochemical results and exploration significance of two uraniferous peat bogs, Geol. Surv. Can., v. 791B, p. 198-206.

Davey P.T. and Scott T.R., 1956, Adsorption of uranium on clay minerals, Nature, v. 178, p. 1195.

Davis G.E., 1967, Radiation and Life, Iowa State Publisher.

Davis J.A. and Leckie J.O., 1978, Envir. Sci. Technol., v. 12, p. 1309-1315.

Davis J.A. and Leckie J.O., 1978, Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions., J. Colloid Interface Sci., v. 67, p. 90-107.

Douglas L.A. and Fiessinger F., 1971, Degradation of clay minerals by H_2O_2 treatments to oxidize organic matter, Clays and Clay Minerals, v. 19, p. 67-68.

Dragun J., Lewis R. and Murray W., 1986, Impact of soil chemistry on contaminant migration from hazardous waste areas, Geotechnical & Geohydrological Aspects of Waste Management, p. 23-29.

Eligwe C.A. and Torma A.E., 1984, Influence of hydrogen peroxide in the extraction of uranium from a New Mexico ore, Uranium, v. 1, p. 211-225.

Eligwe C.A., Torma A.E. and Devries F.W., 1981b, Extration of uranium from a low-grade ore with H_2SO_4-H_2O_2 in an activated reactor, In: Fourth annual uranium seminar, Corpus Christi, TX, Sept., 14-17, 1980. SME-AIME, New York, NY., p. 65-71.

Farmer V.C. and Mitchell B.D., 1963, Occurrence of oxalates in soil clays following hydrogen peroxide treatment, Soil Science, v. 96, n. 4, p. 221-228.

Francis C.W., Mattus A.J., Elless M.P. and Timpson M.E., 1993, Selective leaching of uranium from uranium contaminated soils: carbonate and citrate-based leaching solutions, ORNL, Oak Ridge, TN.

Giblin A.M., Batts B.D. and Swaine D.J., 1981, Laboratory simulation studies of uranium mobility in natural waters, Geochimica et Cosmochimica Acta, v. 45, p. 699-709.

Galichon P., Schechter R.S., Cowley A. and Breland M., 1977, Chemical factors in in-situ uranium leach mining, In-Situ, v. 1, no. 2, p. 125-146.

Gittus J.H., 1963, Uranium, Buttlerwoths University Press Publisher.

Goldsztaub S. and Wey R., 1955, Adsorption of uranyl ions by clay, Bull. Soc. Franc. Miner.Crist., v. 78, p. 242-253.

Gueniot B., Munier-Lamy C. and Berthelin J., 1988a, Geochemical behavior of uranium in soils, part I. Influence of Pedogenetic processes on the distribution of uranium in aerated soils, J. of Geochemical Exploration, v. 31, p. 21-37.

Gueniot B., Munier-Lamy C. and Berthlin J., 1988b, Geochemical behavior of uranium in soils, part II. Distribution of uranium in Hydromorphic soils and soil sequences. Applications for surficial prospecting. J. of Geochemical Exploration, v. 31, p. 39-55.

Ho C.H. and Doern D.C., 1985, The sorption of uranyl species on a hematite sol, Can. J. Chem., v. 63, p. 1100-1104.

Hostetler p.B. and Garrels R.M., 1962, Transportation and precipitation of uranium and vanadium at low temperatures with special references to sandstone-type uranium deposits, Economic Geology, v. 57, p. 138.

Hsi C.D., 1981, Sorption of uranium (VI) by iron oxides, Ph.D. thesis, Colorado School of Mines, Golden, Colorado, 154 p.

Hsi C.D. and Langmuir D., 1980, The effect of carbonate complexing on the adsorption of uranyl by ferric oxyhydroxides, Geol. Soc. Amer. Abstracts with Programs, p. 452.

James R.O. and Healy T.W., 1972, Adsorption of hydrolyzable metals ions at the oxide-water interface, J. Coll. Interface Sci., v. 30, p. 65-81.

Langmuir D., 1978, Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, Geochimica et Cosmochimica Acta, v. 42, p. 547-569.

Landais P., Connan J., Dereppe J.M., George E., Meunier J.D., Monthioux M., Pagel M., Pironon J. and Poty B., 1987, Alterations of organic matter: A clue for uranium ore genesis, Uranium, v. 3, p. 307-342.

