Organic Components of Nuclear Wastes and Their Potential for Altering Radionuclide Distribution When Released to Soil

K. M. McFadden

August 1980

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WHEN RELEASED TO SOIL

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ABSTRACT

Normal waste processing at the Hanford operations requires the use of many organic materials, chiefly in the form of complexing agents and diluents. These organic materials and their chemical and radiolytic degradation products, have potential for complexing fission products and transuranium elements, both in the waste streams and upon infiltration into soil, perhaps influencing future sorption or migration of the nuclides.

Particular complexation characteristics of various nuclides which constitute the major fission products, long-lived isotopes, and the most mobile in radioactive wastes are discussed briefly with regards to their anticipated sorption or mobility in soils. Included in the discussion are Am, Sb, Ce, Cs, Co, Cm, Eu, I, Np, Pm, Pu, Ra, Ru, Sr, Tc, U, and Zr.

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ORGANIC COMPONENTS OF NUCLEAR WASTES AND THEIR POTENTIAL FOR ALTERING RADIONUCLIDE DISTRIBUTION WHEN RELEASED TO SOIL

INTRODUCTION

As of March, 1975, an estimated 58 million gallons of liquid and solidified high level radioactive wastes were stored at the Hanford waste storage site.⁽¹⁾ The waste volume, which is being decreased by evaporation and salt cake formation, was the result of processing fuel from nine production reactors to extract plutonium, and represents about 90% of the total high-level waste expected to be generated through the operation period of the Hanford plutonium production facilities.^(1, 2) The combined output of high-level waste from the one production reactor (N Reactor) still operating and the scheduled reopening of the Purex processing plant is expected to be 1 million gallons per year.⁽¹⁾

In addition to high level liquid wastes, large volumes of low-level liquid wastes are produced during processing. Depending on the nuclides present and their concentration, these wastes face such treatment as: ion exchange, evaporation, retention to allow for radionuclide decay, and release to controlled areas such as soil columns, seepage basins, evaporative ponds, or retention ponds.⁽¹⁾

Normal waste processing requires large amounts of organics (solvent extractants, diluents, etc.). The bulk of the organic wastes are segregated from the aqueous portion⁽²⁾ for storage or subsequent disposal.⁽³⁾ Most of the high-level aqueous waste is a concentrated sodium nitrate solution containing small amounts of organics, mainly resins, sugar, solvents, and miscellaneous organic materials.^(4, 5) Even after evaporation, the organic content is not expected to exceed 1% of the salt cake.^(4, 6) However, the actual state of the organics present is unknown,⁽⁴⁾ and presumed complex. These organics can potentially complex fission products and transuranium elements, both in the waste streams and upon infiltration into soil, greatly influencing future sorption or migration of the nuclides.

COMPLEX FORMATION

Understanding the nature of complex formation^(7, 8) is requisite for analysis of any potential chelate effect in a soil system. Chelating agents are usually Lewis bases, which require electron acceptors for complex formation. When chelation results in bonds of ionic character, the stability of the complex generally increases with increasing metal charge or decreasing metal ionic radius. With more covalent bonding, complex stability tends to increase with increasing electronegativity. The more bonding groups, or the higher the charge of a ligand, the higher the formation constant of the complex. Unlike their analogous simple metal complexes, metal chelates maintain their stability in very dilute solutions and this stability increases markedly with the number of rings formed during the chelation process. For aliphatic groupings, five-membered rings are the most stable. Further stability results if resonance is also possible. The nature of available donor atoms, steric considerations, and the chemical environment also affect complex stability. Stability constants for various ligands, metals, and chemical systems have been tabulated where known.^(9, 10)

A metal chelate or complex will resist further reaction if the number of donor groups equals the coordination number of the metal ion. However, if these numbers differ several reactions are possible: formation of mixed ligand complexes or mixed-metal polynuclear complexes; hydrolysis, with possible hydroxide bridging to form polynuclear complexes; or disproportionation of metal, with possible metal hydroxide precipitation. Since the metal ion serves as an electron receiver, complex formation makes the organic molecule more vulnerable toward nucleophilic attack, which could result in rearrangement, solvolysis, decarboxylation, or oxidation of the organic substrate. When oxidant is present to reoxidize the metal ion, the metal may then act as a catalyst in the latter reaction.

Predictions of behavior of nuclides in the presence of complexing agents must be based on general chemical properties⁽¹¹⁾ when direct measurements are unavailable. Elements from Group I of the Periodic Table would be expected to complex very poorly, due to their small charge and large size. Complexes of Group II elements should be stronger, especially in the presence of

certain ligands which stabilize the lower oxidation states. First transition series metals should complex mainly in the lower oxidation states. Second transition metals should show an increase in stability of the higher oxidation states relative to the first series. In addition, both series are d-group transition metals that have the ability to form complexes with ligand molecules having vacant π orbitals in addition to lone-pairs, resulting in stabilization of lower oxidation states.

