Polyphosphate Remediation Technology for *In-Situ* Stabilization of Uranium - 9093

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ABSTRACT

A labortory testing program has been conducted to optimize polyphosphate remediation technology for implementation through a field-scale technology infiltration demonstration to stabilize soluble, uranium-bearing source phases in the vadose and smear zone. Source treatment in the deep vadose zone will accelerate the natural attenuation of uranium to more thermodynamically stable uranium-phosphate minerals, enhancing the performance of the proposed polyphosphate remediation within the 300 Area aquifer. The objective of this investigation was to develop polyphosphate remediation technology to treat uranium contamination contained within the deep vadose and smear zones. This paper presents the results of an investigation that evaluated the rate and extent of reaction between polyphosphate and the uranium mineral phases present within the 300 Area vadose and smear zones, and autunite formation as a function of polyphosphate formulation and concentration. This information is critical for identifying the optimum implementation approach and controlling the flux of uranium from the vadose and smear zones to the underlying aquifer during remediation. Results from this investigation may be used to design a full-scale remediation of uranium at the 300 Area of the Hanford Site.

INTRODUCTION

Hanford Site and the 300 Area Uranium Plume

The Hanford Site, located in the eastern part of Washington State, contains nuclear facilities operated by the U.S. Department of Energy (DOE) (Figure 1). During the period spanning the startup of Hanford reactors in 1944 through the late 1980s, facilities in the 300 Area of the Hanford Site were primarily involved with the fabrication of nuclear fuel and the range of activities associated with this task resulted in a wide variety of waste streams that contained chemical and radiological constituents (Gerber 1992; DeFord et al. 1994). By 1989, all nuclear reactors were shut down and the activities were shifted towards environmental cleanup and site restoration. Since the early 1990s, extensive remediation of liquid waste disposal sites and solid waste burial grounds has taken place.
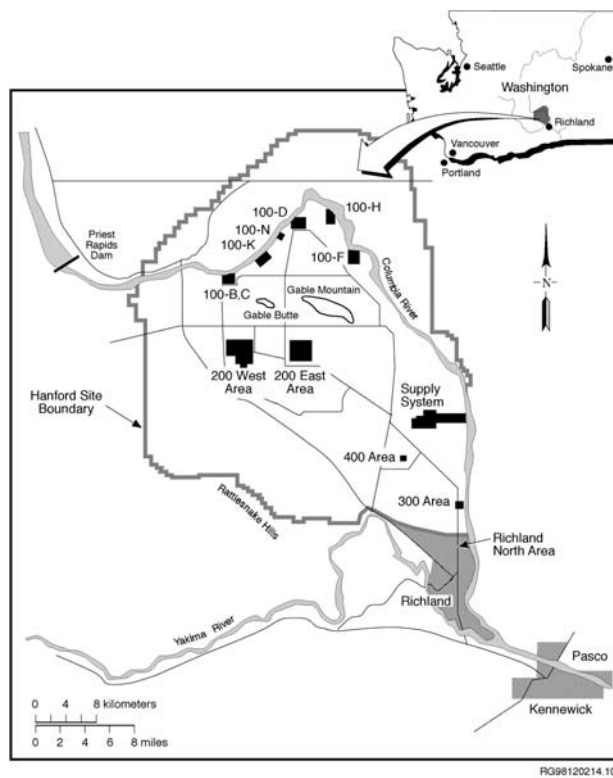

Figure 1. Map of the Hanford Site

The most prominent waste constituent remaining in this environment is uranium. Groundwater beneath the 300 Area contains uranium from past-practice disposal activities at concentrations that exceed the U.S. Environmental Protection Agency (EPA) standards for drinking water supplies (Figure 2). The uranium plume is just upstream of the City of Richland municipal water supply intake on the Columbia River. Elevated uranium concentrations enter the river along the shoreline, and enter the riparian and river biota through seeps. Uranium in its soluble form is of concern because of its chemical toxicity and risk of radiological exposure, even though the concentrations in groundwater for chemical toxicity are lower than those associated with exceeding radiological dose standards.
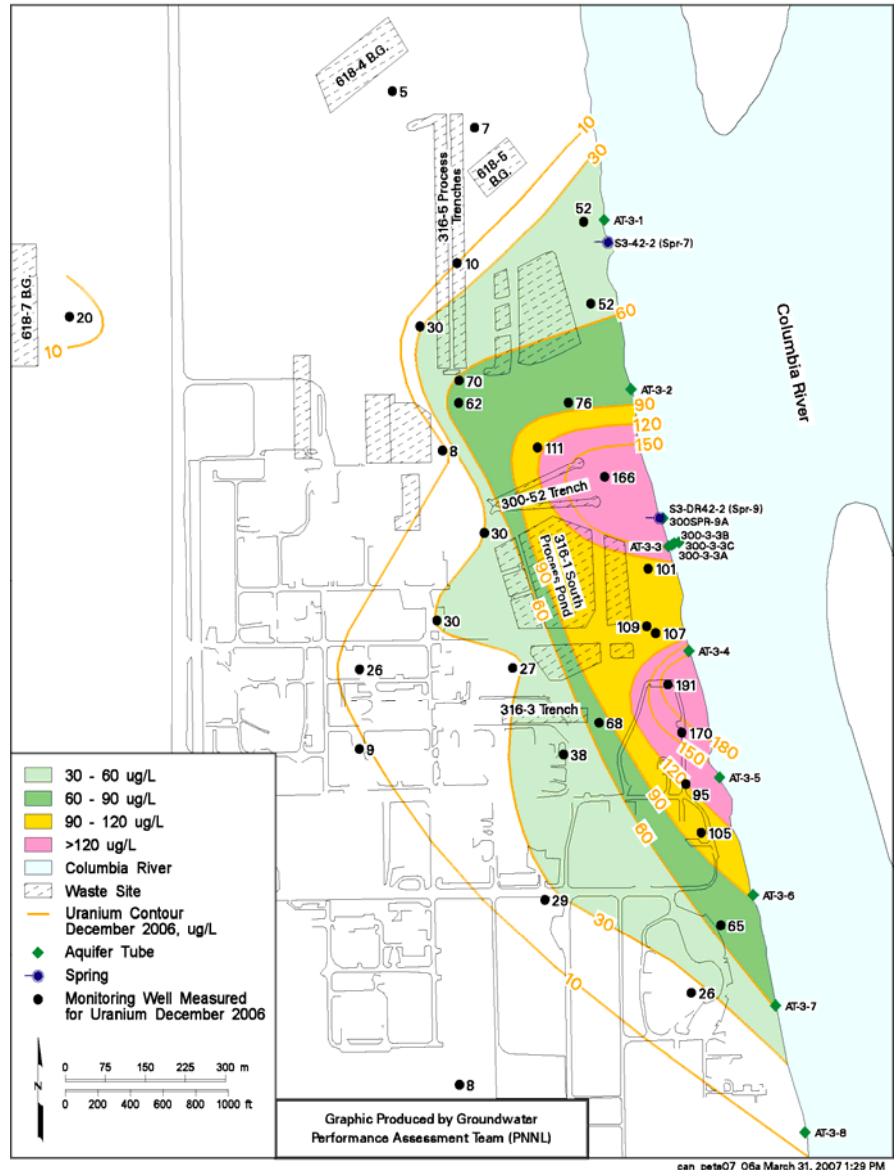

