

## **Uranium Plume Treatability Demonstration at the Hanford Site 300 Area: Development of Polyphosphate Remediation Technology for In Situ Stabilization of Uranium**

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### **ABSTRACT**

A groundwater plume containing uranium, originating from a combination of purposeful discharges of wastewater to cribs, trenches, and ponds, along with some accidental leaks and spills during nuclear fuel-fabrication activities, has persisted beneath the Hanford Site 300 Area for many years. Despite the cessation of uranium releases and the removal of shallow vadose-zone source materials, the goal of less than 30  $\mu\text{g/L}$  has not been achieved within the anticipated 10-year time period. Polyphosphate technology, demonstrated to delay the precipitation of phosphate phases for directed in situ precipitation of stable phosphate phases, can be used to control the long-term fate of uranium. Precipitation occurs when polyphosphate compounds hydrolyze to yield the orthophosphate molecule. Based on the hydrolysis kinetics of the polyphosphate polymer, the amendment can be tailored to act as a time-released source of phosphate for lateral plume treatment, immediate and sustained remediation of dissolved uranium, and to preclude rapid precipitation which could result in a drastic change in hydraulic conductivity of the target aquifer.

Critical to the successful implementation of polyphosphate remediation technology is a site-specific evaluation and optimization of multi-length polyphosphate amendment formulations. A multi-faceted approach has been taken to provide key fundamental science knowledge regarding optimization of the polyphosphate remedy through: 1) phosphorus-31 nuclear magnetic resonance to quantify the effects of Hanford groundwater and sediment on the degradation of inorganic phosphates; 2) static tests to quantify the kinetics, loading, and stability of apatite as a long-term sorbent for uranium; and 3) single-pass flow-through testing to quantify the stability of autunite and apatite under relevant site conditions. Dynamic column tests were utilized to 1) optimize the composition of the polyphosphate formulation for the formation and emplacement of apatite and autunite; 2) understand the rate and extent of reaction between polyphosphate- and uranium-bearing phases; 3) evaluate the effect of chemical microenvironments on the degradation of polyphosphate, and the formation of autunite; and 4) quantify the mobility of polyphosphate as a function of water content. These activities are being conducted in parallel with a limited field investigation, to more accurately define the vertical extent of uranium in the vadose zone, and in the capillary fringe laterally throughout the plume.

### **INTRODUCTION**

#### **Hanford Site and the 300 Area Uranium Plume**

The Hanford Site, located in eastern 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, from 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 [1, 2]. In 1989, all nuclear reactors were shut down, and the activities were diverted to environmental cleanup and site restoration. Since the early 1990s, extensive remediation of liquid waste disposal sites and solid waste burial grounds has taken place. Recently, most liquid waste disposal sites, located in the north half of the 300 Area, have been excavated and backfilled, and the ground surface has been restored. Some unknown amount of contamination remains in the vadose zone beneath the lower extent of the excavation activities. Additional contamination may also remain beneath buildings and facilities in the southern portion of the 300 Area, where decontamination and decommissioning activities have not been implemented.

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). 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. Hanford groundwater is dominated by calcium, sodium, and sulfate, and has a pH of ~8.5 with dissolved  $[\text{CO}_3^{2-}]$  of  $\sim 1.13 \times 10^{-3}$  mol/L [3]. Uranium, as uranyl  $\text{UO}_2^{2+}$ , is predicted to form carbonate complexes in Hanford groundwater, 27% as  $\text{UO}_2(\text{CO}_3)_2^{2-}$ , 68% as  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , 3% as  $\text{UO}_2(\text{OH})_2^0$ , and 2% as  $\text{UO}_2(\text{OH})_3^{1-}$  [3, 4, 5, 6, 7]. Currently, elevated uranium concentrations are entering the Columbia River along the shoreline and enter the riparian and river biota through seeps (Figure 2).