Lanthanides are most stable in the III oxidation state and form fairly weak complexes resembling those of the alkaline earths. Though a large number of complexes are known, these elements are less likely to form complexes than the transition elements. Complex stability increases with decreasing radius of the metal. The most stable and most common complexes are found with chelating oxygen ligands, where stability depends on structure and basicity of the acid, as well as pH of the medium.

The actinides have a wider variety of oxidation states available and are more easily complexed than the lanthanides. The relative complexing strengths vary with valence, and are generally $IV > VI > III > V$, that is, $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$, although in some cases $M^{3+} > MO_2^{2+}$. Like the lanthanides, actinides tend to form strong, higher ligand number complexes with oxygenated anions. Within the actinides, hydrolysis decreases in the order $Am > Pu > Np > U$.

COMPLEXANTS IN WASTE PROCESSING

Complexing agents used in various waste processing procedures include TBP, DBBP, HEDTA, EDTA, HDEHP, NTA, DTPA (Appendix A), citrate, tartrate, hydroxyacetic acid, sucrose^(4, 5, 7, 12,13) Various petroleum fractions and other organics are used as diluents. Chemical and radiolytic degradation products of these organics can interfere with normal separations processes, resulting in poor separation of desired nuclides, poor phase separations, loss of metals to waste streams, and an increase in radioactivity in the recycled organic extractant phase.

Common diluent mixtures^(14, 15, 16) are all primarily aliphatic hydrocarbons varying in chain length and branching, unsaturation, and cyclic or

aromatic character. These solvents give similar decomposition products, in varying proportions.⁽¹⁷⁾ Order of susceptibility of hydrocarbons to thermal or radiolytic degradation is usually olefins > naphthalenes > iso-paraffins > n-paraffins.⁽¹⁸⁾ In irradiation of paraffins, all intermediate products, nearly all dimers, and many of the other products are formed by radical reactions.⁽¹⁹⁾ Therefore, radical scavengers tend to stabilize a solvent system.^(19, 20)

Primary diluent degradation products are nitro-paraffins and carbonyl compounds, with some polymerization and solids formation. Yield is somewhat pH-dependent: high concentration of HNO_3 favors high yield of nitro-paraffins, while carbonyl compounds are maximized at 2-3 M HNO_3 .⁽²¹⁾ Further decomposition yields secondary products of composition highly dependent on the circumstances involved.

Ease of nitration of a carbon atom is usually $3^\circ > 2^\circ > 1^\circ \gg 4^\circ$ (that is, $\text{R}_3\text{CH} > \text{R}_2\text{CH}_2 > \text{RCH}_3 \gg \text{R}_4\text{C}$, where R = any organic branch). An aliphatic side chain of an aromatic compound is more susceptible to nitration than a saturated compound or the aromatic ring itself. Nitration varies with diluent, acid concentration, radiation level, and primary chelate concentration.^(18, 21) Nitrous acid is the chemically active agent for nitration,^(14, 22, 23, 24) existing as a $\cdot\text{NO}_2$ radical in the organic phase.⁽¹⁴⁾ Nitration can yield nitro ($-\text{NO}_2$),^(14, 23, 25) nitrate esters ($-\text{ONO}_2$),^(23, 26) nitrite esters (ONO),⁽²³⁾ nitroso ($-\text{N}=\text{O}$),^(23, 26) isonitro (NOOH)⁽¹⁴⁾ and polynitro compounds.⁽¹⁴⁾ Nitration is accompanied by a considerable amount of oxidation. Carbonyl formation, including carboxylic acids and carbonyls, is maximized at 2-3M HNO_3 .⁽²¹⁾

Nitro and carbonyl formation is highly dependent on minor constituents of a solution. No straight-forward relationship between solvent radiation stability and solution composition was observed for minor additions of 24 compounds or major additions of 9 compounds expected to be present or to act similarly to impurities in process streams.⁽²⁷⁾

Secondary degradation products potentially include such species as nitro-alcohols, nitroolefins, dinitros, acinitro salts, nitrolic acids, hydrozamic acids and oximes.^(18, 28) Radiolysis of paraffins can also yield polymeric

agglomerations.^(19, 23) Olefinic⁽²⁹⁾ and carboxylic acid^(26, 30) dimers have been observed in diluents. Irradiation of amines yielded some polymerization along with large amounts of gaseous product.⁽³¹⁾ Polymers with molecular weights as high as 840 result from radiolysis of TBP.⁽³¹⁾ Sludge formation due to solvent degradation carries with it heavy metals and fission products,^(23, 32) as well as high molecular weight carboxylic acids.^(23, 26) Sludge also hinders the phase separations in reprocessing programs.