Figure 2. Schematic Depicting the Concentration Contours of the Uranium Plume Within the Hanford Site 300 Area Aquifer as of December 2006

Despite the cessation of uranium releases and the removal of shallow vadose zone source materials, the remedial action objective to lower the concentration of groundwater uranium to the U. S. Environmental Protection Agency maximum contaminant level concentration for drinking water of 30 µg/L has not been achieved. The persistence of this plume is enigmatic for several reasons, including: (1) discharges containing uranium-bearing effluent to ground-disposal sites ended in the mid-1980s, (2) contaminated soil associated with these waste sites was removed during the 1990s, with backfilling complete by early 2004, and (3) the aquifer is composed of highly transmissive fluvial sediment, suggesting rapid movement of groundwater. Also, a water-supply well located within the plume has been in operation since 1980, with no observable effect on the plume. The current conceptual site model assumes that re-supply of the plume is occurring, with continuing release from source candidates including the vadose and smear zones beneath waste sites and possibly from aquifer solids (Figure 3). Detailed analyses have previously indicated that uranium occurs as U(VI) through the 300 Area North Process Pond depth profile. Micro-scale X-ray spectroscopy identified uranium-rich calcite (Catalano, personal communication), uranophane, $Ca(UO_2)_2[SiO_3(OH)]_2 \cdot xH_2O$ (Liu et al. 2004; Liu et al. 2006; Zachara et al. 2005; McKinley et al. 2006; McKinley et al. 2007) (Arai et al. 2007), and meta-torbernite, $Cu(UO_2)_2(PO_4)_2 \cdot xH_2O$ (Catalano et al. 2006; Arai et al. 2007), as uranium-bearing solid phases contributing to the flux of uranium from the vadose and smear zones into the aquifer.
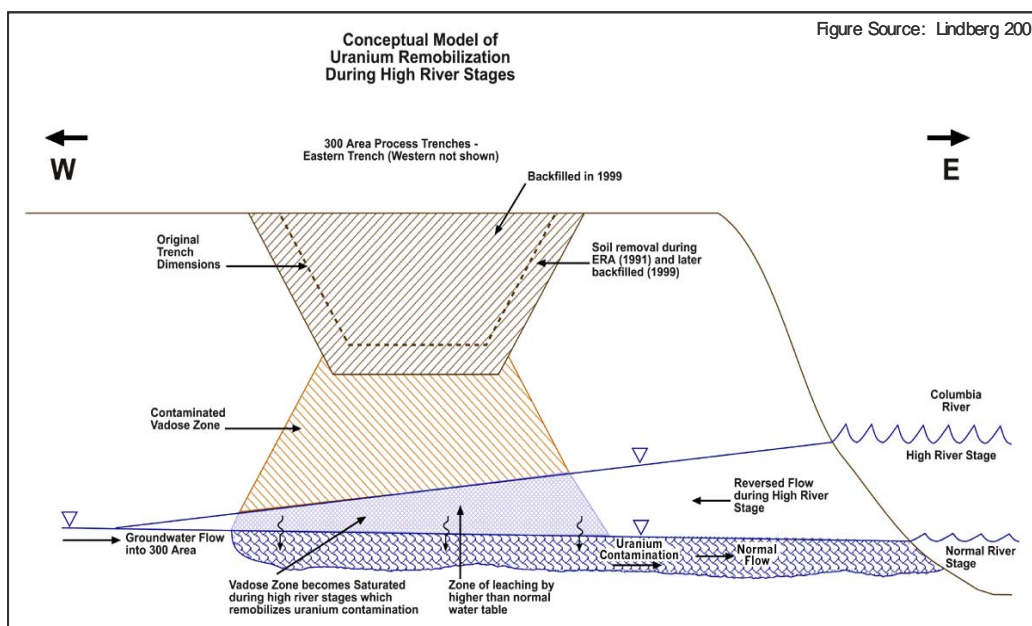

Figure 3. Conceptual Model of Uranium Remobilization During High River Stage

Polyphosphate Remediation Technology

Soluble polyphosphate compounds have been demonstrated to serve as an effective source of orthophosphate for controlled precipitation of phosphate phases to control the long-term fate of uranium (Wellman et al. 2005; Wellman et al. 2006). Injection of a sodium tripolyphosphate amendment into the uranium-bearing saturated porous media has been shown to immobilize uranium through the formation of an insoluble uranyl phosphate mineral, autunite $X_{1-2}[(UO_2)(PO_4)]_{2-1} \cdot nH_2O$, where X is any monovalent or divalent cation. Because autunite sequesters uranium in the oxidized form, U(VI), rather than forcing reduction to U(IV), the possibility of re-oxidation and subsequent re-mobilization of uranium is limited. Release of uranium from autunite may only occur through dissolution of the mineral structure. Extensive

testing demonstrates the very low solubility and slow dissolution kinetics of autunite under conditions relevant to the Hanford subsurface (Wellman et al. 2006).