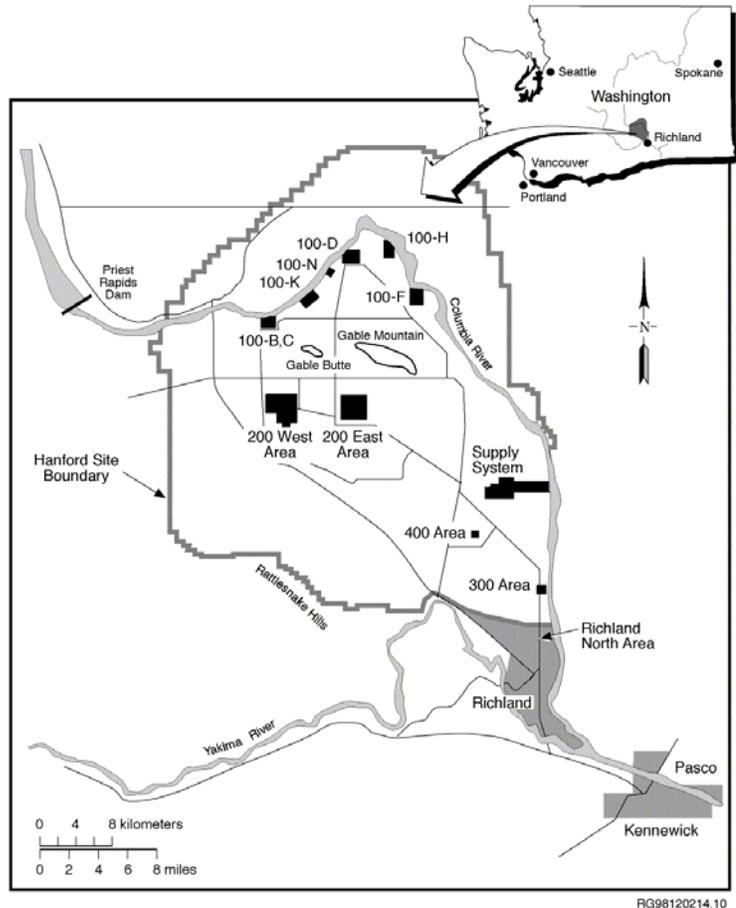


Fig. 1. Map of the Hanford Site.

Despite the cessation of uranium releases and the removal of shallow vadose zone source materials, dissolved uranium concentrations below the EPA maximum concentration level (MCL) have not been achieved within the anticipated 10-year time period. Among several remediation technologies, polyphosphate technology was judged to be the most promising to sequester uranium at this site. Polyphosphate technology works by forming phosphate minerals to directly sequester the existing aqueous uranium in autunite minerals and precipitate apatite minerals for sorption and long-term treatment of uranium migrating into the treatment zone, thus reducing current and future aqueous uranium concentrations [8, 9].