The ability of primary degradation products to act as ligands has been under debate. The enol form of nitro compounds is credited as the major complexing species by Blake et al.,⁽¹⁶⁾ while an activated hydrogen mechanism was proposed to explain complexation in acidic solutions.⁽³³⁾ Still others^(18, 23) found the nitro compounds relatively innocuous. Nitrate esters have been implicated as interfering with normal extraction procedure.⁽²³⁾ Windscale investigators^(18, 22) studied a number of possible types of primary and secondary products and concluded that hydroxamic acids were an important, though certainly not the only, complexing group while all primary products tested were passive. The complexing ability of hydroxamic acids is known^(34, 35, 36, 37) and their presence in degraded solvent has been demonstrated.^(18, 38) Synergistic enhancement of the complexing ability of some chemical species in combination versus either species alone has also been observed for several constituents.^(23, 36, 39)

Once degradation has occurred, the life of the solvent may be extended by using decomposition product scavengers. Alkaline permanganate scavenges well, but requires removal of the resulting MnO_2 sludge.^(16, 18) Alumina adsorbs organics in the decreasing order of aliphatics > TBP > aromatics >> nitro-, carbonyl-, and nitroso-aromatics.⁽²³⁾ Certain alkanolamines remove nitroparaffin-amine salts and polycyclic aromatics^(14, 16, 18, 22, 40) but are costly. Calcium hydroxide reacts with any nitro compound capable of enolization.⁽¹⁶⁾ However, washes with Na_2CO_3 , $NaOH$,^(18, 26) HF ⁽¹⁸⁾ or HNO_3 ⁽²⁶⁾ have proven ineffective. The decomposition products form solvent-soluble (alkali) salts^(14, 18) which may pass through the wash system and be recirculated. Carbonyl impurities of irradiated solutions are partly alkali soluble and would be removed with the phosphate ester impurities in the alkali wash.^(18, 23) The alkali washes would then be routed to the appropriate aqueous waste facilities.

The major chemicals used in separations systems often contain impurities. Both major and minor components are subject to radiolytic and chemical degradation. Commercial TBP usually is contaminated with butyl alcohol and dibutyl ether, and may also contain DBP, MBP and condensed phosphates.⁽²⁴⁾ Hydrolysis and radiolysis of TBP yield DBP and MBP in a molar ratio of nine⁽²⁵⁾ or ten⁽⁴¹⁾ to one. Polymeric TBP appears at about the same rate as DBP.⁽⁴²⁾ Other possible products include hydrogen,⁽²⁵⁾ phosphoric acid, butanol,⁽²⁴⁾ n-methyl nitrate^(24, 43) and C₁-C₄ hydrolysis products.⁽⁴²⁾ Both radical^(25, 42) and ionic⁽⁴⁴⁾ mechanisms have been proposed for the TBP degradation.

Small amounts of mono- and tri-(2 ethylhexyl) phosphoric acid, 2-ethyl hexanol, and other organic and metal contaminants are present in commercial HDEHP.^(39, 45) Primary radiolysis products are H₂MEHP,^(46, 47) 2-ethyl hexanol,⁽⁴⁷⁾ hydrogen-bonded polymer, and reducing agents from the organic extractant.⁽⁴⁶⁾ Unless periodically removed, H₂MEHP can reach a concentration as high as 0.05 M under typical (10⁸ rad) exposure.⁽³⁹⁾

Radiolysis of citric acid causes a loss of some of its acidic protons, finally resulting in formation of dark-brown precipitates containing chiefly oxalates and possibly organic polymers.⁽⁴⁸⁾ Detailed study of radiolysis of aliphatic hydroxypolycarboxylic acids shows hydroxycarboxyalkyl radical formation.⁽⁴⁹⁾ Sucrose undergoes stepwise fragmentation, oxidation and hydrolyzation before ultimately converting to carbon dioxide.⁽⁵⁰⁾ Such a pathway is similar to the sucrose decomposition in sugar denitrification, which yields stepwise products before ultimately converting to the oxides of carbon and nitrogen.⁽⁵¹⁾ If the sucrose is not completely destroyed, these stepwise products (tartaric, oxalic, etc) could be available in waste solutions⁽¹²⁾ for further reaction or complexation.

In addition to the previously mentioned sources of organics in wastes, common maintenance procedures require substances which are potential sources of ligands. Radionuclide sorption in the presence of various detergents varied with detergent type and nuclide.^(52, 53) Fabrication oil (Appendix A) appears relatively innocuous, however. No impairment of ion exchange properties or porosity of soil was observed after addition of this oil or several other organics.⁽⁵⁴⁾ Disposal of the oil did not interfere with subsequent waste

disposal, or entrain the several sorbed nuclides tested.⁽⁵⁴⁾ Fabrication oil has been disposed of in enclosed trenches, along with intermediate level aqueous wastes, miscellaneous organics, and precipitates.⁽⁵⁾