Precipitation of phosphate minerals occurs when polyphosphate compounds hydrolyze to yield the orthophosphate molecule (PO_4^{3-}), which then binds with cations such as uranyl (UO_2^{2+}) (e.g. Figure 4). Based on the hydrolysis kinetics of the polyphosphate molecule, the amendment can be tailored to act as a time-released source of phosphate for lateral treatment of groundwater plumes, immediate and sustained remediation of dissolved uranium, and to preclude rapid precipitation of phosphate phases which could result in a drastic change in hydraulic conductivity of the subsurface.
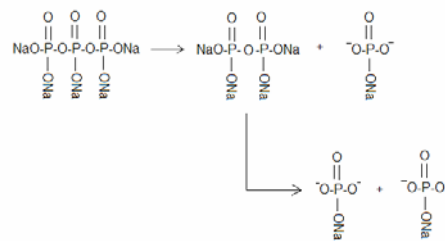

Figure 4. Schematic Depicting the Step-Wise Hydrolysis of Sodium

A laboratory testing program was performed at PNNL to evaluate and optimize polyphosphate remediation technology for infiltration, either from ground surface or some depth of excavation, to provide direct stabilization of source uranium phases within the vadose and smear zones above the 300 Area aquifer. Presented here are the results of a series of unsaturated column experiments, conducted using the pressurized unsaturated flow (PUF) apparatus under site-specific conditions. Three principal objectives were to 1) quantify the ability of the polyphosphate formulations to attenuate the flux of uranium from the sedimentary matrices during remediation, 2) evaluate the immobilization of uranium within these sediments under conditions that simulate the unsaturated, open-flow and transport conditions expected in the vadose zone, and 3) evaluate changes in uranium mineralogy caused by polyphosphate treatment. The results of this investigation provide the necessary information for designing a field-scale remediation test to stabilize soluble uranium phases in the 300 Area vadose and smear zones on the Hanford Site, which serve as a continual source of uranium to the aquifer. Data obtained from this study are being used to identify implementation challenges, develop an implementation plan for deployment of the technology in the field, and investigate the capability of the technology to meet remedial objectives.

MATERIALS AND METHODS

The sediments of the 300 Area vadose and smear zones (Hanford Formation) are open framework sands and gravels, which are highly conductive. Based on the results presented above, the polyphosphate injection developed for deployment within the 300 Area, which consisted of 25% orthophosphate, 25% pyrophosphate, and 50% tripolyphosphate (Wellman et al. 2007), will not degrade and react with uranium solid phases present in the vadose and smear zones at a rate sufficient to control the flux of uranium into the aquifer. Additionally, the rate of transformation of uranyl-carbonate and uranyl-silicate phases with this formulation would require tens of pore volumes of treatment, which is impractical and would exacerbate the flux of uranium to the aquifer. Therefore, a series of unsaturated column tests were conducted using the PUF system (McGrail et al. 1997; 1999; Pierce et al. 2006; Wierenga and Van Genuchten 1989). The PUF system allows controlled dynamic changes in water content that simulate the periodic wet-dry cycling experienced in the deep vadose and smear zones. Additionally, slight changes in pH, conductivity, and water content that occur during dissolution and
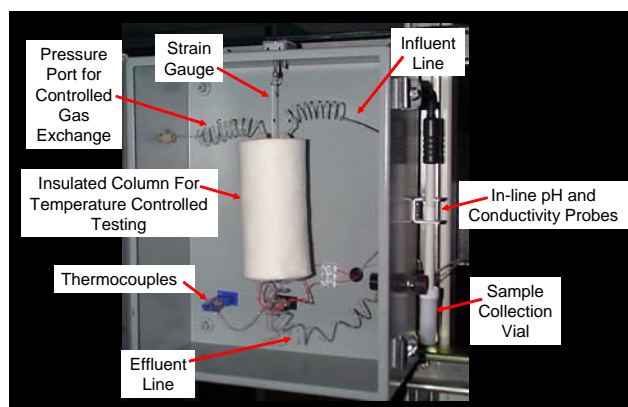

Figure 5. Photo of PUF Column Assembly

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precipitation reactions are continuously logged via the PUF system (Figure 5).

The PUF system, which is similar to a Wierenga column (McGrail et al. 1997; 1999), consists of a polyetheretherketone column ($r = 0.96$ cm, $L = 7.62$ cm) with a porous titanium plate; it has a nominal pore size of 0.2 μm and is sealed in the bottom of the column. Once the porous titanium plate is water saturated, water, but not air, is allowed to flow through the 0.2-μm pores, as long as the applied pressure differential does not exceed the air entry relief pressure, referred to as the bubble pressure of the Ti-plate. If the pressure differential is exceeded, air will escape through the plate and compromise the capability to maintain unsaturated flow conditions in the column (McGrail et al. 1997; 1999). The PUF test computer control system runs LabVIEW™ (National Instruments Corporation) software for logging test data from several thermocouples, pressure sensors, inline sensors that measure effluent pH and conductivity, and from an electronic strain gauge that measures column weight to accurately track water mass balance and saturation level. The column also includes a PUF port, which is an electronically actuated valve that periodically vents the column gases. The purpose of column venting is to prevent reduction in the partial pressure of important gases, especially O_2 and CO_2, which may be consumed in a variety of chemical reactions.

Columns were packed with Hanford vadose zone sediment and ~300 - 900 ppm uranium as uranium-bearing minerals (uranium-rich calcite, uranophane, and meta-torbernite) previously identified as controlling phases in 300 Area sediments (Catalano et al. 2004; Catalano and Jr. 2004; Catalano et al. 2006; Dong et al. 2005; Wang et al. 2005a; Wang et al. 2005b; Zachara et al. 2007; Zachara et al. 2005; Arai et al. 2007) in approximately 5-g increments that were tamped and the surface was scored prior to adding subsequent layers (Table 1). Uranium-rich calcite is a highly soluble uranium-bearing phase previously identified as controlling phases in 300 Area sediments (Catalano et al. 2006). Aside from sorbed uranium, it is a highly labile form of uranium within the 300 Area. Therefore, it is critical that the selected polyphosphate formulation be capable of controlling the potential flux of uranium from this phase during remediation.