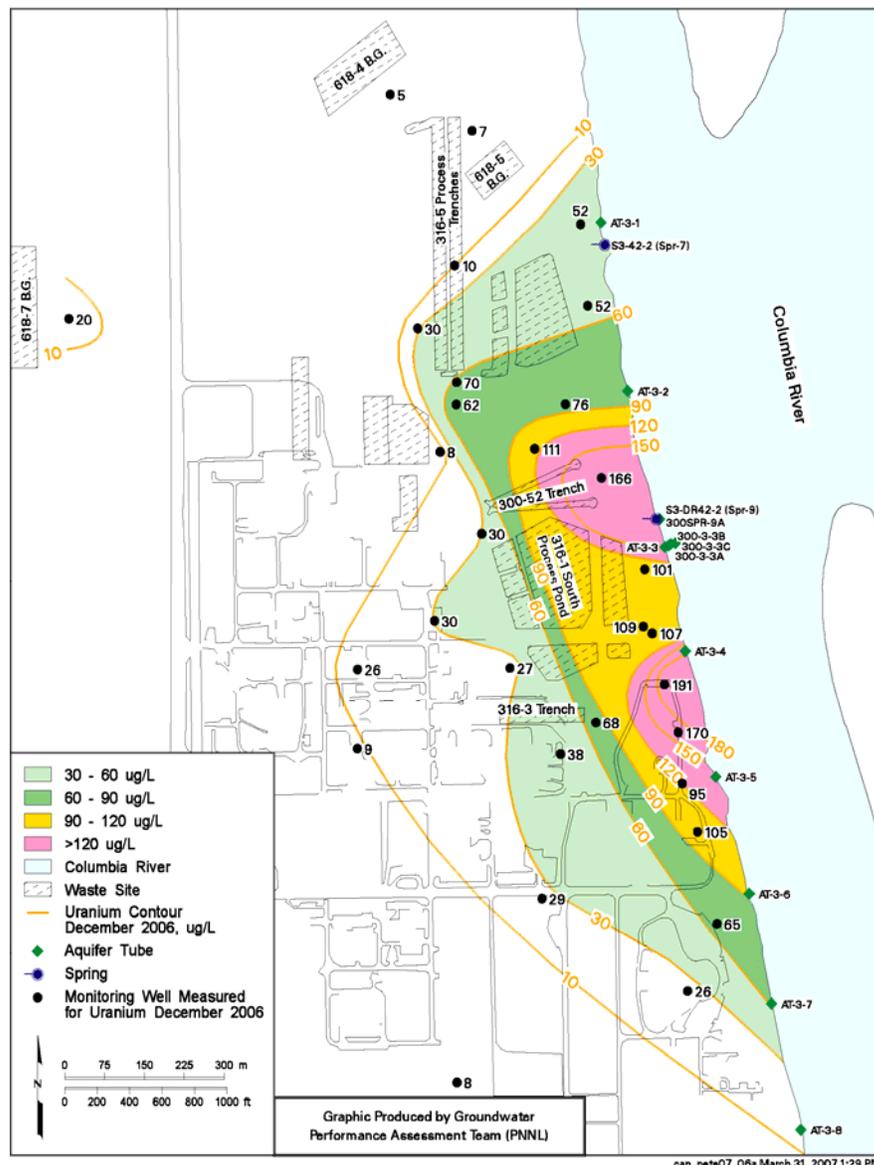


Fig. 2. Schematic Depicting the Concentration Contours of the Uranium Plume Within the Hanford Site 300 Area Aquifer as of December 2006.

### Polyphosphate Remediation Technology

The use of soluble long-chain polyphosphate materials have been demonstrated to delay the precipitation of phosphate phases [8, 9]. Precipitation of phosphate minerals occurs when polyphosphate compounds hydrolyze to yield the orthophosphate molecule ( $\text{PO}_4^{3-}$ ), which then binds with cations, such as uranyl ( $\text{UO}_2^{2+}$ ) (Figure 3).

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  $X_{1-2}[(UO_2)(PO_4)]_2 \cdot nH_2O$ , 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 prevented. 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 [9]. In addition to autunite, excess phosphorous can result in apatite (calcium phosphate) mineral formation, providing a long-term source of treatment capacity.

The degradation kinetics of long-chain polyphosphate molecules, such as sodium tripolyphosphate, affords a time-released source of inorganic phosphate. This allows controlled application and precipitation within deep subsurface-contaminant plumes. However, site-specific optimization of polyphosphate technology is critical to successful implementation of these technologies in the field [9]. A thorough understanding of site-specific geochemical and hydrodynamic conditions enables optimization of polyphosphate technology for controlled remediation without discharging excess phosphorus into the environment, which could detrimentally impact the environment or downgradient drinking water supplies. Research presented herein details the optimization and field testing of polyphosphate technology within the 300 Area of the Hanford Site [10, 11, 12], which underscore the necessity to understand the geochemistry controlling uranium within the subsurface environment and evaluate the resulting effect of phosphate-based remediation technology on the system.

