

SELECTION OF CHELATING AGENTS FOR REMEDIATION OF RADIONUCLIDE-CONTAMINATED SOIL

J.-C. Chao¹, A. Hong¹, R.W. Okey¹, and R.W. Peters²

¹Department of Civil and Environmental Engineering, University of Utah, Salt Lake City, UT 84112; ²Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

Soil contamination by heavy metals and radionuclides is a common problem encountered at many contaminated DOE sites. Lead, chromium, copper, arsenic, uranium, technetium, strontium, cesium, and actinides are among the most often found. Metals and radionuclides in soil pose a serious risk to public safety and groundwater supplies. Once reaching the soil matrix, they can be strongly retained, ensuring prolonged adverse impacts on environmental quality and human health. Chelating extraction has already been shown to have potential for the remediation of heavy metal-contaminated soils either as on-site soil washing agents or for *in situ* remediation. Chelation extraction is well suited as a remediation technique for radionuclide-contaminated soils.

This paper communicates our progress in efforts to develop a predictive tool for the selection of effective chelators for the target radionuclide contaminants and for assessing chelation remediation efficiency based on barest essential test results. This predictive modeling tool is technically and economically beneficial to remediation projects at DOE sites. A regression/empirical model is being developed that predicts radionuclides extraction efficiencies based on input parameters including equilibrium properties of the chelators, laboratory sequential extraction results, and soil characteristics such as composition, texture, organic content, soil pH, cation exchange capacity, carbonate content, mineralogy, and other significant factors.

Results to date of this project are a list of chelators suitable for the extraction of target contaminants including U, Ra, Th, Ba, Pu, and Pb. The selection of chelators is based on aqueous phase equilibrium determination of the chelators's complexation ability, selectivity, and recoverability with respect to the target contaminants.

Key words: *chelators, soil remediation, heavy metals, radionuclides*

INTRODUCTION

Metals and metalloids have long been mined, industrially processed, and used in numerous applications. This has led, especially since the industrial revolution and during the 20th century, to regional and global redistribution and for some—more or less hazardous—elements to a significant increase of other concentration in the upper part of the earth's crust. Therefore, in the plough-layer of soils, in plants, animals, lakes, rivers, and even in the oceanic regions, in foodstuffs and human beings the levels of a variety of elements have substantially increased over time. With increasing industrial demand for metals, there is a continuous need to locate new reserves of ore minerals. Heavy metal contamination of soil is most common and difficult to treat, since the soil is both a sources of metals and also a sink for metal contaminants. The total and bioavailable concentrations of heavy metals in soils are of great importance with regard to both human toxicology and agriculture productivity (Alloway, 1995; Selim and Amacher, 1997; Ferguson, 1990; Stieookerm 1992; and Salomans, Forstner, and Mader, 1995).

A variety of techniques have been investigated for remediation of heavy metal-contaminated soil, such as plant uptake of metals, biological methylation of heavy metals, chemical adsorption of heavy metals, etc. Use of chelating agents to extract heavy metals from contaminated soils is seen as

a treatment method (Hong, Chen, and Macauley, 1995; Truin and Tels, 1990; Pretal et al., 1994; Bart et al., 1990; Kroschwitz and Grant, 1982; Clevenger, 1990; Yong et al., 1993). Complexes with multidentate ligands are usually more stable than those with monodentate ligands. Those chelators with many coordinating sites can penetrate into soil matrix to hold metals and form stable complexes. Results of some investigations show that it is possible to use a suitable chelating agent to extract target metals from soil and recover them both (Hong, Chen, and Macauley, 1995; King, 1987; Bart et al., 1990; Kroschwitz and Grant, 1982; and Stumm and Morgan, 1996). The proper chelator should be capable of extracting target heavy metal from soil and recovering readily. The selectivity between target heavy metals and chelators, and the reuse and recoverability of chelators, will be the major task for this remediation technique.

One other key factor about this technique is the soil environment. The soil is a dynamic system, a heterogeneous mixture of organic and mineral components with differences of pH values, redox conditions, moisture content, and undergoing gradual alterations in response to changes in management and environmental factors. Heavy metals in the soil environment can be involved in a series of complex chemical and biological interactions. Several of the reactions include oxidation-reduction, precipitation-dissolution, volatilization, and surface-solution phase complexation (Alloway, 1995; Selim and Amacher, 1997; Fergusson, 1990; Stoeppler, 1992; Salomans, Forstner, and Mader, 1995). The extraction of heavy metals from contaminated soils by different suitable chelators and soil characteristics will be major task for remediation.

The first step is to identify the selectivity and efficiency of the chelating agents based on available thermodynamic constants and soil characteristics. A regression/empirical method will be developed to predict the complexation ability, selectivity, and recoverability of large numbers of chelators to the target metal contaminants (for example, U, Ra, Th, Ba, Ce, Sr, Pu, Cs, Pb, Hg, and Tc) by inputting acid-base equilibrium constants of chelators, complexation constants of the chelators with heavy metals, heavy metals speciation constants with natural ligands (OH^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , etc), chemical properties, and quantitative structure-activity relationships

THEORY

Chelating extraction is a potential technology of remediation for heavy metals-contaminated soils. Since only limited number of chelators have been investigated for remediation and some of complexation constants for those chelators are not available, the performance of suitable chelators on target metals and the unavailable complexation constants may be evaluated and predicted by equilibrium modeling and mathematical computations (9, 28, 30, 35, MINTEQ2). The chemical equilibrium modeling will be used to predict the efficiency, selectivity, and recoverability of chelating agents for the remediation of target metals in soils based on acid-base equilibrium constants of chelators, complexation constants of the chelators with target metals, speciation constants of target metals with natural ligands (OH^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , etc), and soil characteristics.

