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In-situ Mineralization of Actinides for Groundwater Cleanup:

Laboratory Demonstration with Soil from the Fernald Environmental Management Project

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ABSTRACT

An attractive approach to decreasing the probability of actinide migration in the subsurface is to transform the ions into less mobile forms by remote treatment. The process described herein relies on a polyfunctional organophosphorus complexant to sequester the mobile metal ions by complexation/cation exchange in the near term. The cation exchanger is designed to subsequently decompose, transforming the actinides into insoluble phosphate mineral forms as the medium of stable long-term isolation. This material can be generated in situ in the subsurface thus eliminating the need for excavation to immobilize the actinide ions. Previous investigations have identified a suitable organophosphorus reagent and profiled its decomposition kinetics, verified the formation of phosphate mineral phases upon decomposition of the reagent, determined solubility limits for appropriate metal phosphates under groundwater conditions, and examined the cation exchange behavior of the calcium salt of the organophosphorus reagent. In this report, the focus is on a laboratory-scale demonstration of the concept using a soil sample from the Fernald Environmental Management Plant.

Introduction

Accidental releases, disposal of contaminated materials in landfills and soil pits, and leaking storage tanks in the subsurface have contaminated soils and waters at many DOE sites with a variety of radioactive and chemically hazardous substances [1]. Various technological solutions have been proposed for remediation of sites contaminated with transuranic elements. Protocols have been developed for washing of soils with various solvent/chelating agent mixtures. Radionuclides can be removed from groundwaters by pumping the waters to the surface, treating them (e.g., by cation exchange or membrane separations) and returning the cleaned water to the subsurface, so-called "pump and treat" methods. Installation of reactive barriers into the subsurface, injection of impermeable barriers, and even "glassification", melting the soils to convert them to glass, have been suggested as methods for minimizing the potential for migration of the contaminants to the wider environment. For many chemical contaminants, bioremediation is an attractive option.

These treatment options achieve varying levels of success in cleaning the subsurface soils and ground waters. Many suffer defects/obstacles that inhibit their deployment. Several involve movement of contaminated materials from soils, creating opportunities for increased dispersal of the radionuclides during the treatment process. Other methods are so expensive as to be impractical for implementation on a large scale. Some have proven unacceptable because they performed better in the laboratory than they did in the field. However, most of these options could be applied with good effect to provide solutions to contamination problems in selected sites.

An attractive alternative approach to the pump-and-treat and soil excavation methods of

radionuclide/actinide remediation is to develop in-situ treatment methods that do not require extensive movement and treatment of the contaminated geomedia (soils or waters) but rather immobilize (or otherwise transform) the radioactive elements in place. Introduction of reactive or impermeable barriers into the soil are attractive from this perspective, as the need to excavate contaminated soils or pump contaminated waters is diminished. The ideal in situ treatment option would create a reactive barrier through introduction of water soluble species which would react in the soil (perhaps with soil components) to form the barrier without significant intervention from the surface. Natural processes of this type have been suggested as possible mechanisms for the formation of rich mineral veins of redox active metal ions, for example, at the Oklo mine site in Gabon [2].

The premise of our research project is to immobilize actinides in situ, transforming them into thermodynamically stable mineral phases by introducing a mineralizing agent into the subsurface environment via an aqueous solution. The mineralizing reagent is injected or sprayed on the surface and allowed to percolate downward as a water soluble organic compound which reacts with naturally occurring metal ions to form insoluble compounds. These compounds readily exchange the naturally occurring metal ions (e.g., Ca^{2+}) for the mobile actinide cations which are thus removed from the mobile aqueous phase via a cation exchange mechanism. Under suitable conditions, cation exchange can be greatly superior to sorption mechanisms for metal ion immobilization. The complexant is designed to subsequently decompose, releasing the mineralizing agent and promoting the formation of thermodynamically stable actinide-bearing mineral phases. Incorporation of the target metal ion in a thermodynamically stable species should constitute an ideal matrix for permanent disposal.

