

co-sorption, ternary complexation, and other related phenomena. Interfacial reactions of contaminants in subsurface systems are not well understood, and therefore experimental and modeling studies at different scales are being performed to identify the chemical nature of multi-species sorption reactions and the complex physiochemical factors that control the ultimate manifestation of these reactions in a mineralogically heterogeneous subsurface environment.

Sorption reactions on subsurface materials: General considerations

Sorption is a phenomena that concentrates aqueous phase constituents at the solid-liquid interface. Many radionuclides are strongly sorbed by subsurface minerals and material [2-6], and this sorption retards their transport velocity [7,8]. Sorption generally proceeds via the formation of a surface complex between the sorbate and specific functional groups on the sorbent. Various different types of radionuclide surface complexes have been reported including (1) surface precipitates and (2) inner and outer sphere surface coordination complexes (see references 9 and 10 for definitions). These different types of complexes vary in their chemical bonding environment on the surface which strongly influences the reversibility of sorption if aqueous concentrations or composition changes. Surface precipitates are often irreversibly sorbed, while outer sphere complexes are generally labile and desorb rapidly.

The most important types of surface sites in subsurface materials includes hydroxylated FeOH, AlOH, and MnOH groups on the surfaces of oxides and minerals containing oxide components, fixed charge sites on layer silicates originating from structural cation substitution, surface structural vacancies on carbonate minerals, and carboxylate groups on organic matter [11]. The formation of surface complexes can be described via chemical mass action equations [12]. Radionuclide surface complexation is often a strong function of pH and aqueous speciation [5,13-15]. It is also influenced by other experimental variables such as ionic strength, solution composition, and sorbent surface area or site concentration. The complex dependency of sorption on these different experimental variables precludes the applicability of a univalent K_d . In heterogeneous subsurface materials the overall sorption of a radionuclide may, in fact, represent the contribution of multiple surface complexes on different mineral or organic matter phases.

The presence of organic co-contaminants such as organic acids (i.e., oxalic, citric, or salicylic) and amino-carboxylic acid chelators, and natural organic compounds such as humic substances may have a profound effect on the sorption chemistry of certain radionuclides (see for example reference 16 and later discussions related to speciation). Generally, these effects are not well understood or documented. The formation of strong aqueous complexes with organic ligands may significantly reduce the overall sorption of radionuclide cations, or reverse their surface complexation behavior so they appear to mimic the sorption behavior of the organic ligands [17,18]. Additionally, natural humic substances in subsoil porewater or groundwater may strongly bind to and coat subsurface mineral surfaces with Fe(III)OH and AlOH surface sites [19-21], and function as a co-sorbing surface phase for radionuclide cations [22,18]. Both organic acids and humic substances may compete with anionic radionuclides such as TcO_4^- for strongly binding Fe(III)OH or AlOH surface sites.

Subsurface Sorption Reactions: Research Needs

DOE's massive site restoration effort could be significantly enhanced by improved models that describe and predict radionuclide sorption reactions on subsurface materials in the presence of organic and inorganic

co-contaminant species. Such improved models must derive from a better understanding of (1) the chemical nature of radionuclide surface complexes, (2) the thermodynamics and kinetics of surface complex formation and their dependence on aqueous speciation, and (3) the identity of surface complexes and the properties of sorbents in subsurface materials.

Spectroscopic studies are needed to identify the molecular nature of radionuclides surface complexes on relevant mineral and organic surfaces in the absence and presence of organic co-contaminants. Measurements allowing inference of sorbate valence, speciation, and bonding environment at the solid liquid interface are needed to understand the magnitude and kinetics of sorption. Noninvasive techniques that do not require sample or surface desiccation should be given emphasis. Such studies must be performed under relevant sorbate concentrations and geochemical conditions (i.e., redox potential, pH, electrolyte conditions) to assure that the surface complexes being evaluated are applicable to groundwater conditions on DOE sites. Spectroscopic studies of radionuclide surface complexes should be performed in concert with those on the aqueous phase so that experimental relationships may be drawn between aqueous and surface speciation.

Sorption reactions must also be investigated at the microscopic scale to quantify (1) the thermodynamics and kinetics of formation/dissociation of different types of radionuclide or organic-radionuclide surface complexes and (2) the reaction stoichiometry for surface complex formation and its dependence on solution composition and co-contaminants. Information of this nature is needed for well-characterized sorbents from subsurface environments, and data should be developed within the general context of linked aqueous speciation-surface complexation models [11,12] as these hold the most promise for extrapolation of data over ranges in geochemical and site conditions. Studies of sorption kinetics and thermodynamics must be related to the surface chemical properties of the mineral or organic sorbents as well as the aqueous phase composition to facilitate data transferability to different geochemical conditions. Experimental techniques such as micro-calorimetry, pressure jump excitation, micro-electrophoresis, and various forms potentiometric titration are especially relevant.

