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Actinide immobilization in the subsurface environment by in-situ treatment with a hydrolytically unstable organophosphorus complexant: Uranyl uptake by calcium phytate

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Abstract

An attractive approach to decreasing the probability of actinide migration in the subsurface is to transform the ions into a less mobile form by remote treatment. We have under development a process that relies on a polyfunctional organophosphorus complexant to sequester the mobile metal ions by complexation/cation exchange. The insoluble complex subsequently decomposes, transforming the actinides into phosphate mineral forms as a thermodynamically stable isolation medium. In this report, we briefly describe the process with focus on the cation exchange behavior of the calcium salt of the organophosphorus sequestrant. © 1998 Elsevier Science S.A.

Keywords: Actinides; Environment remediation; Mineralization; Phytic acid; Uranyl

1. Introduction

Fifty years of actinide production at U.S. Department of Energy facilities (and corresponding facilities in the former Soviet Union and elsewhere) have left a substantial cleanup obligation in the post-cold war era. 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]. For those materials possessing appreciable water solubility, transport as soluble or colloidal species in ground or surface waters represents a potential pathway for spread of the contamination to the general environment. Among the long-lived radioactive materials, the transuranic actinides are commonly acknowledged to represent the greatest hazard, though their mobility is strongly a function of conditions. Immobilization of actinide ions is the particular focus of this report.

Various technological solutions have been proposed for remediation of sites contaminated with transuranic elements. Protocols have been developed for washing of soil samples 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. These treatment options achieve varying levels of success in cleaning the subsurface soils.

An attractive alternative approach 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 is attractive from this perspective, as the need to excavate soils or pump waters is diminished. The ideal in-situ treatment option would create a reactive barrier through introduction of water soluble species that 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 work is to immobilize the actinides in situ, transforming them into thermodynamically stable mineral phases by introducing a mineralizing agent into the subsurface environment using an aqueous solution. The

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mineralizing reagent is injected or sprayed on the surface and allowed to percolate downward as a water soluble organic compound that 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 by a cation exchange mechanism. The complexant is designed to subsequently decompose, releasing the mineralizing agent and promoting the formation of thermodynamically stable actinide-bearing mineral phases.

Thermodynamic calculations suggest phosphate as an optimum mineral phase for actinide sequestration. Our studies have focused on the natural product phytic acid (myo-inositolhexakisphosphoric acid, Fig. 1) as the means of delivery of phosphate to the subsurface environment. Phytic acid is a natural product (isolated from beans and leafy vegetables) that 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 agent 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]. This material presently is not isolated for use but rather is 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.

Our earlier investigations have established that phytic acid is hydrolyzed in pH 5–7 solutions of synthetic groundwaters with a half-life of about 100–150 years at 25°C [5]. Literature reports indicate that microbes can significantly promote the rate of hydrolysis of phytate, often by orders of magnitude [6]. We have also established that the hydrolysis of Eu^{3+} (as an analog for trivalent actinides) and UO_2^{2+} salts of phytic acid yield the corresponding metal phosphate solids $EuPO_4 \cdot 0.5H_2O$ and $(UO_2)_3(PO_4)_2 \cdot H_2O$. Radiotracer 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. Parallel experiments with $^{233}UO_2^{2+}$ tracer indicated less efficacious control of uranium solubility by phosphate (soluble uranyl concentrations of 10^{-7} M at pH 6–7). Slightly higher concentrations are observed at pH 8 due to carbonate complexation. Phosphate alone appears to have little impact on the solubility of NpO_2^{+} except at pH above 7 and $[PO_4^{3-}]_t = 0.01$ M. Addition of low concentrations of Ca^{2+} appears to reduce actinide solubility generally, presumably due to the formation of hydroxyapatite ($Ca_5(OH)(PO_4)_3 \cdot xH_2O$) which either coprecipitates or sorbs the actinides from the solution phase.

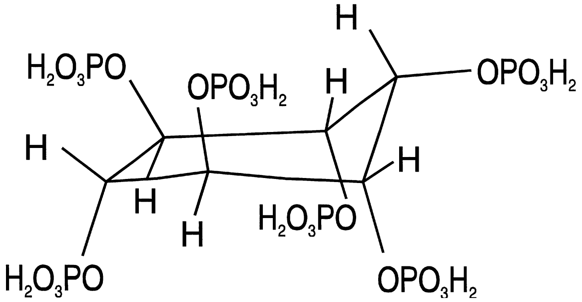

Fig. 1. Structure of myo-inositolhexakisphosphoric acid (phytic acid).