Thermodynamic calculations suggest phosphate as an optimum mineral phase for actinide sequestration. Our studies therefore have focused on the natural product phytic acid (myo-inositolhexakisphosphoric acid, Figure 1) as the means of delivery of phosphate to the subsurface environment. Phytic acid is a natural product (isolated from beans and leafy vegetables) which is used commercially as a starting material in the manufacture of inositol [3], as a dietary supplement, a nutrient source for microorganisms, and a metal chelating and precipitating agent. It complexes polyvalent metal ions moderately and is readily hydrolyzed to release phosphate. In the U. S., phytic acid is produced at an annual rate of several hundred thousand metric tons as a byproduct of fermentation processes [4], but this material is not isolated for use. Instead, most of the insoluble phytate (as phytin) is being recycled along with the other solid fermentation residues for animal feed. Because the calcium salts of phytic acid are insoluble, we projected that these salts would function as cation exchangers for soluble actinides in the environment.

One contaminated site with a fairly well-defined cleanup target is the former Fernald Plant, presently known as the Fernald Environmental Management Project. The Fernald site was

established in the early 1950's for processing uranium and its compounds from natural uranium ore concentrates [5]. Over the operating lifetime of the plant, which extended to 1989, various plant operations resulted in substantial contamination of soils on the site with uranium. This site differs from most of the contaminated environments around the former DOE weapons complex in that the principle contaminant of concern is uranium. With only one element as a target, this site would appear to be most promising for a successful cleanup.

Site restoration activities initially focused on characterization of the uranium in the soil and on soil washing procedures to decontaminate the soils. Removal of uranium to below normal background soil concentrations was envisioned. Unfortunately, soil washing procedures designed to remove uranium contamination have proven less effective than expected, partly as a result of the diversity of soil composition and the chemical/physical state of uranium in the soil. Presently, site closure plans call for the disposition of contaminated surface soils in engineered landfills at the FEMP site. The soil samples are to be excavated, treated, and disposed of in the engineered facility. Specifically, the contaminated soils are to be deposited in the engineered bins in six inch layers of soil, chemically treated, compacted, and another layer of soil deposited [6]. The process will be continued until the bin is filled. The landfill will then be capped and maintained indefinitely. Treatment options for the interbed layers (to minimize the potential for uranium migration) have been considered.

In this report, we present the results of a laboratory investigation of the effect of calcium phytate on the solubility of UO_2^{2+} in contact with a glacial till soil sample from the Fernald Environmental Management Project. For comparison, sorption of UO_2^{2+} by hydroxyapatite has also been examined.

Experimental

Phytic acid was purchased from Aldrich Chemical Company as the dodecasodium salt and used as received. Its characterization has been described previously [7]. All other reagents were of analytical reagent grade and used as received.

Calcium phytate solids were prepared according to the following procedure. A solution of sodium phytate (0.049 M) was adjusted to pH 7 with NaOH. A 0.994 M $\text{Ca}(\text{NO}_3)_2$ solution was added to the sodium phytate solution at metal to ligand ratios of 6:1. A white precipitate formed immediately under all conditions. The solutions were stirred overnight then washed four times with deionized water. After the fourth washing the samples were placed in an oven and dried at 100 °C for 24 hours. After drying, the precipitates were analyzed for Ca, P, Na, C, and H. Results of the elemental analysis of several samples prepared using this and other procedures always result in a solid material of composition $(\text{Ca}_{4.6}\text{Na}_{0.20}\text{H}_{2.6}(\text{CH}(\text{PO}_4))_6 \cdot 6.5\text{H}_2\text{O})$, FW=957 g/mole). The calcium

phytate solids were amorphous to X-rays. Synthesis of stoichiometric hydroxyapatite was performed via a "Gel" route outlined by Takahashi et. al. [8]. X-ray powder diffraction confirmed the formation of hydroxyapatite (Figure 2). This material was ground to a fine powder for uranium uptake testing.