The prediction of radionuclide sorption in mineralogically heterogeneous subsurface material remains a great challenge; however, such capability is needed for effective remediation of DOE lands. Significant research efforts must, therefore, be focused on (1) identifying which surface complexation reactions are of most importance in different subsurface materials, (2) characterizing the reactive sorbent surface in terms of site concentrations and surface properties, and (3) developing chemically realistic, yet tractible approaches for surface complexation modeling of multi-species radionuclide and organic co-contaminant sorption (see reference 12 for a discussion of these issues and reference 23 for an example). Attention must be given to the kinetics of these reactions as certain radionuclides and organic co-contaminants may form surface complexes or phases that do not exhibit equilibrium behavior over the time scale of water movement in waste sites or groundwater. Biological effects must not be ignored since microbes may utilize organic co-contaminants as substrates leading to transient concentrations in complexing organic ligands and changes in geochemical master variables such as redox potential and pH.

AQUEOUS SPECIATION OF RADIONUCLIDES IN THE PRESENCE OF ORGANIC LIGANDS

The speciation of radionuclides is a key consideration in defining their mobility in groundwater systems and establishing their interaction with subsurface materials. Here, speciation is defined as the chemical form (i.e., oxidation state, complexation, and aggregation) of a particular

radionuclide in the aqueous medium of interest. Speciation, in this context, has been the subject of many past investigations related to site-specific studies [24-27], the characterization of high-level waste sites within the U.S. [28,29] and abroad [30,31] and the distribution of radionuclides due to atmospheric fallout from nuclear testing [32,33].

While great progress has been made in understanding radionuclide speciation in aqueous systems, existing information is inadequate to predict aqueous speciation of relevant radionuclides over the broad range of geochemical conditions found in soils and groundwaters on DOE sites. This situation is further complicated by the frequent co-occurrence of both anthropogenic and natural organic compounds along with radionuclides in terrestrial DOE disposal sites and associated subsurface environments.

Data Base for Organic-Radionuclide Mixtures in Groundwaters

The first issue associated with the radionuclide data base is the identification of the important radionuclides and complexants present as subsurface contaminants at DOE sites. Some of the more important of these are listed in Table I. Many of these are known to exist as mixtures at DOE sites [34]. An extensive compilation of the identity and concentration of inorganic and organic contaminants in waste sites on DOE lands and identification of the frequency of occurrence of specific binary, ternary and higher order contaminant mixtures within DOE waste sites is being performed as part of the co-contaminant subprogram.

In addition to the ligands tabulated in Table I, it is important to note that inorganic complexants in groundwater may also have a significant effect on radionuclide speciation. Competition between inorganic and organic ligands will be an important aspect of the final speciation. Inorganic complexants that need to be considered are hydroxide (i.e., hydrolysis), carbonate/bicarbonate, phosphate, halides, and sulfate.

Extensive compilation of the inorganic radionuclide data base has been done elsewhere [35] with critical reviews published on uranium [36], plutonium [37], and americium [38] complexation data. There are still important deficiencies in these data however that preclude quantitative and accurate calculations of speciation under the diversity of geochemical conditions existing on DOE lands. Association quotients for the monocarbonato Pu(IV) complex (PuCO_3^{2+}) of 10^{47} [39] and 10^{13} [40] have been reported with 10^{13} as the more commonly held value based on analogy with similar systems. The first hydrolysis constant of Am suggested [38] by extrapolation of low-pH data is in apparent contradiction with direct observations made in the Cm system [26], which exhibits a similar chemistry to Americium. Values of 10^{-6} to 5×10^{-4} are reported for the first hydrolysis constant of Pu(VI); e.g., formation of PuO_2OH^+ . We [41] are showing that this is likely due to a miss-assignment in the speciation of Pu(VI) in the studies reported. These discrepancies need to be experimentally resolved prior to investigating the more complex radionuclide-organic systems.

