

Thermally Unstable Complexants/ Phosphate Mineralization of Actinides

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EM Focus Area: contaminant plume containment and remediation

Task Description

In situ immobilization is an approach to isolation of radionuclides from the hydrosphere that is receiving increasing attention. Rather than removing the actinides from contaminated soils, this approach transforms the actinides into intrinsically insoluble mineral phases resistant to leaching by groundwater. The principal advantages of this concept are the low cost and low risk of operator exposure and/or dispersion of the radionuclides to the wider environment. The challenge of this approach is to accomplish the immobilization without causing collateral damage to the environment (the cure shouldn't be worse than the disease) and verification of system performance.

This task involves the measured addition of a reagent designed to generate a precipitant in the groundwater or soil in a manner that is most favorable for the formation of thermodynamically stable insoluble mineral phases. The reagent must be compatible with the groundwater and soil, potentially using groundwater/soil components to aid in the immobilization process. The delivery system should first concentrate the radionuclides, removing them from the groundwater flow by a cation exchange process, then release the precipitating anion, which forms thermodynamically stable mineral phases. The most promising means of delivering the precipitant would be to use a water-soluble, hydrolytically unstable complexant that functions in the initial stages as a cation exchanger to concentrate the metal ions. As it decomposes, the chelating agent releases an inorganic precipitant and crystalline mineral phases are formed.

Technology Needs

The mineralization concept can potentially immobilize radioactive metal ions in the environment. It is a safe, simple, and inexpensive alternative to pump-and-treat methods for groundwater decontamination or the installation of massive barriers to prevent nuclide migration (in situ grouting). Alternatively, it could be applied as a finishing step following the removal of most of the radionuclides from the site. The process could be applied to waste disposal sites (used either before or after burial) like Hanford and Idaho National Engineering Laboratory, areas of accidental environmental contamination (Fernald, Rocky Flats), or even to commercial mill tailings piles.

Scientific Background

Unplanned releases and direct discharges have contaminated soils and waters at many DOE sites. Planned disposal of materials contaminated with radionuclides also accounts for a significant portion of the radionuclides in the subsurface environment. Several mechanisms exist for the dispersal of the contaminants to the wider environment. For those materials possessing appreciable water solubility, serious contamination of the local environment may occur through surface water runoff and percolation through underlying geologic strata. This pathway represents a potential direct route for invasion of the biosphere by radioactive metal ions. Among the long-lived radioactive materials, the transuranic actinides are acknowledged to represent the greatest long-term hazard.

Most of the radionuclides in the buried waste disposal trenches are sorbed on surfaces. These surfaces are usually metallic, organic (paper and plastic), or

mineral in nature. The surrounding geologic strata provide additional surface sorption opportunities. The chemical form of the sorbed radionuclides is extremely variable ranging from rather intransigent oxide films to potentially soluble metal nitrate residues. The latter species in particular are susceptible to mobilization when in contact with natural waters. Natural chelating agents like humic and fulvic acids, which are present at low concentration in most groundwater, can facilitate environmental migration of heavy metals even when present in moderately insoluble forms. The potential for migration to the surrounding environment would be greatly decreased if the metal ions were converted to much more insoluble thermodynamically stable forms.

For the actinides, thermodynamic calculations and observation of the natural world suggest that phosphate may be the ideal medium for in situ immobilization. The existence of major deposits of rare-earths, thorium, and uranium in monazite sands in the subtropical environment represented by central Florida is nature's testimony to the stability of this mineral phase. Thermodynamic calculations based on the best available data further supports the low solubility of f element phosphates. Conversion of surface-sorbed actinide ions into thermodynamically stable mineral phases will decrease the tendency of the nuclides to be transported by groundwater and simultaneously improve the predictability of such movement by thermodynamic models.

Technical Approach

The task has as its objectives 1) identification of a hydrolytically unstable organophosphorus complexant and demonstration of its decomposition of under representative groundwater conditions of E_h and pH, 2) demonstration of the formation of crystalline actinide phosphate solids under these conditions, 3) determination of the leachability of actinides from the phosphate solids, and 4) testing with representative geomeia and synthesized analogs. Verification of reduced "solubility" (not thermodynamic solubility

products, but actual radionuclide concentrations) of actinide ions in the III, IV, V, and VI oxidation states as a function of pH and phosphate concentration is a primary goal. Ultimately, the concept could be developed to treat various mill-tailings piles in addition to those media contaminated with transuranics.

Accomplishments

As initially conceived, this program was to rely on the class of compounds called Thermally Unstable Complexants (TUCS). These ligands, diphosphonic acid chelating agents designed to spontaneously decompose under suitable conditions, proved too robust for the purpose under environmental conditions. The organophosphate complexing agent phytic acid (Figure 1) (myo-inositol(hexakisphosphoric acid)) was then identified as a potential substitute for the phosphonate chelating agents. Phytic acid has much better characteristics for the design objective than the phosphonate TUCS compounds. It is a natural product, forms insoluble salts with polyvalent cations (Ca^{2+} , for example) thus potentially serving as a cation exchanger, is known to be readily hydrolyzed releasing phosphate, and the organic residue (inositol) does not complex metal ions and hence will not interfere with the mineralization process.