Uranium concentrations in the solution phase were monitored using ^{233}U tracer, which offers much greater detection sensitivity than the ubiquitous natural uranium in the soil sample. Purification of ^{233}U was carried out by evaporating 2 ml of a $^{233}\text{UO}_2(\text{ClO}_4)_2$ solution to dryness. A 300 μL aliquot of 2 M HNO_3 was added to the vial containing the ^{233}U . The solution was then loaded onto an U/TEVA column (EiChrom) [9]. The column was rinsed with 18 ml of deionized water (10 free column volumes). After rinsing, Th^{4+} was eluted with 16 ml of 2 M HCl , and uranium was eluted by rinsing with 16 ml of 0.01 M HNO_3 . After collection, the solution containing the uranium was evaporated to dryness and dissolved in 1.5 ml of 0.01 M HClO_4 . Radiochemical purity was checked by alpha and gamma spectroscopy using a NaI detector.

Equipment

All pH measurements were made with Beckman $\Phi 71$ and $\Phi 72$ pH meters using Ross combination pH semi-micro electrodes using saturated NaCl as the reference electrolyte. Electrodes and pH meters were calibrated with pH 4.00 and 7.00 buffers (Aldrich). X-ray powder patterns were generated by a Phillips PW 1729 X-ray Generator with a $\text{CuK}\alpha$ source at a wavelength of 1.5418Å. X-ray powder pattern of hydroxyapatite was generated by Scintag Diffractometer operating in the theta-theta mode. Liquid scintillation measurements of ^{233}U were made with a Beckman LS 6000IC counter using Ultima Gold liquid scintillation cocktail (Packard).

Mineral and Solid Phases

A soil sample from Fernald was used for batch experiments. The reported composition of the Fernald soils was 65% quartz, 20% calcite, 2% dolomite, and 13% clay by quantitative XRD [5]. Reported values of the pH of the Fernald soils were between pH 7.3 and 8.1 [10]. All pH measurements taken at Argonne of the Fernald soils were between pH 7.2 and 7.4.

Fernald Soil Batch Experiments

Calcium phytate, sodium phytate, and hydroxyapatite were added to a Fernald soil sample to assess which compound was the most efficient for removing uranyl from solution in contact with soil samples. Blank experiments assessed the inherent uranyl uptake capacity of the Fernald soil sample.

Large culture tubes (10 ml) were acid washed and then rinsed with deionized water. To each of the culture tubes 10, 20, 40, 50, & 100 mg of calcium phytate, sodium phytate, or hydroxyapatite was added. Calcium phytate and hydroxyapatite were added as solids. Sodium phytate was added as a 0.049 M solution (pH 7). After the phosphate sources were added to the culture tubes, one gram of Fernald soil was added to the culture tubes. A solution of 8 ml of simulated groundwater (0.1 M

NaCl, 0.5 mM NaHCO₃, and 10 mM Ca(NO₃)₂) and 3-5 µl of ²³³U tracer solution ([U]_{tot} = 2.2-3.6 x 10⁻⁶ M) was added to the culture tubes. The solution was mixed continuously on a stir plate (at room temperature) and sampled periodically. When sampling, the culture tubes were centrifuged and 800 µl was removed and filtered through a 0.2 µm filter. A 400 µl aliquot of the filtered sample was taken for liquid scintillation counting. The pH of the solutions was measured at each sampling interval.

Results

The rate of equilibration of uranyl in this system was rapid as indicated in Table 1 for pure materials and Figure 3 for soil/calcium phytate mixtures. Under the conditions of these experiments, a 250 mg sample of the Fernald soil exhibited minimal tendency to adsorb UO₂²⁺ from the simulated groundwater. Over a three week equilibration period, only about a third of the tracer was removed from the solution. In contrast, only 30 mg of calcium phytate were sufficient to adsorb 99.9% of the ²³³U tracer within one hour. The uranyl tracer contacting 30 mg of calcium phytate was below detection limits (<1 x 10⁻¹⁰ M) at 2 days. Follow-on experiments (to be described in a future publication) demonstrated similar uranyl sorption efficiency by freshly prepared hydroxyapatite as sorbent.