A typical high salt aqueous waste stream⁽⁵⁵⁾ contains large amounts of Al, Mg, Ca, and Fe nitrates⁽⁵⁾ in addition to the major component, NaNO_3 . Without pretreatment such a solution would not be buffered to a lower pH by even a great excess of soil,⁽⁵⁵⁾ and sorption of radionuclides would be inhibited. Reduction in pH greatly improves sorption of most radionuclides in the absence of organics. However, the presence of chelating agents or organics is known to alter nuclide distributions significantly.⁽⁵⁵⁾

After deacidification, high level aqueous wastes are sent to tanks for evaporation and salt cake formation. In the absence of ligands, plutonium and strontium are present as a precipitate. Complexation prevents their precipitation and enables the nuclides to remain mobile if released to the soil.^(12, 13) For example, a considerable rate of migration of Sr from an actual waste site which had received chelating agents was observed.⁽⁵⁶⁾ Presence of Sr-chelate in a tank liquor has been confirmed.^(12, 13) It is reasonable to assume that other radionuclides will be complexed as well.

METAL COMPLEXATION IN SOIL

The significance of soil properties on complexation has been reviewed for selected elements.⁽⁵⁷⁾ Many complexing agents are present naturally in the soil,^(58, 59, 60, 61, 62, 63, 64) plant excretions,⁽⁶⁵⁾ or microorganism products⁽⁷⁶⁾ and are therefore available for potential reaction with any metals present in, or added to, the soil. In addition, ligands may enter the soil via fertilization or waste disposal. Metal chelates are highly subject to environmental influences. Weaker chelates often require correspondingly higher pH before complexation can occur. Alkaline hydrolysis may negate the effect of chelates in calcareous soils.^(66, 67) Sorption of the chelate onto clay minerals varies with the type and concentration of the ligand, as well as with soil pH and type of clay mineral involved.^(67, 68, 69, 70, 71, 72, 73) Direct ion exchange, isotopic exchange,^(70, 72) and competition among the

available metal ions^(71, 72) alter the ratio of soluble and sorbed metals. Bio-degradation can alter solubility and valence state of a metal⁽⁷⁴⁾ and the effectiveness of the ligands present.⁽⁷⁵⁾ Microbial metabolites can themselves become ligands for metal complexation⁽⁷⁶⁾ and thereby alter their mobility in soil. The availability of ligands for complexation also depends on the relationship between rates and equilibriums of possible competing reactions in the system.⁽⁷¹⁾

Synthetic polyamine carboxyl chelating agents have been extensively employed in soil studies. Stability of the complex increases with increasing number of available functional groups on the ligand. Metal chelates formed by these ligands have a net negative charge, but are probably still dipoles,⁽⁶⁸⁾ accounting for the ability to sorb to soils. Since many such chelates are used in radioactive waste processing, and since little is known about the nature of potential chelates found in the waste processing streams, analogs must be drawn from available data, principally using the polyamine carboxyl chelates.

NUCLIDES PERTINENT TO WASTE CONTAINMENT ANALYSES

The following discussion is directed toward the particular complexation characteristics of various elements. These elements constitute the major fission products, long-lived isotopes, and the species most mobile in radioactive wastes that are currently being generated. Notably, tritium and ¹⁴C have been omitted, since this discussion is primarily concerned with mobility due to nuclide complexation. Although not normally studied in terms of nuclide complexation, iodine is included since it is normally a highly mobile, high-yield fission product.

Americium (Am)

A comprehensive list of Am III complex data prior to 1974 has been published.⁽⁷⁷⁾ With the exception of Am V complexes with EDTA, DTPA, and oxalate, little is known about complexes in other oxidation states. The higher oxidation states are strong oxidizing agents and are not stable in the presence of most organic ligands.

Stability of Am complexes is equal to or greater than that of the corresponding lanthanide complex.⁽⁷⁷⁾ Am was not sorbed on a soil column from organic wastes containing one or a combination of: DBBP, HDEHP, hexone, NPH, TBP, or hydroxyacetic acid.⁽⁵⁴⁾ Hydroxyacetic acid or a mixture of HDEHP and TBP in NPH removed large quantities of previously sorbed Am.⁽⁵⁴⁾ Am sorption from a typical high salt acidic waste stream was shown to be negligible despite partial neutralization in soil.⁽⁵⁵⁾ Sorption was high from aqueous alkaline solution if organics were present in amounts that only saturated soil sites; higher concentrations of organics caused reduction of sorptive ability.⁽⁵⁵⁾

Antimony (Sb)

Principal oxidation states of Sb in solution are III and V. The Sb III oxide, Sb_2O_3 , dissolves in alkali to yield SbO_2^- salts. Sb_2O_5 is formed by the action HNO_3 on Sb_2O_3 ; when dissolved in basic media, it yields $\text{Sb}(\text{OH})_6^-$. Sb shows increasing cationic behavior relative to the other group V elements (N, P, As). Sb III is usually described as the cation SbO^+ in solution and is hydrolyzed except when involved in complex formation. Cation exchange separations usually employ a complexing agent in the elution of Sb III; anion exchange methods are highly dependent on system employed. Sb chemistry is particularly complicated by the wide range of organometallic compounds formed, and the ability of Sb species to act as ligands themselves.⁽⁷⁸⁾ Sb chelated with EDTA has been evaluated as a groundwater trace.⁽⁷⁹⁾