Much less has been determined about the effect of temperature on the formation constants for both inorganic and organic radionuclide complexes. For actinides, no temperature dependent data exists although theoretical estimates of the thermodynamic data have been made by Langmuir [36] for uranyl and Lemire and Tremaine [37] for plutonium. The initial hydrolysis of Pu(VI) is being systematically investigated in noncomplexing media by spectrometric techniques [41]. The spectra obtained at 10, 25 and 45°C are shown in Figure 1. After correction for the effects of temperature on pH and the extinction coefficients is made, there is no effect of temperature on the relative concentration of the aquo and first hydrolysis product. This does not compare well with the relatively large (an order of magnitude over 30-40°C changes in temperature) temperature effects predicted.

TABLE I
Selected DOE Site Contaminants

Inorganic Species	Organic Species
Radionuclides	Contaminants
Plutonium-238, 239	Chlorinated hydrocarbons
Americium-241	Methyl ethyl ketone, cyclohexanone, acetone, hexone
Uranium-234, 238	Tetraphenyl boron
Technetium-99	Tributyl phosphate
Strontium-90	PCBs, select PAH
Cesium-134, 137	Toluene
Cobalt-60	Benzene
Radium-224, 226	
Thorium-228, 232	
Metals	Facilitators^a
Lead, chromium, copper, nickel	Aliphatic organic acids (citric, lactic, succinic, oxalic to octadecanoic)
Mercury	Aromatic acids (humic substances)
Cyanides	Chelating agents (EDTA, NTA, HEDTA, DTPA, TTA, Di-2-EHPA)
	Solvent, diluent, and chelate radiolysis fragments

^aFacilitators are organic compounds that interact with and modify metal/radionuclide geochemical behavior.

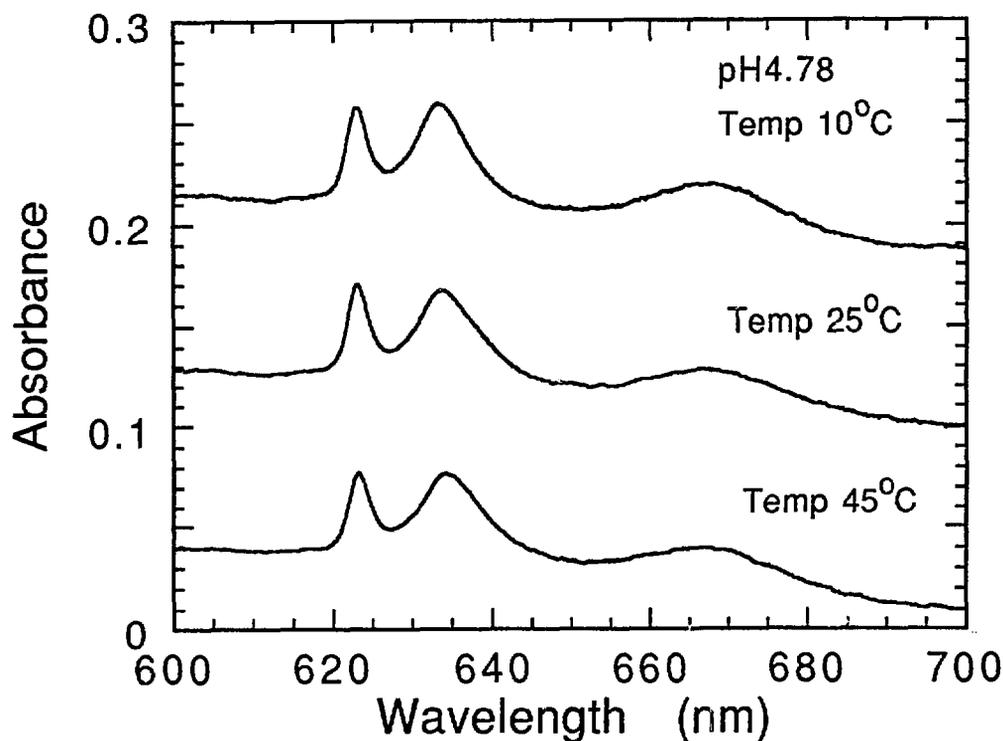


Figure 1. Effect of Temperature on the Relative Concentration of the Pu(VI) Aquo (at 622 nm) and First Hydrolysis Product (at 632 nm) in 0.1M Sodium Perchlorate. Spectra are offset to show spectral features.

The organic-radionuclide data base, in comparison to the inorganic data base, is much weaker. Organic complexation has not been identified as an important factor in considerations related to the high-level nuclear waste effort. At DOE sites, emphasis has been on tracking inorganic species with, until recently, lesser emphasis on the organics also present in the groundwater. This contrasts with the clear association of radionuclides with organic species (mostly fulvic and humic acids) as the mobile species in far-field studies performed [42,43].