In the following discussion, we will present new information on the preparation, stoichiometry, and cation exchange behavior of calcium phytate with particular focus on its ability to complex and/or sorb uranyl.

2. Experimental

Phytic acid was purchased from Aldrich Chemical Company as the dodecasodium salt and used as received. The material was characterized by NMR spectroscopy and potentiometric titration. The phytic acid concentration was determined by potentiometric titrations of sodium phytate solutions with 1 M $HClO_4$. The total phytate was quantified using the difference of the equivalence points at 6 and 8 equivalents of acid added, where clear breaks are observed in the titration curve [7]. All other reagents were of analytical reagent grade and used as received.

Stoichiometry of solid calcium phytate was determined as a prerequisite for actinide cation exchange studies according to the following procedure. A solution of sodium phytate (0.049 M) was adjusted to pH 7 with NaOH. A 0.994 M $Ca(NO_3)_2$ solution was added to the sodium phytate solution at metal-to-ligand ratios of 1:1, 2:1, 3:1, 4:1, 5:1, and 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 h. After drying, the precipitates were analyzed for Ca, P, Na, C, and H.

The second phase of the cation exchange experiments was designed to test the relative affinity of phytate for Ca^{2+} and UO_2^{2+}. Solutions of calcium nitrate (0.9945 M) and uranyl nitrate (0.1123 M) were added to the vials in mole ratios of 5:1, 4:2, 3:3, 2:4, 1:5, and 0:6, respectively. A solution of sodium phytate (0.049 M) adjusted to pH 7 was then added to the Ca^{2+}/UO_2^{2+} solutions so that the ratio of the total metal concentration to ligand was 6:1. The vials were placed on a stir plate and mixed continuously for 72 h. They were subsequently centrifuged, the solids washed with deionized water, dried in an oven at 110–125°C and analyzed for Ca, U, P, and Na.

The final phase of the cation exchange experiments was to test uranyl substitution for calcium on solid calcium phytate samples. A known amount of calcium phytate

(F.W. = 957 g mol^{-1}) of known stoichiometry ($Ca_{4.6}Na_{0.20}H_{2.6}(CH(PO_4))_6 \cdot 6.5H_2O$, see below) was added to six 40 ml test tubes of a predetermined weight. Ten ml of deionized water were added to the vials. A solution of uranyl nitrate was added to the mixture with a uranyl-to-phytate mole ratio of 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1. The pH of the solutions was in the range of 6–7.5. The vials were placed on a stir plate and mixed continuously for 72 h. After mixing, the vials were centrifuged and the mother liquor removed. The precipitate was washed once with deionized water. The vials containing the precipitate were then placed in an oven and dried at 110–125°C to constant weight. When drying was complete the precipitates were analyzed for Ca, U, P, and Na.

3. Results

Results for elemental analysis of C, H, Ca, Na, and P and the calculated stoichiometries of the calcium phytate solids are reported in Table 1. The column labeled C/P is the weight ratio of carbon/phosphorus obtained analytically, which compares favorably with the theoretical ratio of 0.387 for phytic acid. Because of the good agreement between experimental and calculated values, we elected to analyze only for phosphorus (as an indicator of phytate) in the uranyl substituted samples. The composition of calcium phytate derived from precipitation studies as a function of calcium/phytate mole ratios indicates a surprisingly constant stoichiometry for Ca^{2+} substitution onto phytate of 4.6(±0.2). An earlier report noted a maximum Ca/phytate stoichiometry of 4.8:1 [8], though the authors suggest that higher substitution is possible. The present results seem to contradict that suggestion. The water content of the calcium phytate is also constant at 6.7(±0.6). The only variation in the composition of the solids is in the ratio of Na^+ to H^+, which probably changes as a function of the pH at which the precipitate was formed. We prepared a relatively large sample of $Ca_{4.6}(H,Na)_{2.8}(phytate) \cdot 6.5H_2O$ for an investigation of actinide cation exchange.