The results of subsequent experiments in which calcium phytate, soluble sodium phytate and hydroxyapatite were mixed with the Fernald soil sample (in the presence of the ²³³U tracer) are shown in Figure 4 (12 days equilibration results plotted). Surprisingly, under the conditions of these experiments our freshly prepared hydroxyapatite appears to have little effect on the uranyl concentration in the simulated groundwater (0.1 M NaCl, 0.0005 M NaHCO₃, 0.01 M Ca²⁺ at pH 7). Both solid calcium phytate and soluble sodium phytate are significantly more effective than hydroxyapatite in contact with the Fernald soil.

Discussion

Our earlier investigations have established the fundamental validity of the phytate-phosphate mineralization concept, briefly summarized as follows:

1) Phytic acid is hydrolyzed in pH 5-7 solutions of synthetic groundwaters with a half-life of about 100-150 years at 25°C [7]. Literature reports indicate that microbes can significantly promote the rate of hydrolysis of phytate, often by orders of magnitude [11];

2) Hydrolysis of Eu³⁺ (as an analog for trivalent actinides) and UO₂²⁺ salts of phytic acid yield the corresponding metal phosphate solids EuPO₄•½ H₂O and (UO₂)₃(PO₄)₂•H₂O, which are species of known properties;

3) Radiotracer solid-solution distribution experiments established that the concentration of

Eu^{3+} was controlled in the 10^{-10} M concentration range over the pH range of 5-8 by 10^{-3} M phosphate in citrate media, uranyl concentrations are controlled at around 10^{-7} M by 10^{-3} M phosphate at pH 6-7 with slightly higher levels at pH 8 due to carbonate complexation, concentrations of NpO_2^+ are minimally affected by phosphate except at pH above 7 and $[\text{PO}_4^{3-}]_t = 0.01$ M;

4) Addition of low concentrations of Ca^{2+} (in the presence of phosphate) appear to reduce actinide solubility generally, due either to the formation of hydroxyapatite ($\text{Ca}_5(\text{OH})(\text{PO}_4)_3 \cdot x\text{H}_2\text{O}$) which coprecipitates or sorbs the actinides from solution, or to the formation of discrete mineral phases incorporating both actinides and calcium;

5) $\text{Ca}_{4.6}\text{H}_{2.8}(\text{phytate}) \cdot 6.5 \text{ H}_2\text{O}$ has been established as the dominant form of insoluble calcium phytates and as an effective cation exchange medium for UO_2^{2+} and NpO_2^+ [12]. These basic concepts were established in the absence of actual geomedial media to demonstrate the fundamental characteristics of our approach.

Additional complexity is introduced into both the performance of the isolation system and its interpretation with the inclusion of a mineral. In addition to surface adsorption opportunities for metal ion removal and the production of colloidal particles, mineral components may partially dissolve in the aqueous medium and the concentrations of "groundwater" solutes may be altered as a result. We have not analyzed the synthetic groundwater samples after equilibration with the soil sample. Based on the known composition of the solid (65% quartz, 20% calcite, 2% dolomite, 13% clay) there is little reason to expect a significant change in composition in any soluble components other than Ca^{2+} and total carbonate. Taking into account our synthetic groundwater composition of 0.1 M NaCl, 0.01 M Ca^{2+} , 0.0005 M NaHCO_3 , the 20% by mass of calcite in the soil sample, and fixing the pH at 7.0, we calculate a baseline water composition of 0.0096 M Ca^{2+} , 9.4×10^{-5} M total carbonate and ionic strength 0.1. The $[\text{UO}_2^{2+}]$ observed in the absence of any added sequestrant (in Figure 4) is consistent with this composition.