Cerium (Ce)

Cerium is soluble under acidic conditions but forms colloids under alkaline conditions.⁽⁶⁹⁾ Ce^{3+} has a tendency to oxidize to Ce^{4+} in the process of complex formation. Ce^{4+} acts much like a tetravalent actinide, and is the only tetravalent lanthanide stable enough to exist in aqueous solutions. Ce is readily sorbed by soils,⁽⁶⁹⁾ and is highly complexed by soil humic acid.⁽⁵⁸⁾ Ce shows maximum sorption to soil between pH 6-8 and above 11; between pH 8-11 peptization of the Ce-bearing particles of colloidal dimensions is suspected, while below pH 6 sorption decreases rapidly.⁽⁶⁶⁾

Sorption is prohibited by addition of chelating agents such as citrate, acetate, EDTA, or DTPA.⁽⁶⁶⁾ Considerable desorption of previously sorbed Ce results from these chelating agents,^(66, 80, 81) while CDTA or EDDHA had

little effect, evidently due to alkaline hydrolysis.⁽⁶⁶⁾ The low stability of lanthanide-EDDHA complexes relative to Ca or Fe would allow these elements to compete for the ligand in the soil and preclude significant movement of Ce.⁽⁶⁶⁾

Ligand solutions of large volume or high concentration would eventually move all the sorbed Ce in the soil. If the Ce is chelated prior to addition to the soil, only a small amount of chelate would be necessary to maintain solubility and mobility.⁽⁶⁶⁾

Cesium (Cs)

Like K and NH_4^+ , Cs is retained in the interlattices of montmorillonitic clay mineral and is bound tightly in soils in which this clay mineral is present. Since Cs^+ is a large ion with a small charge, it would be expected to form complexes with difficulty. Maximum Cs sorption occurs at pH 7-9 from low ionic strength soil solutions.⁽⁶⁶⁾ Cs is poorly complexed by humic acids, as shown by the relative order of complexation: $\text{Ce} > \text{Fe} > \text{Mn} > \text{Co} \geq \text{Ru} \geq \text{Sr} > \text{Cs} > \text{I}$.⁽⁵⁸⁾ The low relative stabilities of Cs chelates prevent any direct chelate effect on Cs migration: competition for the ligands by Ca, Sr, Mg, Al, Mn, Zn, or Fe, all elements common to soil solution, would negate Cs complexation.^(66, 80) Cs was not removed from soil by hydroxyacetic acid,⁽⁵⁴⁾ EDTA,⁽⁷⁹⁾ DTPA,^(66, 79, 80) EDDHA, or CDTA.⁽⁶⁶⁾ Cs sorption to soil was impaired, however, by the addition of several detergents,⁽⁵²⁾ or by high concentrations of Na^+ .⁽⁸⁴⁾ Cs, but not Sr, can be removed from complexant wastes by an ion exchange process.⁽¹²⁾

Cobalt (Co)

Cobalt can form a great many complexes in both the II and III oxidation states. Co III has particular affinity for N-donors, and complexes are usually stable. The reactive species is considered to be $\text{Co}(\text{OH})^{2+}$.⁽⁸⁾ In contrast, Co II complexes are readily oxidized. Cationic cobalt would be expected to be retained on the soil ion exchange sites. Co is complexed by amino acids and mercapto carboxylic acids found in reducing soils.⁽⁵⁹⁾ Uncomplexed Co was sorbed by a test soil column, while Co complexed with EDTA did not sorb from pH 1.0, 5.0, or 8.2 solutions.⁽⁸³⁾ Sorbed Co was released using EDTA and DTPA.⁽⁸⁰⁾ Migration of Co EDTA at a rate correlated with precipitation has

been detected from a waste disposal trench.⁽⁸⁴⁾ Field studies suggested that EDTA was the primary agent for Co mobilization in some ORNL burial grounds.⁽⁸⁵⁾ The Co detectable in ground water has been assumed to be an anionic species⁽⁸⁶⁾ but has not been specifically identified.

Curium (Cm)

Cm III, the only oxidation state found in solution, resembles Am III and the trivalent lanthanides.⁽⁸⁷⁾ Since little work has been done using Cm complexes directly, any prediction of responses to ligands must be based on Am III or the lanthanides as analogs. On this basis, it would be expected to be mobilized by the presence of the proper complexing agents in a soil system. Chelates that have been studied include DTPA, acetic acid, glycolic acid, and tartaric acid.⁽¹⁰⁾

Europium (Eu)

Generally, Eu would be expected to resemble the other lanthanides. Complexes formed by Eu III should show increased stability relative to Ce III and Pm III.⁽⁸⁸⁾ Several complexing systems have been studied,⁽¹⁰⁾ but most environmental studies have been concerned with monitoring concentrations rather than studying mechanisms of transport and uptake.