The elemental analyses and calculated stoichiometries of the solid samples prepared from soluble calcium and uranyl phytate are presented in Table 2. As noted above, the phosphorus analysis was used to calculate the phytate content of the solid. Hydrogen ions (H^+) were added to achieve charge balance in the solid. The excess weight not accounted for by Ca^{2+}, Na^+, $phytate^{12-}$, and UO_2^{2+} was assumed to represent waters of hydration. Corresponding results for samples prepared by contacting soluble uranyl nitrate with solid calcium phytate are given in Table 3. The elevated ratio of UO_2^{2+}/Ca^{2+} in the solids prepared with low ratios of uranyl/calcium suggest that, as expected, phytate has a much higher affinity for uranyl than calcium. The highest stoichiometry for UO_2^{2+} is 5.4 equivalents/phytate, 91% of the theoretical maximum of 6 equivalents. In the two phase experiments, the trend of uranyl substitution for calcium is less regular for 1–3 equivalents of uranyl, but ultimately reaches a maximum substitution of 96% at the 6:1 mole ratio.

4. Discussion

The requirements for a viable cation exchanger based on Ca-phytate are (1) the calcium phytate should preferably have consistent, well-defined stoichiometry, (2) Ca^{2+} should be readily displaced by the target metal ions, (3) the calcium salt, the target metal ion salt and mixed cation salts of the phytate must all be insoluble, and (4) the capacity of the solid phytate for the metal ion should be known. Assuming electroneutrality of the insoluble metal phytate, the theoretical maximum capacity of phytic acid for divalent cations is 6 eq(R-PO_4^{2-})/(660.04 g mol^{-1}) = 9.1 meq g^{-1}. The acid (H^+) capacity is 18.2 meq g^{-1}. By comparison, the total acid capacity of strongly acidic

Table 1
Elemental analysis of calcium phytate samples (±10%) and calculated stoichiometries of the solids

Ca/phytate mole ratio	C (wt.%)	H (wt.%)	Ca (wt.%)	Na (wt.%)	P (wt.%)	C/P
1:1	7.65	2.19	20.3	0.76	18.9	0.405
2:1	7.57	2.20	19.7	0.57	19.3	0.392
3:1	7.71	2.17	19.5	0.29	19.6	0.394
4:1	7.74	2.23	19.2	0.27	20.3	0.381
5:1	7.68	2.31	18.8	0.24	19.3	0.398
6:1	7.85	2.26	18.7	0.22	19.4	0.405

Starting Ca/phytate mole ratio	Calculated stoichiometry of solid calcium phytate
1:1	$Ca_{4.88}Na_{0.32}H_{1.92}(CH(PO_4))_6 \cdot 7.0H_2O$
2:1	$Ca_{4.71}Na_{0.24}H_{2.34}(CH(PO_4))_6 \cdot 6.8H_2O$
3:1	$Ca_{4.54}Na_{0.10}H_{2.82}(CH(PO_4))_6 \cdot 6.5H_2O$
4:1	$Ca_{4.43}Na_{0.11}H_{3.03}(CH(PO_4))_6 \cdot 5.6H_2O$
5:1	$Ca_{4.47}Na_{0.10}H_{2.96}(CH(PO_4))_6 \cdot 7.4H_2O$
6:1	$Ca_{4.41}Na_{0.09}H_{3.09}(CH(PO_4))_6 \cdot 7.2H_2O$

Table 2
Elemental analysis and solid stoichiometry of calcium/uranyl phytate samples (±10%) prepared from homogeneous aqueous solution

U/Ca/phytate mole ratio (initial)	Ca (wt.%)	P (wt.%)	U (wt.%)	Na (wt.%)
1:5:1	5.43	11.3	35.2	1.99
2:4:1	2.65	10.0	37.4	1.21
3:3:1	1.83	10.5	43.4	0.81
4:2:1	0.72	9.11	48.4	0.35
5:1:1	0.10	7.86	52.4	0.36
6:0:1	0.01	7.71	53.6	0.08