Lavkulich L.M. and Wiens J.H., 1970, Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents, Soil Sci. Soc. Amer. Proc., v. 34, p. 755-758.

Lawes B.C., 1978, Effect of sodium silicate on leaching uranium ores with hydrogen peroxide, In-Situ, v. 2, n. 2, p. 75-92.

Lopatkina A.P., 1967, Conditions of accumulation of uranium in peat, Geochem. Int., v. 4, p. 577-588.

Maya L., 1982a, Sorbed uranium (VI) species on hydrous titania, zirconia and silica gel, Radiochim. Acta, v. 31, p. 147-151.

McLean W., 1930, Effect of hydrogen peroxide on soil organic matter, J.Agric. Sci., p. 251-261.

Merritt R.C., 1971, The extract metallury of uranium, Colorado School of Mines Research Institute, 576p.

Perry R.H. and Green D., 1973, Perry's Chemical Engineerings' Hanbook, 6th Ed, McGraw-Hill.

Read D., Bennett D.G., Hooker P.J., Ivanovich M. and Longworth G., 1993, The migration of uranium into peat-rich soils at Broubster, Caithness, Scotland, U.K., J.of Contaminant Hydrology, v. 13, p. 291-308.

Rodden C.J. and Warf J.C., Analytical Chemistry Manhattan Project, New York, McGraw-Hill Book Company.

Scharpenseel H.W., Pietig F. and Kruse E., 1975, Uranium concentration in soils and their use in prospecting, Pflansenern, Bodenkd, v. 138, p. 131-139.

Sheppard S.C., Gibb C.L. and Hawkins J.L., 1989, Fate of contaminants during utilization of peat materials, J. of Environmental Quality, v. 18, p. 503-506.

Snoeyink V.L. and Jenkins D., 1980, Water Chemistry, John Wileys & Sons, Inc.

Sposito G., 1983, Surface complexation model of the oxide-aqueous solution interface, J. Colloid Interface Sci., v. 91, n. 2, p. 329-340.

Szaley A., 1964, Cation exchange properties of humic acids and enrichment of UO_2^{2+} , Geochem. et Cosmochem. Acta, v. 28, p. 1605-1614.

Tatsch J.H., 1976, Uranium Deposits : Origin, Evolution, & Present Characteristics, Tatsch Associates Publisher.

Tessier A., Cambell P.G.C. and Bisson M., 1979, Sequential extraction procedures for the speciation of particulate trace metals, Analytical Chemistry, v. 51, p. 844-850.

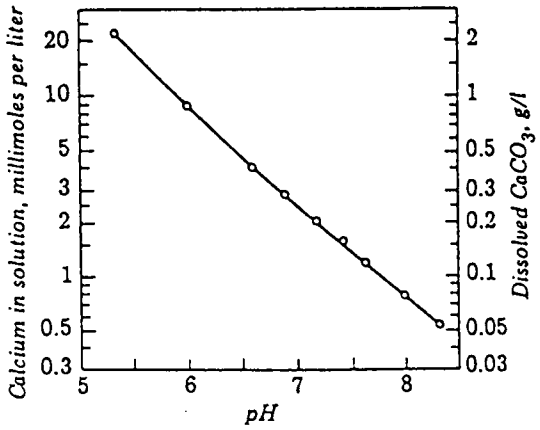
Torma A.E. and Eligwe C.A., 1982, Leaching of uranium ores with H_2O_2-Na_2SO_4-H_2SO_4 system, Hydrometallurgy, v. 9, p. 83-95.

Tsunashima A., Brindley G.W. and Bastovanov M., 1981, Adsorption of uranium from solutions by Montmorillonite: Compositions and properties of uranyl montmorillonites, Clays and Clay Minerals, v. 29, n. 1, p. 10-16.