Coordination Chemistry

Coordination compounds or complexes consist of one or more central atoms or central ions, usually metals, with a number of ions or molecules, called ligands, surrounding them and attached to them. The complex can be nonionic, cationic, or anionic, depending on the charge of the central ions and the ligands. Usually, the central ions and ligands can exist individually as well as combined in complexes. The total possible number of attachments to a central atom or central ion, or the total possible number of coordinated species, is referred to as the coordination number. Ligands are attached to the central species by coordinate covalent bonds in which both of the electrons participating in the bond are derived from the ligand. Thus we can regard the central species as an electron acceptor and the ligand as electron donor. The central species is a Lewis acid and the ligands are Lewis bases. Since metal ions have an affinity for accepting electrons, they all form coordination compounds with a tendency that increases as the electron-accepting affinity of the metal ion increases. Molecules and ions with free electron pairs tend to form complexes whose strength is a function of their ability to donate or share that pair of electrons.

Ligands that attach to a central ion at only one point, such as H_2O , OH^- , Cl^- , and CN^- , are called monodentate ligands. Ligands that attach at two or more sites are multidentate ligands or chelating agents. The complex formed by a chelating agent and a metal ion is known as a chelate. For example, the chelating agent EDTA^{4-} can attach at six sites, since each of the acetate groups and the two nitrogen atoms have free electron pairs necessary for coordinate bond formation. Complexes containing one central ion are called mononuclear complexes; when there is more than one central ion or molecule the complexes are polynuclear complexes.

Just as a metal can coordinate with more than one chelating molecule, a ligand having enough donor atoms on the proper configuration can bind with more than one metal. These metal atoms may be the same or different. A chelate compound may be either a neutral molecule or a complex ion associated with the appropriate counterions to produce electroneutrality—the formal charge on the ligand or ligands and the charge of the metal. The ligand may be neutral or completely or partially ionized before chelation occurs. Changes in the charge of either or both the metal atom and chelating agent may occur during the chelating reaction as, for example, by the displacement of hydrogen atoms or ions from the ligand donor atoms, or by an oxidation-reduction reaction between the metal and the chelant. After the chelate is formed, the charge of the complex can also change. Charge change often involves ionization of groups on the ligand that are not involved in the chelate structure, usually as a result of changes in the pH, or by oxidation or reduction of the chelated metal atom (Kroschwitz and Grant, 1982; Snoeyink and Jenkins, 1982; Stumm and MorGan, 1996).

Most chelating agents are linear or branched chains where the donor atoms are separated by suitable numbers of other atoms to allow the formation of the chelate rings. However, there are also classes of chelating agents where the donor atoms are contained within macrocyclic structures. The

pattern of fused rings centered about the metal. Another group of macrocyclic ligands that have been extensively studied are the cyclic polyethers in which the donor atoms are either oxygen functions separated by two or three carbon atoms.

Compounds having more than one kind of heteroatom in the ring are called mixed-donor macrocycles. Three-dimensional, polymacrocyclic chelating agents are formed by joining bridgehead structures with chains that contain properly spaced donor atoms. Such bicyclic structure forms a cavity that holds a metal coordinated to the donor atoms in the surrounding chains. Other groups that are at least trifunctional can serve as bridgeheads. The donor atoms of the bridge may all be O, N, or S, or the compounds may be mixed donor macrocycles in which the bridge strands contain combinations of these donor atoms. Incorporating ligand groups into a cross-linked polymer structure gives the chelate-forming resins that perform ion-exchange functions by chelation. The ligand groups may either be present in the monomer before polymerization, or they may be attached to be performed polymer by appropriate reactions (Kroschwitz and Grant, 1982; Snoeyink and Jenkins, 1982; Stumm and MorGan, 1996).

Chelating agents may be either organic or inorganic compounds, but the number of inorganic agents is very small. The best known inorganic chelating agents are polyphosphates. The annual consumption of these compounds exceeds that of all the organic chelating agents combined. Besides the conventional empirical and structural formulas, chelating compounds and chelates are often represented by type formulas. Chelators having proton acid groups may be shown as H_nA , or if partially dissociated, as H_mA^{n-} . Alcohol or phenol groups that lose protons on chelation are shown as $A(OH)_n$. The letter A may be used to represent an entire multidentate ligand molecule or to show only a donor atom as in A-A-A-A for a tetradentate ligand (Kroschwitz and Grant, 1982; Stumm and MorGan, 1996).

The rates of formation and dissociation of displacement reactions are important in the practical applications of chelation. Complexation of many metal ions, particularly the divalent ones, is almost instantaneous, but reaction rates of many higher valence ions are slow enough to measure by ordinary kinetic techniques. Rates with some ions, notably Cr(III) and Co(III), may be very slow. Systems that reach equilibrium rapidly are termed kinetically labile, and those that are slow are called kinetically inert and may be unstable in the thermodynamic equilibrium sense. The stability constants of the multidentate complexes usually are from one to several orders of magnitude greater than those of monodentate complexes. The greater stability of chelates is largely the result of an increase in entropy resulting from an increase in number of free molecules, usually solvent or other monodentate ligand, liberated as the chelate is formed. This extra stabilization produced by the ring formation is called the chelate effect (Kroschwitz and Grant, 1982; Snoeyink and Jenkins, 1982; Stumm and MorGan, 1996).

Many parameters influence the stability of chelates. Several of the stability factors common to

all chelate systems are the size and number of rings, substituents on the rings, and the nature of the metal and donor atoms. In the macrocyclic complexes, the degree to which the size of metal ion fits the space enclosed by the macro rings is a significant factor. In chelation, five- and six-membered rings are most stable: coordination angles on the metal atoms prohibit the formation of three-membered rings, and ring closure is improbable for rings having more than seven members. In these latter systems, coordination in linear chains is a competing reaction. Formation of each additional ring by the same ligand contributes extra stability from the entropy effect of displacing coordinated solvent molecules. Substituents on a ring may also produce steric hindrance, or otherwise alter the availability of the donor atom electrons for coordination. The stability constants are usually influenced by more than one of the parameters that are known to affect chelate stability. In some cases, the size of ring, number of rings for similar donor atoms, and whether one or more ligand molecule forms the rings will influence the chelate stability.