We have established independently by both experiment and calculation [7] that phosphate concentrations as low as 10^{-4} M control the concentration of UO_2^{2+} in this synthetic groundwater at about 10^{-7} M due to the insolubility of $(\text{UO}_2)_3(\text{PO}_4)_2$. In light of this observation, it is surprising that hydroxyapatite apparently has minimal effect on uranyl concentrations in the synthetic groundwater in contact with the Fernald soil sample. Equilibrium calculations based on the composition of the system indicate that the free phosphate concentration (limited by the solubility of hydroxyapatite) falls in the range 1.5 to 3.1×10^{-10} M, a free phosphate concentration too low to have significant impact on the speciation of uranyl phosphates. In addition, since the concentration of UO_2^{2+} in contact with the soil samples with hydroxyapatite do not differ appreciably from the soil sample alone, we conclude that sorption of uranyl onto the hydroxyapatite surface also is inconsequential in these experiments. Previous investigations (as a part of this project) have established a correlation

between the concentration of UO_2^{2+} in solution and the concentrations of Ca^{2+} and PO_4^{3-} (uranyl solubility decreases as calcium concentration increases) which we have interpreted as an indication of calcium phosphate sequestration of uranyl. As the present experiment suggests surface sorption is not important in this system, we suggest that the most effective method of uranyl solubility control by calcium phosphate relies on a coprecipitation mechanism rather than adsorption. This would suggest that mineral apatite might not be an optimum choice for uranyl solubility control in the Fernald soil/synthetic groundwater system.

In contrast, the results shown in Figure 4 indicate that phytate is superior to hydroxyapatite for controlling the concentration of UO_2^{2+} under the conditions of these experiments, though in this system as well uranyl concentrations are higher than the results in Table 1 would predict. The soluble uranyl concentration decreases exponentially (linear in the semilog presentation) with the percent addition of calcium phytate. Addition of soluble sodium phytate results in a more dramatic decline in the soluble uranium fraction up to 4 weight percent sodium phytate. At higher concentrations of soluble phytate, uranyl concentrations increase slightly. Assuming a Ca^{2+} :phytate stoichiometry of 4.6:1 in the stable calcium salt, the calculated soluble calcium will be fully depleted from the solution phase at about 2-3 weight percent phytate. Therefore, at higher concentrations the added phytate remains in solution and apparently complexes uranyl to keep it in solution. Ongoing research suggests a similar effect in the chemistry of Pu(VI). The sodium phytate results indicate that prompt precipitation of uranyl as uranyl/calcium phytate is a more effective solubility control mechanism than the cation exchange, though within the 12 day equilibration comparable uranyl concentrations are observed at 10% substitution for the calcium phytate and sodium phytate systems.

The relative effectiveness of calcium phytate and hydroxyapatite is particularly striking and potentially important. Hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, formula weight 1004.8 g/mole) is under consideration at several DOE environmental restoration sites as a soil additive to reduce the environmental mobility of radionuclides, including actinides. Hydroxyapatite could function as a potential source of phosphate for actinide mineralization, but, the low solubility product of hydroxyapatite ($\log K_{\text{sp}} = -58.33$ - $K_{\text{sp}} = [\text{Ca}^{2+}]^5[\text{OH}][\text{PO}_4^{3-}]^3$, [13]) probably maintains phosphate at too low a concentration for this mechanism to be very important. It is likely that the principal mechanism for actinide solubility control is surface sorption, which is clearly not very effective in our laboratory soil tests. As the relative percentages of phosphate in hydroxyapatite and calcium phytate is similar (57% vs. 60% by weight), the difference between hydroxyapatite and calcium phytate cannot be attributed to the amount of phosphate present. The phosphate in phytic acid must be in a more suitable form for metal ion sequestration, almost certainly reflecting the more favorable orientation of the phosphate groups in phytate as compared with hydroxyapatite.