Table 1.   Sediment and Uranium Mineral Composition of Columns Used in the Evaluation of Polyphosphate Remediation Under Vadose Zone Conditions

Sediment	Uranium Mineral	Uranium Content	Polyphosphate Amendment
Uncontaminated 300 Area	Uranium-rich calcite	900 mg/kg	25% ortho-, 65% pyro-, 10% tripolyphosphate in Hanford Groundwater
Uncontaminated 300 Area	Uranium-rich calcite	900 mg/kg	70% ortho-, 20% pyro-, 10% tripolyphosphate in Hanford Groundwater
Uncontaminated 300 Area	Uranium-rich calcite	900 mg/kg	90% ortho- and 10% tripolyphosphate in Hanford Groundwater
Uncontaminated 300 Area	Uranophane	300 mg/kg	90% ortho- and 10% tripolyphosphate in Hanford Groundwater
Uncontaminated 300 Area	Meta-Torbernite	300 mg/kg	90% ortho- and 10% tripolyphosphate in Hanford Groundwater

Flow was initiated through the columns with Hanford groundwater until steady-state water content was attained at the desired degree of saturation. The process of fully saturating the column and reducing the water content to the desired level minimizes preferential flow paths and hysteresis verifies the most

consistent, uniform attainment of water content within a series of unsaturated columns, and affords a consistent method for establishing unsaturated conditions. After the attainment of hydraulic and chemical equilibrium, the influent solution was changed to Hanford groundwater containing one of the three respective polyphosphate formulations (Table 2). The polyphosphate formulations all contained 5000 ppm phosphate, but the relative percent contributions of ortho-, pyro-, and tripolyphosphate were varied. Sediment bulk density, ρ_b (g cm^{-3}), and volumetric water content, θ (cm cm^{-3}), were determined from the mass of the sediment and water. The percent saturation was calculated from the ratio of the volumetric water content to the total porosity, ϕ, which was calculated from the bulk density and particle density, ρ_p (g cm^3).

Table 2.   Polyphosphate Formulations for Uranium Stabilization via Infiltration Under Unsaturated Conditions

Formulation	Nominal Percentage	Composition	Formula	Formula Wt, g/mol	Conc., g/L	Conc., M
1	25	Sodium phosphate, tribasic	$Na_3PO_4 \cdot 12H_2O$	380.13	5.003	1.32×10^{-2}
	65	Sodium pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	446.06	7.632	1.71×10^{-2}
	10	Sodium tripolyphosphate	$Na_5P_3O_{10}$	367.86	0.646	1.75×10^{-3}
2	70	Sodium phosphate, tribasic	$Na_3PO_4 \cdot 12H_2O$	380.13	14.009	3.69×10^{-2}
	20	Sodium pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	446.06	2.348	5.26×10^{-3}
	10	Sodium tripolyphosphate	$Na_5P_3O_{10}$	367.86	0.646	1.75×10^{-3}
3	90	Sodium phosphate, tribasic	$Na_3PO_4 \cdot 12H_2O$	380.13	18.011	4.74×10^{-2}
	10	Sodium tripolyphosphate	$Na_5P_3O_{10}$	367.86	0.646	1.75×10^{-3}

The effect of wet-dry cycling was simulated by periodically resaturating the column, with continuous flow, and then desaturating the column to the initial water content. All effluent solutions were monitored for pH with in-line sensors. Prior to starting the experiments, the in-line pH probe was calibrated with National Bureau of Standards pH buffers (pH 7.00, 10.00, or 12.00 at 25°C). Precision of pH measurement was ±0.02 pH units. Concentrations of Al, Ca, Cd, Co, Cr, Fe, K, Mg, Na, P, S, Sr, and Si in the effluent solutions samples were monitored with ICP-OES methods; whereas the concentration of uranium was determined by ICP-MS methods. After passing through the 0.2-μm Ti porous plate and the inline sensors, aliquots of the effluent solutions were acidified with ultra-high-purity concentrated HNO_3 and analyzed using ICP-OES and ICP-MS methods.

Upon termination of the column tests, the solid-phase speciation of U(VI) was assessed using XRD and EXAFS to develop a mechanistic understanding of the formation and/or transformation and identity of resulting uranium phase(s) during phosphate remediation. The thermodynamic database and reaction code EQ3/6 (Wolery and Jarek 2003) was used to evaluate the uranium aqueous speciation and saturation state of the effluent solutions with respect to uranium solid phases using an updated thermodynamic database for uranium.

RESULTS AND DISCUSSION

Polyphosphate Formulation for Vadose and Smear Zones Infiltration

Formulation 1: 25% Ortho-, 65% Pyro-, and 10% Tripolyphosphate

Because pyrophosphate displayed the greatest degree of retardation under unsaturated conditions, the initial reformulation of polyphosphate contained 25% ortho-, 65% pyro-, and 10% tripolyphosphate. Figure 6 presents effluent uranium concentrations. The initial uranium concentration measured in the Hanford groundwater effluent was ~6.0 × 10^3 g/L. Initial treatment of the column with the polyphosphate-amended Hanford groundwater resulted in a spike in uranium concentration of ~ 3.0 x 10^5 g/L. The effluent uranium concentration rapidly decreased during the subsequent 2 pore volumes of treatment and the total amount of uranium released during testing was ~1%. The increase in pyrophosphate and decrease in tripolyphosphate, relative to the original polyphosphate formulation developed for treatment of the aquifer, decreases the necessary degradation time for production of orthophosphate.