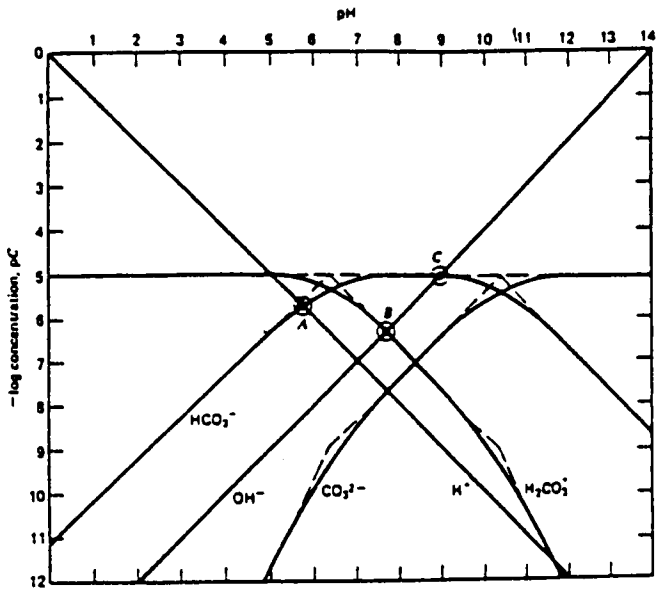
Van Der Weijden, Arthur R.C. and Langmuir D., 1976, Sorption of uranyl by hematite: Theoritical and geochemical implications, Geol. Soc. Amer. Abstracts with Programs, p. 1152.

Zielinski R.A., Otton J.K., Wanty R.B. and Pierson C.T., 1988, The aqueous geochemistry of uranium in a drainage containing uraniferous organic rich sediment, Lake Tahoe area, Nevada, U.S.A., v. 4, p. 281-305.

APPENDIX



A-1: Solubility of $CaCO_3$ vs pH in an equilibrium solution of $CaCO_3$-CO_2-H_2O at 25^0C. Source: Birkeland P.W.,1974.



B-1: The pC-pH diagrams for a 10^{-5} M Carbonate solution at 25^{0}C. Source: Snoeyink and Jenkins, 1980.

$$[H_2CO_3^*] = K_H P_{CO2}$$
$$= 10^{-1.5} * 10^{-3.5}$$
$$= 10^{-5} \text{ M}$$

Determine U-complexes in solution from:

a/ Binding isotherm:

MINTEQ program was utilized to calculate U speciations.

At pH 7: $[CO_3^{2-}] = 10^{-8.5}$ M (from B-1)

B-2: % U complexes in solution at 25°C and pH 7 from equilibrium concentration U_e (mol/L).

U_e (mol/L)	UO_2^{2+} (%)	UO_2OH^+ (%)	$(UO_2)_3(OH)_5^+$ (%)	UO_2CO_3 (aq) (%)
2.8×10^{-9}	1.2	98.6	0	0
1.9×10^{-8}	1.2	94.4	4.3	0
2.2×10^{-8}	1.1	93.1	5.6	0
1.1×10^{-7}	0	60.8	38.1	0
0.8×10^{-6}	0	20.4	79.1	0
1.0×10^{-6}	0	18.2	81.3	1.0

At pH 9: $[CO_3^{2-}] = 10^{-6}$ M

B-3: % U complexes in solution at 25°C and pH 9 from equilibrium concentration U_e (mol/L).

U_e (mol/L)	UO_2OH^+ (%)	$(UO_2)_3(OH)_5^+$ (%)	UO_2CO_3(aq) (%)	$UO_2(CO_3)_2^{2-}$ (%)	** (%)
2.0×10^{-9}	45.3	50.5	3.1	1.1	0
5.6×10^{-9}	25.4	72.3	1.7	0	0
1.9×10^{-8}	11.0	68.0	0	0	21
4.0×10^{-8}	5.2	31.3	0	0	63.5
0.2×10^{-6}	1.0	5.7	0	0	93.3
0.4×10^{-6}	0.5	3.3	0	0	96.2

** $UO_2(OH)_2 H_2O$

Based on amount formed, results showed that carbonate complexes were insignificant in solution. Hydroxy complexes, on the other hand, predominated at the pH's tested.

b/ U mobilization:

Data was taken from U mobilization from Hanford (I) soil. The final pH treatment solution ranged from 6-8. At pH 7, dissociation of calcite is approximately 0.2 g/L (A-1) or 2×10^{-3} M.

At 0.6% H_2O_2 treatment, U mobilization was 6.61×10^{-5} M.

MINTEQ program was utilized to determine U speciations.

B-4: % U complexes in treatment solution at 25°C from U mobilization at 0.6% H_2O_2.

U (mol/l)	$UO_2(CO_3)_2^{2-}$ (%)	$UO_2(CO_3)_3^{4-}$ (%)	UO_2CO_3 (aq) (%)	$(UO_2)_3(OH)_5^{+}$ (%)
6.6×10^{-5}	84.4	2.1	13.2	0

Based on amount formed, U-carbonate complexes was the dominant species in the treatment solution.