The more effective uranyl getting power of soluble phytate probably reflects a difference in

mobility and therefore accessibility of the phytate to the uranyl ion. Its effectiveness in reducing soluble uranyl concentrations at low weight percent suggests that either the solubility of uranyl phytates is very low [12] or that some of the phosphate groups of phytate are forming strong bonds with metal ions at the water mineral interface. If the latter assumption proves true, it constitutes a most significant development in the evolution of this technology, as it provides evidence of a mechanism by which phytate can be bound to the soil. Surface complexation of phytate by clay minerals will have the effect of anchoring phytate in the soil matrix and further reducing radionuclide mobility.

Conclusions

The experiments described above allow us to conclude: 1) that solid hydroxyapatite (as opposed to hydroxyapatite generated in situ) reduces the concentration of uranyl ion in solution by only a small amount when mixed with soil from the Fernald site; 2) Substitution of 1-10% calcium phytate results in an exponential decrease in the uranyl concentration (linear log vs. weight percent) reducing the concentration of uranyl by a factor of 100 at 10% substitution. 3) Sodium phytate achieves more spectacular results at lower concentrations, but give indication of possible resolubilization at higher weight percents (under calcium deficient conditions). 4) The rate of achievement of a steady state is rapid for all systems.

Phytic acid cation exchange and phosphate mineralization is an attractive method for improving the viability of various disposal options. Phytate, either as the pH adjusted, water soluble sodium salt or as the insoluble calcium salt, could be applied to the surface of contaminated soils. The soluble phytate would penetrate the layers to some degree and distribute through the porous soil zones reacting with soil components and precipitating as phytin (Ca/Mg salts of phytic acid). Phytin has been demonstrated as an effective cation exchanger for uranyl and other actinides. Alternatively, insoluble calcium phytate could either be mixed homogeneously into the soil samples to sequester mobile cations where soil excavation is feasible. The raw unrefined phytate presently disposed of as an undesirable component of animal feed [4] could be recovered for this use. Application of soluble phytate and calcium salts via injection wells could be used to prepare calcium phytate barriers at depth thus avoiding excavation. A variety of other potential applications can also be envisioned for this technology.

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Table 1. Sorption of ^{233}U tracer (2.9×10^{-6} M total concentration in Fernald soil experiments, 2.2×10^{-6} M in calcium phytate experiment) from 0.1 M NaCl/0.0005 M NaHCO_3 (total volume 8 ml) onto soil sample from Fernald (pH 7.8) and calcium phytate (pH 7.9 decreasing to 6.6).

Contact time	Fernald Soil 250mg	$\text{Ca}_{4.5}\text{H}_3(\text{phytate})$ 30 mg
1 hour	2.26×10^{-6} M	3×10^{-9} M
1 day	1.81×10^{-6} M	6×10^{-10} M
2 day	1.84×10^{-6} M	nd
19 days	2.31×10^{-6} M	nd

nd. Below detection limit of 2×10^{-10} M.

Figure Captions:

Figure 1. Phytic acid

Figure 2. X-ray powder diffraction pattern for hydroxyapatite sample generated in this investigation.

Figure 3. Concentrations of UO_2^{2+} in synthetic groundwater solution (8.0 ml of 0.0005 M NaHCO_3 , 0.1 M NaCl , 6.0×10^{-6} M total uranium) in contact with 100 mg of Fernald soil sample plus variable amounts of calcium phytate cation exchanger as a function of equilibration time.

Figure 4. Concentration of UO_2^{2+} in synthetic groundwater solution (8.0 ml of 0.0005 M NaHCO_3 , 0.1 M NaCl , 0.01 M Ca^{2+} , pH 7) in contact with 1 g Fernald soil sample plus varying amounts of hydroxyapatite, calcium phytate and soluble sodium phytate after 12 days equilibration.

Intensity (A. U.)