By bulk, most of the organics present at DOE sites are aromatic or aliphatic (halogenated hydrocarbons) that are known to be very weak complexants of radionuclides. These organic compounds are primarily of importance due to their own toxicity. There are, however, documented cases as well as historical reports of the codisposal of complexing agents (listed as facilitators in Table I) and radionuclides. Extensive data on their complexation behavior have been tabulated [44] for high ionic strength and low pH media. Two issues, therefore, associated with the co-existence of organics and radionuclides are: (1) a corresponding set of complexation data that is more applicable to the higher pH, more reducing and more complex groundwater systems is needed and (2) the evolution/ degradation of the organic material present as waste due to interactions with the host environment (redox, microbial activity, etc.) and radioactive species present (radiolysis) needs to be investigated.

The potential for enhanced radionuclide mobility due to the co-disposed organic compounds present at DOE sites cannot be ignored and is an important component of groundwater speciation that is not properly taken into account by existing models. Further work is also needed to (1) identify highly complexing organic substances in soils and groundwaters and (2) relate the functionality/structure of these and natural organics to their ability to complex radionuclides.

Speciation: Mechanism of Transport

From the perspective of developing remediation technology, the most important aspect of radionuclide speciation is not simply the characterization of what is likely to exist in a particular site/groundwater but an understanding of the mechanism by which species are mobilized or immobilized. An important consideration, that is unique to the current DOE site restoration effort, is that for far-field transfer to occur in many cases the radionuclide in the waste must be initially transported through unsaturated zones and may initially encounter biphasic (mixed groundwater and organic solvents) rather than purely aqueous media. In addition, the oxidation state of the radionuclide may be affected by its migration into anoxic or oxygen-depleted zones and interaction with the organic compounds present, leading to marked changes in speciation and ligand distribution.

Research designed to investigate the potential effect of the sequence by which radionuclides are introduced to the groundwater on its final speciation is critical since, it is in these regimes that the need for remediation exists. Experimentally, the way in which radionuclides are introduced into groundwaters and simplified groundwater systems is often an important factor in the final speciation obtained in the laboratory since irreversible colloid formation, polymerization and precipitation may occur. For example, Pu(IV) introduced directly to carbonate media at $\text{pH} > 10$ will polymerize whereas its introduction as Pu(III) and subsequently air-oxidized to Pu(IV) will result in the formation of Pu(IV)-carbonate complexes that are stable for long periods of time. Investigations that carefully track the oxidation state are, therefore, needed to characterize these effects.

Speciation: Experimental Aspects

The last research need with respect to radionuclide speciation is the continued development of in-situ monitoring and detection techniques. Direct methods, such as spectroscopy and potentiometry, circumvent what are often formidable obstacles in identifying and synthesizing pure solid phases that are needed to unambiguously establish speciation through more indirect means (solubility effects, etc.).

Currently, the most sensitive and versatile of these techniques, are the laser-based high sensitivity methods of photoacoustic spectroscopy, laser-induced fluorescence, and thermal lensing. The applicability of these techniques to radionuclide systems have been assessed with the combination of LPAS and LIF having the most overall sensitivity. These are also conducive to performing temperature-dependent studies which are needed to obtain solution thermodynamic data on the complexes. The IV, V, and VI oxidation states for actinides, with the exception of uranyl, are primarily photoacoustically active with the trivalents, when not strongly complexed, tending towards fluorescence. The best published sensitivity for photoacoustic spectroscopy [45] is 2×10^{-7} absorption units/cm (signal to noise ratio of 1) which is on the order of a thousand times more sensitive than more conventional spectrometric techniques. Substantially greater sensitivity is obtained with fluorescence in some cases with sub pico-molar concentrations of Cm detectable [26]. Considerable spectral data base development is, however, needed to apply these techniques reliably to understand spectra obtained in complex systems such as real groundwaters.

Although the laser-based techniques currently provide the best overall sensitivity there are important limitations to these techniques that need to be addressed. All laser-based techniques rely on relatively narrow bandwidth dyes for tunability. This limits their applicability to species that have relatively narrow absorption bands (such as those with f-electron transitions). The development of broadband laser dyes will therefore increase the general versatility of these techniques. In addition, even though the sensitivity of these techniques is high, greater sensitivity is needed to directly characterize radionuclide speciation in groundwaters that are presently contaminated. Current extraction methodology, at best, only provides information about the oxidation state of the radionuclide. Improved overall experimental sensitivity to contaminants present in DOE lands is, therefore, an important research need.