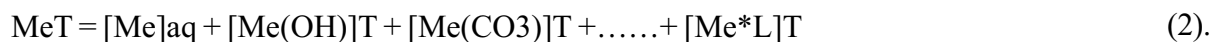
Equilibrium Chemistry

Equilibrium chemistry is important when considering the solubility of a particular metal. In homogeneous solution, the equilibrium constant for the formation of the chelate complex from the solvated metal ion and the ligand in its fully dissociated form is called the formation or stability constant. Whereas the ligand displaces solvent molecules coordinated to the metal, these solvent molecules do not generally enter into the equations. When more than one ligand molecule complexes with a metal atom, the reaction usually proceeds stepwise. Equilibrium constant for complex are usually stated for reactions written in the direction of the following complex formula:



Thus, $K(\text{equilibrium constant}) = \frac{\{\text{complex}\}}{[\{\text{ligand}\}^n \{\text{central metal ion}\}^m]}$.

When stated for a complex formation reaction, the equilibrium constant is called a formation or a stability constant. Conversely, if the equilibrium constant is stated for the dissociation of the complex, it is called dissociation or an instability constant (Smeth and Martell, 1989; Snoeyink and Jenkins, 1982; Stumm and MorGan, 1996). Large values of stability constants indicate stable complexes. For example,



In order to be effective at extracting metals from soil or the aqueous phase, a ligand must overcome competing metal precipitation as hydrous oxide and/or as carbonate precipitates, and surface complexation and precipitation on soil particles.

Experimentally determined equilibrium constants are usually calculated from concentrations rather than from the activities of the species involved (Tuin and Tels, 1990; Bart et al., 1990; Yu and Klarup, 1994; Nigond, Musikas, and Cuillerdier, 1994; Cerna, 1995; Dietz et al., 1996; Clevenger,

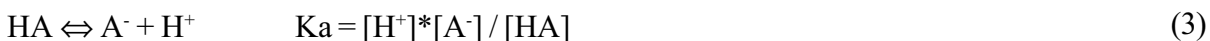
1990; Yong, Galvez-Cloutier, and Phadungchewit, 1993). Thermodynamic constants, based on ion activities, require activity coefficients. Because of the inadequacy of present theory for either calculating or determining activity coefficients for the complicated ionic structures involved, the relatively few known thermodynamic constants have usually been obtained by extrapolation of results to infinite dilution. The constants based on concentration have usually been determined in dilute solution in the presence of excess inert ions to maintain constant ionic strength. Thus concentration constants are accurate only under conditions reasonably close to those used for their determination. Beyond these conditions, concentration constants may be useful in estimating probable effects and relative behaviors, and chelation process designers need to make allowances for these differences in conditions. The practical significance of formation constant is that a high log K value means a large ratio of chelated to unchelated or free metal when equivalent amounts of metal and ligand are present.

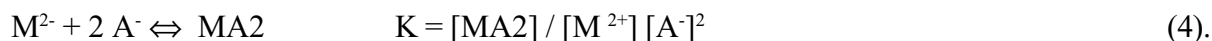
Species in solution are generally in formation-dissociation equilibrium, and displacement reactions of any given metal or ligand by another are possible. The addition of a chelating agent to a solution of two or more metal ions leads to an order of metal ion complexation that is regulated by displacement equilibrium constants. If the objective is to bind only a particular ion, then enough chelant to combine with the target ion and all the other ions that are capable of displacing the target ion should be added. For selective complexation of one metal in the presence of another, a chelating agent with sufficiently different stability constants for the two metals is necessary.

pH Effects

Being Lewis bases, the donor atoms of chelating agents react with Lewis acids such as metal and hydrogen ions. In the pH range of aqueous solution, most of the well-known chelating agents exist as an equilibrium mixture of both protonated and unprotonated forms. Metal ions compete with hydrogen ions for the available donor atoms, and therefore, simultaneous equilibria exist that are treated mathematically by the simultaneous equations for the formation constants of the chelates and the acid dissociation constants of the chelating agents.

In aqueous systems, water is a competing ligand, and its dissociation into hydrogen and hydroxyl ions must often be considered in the system of simultaneous equilibria. In nonaqueous solvents, similar treatment is possible with appropriate modifications for the acidity in those systems. The pH-leveling effect of water affects and limits the acid dissociation behavior of chelating agents in aqueous systems. However, coordination with certain metals in aqueous solution can result in loss of a proton from aliphatic –OH and –NH₂ groups. Consider the equilibrium in an aqueous system composed of a bidentate ligand HA, eg, the enol form of acetylacetone, and a tetracoordinate metal M²⁺. The equations are





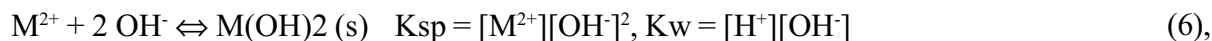
Given the relation

$$[M^{2+}] = [H^+]^2 * \{[MA_2] / [HA]^2\} * \{1/K * K_a^2\} \quad (5),$$

equation (5) shows that an increase in acidity of the solution increases the concentration of uncomplexed metal, which must result from the displacement of M^{2+} from MA_2 , causing a simultaneous decrease in the ratio of complexed to free ligand $[MA_2]/[HA]$. The opposite effects result upon decreasing the acidity. This behavior occurs in the pH range where appropriate amounts of both HA and A^- coexist. Outside this range, the ligand is present almost entirely as either HA or MA_2 and A^- , and the system is essentially independent of pH.

The displacement of hydrogen ions by a metal ion from a protonated form of the chelating agent generates an autogenous pH that depends on the base strength of the counterions of the metal salt. The pH of the solution can become quite low if these counterions are those of a strong acid, eg, Cl^- or SO_4^{2-} . However, the pH of chelate solutions can be controlled by the use of compatible buffers, and the chelating agent itself can sometimes serve as the pH buffer if its acid dissociation stages occur in the desired pH range.