Iodine (I)

Since sorption by soils is mainly a cationic process, anionic iodide would be expected to remain mobile. Iodine can combine with iodide to form polyiodide anions, the most stable of which is I_3^- . These anions form stable salts with large cations, such as Cs^+ . All halides can function as ligands, but the stability of the complex decreases through the series $F > Cl > Br > I$ for most metals. With metals having a variety of oxidation states, the covalent character of the metal-halide bond increases with increasing oxidation state of the metal.

A major portion of iodine escaping from radioactive waste reprocessing is initially in the form of volatile methyl iodide and other organic iodides. While migration of I^- is easily monitored, that of organic iodides is more difficult.^(89, 90) The efficiency of sampling methods for the various forms of iodine is questionable.⁽⁹¹⁾ Nevertheless, iodine migration and availability

for plant uptake has been observed for some time.⁽⁹¹⁾ Iodine accumulates in plant cells mainly as iodide, but organic iodine compounds have been found in wheat roots.⁽⁹²⁾ A study of methyl iodide retention on 22 diverse soils showed retention positively correlated with percent clay, organic carbon content, and cation exchange capacity, and negatively correlated with pH.⁽⁹³⁾

Neptunium (Np)

Np can exist in any oxidation state from III to VII; Np V is the most stable in aqueous solutions. Stability of complexes usually follow the order $\text{Np}^{4+} > \text{Np}^{3+} > \text{NpO}_2^{3+} > \text{NpO}_2^{2+} > \text{NpO}_2^{+}$. Because Np^{4+} and NpO_2^{+2} form more stable complexes than NpO_2^{+} , addition of complexing agents to a system containing Np V would be expected to increase the disproportionation to Np IV and Np VI. Stabilities of Np V complexes are comparable to those of Mg^{2+} , Ca^{2+} , and Zn^{2+} , and are much more stable than those of U V, Pu V, or Am V.⁽⁹⁴⁾

Promethium (Pm)

The primary oxidation state of Pm is as Pm III; its smaller radius should increase complex stabilities relative to Ce III. Like Ce, Pm showed maximum sorption by soil at pH 6-8 and greater than 11.⁽⁶⁶⁾ Retention would be expected to be influenced by chelation in much the same manner as for Ce. The effectiveness of citrate, acetate, EDTA and DTPA in reducing retention of Pm, and the lack of effect by CDTA and EDDHA⁽⁶⁶⁾ exemplifies this similarity. Pm complexes should remain soluble if added to soil along with only a small amount of excess chelate. However, if added initially as an uncomplexed species, Pm, like Cs, would require chelate solutions of large volumes or high concentrations to cause eventual removal from soil.⁽⁶⁶⁾

Plutonium (Pu)

Pu can exist in solution in four oxidation states simultaneously (III, IV, V, VI). Complexing ability usually follows the order: $\text{Pu}^{4+} > \text{Pu}^{3+} > \text{PuO}_2^{2+} > \text{PuO}_2^{+}$. In any given valence state, complexing ability for Pu is greater than the corresponding U or Np ion.

Pu sorbs to soils to a high degree in the absence of ligands. Hydrolyzed Pu is taken up by soil nearly irreversibly at neutral pH, but is not well sorbed at a higher pH.⁽⁸²⁾ The effect of ligand addition varies with agent used.

Pu solutions containing citric acid showed a steady low bleed in soil column studies.⁽⁵⁵⁾ Like Am, Pu was not sorbed on a soil column from organic wastes containing one or a combination of: DBBP, HDEHP, hexone, NPH, TBP, or hydroxyacetic acid.⁽⁵⁴⁾ Pu was essentially sorbed from fabrication oil.⁽⁵⁴⁾ Hydroxyacetic acid, or a mixture of HDEHP and TBP in NPH removed 35 to 40% of previously sorbed Pu.⁽⁵⁴⁾ Pu sorption from a typical-high salt, acidic, waste stream was shown to be minor despite partial neutralization by soil.⁽⁵⁵⁾ Sorption from alkaline solutions was high if only saturation amounts of organic materials were present; sorption was reduced with excess organic materials.⁽⁵⁵⁾ Pu in complexed waste is expected to remain mobile in soil, and no practical method for Pu removal from these wastes has yet been implemented.⁽¹²⁾

Radium (Ra)

Ra is limited to one oxidation state, Ra II. Due to its highly basic character, Ra displays the least tendency to complex of all alkaline earths. Complexes which are known to consist of one ligand per Ra atom, and are often formed only at higher pH values.⁽⁹⁵⁾ Ra would be expected to sorb easily on soil, and be removed by chelating agents only after those elements of higher KD values are depleted.