C-1: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Kaolinite.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.50	5.35	5.47
6	4.51	4.30	4.20
24	3.50	3.25	3.46
30	2.89	2.99	3.01

C-2: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Kaolinite.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.42	5.20	5.21
6	4.28	4.23	4.05
24	3.23	3.27	3.41
30	2.80	3.01	2.89

C-3: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Illite.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.49	5.95	5.90
0.6	4.58	4.57	4.60
2.8	3.35	3.12	3.20
18	2.18	2.32	2.65

C-4: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Illite.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.80	6.14	5.92
0.6	5.10	3.13	2.90
2.8	4.54	2.64	2.94
18	2.38	2.59	2.60

C-5: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Ca-Montmorillonite.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.52	5.58	5.90
6	4.51	4.20	4.10
12	4.01	3.87	3.89
24	3.22	3.44	3.25
30	2.79	2.89	3.00

C-6: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Ca-Montmorillonite.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.55	5.67	5.25
6	4.25	4.00	4.34
12	4.41	4.21	4.31
24	3.35	3.45	3.28
30	2.99	3.01	2.81

C-7: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Al oxide.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	6.60	5.43	5.13
0.6	4.80	4.92	4.92
2.8	4.16	4.62	4.63
6	3.85	3.64	3.65
18	2.99	2.97	3.00

C-8: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Al oxide.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	4.48	4.42	4.47
0.6	7.05	6.08	5.63
2.8	6.09	5.75	5.40
6	4.02	4.06	3.94
18	2.54	2.87	2.93

C-9: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Fe oxide.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	4.50	4.58	4.51
0.6	4.06	4.10	3.96
2.8	3.54	3.50	3.41
6	3.18	3.55	3.08
18	3.04	3.08	3.08

C-10: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Fe oxide.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	3.99	3.87	3.87
0.6	4.12	4.10	4.07
2.8	3.13	3.13	3.23
6	2.99	3.03	3.17

C-11: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Hanford (I) soil.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.11	5.40	5.40
0.6	7.13	6.93	7.05
2.8	6.70	6.45	6.50
6	7.04	7.00	7.00
18	6.32	6.11	6.15

C-12: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Hanford (I) soil.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	7.36	7.47	7.64
0.6	7.02	7.06	7.09
2.8	6.47	6.41	6.61
6	6.80	6.70	7.05
18	6.15	6.30	6.30
24	5.57	6.00	6.05

C-13: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Hanford (II) soil.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	7.35	7.25	7.25
3	6.64	6.72	6.67
15	6.40	5.01	4.54
30	4.98	3.88	3.62

C-14: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Hanford (II) soil.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	8.05	8.22	8.66
3	6.76	7.23	7.30
15	8.15	8.09	9.85
30	8.84	8.90	8.69

C-15: Solution pH after multiple 1-hour peroxide treatments of U-contaminated Portsmouth soil.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	5.31	5.25	5.79
3	6.57	6.38	6.29
15	5.72	6.47	7.46
30	5.46	6.35	7.25

C-16: Solution pH after multiple 24-hour peroxide treatments of U-contaminated Portsmouth soil.

% H_2O_2	Treatment # 1	Treatment # 2	Treatment # 3
0	7.85	7.17	6.93
3	6.28	6.05	4.69
15	7.60	6.94	6.59
30	7.46	6.96	6.80

C-17: Solution pH after 24-hour treatment of DOE soils utilizing water at different initial pHs.

DOE soils	pH_0	pH_f	pH_0	pH_f	pH_0	pH_f	pH_0	pH_f
Hanford (I)	1.95	4.78	3.03	6.76	7.02	8.64	8.00	8.72
Hanford (II)	1.95	4.32	3.03	6.37	7.02	7.33	8.00	8.30
Portsmouth	1.95	2.54	3.03	5.36	7.02	7.40	8.00	7.40

pH_0 = Initial pH

pH_f = Final pH

VITA

Son H. Nguyen was born in DaNang, South Vietnam. He graduated from The University of Minnesota, Minneapolis with a Bachelor of Science degree in Chemical Engineering (1989). After working for 2 years at 3M Company, he entered the Master's program in Environmental Engineering at The University of Tennessee, Knoxville in September 1992, officially receiving the Master's degree in December 1995.