In the aqueous solution, metal ions may form insoluble forms of metal hydroxides with hydroxides:



and from these

$$pM = 2 pH + \log (K_w^2 / K_{sp}) \quad (7).$$

Equations 6 and 7 indicate that the more stable the chelate, the higher the pH it can maintain, and the higher pH required to precipitate the metal hydroxide. It also can be seen that the smaller the solubility product constant K_{sp} , i.e., the more insoluble the metal hydroxide, the higher the pM that a chelate must maintain to prevent precipitation. If instead of hydroxyl ion the precipitating agent is the anion of an acid stronger than or comparable in strength to the chelating agent, the metal salt may be insoluble at higher pH where the complexing form of the ligand is relatively more available. The pH effect in chelation is utilized to liberate metals from their chelates that have participated in another stage of a process, so that the metal, chelant, or both can be separately recovered. Metals can also be displaced as insoluble salts or hydroxides in high-pH domains where the pM that can be maintained by the chelate is less than that allowed by the insoluble species (Hong, Chen, and Macauley, 1995; Snoeyink and Jenkins, 1982; Stumm and Morgan, 1996).

APPROACH

Effectiveness of Complexation

The soil is a dynamic system, a heterogeneous mixture of organic and mineral components with differences of pH values, redox conditions, moisture content, and undergoing gradual alterations in response to changes in management and environmental factors. Heavy metals in the soil environment can be involved in a series of complex chemical and biological interactions. Humic substances are an extremely complex and diverse group of organic materials in soil. Humic substances with function groups of carboxyl, carbonyl, ether, ester, phenolic, alcohol, and methoxyl undoubtedly have the ability to combine or bind with considerable quantities of metal ions. Several of the reactions include oxidation-reduction, precipitation-dissolution, volatilization, and surface-solution phase complexations are taking place in soil environment (Alloway, 1995; Selim and Amacher, 1997; Cernik et al., 1994; Snoeyink and Jenkins, 1982; Yong, Galvez-Cloutier, and Phadungchewit, 1993). The strength of the chelating agent must overcome those reactions in order to extract the target metal from the soil environment. The strong chelators with target metals will have much greater solubility and stability (i.e., stability constant pK) than other reactions with metals in the aqueous phase (Hong, Chen, and Macauley, 1995; King, 1987; Kroschwitz and Grant, 1982; Smith and Martell, 1989; Snoeyink and Jenkins, 1982; Stum and MorGan, 1996). This strength can be shown as $pK_{\text{chelators}}/pK_{\text{natural ligands}}$. The greater this ratio, the stronger this chelator will be.

Selectivity to Target Metals

The selectivity of chelating agents to target metal can be shown as “selectivity ratio (SR)” which is defined as $M\text{-}L_{\text{tot}} / \text{Fe-}L_{\text{tot}}$, $M\text{-}L_{\text{tot}} / \text{Ca-}L_{\text{tot}}$, $M\text{-}L_{\text{tot}} / \text{Mg-}L_{\text{tot}}$, or $M\text{-}L_{\text{tot}} / \text{Al-}L_{\text{tot}}$, since we do not want to extract those ambient cations out of the soil environment. The greater selectivity ratio for the target metal indicates a strong preference of the target metals by the chelating agent.

Recoverability of Chelators

The major mechanisms to retain heavy metals in soil are carbonate, hydroxide, and organic function groups with humic substances. The retention of heavy metals depends on type of heavy metal, soil constituents, and pH of soil solution (2, 3, 10, 26, 33). In general, precipitation mechanisms dominate at high pH of soil solution and cation exchanges become dominant at low pH soil solution. After chelators extract the target metal or radionuclides, the same approach is used to increase pH to form metal salts with hydroxide, carbonate, or other natural inorganic ligands. The metal salt is usually insoluble at higher pH. The pH effect in chelation is utilized to liberate metals from their chelates that have participated in another stage of a process so that the metal, chelant, or both can be separately recovered.

RESULTS AND DISCUSSIONS

The major objectives of this project are to 1) determine the complexation effectiveness of numbers of chelating agents with various target metals, 2) determine the selectivity of target metal contamination, and 3) determine the reusability of selected chelating agents.

Determine the complexation effectiveness of numbers of chelating agents with various target metals

In this task, a large number of thermodynamic databases will be collected from existing literatures (Hogfeldt, 1982; Smith and Martell, 1989; National Bureau of Standards; Stumm and MorGan, 1996). These data include acid-base equilibrium constants of the chelators, complexation constant of the chelators with target metals, and target metal speciation constants with natural ligands. Since only a limited number of chelators have been investigated for remediation and some of complexation constants for those chelators are not available, the performance of suitable chelators on target metals and the unavailable complexation constants may be evaluated and predicted by equilibrium modeling and computations based on connectivity index, structure-activity relationship, and mathematical computation. This will be done by using mathematical computation of this thermodynamic database to determine the strength, stability, and effectiveness of chelators with target metals.

About 291 different kinds of chelating agents vs. 30 different kinds of heavy metals or radionuclides have been collected in one database. Some surrogate metals are used because of very limited stability constants available. All surrogate metals were chosen based on correlation of available and mutual pK values and also consideration of similar chemical properties, such as oxidation states, hydrolysis, complex ion formation, metallic state, and solid compounds. In general, the same group of metals in the periodical table will be the primary candidates of correlation. We accept the same group of metals and/or with 90% of correlation to our target metals as surrogate metals. As a result, barium is the surrogate metal for radium (only 2 pK value available); lead is the surrogate metal for thorium (only 23 pK value available); and uranium is the surrogate metal for plutonium (only 11 pK value available).