Ruthenium (Ru)

Ru can exist in any oxidation state from 0 to VIII. The highly volatile RuO_4 becomes the perruthenate (RuO_4^-) or ruthenate (RuO_4^{2-}) under appropriate aqueous conditions. The lower oxidation states (II, III) exist in aqueous solutions chiefly as complexes. Ru displays marked affinity for N-bonding in the lower oxidation states. Since nitric acid is widely used in waste processing, the highly stable group $\text{Ru}(\text{NO})^+$ should be anticipated in waste solutions, probably as a complexed species. In addition, many oxygen ligands of Ru II and III are known.

The many oxidation states of Ru greatly complicate its chemistry. Typically one of the more mobile nuclides, Ru shows evidence of at least two mobile species.⁽⁶⁶⁾ Like the lanthanides, Ru sorbs on soils and minerals easier from neutral or highly alkaline solutions than from acid or mildly alkaline solutions.⁽⁶⁶⁾ Leaching by rain releases Ru as Ru-fulvate complexes.⁽⁵⁸⁾

Amine and nitrosyl Ru complexes are formed in radioactive waste systems or during nitric acid processing of spent fuels. The nitrate complexes are more unstable relative to the nitro complexes. Depending on the specific makeup of the complex, nitro complexes can have neutral, cationic, or anionic character.⁽⁹⁶⁾ Seventy percent of Ru being released from nuclear facilities is reported to be in the form of nitronitrosyl Ru complexes best represented by the dinitro $[\text{RuNO}(\text{NO}_2)_2\text{OH}(\text{H}_2\text{O})_2]$ and nitrodinitrate $[\text{RuNONO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ complexes.⁽⁹⁷⁾ The former has anionic and the latter cationic character in the soil.

A comprehensive review on behavior of Ru in plants and soils has been published.⁽⁹⁶⁾ Maximum sorption on soil occurred between pH 7-8.⁽⁹⁷⁾ Apparently cationic Ru sorbs well and becomes relatively unavailable to plants.

Ru sorption by soils is reduced with DTPA, EDDHA, CDTA,⁽⁶⁶⁾ and EDTA.⁽⁸⁰⁾ The effect was small, however, probably due to the low concentration of Ru cations available for complexation.⁽⁶⁶⁾ Soil properties have great effect on the effectiveness of chelate additions.⁽⁸¹⁾

Strontium (Sr)

Of the Group II elements, only Mg and Ca show any appreciable tendency to form complexes, usually with oxygen-ligands. Sr does form complexes, but of weaker relative stability. The inability of plants to distinguish between Ca and Sr⁽⁶⁸⁾ makes the presence of soluble Sr species very important. In isolated cases, Sr has proven to be of equal or greater mobility than Ru.⁽⁶⁶⁾ Sr sorbs poorly on clays at low pH,⁽⁶⁸⁾ but sorbs well on soils at pH 7-11 and is retained at pH greater than 8.⁽⁶⁶⁾ Sr can be retained by soil organic matter⁽⁶⁰⁾ or precipitated in phosphate compounds.⁽⁶⁶⁾ Microbiological activity can hinder Sr migration.⁽⁶⁸⁾ Retention is affected by the presence of competing ions in order of decreasing effect: $\text{Al} > \text{Fe} > \text{Ba} \geq \text{Ca} > \text{Mg} \geq \text{H}$; and $\text{Cs} > \text{K} > \text{Na} > \text{NH}_4$.⁽⁶⁶⁾ Sorption increases in the presence of detergents.⁽⁵²⁾ While presence of high concentrations of Na^+ decrease sorption, addition of relatively small amounts of PO_4^{3-} negate the effect.⁽⁸¹⁾ Sorbed Sr may be mobilized by leaching with competing ions^(69, 82) or with chelates such as EDTA^(66, 81) if the soil properties such as pH or organic matter do not interfere.⁽⁶⁸⁾ However, effectiveness of DTPA, CDTA, or EDDHA is highly dependent

on soil properties.^(66, 68) Prior chelation with DTPA has little effect.⁽⁶⁶⁾ A high concentration of competing ions, such as Ca, in a calcareous soil can cause migration of Sr independent of any chelate effect.⁽⁶⁶⁾ Sr in complexed waste solutions remained mobile in soil test columns,⁽¹²⁾ and rapid migration from a radioactive waste disposal site in the presence of chelates has been documented.⁽⁵⁶⁾

Technetium (Tc)