INTERMEDIATE/LARGE SCALE INTERACTION STUDIES

The research needs identified in the previous two sections will be obtained by predominantly performing laboratory/bench scale experiments. An important link between the data generated by these experiments and that needed to reliably and quantitatively model the migration of radionuclides on DOE lands is a scale-up of the laboratory experiments to include the effects of transport and heterogeneity on radionuclide speciation and sorption. Reliable methodologies for doing this have not yet been fully demonstrated.

The need for intermediate-scale experimentation was critically evaluated in recent DOE-sponsored workshops. Priority experiments needed to advance the state of the science were identified. The results of these workshops were summarized by Zachara [46] and Streile et al. [47]. The initial focus identified was on the influence of controlled heterogeneities (layers, inclusions) as coupled processes including multiphase transport, and integrated effects of chemical and microbiological processes. Particular attention should be directed toward processes at porous media interfaces or at the saturated/unsaturated zone boundaries.

Progress in intermediate-scale experimentation is relatively recent. While several intermediate-scale experiments have been conducted on water flow and nonreactive/reactive inorganic solute transport in homogeneous and heterogeneous (i.e., having layers or inclusions) porous media systems, intermediate-scale studies on organic systems have been limited to organic liquid-flow experiments [48-50].

In the absence of knowledge of process interactions, it is often assumed that processes occurring simultaneously will not directly affect one another, but will instead be strictly additive in their effect. Some conceptual/mathematical models account for simultaneous processes merely by superimposing individual conceptual/mathematical submodels. (As examples, see the solute transport/sorption/degradation models of Van Genuchten [51] and Jury et al. [52].) In contrast, the studies that have incorporated more complex, mechanistically based descriptions of sorption and biodegradation during transport are theoretical model development and simulation efforts without rigorous experimental corroboration [53-55].

The assumption of noninteracting processes and superposition of models is invalid in certain circumstances. The interaction of solute transport and sorption has received, by far, the most experimental and theoretical investigation. These investigations have highlighted the importance of physical and chemical kinetic limitations on sorption imposed by porous media-flow and solute transport processes [56]. Explicit accounting of this sorption/flow interaction is now a standard consideration in describing reactive-solute transport. Microbial activity and growth in response to contamination has been shown to affect porous-media hydraulic properties (through pore clogging), with a subsequent feedback alteration of plume transport rate and direction [57]. Sorption has been shown to affect biodegradation because of the different abilities that sorbed or solution-phase microbes have for degrading either sorbed or solution-phase compounds [58]. Furthermore, sorption may directly affect degradation when the sorbed compound must desorb before being degraded and when the desorption rate is slower than the solution-phase degradation rate. Conversely, biodegradation can affect compound sorption by coating the surface with organic exopolymer degradation byproducts or through competition for sorption sites by the compound transformation products.

Field-scale contaminant transport is also significantly affected by spatial heterogeneity. Processes related to nonreactive solute transport (e.g., dispersion) exhibit a scale effect when transport models originally validated in macroscopic-scale systems are extended to field-scale application; that is, the magnitude of a supposed medium property appears to vary as the spatial extent of the contaminant migration increases. Only a few recent investigations of this scale effect in nonreactive solute dispersion have attempted to develop a mechanistic understanding of it through a series of controlled, intermediate-scale experiments [59,60]. No similar series of experiments has been conducted for reactive solutes to ascertain whether scale effects in chemical and microbiological parameters appearing in transport equations exist and, if so, to ascertain what mechanisms give rise to them.

Lastly, there is currently only the beginning of an adequate theory on how to deal with problems involving different spatial scales of observation [61]. Moreover, it is now recognized that any adequate mathematical theory should include the role of specific measuring instruments that would ultimately be used to quantify and validate a predictive theory [62,63]. Stochastic mathematical theories have been suggested to treat conceptual problems associated with heterogeneity [64]. However, documented and operational stochastic models are not yet available, because the difficulty of obtaining the needed additional statistical characteristics for a system remains an unsolved problem.

The performance of intermediate-scale investigations that address the issues just identified will aid in the development of the next generation of computer codes for describing contaminant transport in the field by

allowing incorporation of more mechanistically based formulations of the quantitative effects of simultaneous mesoscopic-scale processes and aiding in measurements of these processes at the appropriate scale. They will also aid in the qualitative general assessment of the overall extent of contaminant migration at DOE sites, the possibility of contaminant immobilization, the potential for aquifer bioremediation, and the most suitable remediation methodology.

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