Determine the Selectivity of Target Metal Contamination

Since only certain target metals in contaminated soils would be extracted out of the soil environment, other metals (i.e., Fe, Ca, Mg, and Al) will stay in soils. The selectivity of chelating agents to the target metal can be shown as a "selectivity ratio (SR)" which is defined as $M\text{-L}_{\text{tot}} / \text{Fe-L}_{\text{tot}}$, $M\text{-L}_{\text{tot}} / \text{Ca-L}_{\text{tot}}$, $M\text{-L}_{\text{tot}} / \text{Mg-L}_{\text{tot}}$, or $M\text{-L}_{\text{tot}} / \text{Al-L}_{\text{tot}}$. In this task, the selectivity to target metals will be computed on the basis of a large number of data for chelating agents. Many mathematical computations have been performed on those target metals and radionuclides (Ra, Ra, Th, Pb, Pu, and U). Chelators with an SR ratio greater than 1.5 were chosen (especially for Ca and Mg), because of the indication that chelators have greater tendency to form complex with target metal/radionuclides rather than ambient metals (see Tables 1, 2, and 3).

Determine the Reusability of Selected Chelating Agents

It is more cost-effective if the chelating agents can be used repeatedly. Changing the pH level to precipitate out metal salts from chelating complexes is major method to recover the chelators. In addition to recovery of chelators and heavy metals by pH adjustment, this work will also evaluate the other cationic and anionic precipitants. Numbers of the computation will be performed to determine the recoverability of chelators. Complexity calculations and diagrams have been performed to evaluate the recoverability of target metals (Ra, Ra, Th, Pb, Pu, and U) under certain controlled solids. Some degrees of complexation diagrams of various chelating agents to target metals or radionuclides as a function of pH are shown in Figures 1, 2, and 3. Chelators with a pK_M to pK_L inorganic ligands ratio smaller than 1.0 were chosen, which indicates the inorganic ligands have the ability to replace the chelators by increasing the pH (see Tables 1, 2, and 3).

Since we would like to have a recoverable chelator with enough strength to overcome all kinds of reactions in soils to form a stable complex and one also likely to extract less ambient metals from soils, the order of choosing suitable chelators to target metal/redionuclide will be recoverability, effectiveness, and selectivity. For Ra and Ba as shown in Table 1, EDTA, DTPA, and NTPA all are reusable and have good strength but relative less selectivity to ambient metals. The reason for poor selectivity is that Ra, Ba, Ca, and Mg are in the same II A group, which has a very similar chemical property. For Th and Pb, as shown in Table 2, 2-Aminoethanethiol, EDTA, DTPA, TEDTA, and ADA are the proper chelators to met the criteria, especially for good selectivity. For Pu and U, as shown in Table 3, IDA, NTA, and EDDA are chosen. Both radionuclides exist in the oxidation state of III, IV, V, VI, and even VII for Pu, the reason to present as VI is simply because more stability constants are available. The metal salts can be carried out as solids are varied with different oxidation states. Although we chose UO₂CO₃(s) as a product of precipitation as shown in Figure 3, other metal salts may also be present; for example, (UO₂)₃(PO₄)₂·4H₂O(S) with solubility product constant about 10^{-53.28}, U(OH)2SO₄(S) with solubility product constant about 10^{-31.17}, U(HPO₄)₂(S) with solubility product constant about 10^{-30.49}, and Pu(OH)₄(S) with solubility product constant about 7*10⁻⁵⁶ (Suresh, Srinivasan, and Vasudeva Rao, 1994; McKetta, et al., 1983; Kroschwitz and Grant, 1982; Preston and du Preez, 1995; Nigond, Musikas, and Cuillerdier, 1994).

CONCLUSIONS

Based on the sequence order of recoverability, effectiveness, and selectivity to screen all chelating agents to target contaminants, heavy metals or radionuclides seem to be the most cost-effective way to obtain suitable and inexpensive chelators. Even though limited numbers of thermodynamic stability constants are available, mathematical computation, basic chemical structure relationships, and chemical properties can be also beneficial to evaluate the proper chelating agents. For remediation of radium- and barium-contaminated soils, EDTA, DTPA, and NTPA are the

suggestions. For remediation of lead- and thorium-contaminated soils, 2-Aminoethanethiol, EDTA, DTPA, TEDTA, and ADA are recommended. For soils contaminated by plutonium and uranium, IDA, NTA, and EDDA are good choices for remediation. For future work, laboratory verification of predicted results are ongoing. Evaluation of predictive methods will be benefited by comparison of laboratory results to predicted data.

ACKNOWLEDGMENT

We thank the Argonne National Laboratory for funding of this work.

REFERENCES

- Alloway, B.J., *Heavy metal in soils*, 2nd Edition, Blackie Academic & Professional, NY, 1995.
- Bart, H.-J., R. Marr, J. Drexler, and J. Hartl, "Heavy Metal Recovery by Extraction and Permeation in Incineration Processes," *Chem. Eng. Technol.* 13 (1990), pp.313-318.
- Bosilovich, B.E., and N.J. Kardos, "Emerging Technology Summary: Acid extraction treatment system for treatment of metal contaminated soil," EPA report 540/SR-94/513, Aug 1994.
- Cerna, M., "Use of solvent extraction for removal of heavy metal from liquid wastes," *Environmental Monitor Assessment*, Jan 1995, v34, n2, p151.
- Cernik, M., P. Federer, M. Borkovec, and H. Sticher, "Modeling of Heavy Metal Transport in a Contaminated Soil," *J. Environ. Qual.* 23: 1239-1248 (1994).
- Clevenger, T.E., "Use of Sequential Extraction to Evaluate the Heavy Metals in Mining Wastes," *Water, Air and Soil Pollution* 50: 241-254, 1990.
- Dietz, M.L., E.P. Horwitz, S. Rhoads, R.A. Bartsch, and J. Krzykawski, "Extraction of Cesium from Acidic Nitrate Media Using Macrocylic Polyethers: The Role of Organic Phase Water," *Solvent Extraction and Ion Exchange*, 14(1), 1-12 (1996).
- Fergusson, J.E., *The heavy elements chemistry, environmental impact and health effects*, 1st Edition Pergamon Press, Inc. NY 1990.
- Hogfeldt, E., "Analytical Chemistry Division, Commission on Equilibrium Data-Stability Constant of Metal-ion Complexes, Part A: Inorganic Ligands," *International Union of Pure and Applied Chemistry*, IUPAC Chemical Data Series, No 21, Pergamon 1982, NY.
- Hong, A., T.C. Chen, and E. Macauley, "Selection and Test of Effective Chelators for Removal of Heavy Metals from Contaminated Soils," *Canadian Journal of Civil Engineering*, Vol 22, n 6, 1995, pp.1185-1197.
- Judson King, C., "Separation processes based on reversible chemical complexation" *Handbook of Separation Process Technology*, 1987 John Wiley & Sons. Inc.
- Kroschwitz, J.I., and M.H. Grant, "Actinides and Transactinides," *Encyclopedia of Chemical Technology*, 4th Edition, 1982 John Wiley & Sons Inc. Vol 1, pp. 456-488.
- Kroschwitz, J.I., and M.H. Grant, "Barium," *Encyclopedia of Chemical Technology*, 4th Edition, 1982 John Wiley & Sons Inc. Vol 3, pp. 902-931.