25% Ortho, 65% Pyro, 10% Tripoly
Approx. Saturation level = 60%
Approx. Pore Volume = 9 mL
Total U = 859 ppm U-Calcite
Total U leached = ~0.97%

Figure 6. Concentration of Uranium,   g/L, Released from 25% Ortho-, 65% Pyro-, 10% Tripolyphosphate-Treated Column Measured in the Effluent Solutions as a Function of Time (days) and Pore Volume. The dashed vertical line represents the initiation of flow for the phosphate amended

However, as previously noted, the solubility of pyrophosphate metal complexes are greater than those of tripolyphosphate (Onaka et al. 1981; van Wazer and Callis 1958). Thus, reaction of uranium-rich calcite with pyrophosphate can result in the formation of more stable aqueous uranium complexes, which limit precipitation and result in greater mobilization of uranium during polyphosphate-based remediation. Although results presented here suggest that the higher proportion of pyrophosphate does provide a more readily available source of orthophosphate for stabilization of uranium solid phases and attenuation of the aqueous uranium flux, the abundance of pyrophosphate in formulation 1 may produce a significant pulse of uranium to the aquifer during initiation of the remedial action.
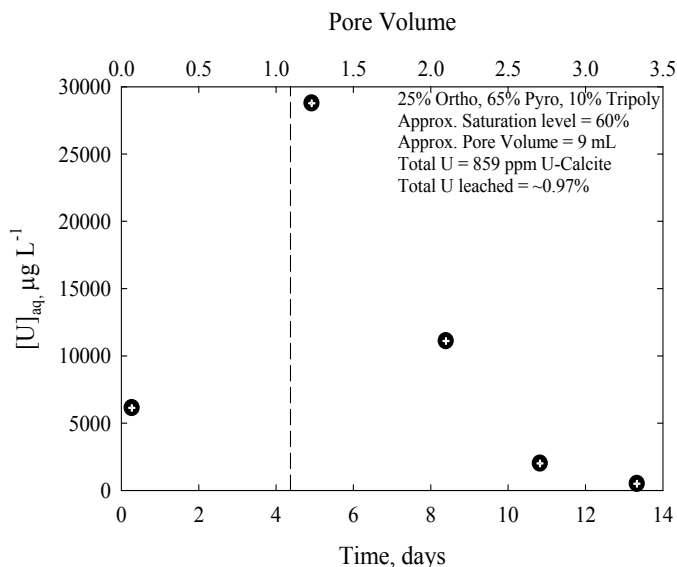
Formulation 2: 70% Ortho-, 20% Pyro-, and 10% Tripolyphosphate

Figure 7 presents effluent uranium concentration from the 70% ortho-, 20% pyro-, 10% tripolyphosphate-amended column. The initial uranium concentration measured in the Hanford groundwater effluent was ~6.0×10^3 g/L. This concentration was comparable to that measured in Hanford groundwater effluent from the PUF column treated with formulation 1, 25% ortho-, 65% pyro-, 10% tripolyphosphate. Initial treatment of the column with the polyphosphate-amended Hanford groundwater resulted in a spike in uranium concentration of ~ 2.3×10^5 g/L. This increase in uranium concentration was ~24% lower than that exhibited by the column treated with formulation 1. Comparable to the column treated by formulation 1, the effluent uranium concentration rapidly decreased during the subsequent 2 pore volumes of treatment. The total amount of uranium released during testing was ~1%.

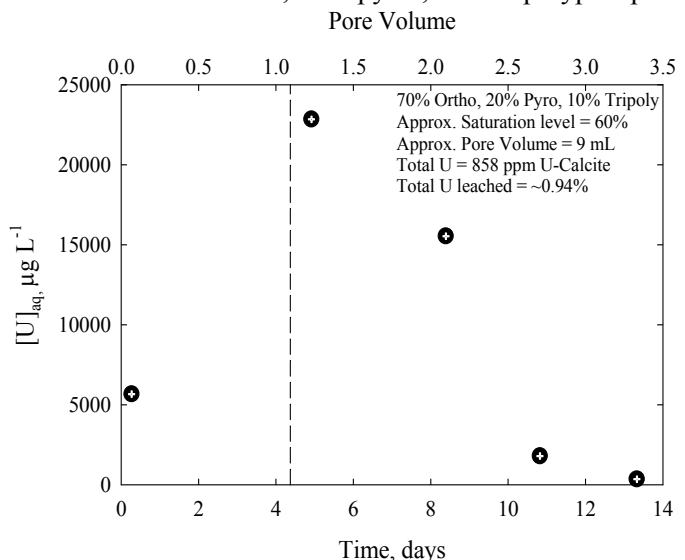**Figure 7**. Concentration of Uranium,   g/L, Released from the 70% Ortho-, 20% Pyro-, 10% Tripolyphosphate-Treated Column Measured in the Effluent Solutions as a Function of Time (days) and Pore Volume. The dashed vertical line represents the initiation of flow for the phosphate amended groundwater
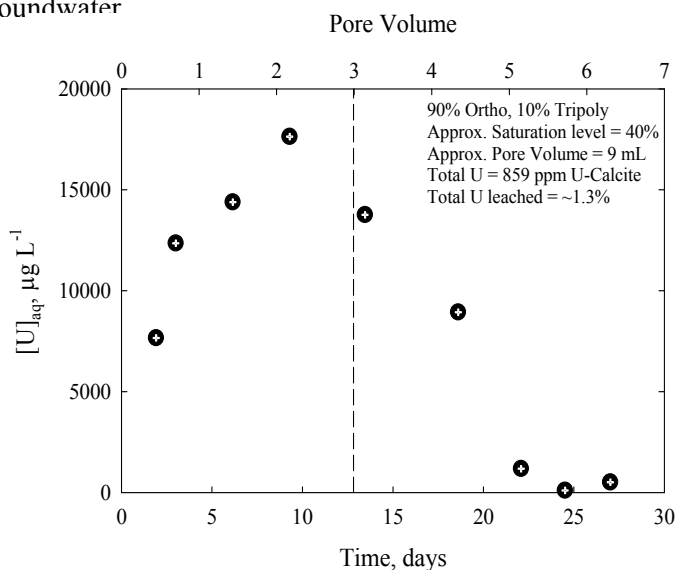
Formulation 3: 90% Ortho- and 10% Tripolyphosphate