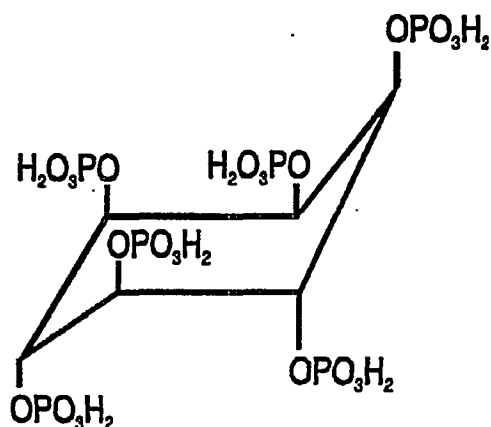


Figure 1. Structure of the organophosphate complexing agent phytic acid.

The rate of production of phosphate from phytate as a function of temperature and pH has been investigated using spectrophotometric techniques and NMR spectroscopy. Independent of the starting pH, all systems tend toward a final pH of 6, buffered by the $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ hydrolysis product. NMR spectroscopy indicates inositol as the major immediate organic product. No evidence was found for significant buildup of intermediate inositol(phosphate) species ($\text{I}(\text{PO}_4\text{H}_2)_{6-x}$). Extrapolation of the rate parameters using the Arrhenius relationship at pH 5 and 6 gives the lifetime for phytate 104 ± 22 years at pH 5.1 and 156 ± 42 years at pH 6.0. Literature reports indicate that microbiological effects can shorten this lifetime by orders of magnitude. Other reports have implicated polyvalent metal ions in accelerated phytate hydrolysis. The lifetime of phytic acid in the environment becomes immaterial if it functions in the intermediate term as an effective cation exchange medium.

Crystalline lanthanide (EuPO_4 and $\text{EuPO}_4 \cdot 1/2 \text{H}_2\text{O}$) and uranyl phosphate ($(\text{UO}_2)_3(\text{PO}_4)_2$) solids have been identified in pH 1-5 phosphate media and further demonstrated to exist as a result of the hydrolysis of lanthanide and uranyl phytates. Results for thorium (as representative of the tetravalent actinides) indicated no evidence for the formation of crystalline thorium phosphates, though the existence of amorphous thorium phosphates cannot be ruled out. Weak $\text{Th}(\text{OH})_4/\text{ThO}_2$ lines appear in the X-ray powder diffraction pattern indicating that these species may control the solubility of thorium.

The "solubility" of europium, uranyl, and neptunium(V) as a function of pH and phosphate concentration in a synthetic groundwater solution ($I = 0.1 \text{ M}$, $[\text{NaHCO}_3] = 0.5 \text{ mM}$) has been determined in a series of experiments using radiotracers. Solid films of metal nitrates, hydroxides, citrates, and TRUEX process solvent solutions were deposited on glass surfaces and contacted with the synthetic groundwater solutions. In both the europium and uranyl systems, the concentration of the radionuclide in the synthetic groundwater was controlled by phosphate

even at 0.1 mM total phosphate. Europium concentrations were less than $2 \times 10^{-9} \text{ M}$ even at the lowest phosphate concentration. Uranyl concentrations were below $2 \times 10^{-7} \text{ M}$ in the presence of phosphate with concentrations decreasing at higher pH. Each of these solubility limits is at least 10 times lower than that observed in the absence of phosphate and generally consistent with thermodynamic calculations. NpO_2^+ concentrations were not appreciably affected by phosphate except at $[\text{PO}_4]_i > 1.0 \text{ mM}$ and at pH 7-8. Under these conditions, neptunium solubility is controlled at about 10^{-6} M . Ongoing experiments are investigating the effect of coprecipitation on $[\text{NpO}_2^+]$ in solution.

Benefits

Because it involves only the application of inexpensive reagents, phosphate mineralization promises to be an economical alternative for in situ immobilization of radionuclides (actinides in particular). The method relies on the inherent (thermodynamic) stability of actinide mineral phases. This has the dual benefit of reduced radionuclide solubility, and predictability based on the application of thermodynamic models for performance verification. In situ immobilization eliminates the need for excavation, thus reducing the risk of operator contamination and airborne dispersion of radionuclides to the surrounding environment.

The principal benefits to be derived from the demonstration of this process are the elimination of the need for pumping of groundwater or excavation of soils to maximize the environmental (geochemical) stability of radionuclides in buried wastes. Immobilization of radionuclides in the subsurface environment can be accomplished by this method at low cost and without the construction of massive barriers to restrict groundwater flow. Because thermodynamically stable actinide phosphates are formed, accurate prediction of the potential for radionuclide migration will be possible via thermodynamics-based geochemical models. The

concept also has potential for commercial development as a means of immobilizing radioactive elements in uranium or thorium mill tailings piles, or for the stabilization of nonradioactive heavy metals in mill-tailings piles resulting from surface mining activities to recover strategic metals.

Keywords

mineralization, actinides, phosphate, groundwater, in situ treatment, environment remediation.

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