- Kroschwitz, J.I., and M.H. Grant, "Chelating Agents," *Encyclopedia of Chemical technology* 4th Edition 1982 John Wiley & Sons, Inc. Vol 5, pp764-795.
- Kroschwitz, J.I., and M.H. Grant, "Radioactivity, Natural," *Encyclopedia of Chemical Technology*, 4th Edition, 1982 John Wiley & Sons Inc. Vol 19, pp. 639-681.
- Kroschwitz, J.I., and M.H. Grant, "Radioisotopes," *Encyclopedia of Chemical Technology*, 4th Edition, 1982 John Wiley & Sons Inc. Vol 19, pp. 682-785.
- Kroschwitz, J.I., and M.H. Grant, "Thorium and Thorium Compounds," *Encyclopedia of Chemical Technology*, 4th Edition, 1982 John Wiley & Sons Inc. Vol 22, pp. 989-1002.
- Kroschwitz, J.I., and M.H. Grant, "Plutonium and Plutonium Compounds," *Encyclopedia of Chemical Technology*, 4th Edition, 1982 John Wiley & Sons Inc. Vol 18, pp. 278-301.
- Mcketta, J.J., "Barium Compounds," *Encyclopedia of Chemical Processing and Design*, Vol 2, Marcel Dekker. Inc. NY 1983, pp. 50-63.
- Miller, R.L., A.B. Pinkerton, P.K. Hurlburt, and K.D. Abney, "Extraction of Cesium and Strontium into Hydrocarbon Solvents Using Tetra-c- Alkyl Cobalt Dicarbollide," *Solvent Extraction and Ion Exchange*, 13(5), 813-827 (1995).
- National Bureau of Standards, *Selective Values of Chemical Thermodynamic Properties-Series 1*, Technical Note 270-8, Table 88 &90.
- Nigond, L., C. Musikas, and C. Cuillerdier, "Extraction by N, N, N',N'- Tetraalkyl- 2 Alkyl Propane-1,3 Diamines. II. U(VI) and Pu(IV)," *Solvent Extraction and Ion Exchange*, 12(2), 297-323 (1994).
- Preston, J.S., and A.C. du Preez, "Solvent Extraction of Uranium(VI) and Thorium(IV) from Nitrate Media by Carboxylic Acid Amines," *Solvent Extraction and Ion Exchange*, 13(3), 391-413 (1995).
- Pretel, E.J., P.A. Lopez, S.B. Bottini, and E.A. Brignole, "Computer-Aided Molecular Design of Solvents for Separation Processes," *AIChE Journal*, Aug 1994 Vol. 40, No. 8, pp.1349-1360.
- Reed, B.E., M.R. Matsumoto, J.E. Van Benschoten, and P.J. Mcgarvey, "Metal removal by soil washing for an Iron oxide coated soil," *Water Environment Research*, Mar-Apr 1994, v66, n2, p168.
- Salomons, W., U. Forstner, and P. Mader, *Heavy metals*, Springer-Verlag Berlin Heidelberg 1995.
- Selim, H.M., and M.C. Amacher, *Reactivity and transport of heavy metals in soils*, CRC Press Inc. NW 1997.
- Smith, R.M., and A.E. Martell, *Critical Stability Constants*, 1989 Plenum Press Vol 1-6.
- Snoeyink, V.L., and D. Jenkins, *Water Chemistry*, John Wiley & Sons, Inc. 1982, NY.
- Srinivasan, T.G., A. Suresh, R. Prasanna, N. Jayanthi, and P.R. Vasudeva Rao, "Metal-Solvate Stoichiometry Evaluation in Extractions by Slovating Type Neutral Extractions-a Novel Approach," *Solvent Extraction and Ion Exchange*, 14(3), 443-458 (1996).

- Stoeppler, M., *Hazardous metals in the environment*, Elsevier Science Publishers B.V. 1992.
- Stumm, W., and J.J. MorGan, *Aquatic Chemistry*, 3rd Edition, 1996 John Wiley & Sons, Inc. pp252-424.
- Suresh, A., T.G. Srinivasan, and P.R. Vasudeva Rao, "Extraction of U(VI), Pu(IV) and Th(IV) by Some Trialkyl Phosphates," *Solvent Extraction and Ion Exchange*, 12(4), 727-744 (1994).
- Tuin, B.J.W., and M. Tels, "Removing heavy metals from contaminated clay soils by extraction with hydrochloric acid, EDTA or hypochlorite solutions," *Environmental Technology*, Nov 1990, v11, n11, p1039.
- Yong, R.N.; Galvez-Cloutier, R., and Phadungchewit, Y., "Selective Sequential Extraction Analysis of Heavy –Metal Retention in Soil," *Canadian Geotechnical Journal*, Vol 30 n5 Oct 1993, pp. 834-847.
- Yu, J., and D. Klarup, "Extraction Kinetics of Copper, Zinc, Iron, and Manganese from Contaminated Sediment Using Disodium Ethylenediaminetetraacetate," *Water, Air and Soil Pollution* 75: 205-225, 1994.