Starting U/Ca/phytate mole ratio	Calculated stoichiometry of solid calcium phytate
1:5:1	$(UO_2)_{2.43}Ca_{2.24}Na_{1.42}H_{1.24}$phytate·$12.1H_2O$
2:4:1	$(UO_2)_{2.92}Ca_{1.23}Na_{0.98}H_{2.72}$phytate·$19.6H_2O$
3:3:1	$(UO_2)_{3.23}Ca_{0.81}Na_{0.63}H_{3.29}$phytate·$11.4H_2O$
4:2:1	$(UO_2)_{4.15}Ca_{0.37}Na_{0.32}H_{2.64}$phytate·$13.9H_2O$
5:1:1	$(UO_2)_{5.21}Ca_{0.06}Na_{0.38}H_{1.08}$phytate·$16.7H_2O$
6:0:1	$(UO_2)_{5.43}Ca_{0.00}Na_{0.07}H_{1.07}$phytate·$16.4H_2O$

sulfonic acid cation exchangers (e.g., Dowex 50) is typically 4–6 meq g^{-1}, that for Ca^{2+} is 2–3 meq g^{-1}. For the intended application, the kinetics of cation exchange are probably of little consequence. Nevertheless, kinetics of cation exchange onto calcium phytate should be rapid. The experiments conducted in this study had apparently achieved a steady state within 72 h.

The calcium/uranyl phytate solids formed as a result of precipitation from mixed calcium/uranyl phytate solution indicate that the insoluble material has a higher affinity for uranyl than calcium and tends to be more strongly hydrated. Overall hydration of the solid increases more or less in direct proportion to the degree of uranyl substitution. Though these experiments were designed primarily to determine only the stoichiometry of the precipitated solids, in all cases most of the uranium was removed from the solution phase. The high degree of loading of uranyl onto phytate (91% at 6:1 mole ratio) indicates that the sequestering ability of phytate is not reduced as uranyl loading increases to the theoretical maximum. In the two phase uptake experiments involving soluble UO_2^{2+} and solid $Ca_{4.6}H_{2.8}$phytate, uranyl is taken up to a slightly greater degree. The calcium residue is somewhat higher in these experiments than in the parallel aqueous mixing experiment. The quality of the agreement between the initially homogeneous mixing and the solution solid mixing experiments with uranyl also argue that the system is at a steady state within the 72 h period of mixing.

5. Conclusions

In this report, we have reported the dominant stoichiometry of the calcium salt of phytic acid and summarized the binding characteristics of UO_2^{2+} to the dominant calcium phytate salt. This series of experiments describes one aspect of our proposed two-step process for the removal of actinide ions from groundwaters. We have

Table 3
Elemental analysis and solid stoichiometry of calcium/uranyl phytate samples (±10%) prepared by contact of soluble uranyl nitrate with solid calcium phytate

Solid calcium phytate and UO_2^{2+} (initial)	Ca (wt.%)	P (wt.%)	U (wt.%)	Na (wt.%)
1:4.6:1	13.6	14.4	20.3	<0.05
2:4.6:1	8.55	11.3	34.3	0.13
3:4.6:1	11.1	13.0	28.4	<0.05
4:4.6:1	2.36	8.76	49.3	<0.05
5:4.6:1	0.99	7.97	52.7	<0.05
6:4.6:1	0.29	7.50	55.4	<0.05

Starting U/Ca/phytate mole ratio	Calculated stoichiometry of solid
1:4.6:1	$(UO_2)_{1.10}Ca_{4.38}Na_{0.07}H_{0.97}$phytate·$9.4H_2O$
2:4.6:1	$(UO_2)_{2.37}Ca_{3.51}Na_{0.00}H_{0.24}$phytate·$12.0H_2O$
3:4.6:1	$(UO_2)_{1.71}Ca_{3.96}Na_{0.00}H_{0.66}$phytate·$9.0H_2O$
4:4.6:1	$(UO_2)_{4.39}Ca_{1.25}Na_{0.00}H_{0.72}$phytate·$17.2H_2O$
5:4.6:1	$(UO_2)_{5.16}Ca_{0.58}Na_{0.00}H_{0.52}$phytate·$14.8H_2O$
6:4.6:1	$(UO_2)_{5.77}Ca_{0.18}Na_{0.00}H_{0.10}$phytate·$14.9H_2O$

demonstrated that $Ca_{4.6}H_{2.8}$(phytate)·$6.7H_2O$ is readily and consistently formed upon contact between soluble phytic acid and Ca^{2+}. This material completely exchanges Ca^{2+} for UO_2^{2+} when contacted with solutions containing macroscopic concentrations of $UO_2(NO_3)_2$. Similar quantitative substitution of UO_2^{2+} for Ca^{2+} is observed when the solids are prepared from aqueous solution. Other aspects of the overall actinide isolation process have either been previously reported or are under continuing study.

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