Figure 8 presents effluent uranium concentration from the 90% ortho- and 10% tripolyphosphate-amended column. The initial uranium concentration measured in the Hanford groundwater effluent was ~7.5×10^3 g/L. Because of challenges establishing steady-state unsaturated flow conditions, flow of Hanford groundwater through the column continued for the first three pore volumes. In comparison, Hanford groundwater was only displaced for approximately one pore volume through unsaturated columns used to evaluate formulations 1 and 2. The effluent uranium concentration increased to ~1.8×10^5 g/L over the first three pore volumes, prior to treatment with polyphosphate formulation 3. Contrary to formulations 1 and 2, there was no spike in uranium concentration upon initial treatment of the column with the polyphosphate-amended Hanford groundwater. Rather the effluent uranium concentration decreased from ~1.8×10^5 g/L to ~ 1.4×10^5 g/L. Comparable to the column treated by formulations 1 and 2, the effluent

Figure 8. Concentration of Uranium,   g/L, Rreleased from 90% Ortho- and 10% Tripolyphosphate-Treated Column Mmeasured in the Effluent Solutions as a Function of Time (days) and Pore Volume. The dashed vertical line represents the initiation of flow for the phosphate amended groundwater.

uranium concentration rapidly decreased during the subsequent two pore volumes of treatment. The total amount of uranium released during testing was ~1.3%. The increased amount of uranium released, relative to columns treated with formulation 1 and 2, was a result of two additional pore volumes of leaching with Hanford groundwater, prior to initiation of the polyphosphate amendment.

EXAFS analyses were conducted on reacted materials extracted from the uranium-rich calcite columns treated with the three different polyphosphate formulations. Evaluation of the uranium L_{III}-edge EXAFS spectra (Figure 9) suggests that the chemical speciation of uranium changed upon treatment with polyphosphate. The data were well fit using a linear combinations of the data from k = 3-12, k^3 weighted for U-calcite and autunite-group minerals. The fitted data suggest that treatment with formulation 1 (consisting of 25% ortho-, 65% pyro-, and 10% tripolyphosphate), resulted in only 1% conversion of the uranium to a uranium-phosphate phase after ~3 pore volumes of treatment; the remaining fraction was still uranium coprecipitated with calcite. EXAFS results indicated that in the uranium-calcite rich column treated with formulation 2 (consisting of 70% ortho-, 20% pyro-, and 10% tripolyphosphate), 10% of the uranium was converted to a uranium-phosphate phase after nearly a comparable ~3 pore volumes of treatment. The remaining fraction was still coprecipitated with calcite. Treatment of uranium-rich calcite under unsaturated conditions was best achieved using polyphosphate formulation 3, 90% ortho- and 10% tripolyphosphate. After 3 pore volumes of treatment, 40% of the uranium was converted to uranium-

Figure 9. EXAFS of (a) autunite-group mineral, [(UO2)(PO4)]2 · xH2O, (b) U-calcite, and EXAFS of Uranium-Rich Calcite Reacted with (c) 90% Ortho-/10% Tripolyphosphate, (d) 70% Ortho-/20% Pyro-, and 10% Tripolyphosphate, and (e) 25% Ortho-/65% Pyro-, and 10% Tripolyphosphate. The dashed line is the

phosphate. Even though < 1% of the total uranium contained within the column had been removed, the formation of an autunite-group mineral "rind" on the uranium-rich calcite surface decreased the flux of uranium from the column. Subsequent release of uranium is limited by the rate of dissolution for autunite-group minerals. Because autunite sequesters uranium in the oxidized form, U(VI), rather than forcing reduction to U(IV), the possibility of re-oxidation and subsequent re-mobilization of uranium is negated.
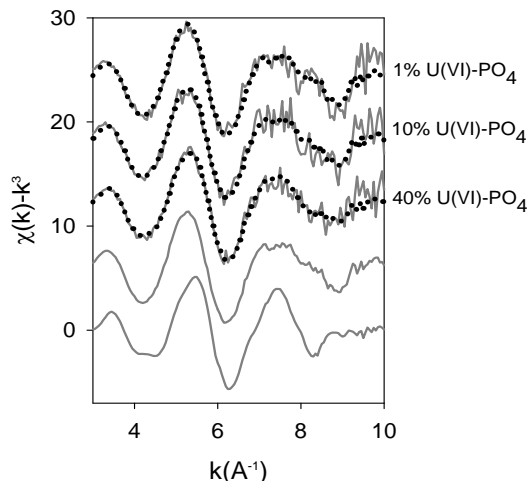
The results of unsaturated column tests conducted as a function of polyphosphate composition indicate that a formulation consisting of 90% orthophosphate and 10% tripolyphosphate will provide the most rapid and complete stabilization of uranium-solid phases through transformation to uranium-phosphate phases and mitigate the flux of uranium from the vadose and smear zones during infiltration. A polyphosphate formulation consisting of 100% orthophosphate is not permissible in Hanford groundwater because in the absence of 10% tripolyphosphate, the orthophosphate rapidly precipitates with cations present in Hanford groundwater. This results in the formulation of a slurry of phosphate phases that will rapidly occlude pore space, limiting infiltration. Moreover, attempting to prepare a polyphosphate amendment consisting of 100% orthophosphate in an aqueous media other than Hanford groundwater, such as deionized water, to reduce precipitation with cations, will not mitigate the rapid precipitation that will occur within the subsurface pore water (Wellman et al. 2006).

Unsaturated Weathering of Uranium Minerals during Polyphosphate Remediation

Stabilization of Uranium-Rich Calcite with Polyphosphate Remediation Technology Under Unsaturated Conditions

Figure 10 presents effluent uranium concentration from an unsaturated column containing uranium-rich calcite that was treated with the 90% ortho- and 10% tripolyphosphate-amended column. The dashed vertical line on the graph indicates the start of polyphosphate treatment; the solid vertical line indicates the termination of polyphosphate treatment and the flow of Hanford groundwater. Prior to the infiltration of polyphosphate the uranium concentration measured in the Hanford groundwater effluent was $\sim 3.9 \times 10^5$ g/L. The effluent uranium concentration rapidly decreased to $\sim 2.9 \times 10^5$ g/L upon initial infiltration of polyphosphate. The effluent uranium concentration continued to decrease during the subsequent six pore volumes of treatment. After the cessation of polyphosphate infiltration, the effluent uranium concentration remained 2 to 3 orders of magnitude lower than that quantified in the effluent prior to treatment.