The sources of Tc and its behavior in the environment are the subject of a recent review.⁽⁹⁸⁾ Tc can exist in all valence states from +7 to -1, with +7 and +4 the most stable in solution. Nuclear fuels processed in a gaseous diffusion plant release Tc as the highly volatile hexafluoride, which is normally trapped on MgF_2 .⁽⁹⁹⁾ In highly alkaline waste streams, Tc remains in the supernate.⁽¹⁰⁰⁾ The most stable soluble form of Tc is anionic pertechnetate (TcO_4^-), which would migrate with the ground water⁽¹⁰¹⁾ if stable in soil. The lower oxidation states show strong tendency to complex. Tc VI and V would be expected to form highly labile complexes which would easily disproportionate in aqueous solutions. Tc IV complexes are widely used as diagnostic pharmaceuticals. At neutral pH hydrolysis tendency is high, with Tc IV forming the hydrated dioxide as a soluble or colloidal species which precipitates at concentrations above 10^{-4} M.⁽¹⁰²⁾ In highly alkaline solutions, the dioxide dissolves to yield Tc(OH)_6^{2-} .⁽⁹⁹⁾

Reduced Tc is known to complex with polyalcohols,⁽¹⁰³⁾ and complex alcohols are available in the soil solution, especially in the vicinity of plant roots. The ready uptake by plants suggests that Tc is acting as a nutrient analog.⁽¹⁰⁴⁾ Although this information suggests that Tc may be highly mobile in the environment, some physiochemical, biological, and time factors, which may be important in reducing mobility, have been reviewed.⁽⁹⁸⁾ The reduction of pertechnetate mobility by igneous rock structures not in contact with the atmosphere has been observed but the reduction could be reversed by the introduction of oxidizing conditions.⁽¹⁰⁵⁾ These findings could be very important in analysis of sites for geologic storage of this long-lived radionuclide.

Uranium (U)

U can exist in several oxidation states in solution. UO_2^{2+} is the most stable ion in solution. U^{3+} is easily oxidized to U^{4+} , while UO_2^+ readily disproportionates to U^{4+} and UO_2^{2+} . The general tendency to complex or to hydrolyze follows the order: $\text{U}^{4+} > \text{UO}_2^{2+} > \text{U}^{3+} > \text{UO}_2^+$. Hydrolysis leads to polymeric species. Many organic complexes with the various valence states of U have been studied, but the conclusions often show contradictions.⁽¹⁰⁶⁾ Evidence of U mobilization by organic complexes similar to Co migration from ORNL burial grounds has been suggested.⁽⁸⁵⁾

Zirconium (Zr)

Aqueous Zr chemistry is almost exclusively limited to the quadravalent state. Insoluble ZrO_2 is favored in basic systems, while acid solutions produce polymeric, partially hydrolyzed species. Since hydrolysis is incomplete in either system, some soluble Zr IV is available for complex formation. Some known complexes are formed with EDTA, NTA and oxalate.⁽¹⁰⁷⁾

CONCLUSION

Organic complexing agents can be expected to be found in aqueous wastes, either through direct addition or chemical degradation. Interference with the normal sorption of nuclides by soil has been observed for several ligands. Positive identification of chelating species present in wastes has not yet been accomplished. In the interim, only general predictions can be made as to the relative ease of complexation of the elements of concern. Such predictions depend on the strength of the ligand and the environment of the reaction, as well as the nuclide involved.

The stabilities of complexes involving actinides and fission products must be compared with those of metals commonly found in soil, and their relative availability. It is reasonable to assume that generally complexes would be formed in order of decreasing stability, if the environmental conditions required for complexation are met and the rates of formation do not differ greatly. Actinides form complexes much more readily than lanthanides, and lanthanides are generally less likely to form complexes than transition

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metals, even though the number of complexes known to form with the lanthanides is great. Stabilities tend to increase with decreasing radii of the metal ions. Oxidation state often determines the relative stability of complexes with nuclides. Chelation affords additional stability relative to a simply complexed nuclide. As the data shows, conditions may be present which could greatly decrease the mobility of a highly mobile species such as Tc or increase the mobility of an otherwise relatively immobile species such as Pu. It is likely that the proper conditions could be generated to cause increased mobility of most, if not all, of the nuclides discussed above. The number of variables involved in prediction of mobility due to presence of complexing agents is large. Rigorously controlled experiments are necessary to correlate mobility of each nuclide with species added, soil properties, and ligands present.

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APPENDIX A

ABBREVIATIONS

APPENDIX A

ABBREVIATIONS USED IN TEXT

CDTA	cyclohexane-1,2-diaminetetraacetic acid
DBP	dibutyl phosphate
DBBP	dibutyl butyl phosphonate
DTPA	diethylene triamine pentaacetic acid
EDDHA	ethylenediamine di-o-hydroxyphenyl acetic acid
EDTA	ethylene diamine tetraacetic acid
HDEHP	di (2-ethyl hexyl) phosphoric acid (also = D2EHPA)
HEDTA	hydroxyethyl ethylene diamine triacetic acid
MBP	monobutyl phosphate
NPH	normal paraffin hydrocarbon (commercial mix of nC_{10} - nC_{14})
NTA	nitrilo triacetic acid
TBP	tributyl phosphate

Fabrication oil (25% lard oil, 75% CCl_4)

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