Chelating Agents	Formula	^a pK _{eq} -Ba ²⁺ ML/M.L.	^b pK-Ba/pK _{sp} -Ba(OH) ₂ Recoverability	^c pK-Ba ²⁺ / pK-Mg ²⁺	pK-Ba ²⁺ / pK-Fe ²⁺	pK-Ba ²⁺ / pK-Fe ³⁺	pK-Ba ²⁺ / pK-Ca ²⁺	pK-Ba ²⁺ / pK-Al ³⁺	^d Estimated Price
Ethylenedinitrilotetra- acidic acid (EDTA)	*C ₁₀ H ₁₆ O ₈ N ₂	7.86	0.59	0.89	0.31	0.55	0.74	0.48	\$17.90 (500g) \$78.50 (3 Kg)
Diethylenetrinitri- pentaacetic acid (DTPA)	C ₁₄ H ₂₃ O ₁₀ N ₃	8.78	0.66	0.94	0.31	0.54	0.82	0.47	
Nitritoltris(methylene)tri- phosphonic acid (NTTA)	*C ₃ H ₁₂ O ₉ NP ₃	6.5	0.49	0.9	N/A	N/A	0.87	N/A	\$17.00(100g) \$22.05(1 Kg)

^{*}Correlations between pK-Ca²⁺ to pK_{Ba}²⁺ (r=0,883) and pK-Mg²⁺ to pK-Ca²⁺ (r=0,914) => pK-Ra²⁺ will have good correlation with pK-Ba²⁺
^aThe value of pK_{eq}-Ba²⁺ indicates the strength/stability of chelating complexation.
^bThe value of recoverability (pK-Ba²⁺/pK_{sp}-Ba(OH)₂) => The smaller value indicates greater recoverability.
 pK_{eq} value of Ba(OH)₂ = 13,3 from Minteq2 software.
^cThe selectivities are based on pK_{eq}-Ba²⁺ / pK_{eq}-M (Ca, Mg, Fe, Al, etc.)
^dAvailable on "Aldrich Chemical Comany" (Catalog handbook of fine chemicals 1996-1997); Price also from Aldrich Chemical Company.

Chelating Agents	Formula	^a pK _{eq} -Pb ²⁺ ML/M.L.	^b pK-Ba/pK _{sp} -Pb(OH) ₂ Recoverability	^c pK-Pb ²⁺ / pK-Mg ²⁺	pK-Pb ²⁺ / pK-Fe ²⁺	pK-PbBa ²⁺ / pK-Fe ³⁺	pK-Pb ²⁺ / pK-Ca ²⁺	pK-Pb ²⁺ / pK-Al ³⁺	^d Estimated Price
2-Aminoethanethiol	C ₂ H ₇ NS	11.1	0.56	4.83	N/A	N/A	5.02	N/A	\$21.75 (25g) \$69.45 (100g)
Ethylenedinitrilotetra- acidic acid (EDTA)	C ₁₀ H ₁₆ O ₈ N ₂	18.0(23.2)	0.91	2.03	1.26	0.72	1.69	1.09	\$17.90 (500g) \$78.50 (3 Kg)
Diethylenetrinitri- pentaacetic acid (DTPA)	C ₁₄ H ₂₃ O ₁₀ N ₃	18.66(26.40)	0.94	2.00	1.14	0.67	1.74	1.00	\$17.90 (500g) \$78.50 (3 Kg)
Thiobis(ethylenitrilo) tetraacetic acid (TEDTA)	C ₁₂ H ₂₀ O ₈ N ₂ S	13.69	0.69	2.94	1.18	0.67	2.21	N/A	
N-2-acetamidoimino- diacetic acid (ADA)	C ₆ H ₁₀ O ₅ N ₂	8.4	0.42	3.31	N/A	N/A	2.12	N/A	\$12 (5 g) \$88 (100 g)

^{*}Correlations between pK_{eq}-Th⁴⁺ and pK_{Pb²⁺ is 0,911(R=0,911, R²=0,83). Pb is end product of Thorium after any kind of decay.}

^aThe value of pK_{eq}-Pb²⁺ indicates the strength/stability of chelating complexation.

^bThe value of recoverability (pK-Pb²⁺/pK_{sp}-Pb(OH)₂) => The smaller value indicates greater recoverability.

pK_{sp} of Pb(OH)₂ = 19,8447 (from "Handbook of Chemistry & Physics," 77th edition 1996-97, CRC Press, Inc., New York.

^cThe selectivities are based on pK_{eq}-Pb²⁺ / pK_{eq}-M (Ca, Mg, Fe, etc.)

^dAvailable on "Aldrich Chemical Company" (Catalog handbook of fine chemicals 1996-1997); and Fluka Chemical Company.

Chelating Agents	Formula	^a pK _{eq} -UO ₂ ²⁺ (pK-PuO ₂ ²⁺)	^b pK-U/pK _{sp} UO ₂ CO ₃ Recoverability	^c pK _{eq} -UO ₂ ²⁺ / pK _{eq} -Mg ²⁺	pK _{eq} -UO ₂ ²⁺ / pK _{eq} -Fe ²⁺	pK _{eq} -UO ₂ ²⁺ / pK _{eq} -Fe ³⁺	pK _{eq} -UO ₂ ²⁺ / pK _{eq} -Ca ²⁺	pK _{eq} -UO ₂ ²⁺ / pK _{eq} -Al ³⁺	^d Estimated Price
Iminodiacetic acid (IDA)	C ₄ H ₇ O ₄ N	8.96(8.50)	0.62	3.01	1.55	0.84	3.33	1.11	\$7.4 (25 g) \$20.5 (500 g)
Nitrilotriacetic acid (NTA)	C ₆ H ₉ O ₆ N	9.5(6.91)	0.66	1.73	1.08	0.6	1.48	0.83	\$10.85 (100 g) \$26.8 (500 g)
Ethylenediiminodiacetic acid (EDDA)	C ₆ H ₁₂ O ₄ N ₂	11.41	0.79	2.96	N/A	N/A	N/A	N/A	\$16.35 (1g) \$54.35 (5 g)

^aCorrelations between pK_{eq}-UO₂²⁺ and pK_{eq}-PuO₂²⁺ is 0,903(R=0,903, R²=0,815). Both are *Actinides. (Atomic number U[92], Pu[94]). The actinide elements are a group of chemically similar elements with atomic numbers 90 through 103.