Figure 10. Concentration of Uranium, g/L, in the Effluent Solutions as a Function of Time (days) and Pore Volume Released from Uranium-Calcite-Bearing Column Treated with 90% Ortho- and 10% Tripolyphosphate. The dashed vertical line represents the initiation of flow for the phosphate-amended groundwater; the solid line represents the point at which polyphosphate infiltration was terminated and flow of groundwater was reinitiated.

Stabilization of Uranophane with Polyphosphate Remediation Technology Under Unsaturated Conditions

Figure 11 presents the effluent uranium concentration from an unsaturated column containing uranophane that was treated with the 90% ortho- and 10% tripolyphosphate-amended column. The dashed vertical line on the graph indicates the start of polyphosphate treatment; the solid vertical line indicates the termination of polyphosphate treatment and the flow of Hanford groundwater. Prior to the infiltration of polyphosphate the uranium concentration measured in the Hanford groundwater effluent was $\sim 2.5 \times 10^5$ g/L. Relative to the uranium-rich calcite column, the lower effluent concentration of uranium measured in the uranophane effluent reflects the higher stability of the uranyl-silicate mineral. As observed for polyphosphate remediation of uranium-rich calcite, the effluent uranium concentration rapidly decreased to $\sim 4.8 \times 10^3$
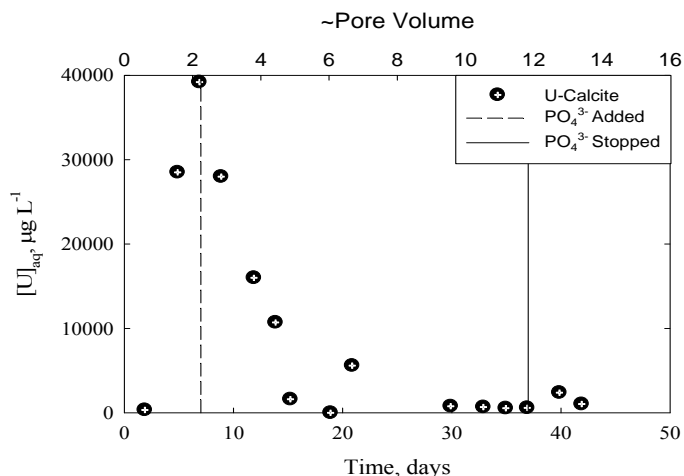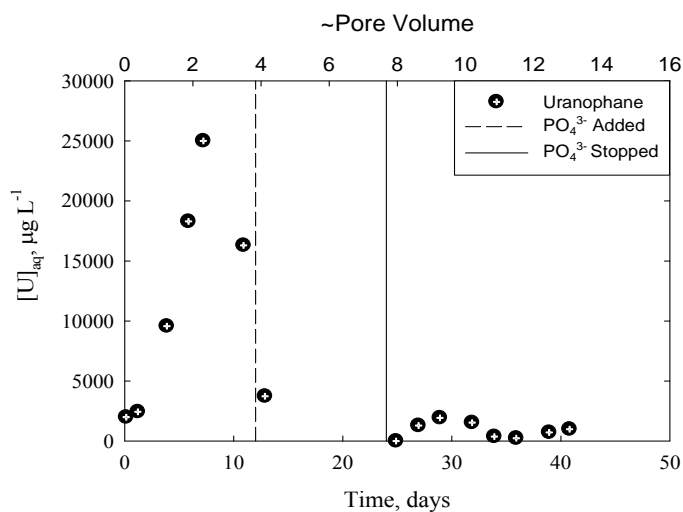

Figure 11. Concentration of Uranium, g/L, in the Effluent Solutions as a Function of Time (days) and Pore Volume Released from the Uranophane-Bearing Column Treated with 90% Ortho- and 10% Tripolyphosphate. The dashed vertical line represents the initiation of flow for the phosphate-amended groundwater; the solid line represents the point at which polyphosphate infiltration was terminated and flow of groundwater was reinitiated.

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g/L upon initial infiltration of polyphosphate. Following the cessation of polyphosphate infiltration the effluent uranium concentration remained 3 orders of magnitude lower than that quantified in the effluent prior to treatment.

Stabilization of Meta-Torbernite with Polyphosphate Remediation Technology Under Unsaturated Conditions

Figure 12 presents effluent uranium concentration from an unsaturated column containing meta-torbernite that was treated with the 90% ortho- and 10% tripolyphosphate-amended column. The dashed vertical line on the graph indicates the start of polyphosphate treatment; the solid vertical line indicates the termination of polyphosphate treatment and the flow of Hanford groundwater. Prior to the infiltration of polyphosphate the uranium concentration measured in the Hanford groundwater effluent was $\sim 4.5 \times 10^4$ g/L. Relative to the uranium-rich calcite or uranophane columns, the lower effluent concentration of uranium measured here, from meta-torbernite, reflects the high stability of the uranyl-phosphate mineral. Upon infiltration of polyphosphate the effluent uranium concentration rapidly decreased within two pore volumes. Following the cessation of polyphosphate infiltration the effluent uranium concentration remained 2 orders of magnitude lower than that quantified in the effluent prior to treatment.
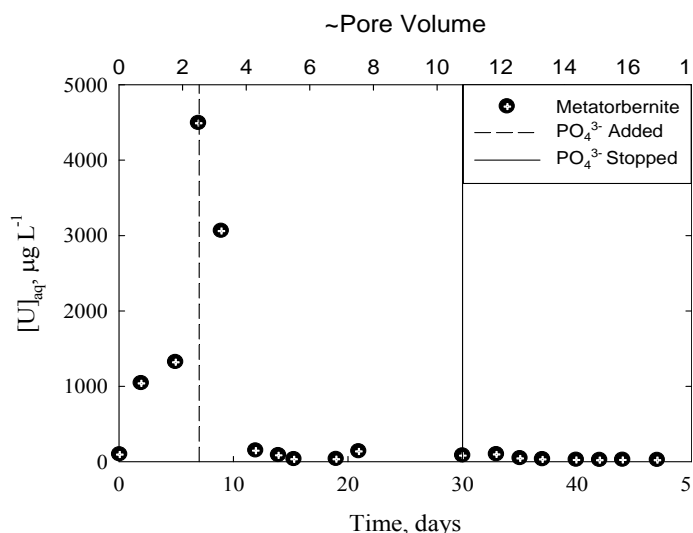
Figure 12. Concentration of Uranium, g/L, in the Effluent Solutions as a Function of Time (days) and Pore Volume Released from the Meta-Torbernite-Bearing Column Treated with 90% Oortho- and 10% Tripolyphosphate. The dashed vertical line represents the initiation of flow for the phosphate-amended groundwater; the solid line represents the point at which polyphosphate infiltration was terminated and flow of groundwater was reinitiated.