^bThe value of pK_{eq}-UO₂²⁺ indicates the strength/stability of chelating complexation.

^cThe value of recoverability (pK-UO₂²⁺/pK_{sp}-UO₂CO₃) => The smaller value indicates greater recoverability.

-pK_{sp} of UO₂CO₃ = 14.47 (from "Chemical Thermodynamics of Uranium," North-Holland, NY, 1992)

^dThe selectivities are based on pK_{eq}-UO₂²⁺ / pK_{eq}-M (Ca, Mg, Fe, Al, etc.)

^ePrices are available on "Aldrich Chemical Company" (Catalog handbook of fine chemicals 1996-1997; and Fluka Chemical Company).

Figure 1. Degree of complexation Ba²⁺ (Ra²⁺).

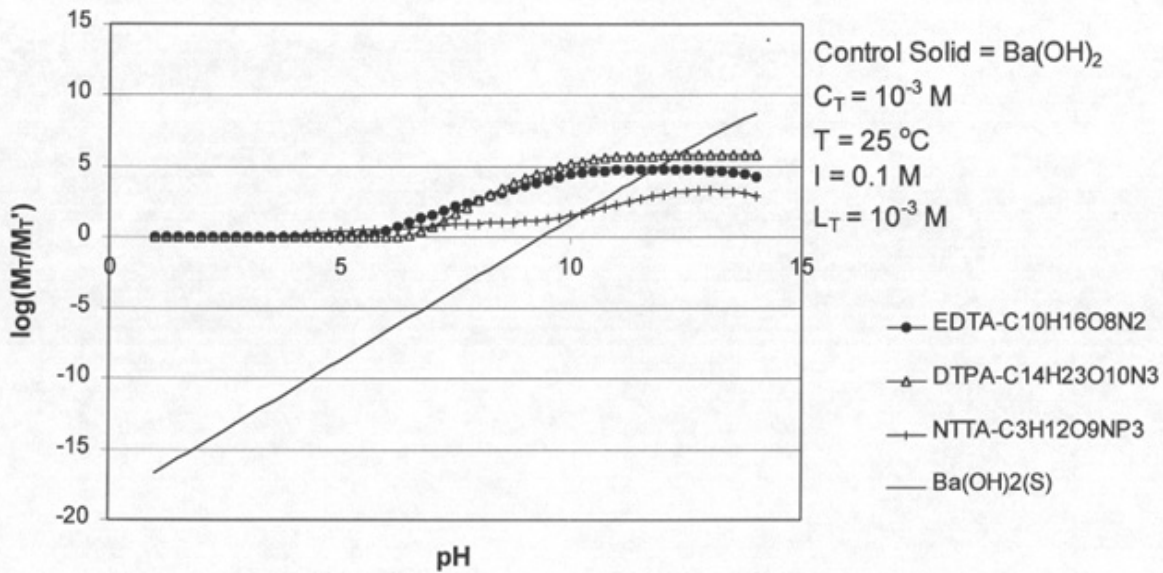


Figure 2 Degree of complexation Pb²⁺ (Th⁴⁺)

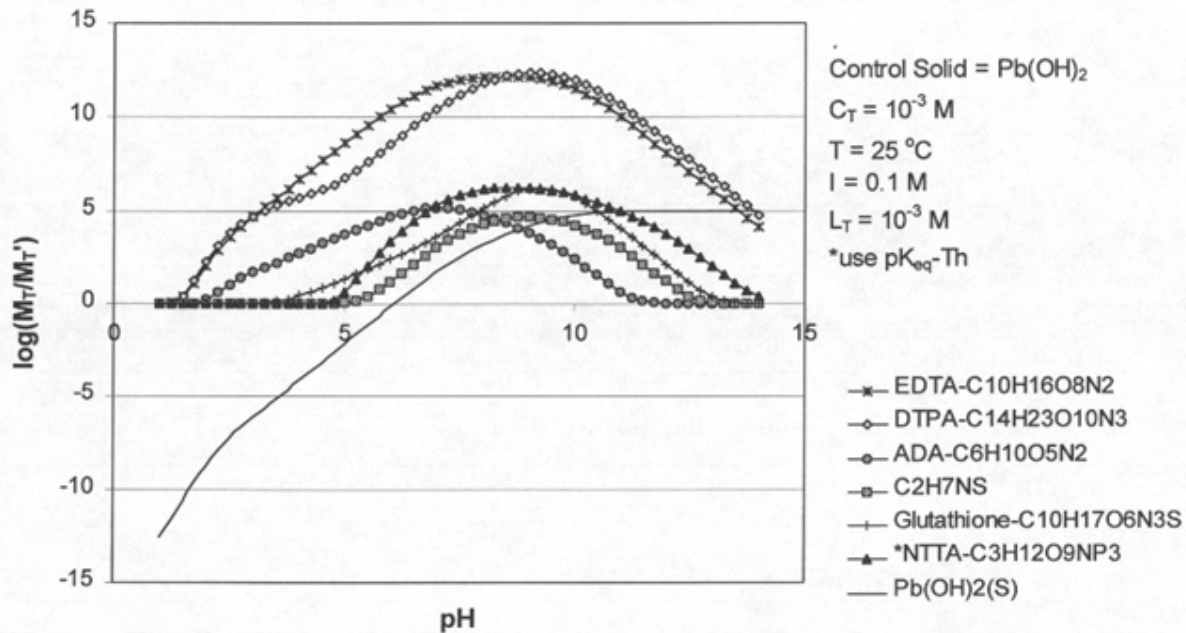


Figure 3. Degree of complexation UO_2^{2+} (PuO_2^{2+}).