SUMMARY AND CONCLUSIONS

The results of this investigation underscore the necessity to understand the geochemistry that controls uranium within this environment and evaluate the resulting effect of polyphosphate amendments on the uranium geochemistry. Laboratory results indicate:

- Concentration of uranium potentially released during the infiltration of polyphosphate remedial solution is lower than that released through the dissolution of uranium-rich calcite, uranophane, or meta-torbernite in natural pore waters.

- Controlled infiltration of polyphosphate will not increase aqueous uranium concentrations.

- Orthophosphate affords the greatest control over the aqueous concentration of uranium under the pH range of 6 to 8, maintaining aqueous uranium concentrations less than 30 g/L at a g $[PO_4^{3-}]_{aq}$/g uranium-calcite ratio of ≤ 0.05. Pyrophosphate and tripolyphosphate required g $[PO_4^{3-}]_{aq}$/g uranium-calcite ratios of ~ 0.15 to maintain aqueous uranium concentrations < 30 g/L.

- A polyphosphate formulation consisting of 90% orthophosphate (4.74×10^{-2} M) and 10% tripolyphosphate (1.75×10^{-3} M) will provide the rapid stabilization of uranium-solid phases

through transformation to uranium-phosphate phases, and mitigate the flux of uranium from the vadose and smear zones during infiltration.

- Stabilization of soluble uranium-bearing minerals occurs by the formation of a uranium-phosphate "rind" on the surface of uranium-rich calcite and uranyl-silicate minerals.

Application of Polyphosphate Remediation Technology

The results of this investigation provide the necessary information for designing a field-scale remediation test to stabilize soluble uranium phases in the 300 Area vadose and smear zones on the Hanford Site, which serve as a continual source of uranium to the aquifer. A conceptual design of a treatability test is the construction of an infiltration array at the ground surface above an area of potential contamination such as one of the process ponds, which has been previously excavated and backfilled, but may contain some unknown amount of contamination in the vadose and smear zones beneath the lower extent of the excavation activities (e.g., Figure 13). Geochemical and thermodynamic data obtained from
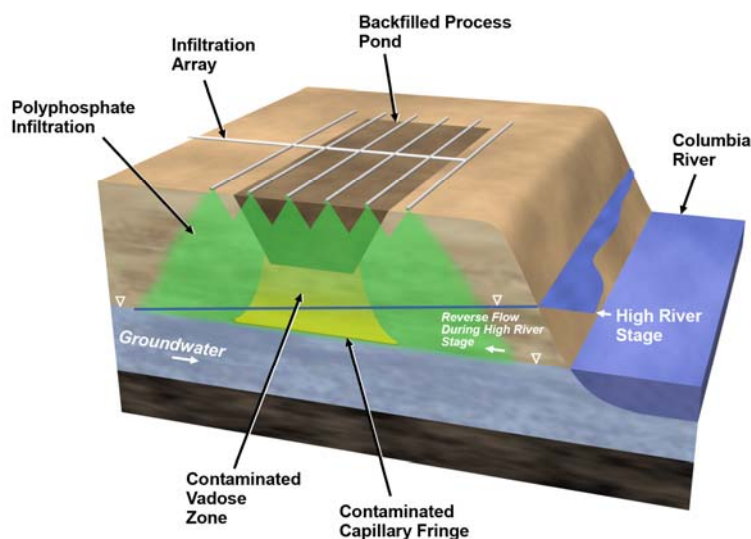

Figure 13. Schematic Depicting a Proposed Treatability Test of Polyphosphate to Stabilize Uranium in the Vadose and Smear Zone

this investigation were used to update the database for EQ3/6, version 8.0, to allow reactive transport simulation of polyphosphate infiltration at the intermediate- and field-scale using STOMP. The results of reactive transport simulations suggest that drip infiltration at an application rate of 0.05 L/hr over a scale 102 cm wide x 80 cm high x 5.5 cm deep controls the saturation beneath a drip infiltration source; the vertical average linear velocity 20 cm beneath the point source is 10.4 cm/hr. This results in a travel time of 5.79 hours vertically through the 60-cm-deep vadose zone. Assuming a K_d of 0.0037 (Wellman et al. 2008) for phosphate simulations indicates that a low water application rate will increase contact time of dissolved phosphate with U-bearing minerals in the sediment and minimize flushing. The presence of heterogeneities and the uncertainty regarding the true reactive surface area of the fine-grained materials at the field scale may have a significant effect on the efficacy and emplacement of the remedial action. Currently, additional intermediate-scale tests are being conducted to evaluate the effect of heterogeneities on the remediation of uranium minerals under conditions relevant to the vadose and smear zones. These results will be used to test and verify a site-specific, variable-saturation, reactive-transport model and to aid in the design of a pilot-scale field test of this technology. In particular, the infiltration approach and monitoring strategy of the pilot test will be based primarily on results from intermediate-scale testing.

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