## MATERIALS AND METHODS

### Polyphosphate Hydrolysis

Controlled phosphorus-31 nuclear magnetic resonance ( $^{31}P$  NMR) experiments were conducted to quantify the kinetic degradation rate of the tripolyphosphate molecule under conditions present within the Hanford 300 Area subsurface. The effect of cations representative of some of the major components of Hanford Site sediment and groundwater (e.g.,  $Al^{3+}$ ,  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Mg^{2+}$ , and  $Na^+$ ) and sedimentary materials (e.g., FeOOH, and native Hanford sediment) on the hydrolysis of polyphosphates was evaluated in potassium carbonate ( $K_2CO_3$ ) buffered solutions at 23°C. The  $K_2CO_3$  buffer was used 1) to maintain the pH in a range near that of Hanford groundwater, pH = 7.5 to 8.5, 2) because carbonate is a major component of Hanford subsurface and groundwater, and 3) because potassium has been shown to have a low catalytic effect on phosphate hydrolysis [13].

Homogeneous hydrolysis experiments were conducted by preparing buffered metal chloride stock solutions by mixing 700 mL of 0.1 M  $K_2CO_3$  in deuterated water ( $D_2O$ ) and adjusting the pH by adding 4.86 mL of HCl. The stock buffer was then divided into five 100 mL fractions and one 200 mL fraction. To each 100 mL fraction, 1 mM equivalent of one of the following metal chlorides was added:  $AlCl_3$ ,  $CaCl_2$ ,  $FeCl_3$ , and  $MgCl_2$ . Precipitation occurred in the  $AlCl_3$ ,  $CaCl_2$ , and  $FeCl_3$  stock solutions; probably as  $Al(OH)_3$ ,  $CaCO_3$ , and  $Fe(OH)_3$ , respectively. Therefore, the final dissolved concentration for aluminum ( $4.10 \times 10^{-16}$  M), iron ( $8.36 \times 10^{-22}$  M), and calcium ( $4.0 \times 10^{-8}$  M) are based on the solubility limit of the aforementioned phases. Each homogeneous hydrolysis experiment was conducted by mixing approximately 5 mL of the appropriate buffered metal solution with 0.366 g of solid sodium tripolyphosphate, which corresponded to 0.2 M tripolyphosphate solution.

Heterogenous solid experiments contained 2.5 g of Hanford sediment or 44 mg of FeOOH per 5 mL of 0.2 M sodium tripolyphosphate carbonate buffered solution. Each experiment was sampled weekly for four weeks. Approximately 1.5 mL of sample was removed, filtered, and placed in a 5-mm outer-diameter, thin-walled precision Wilmad<sup>®</sup> glass NMR tube and analyzed immediately.

Non-proton decoupled  $^{31}P$  NMR spectra were recored on a two-channel Varian-VXR, operating at 300 MHz proton frequency (i.e., 7.0T). A 4.5- $\mu$ sec  $90^\circ$  pulse was used with a 0.5-sec pulse delay, 1.813-sec acquisition time, a frequency of 121.43 MHz, and 300 acquisitions per sample. Spectra were referenced to the resonance peak of 85% phosphoric acid ( $H_3PO_4$ , 37.9 ppm), which was used as an external chemical-shift standard. All  $^{31}P$  NMR experiments were conducted at room temperature in  $D_2O$ .

### Polyphosphate Amendment Formulation

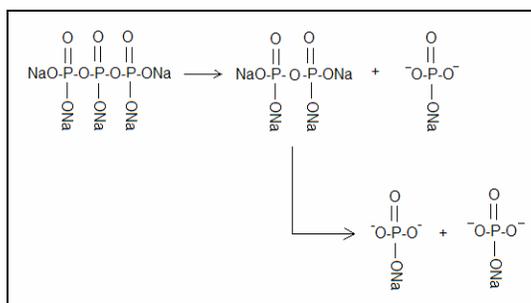


Fig. 3. Schematic Depicting the Step-Wise Hydrolysis of Sodium Tripolyphosphate.

Preliminary field-tracer investigations indicated a field pore velocity of ~50 ft/day, suggesting rapid formation of autunite and apatite was required within the 300 Area subsurface for remediation. Therefore, nine potential phosphate compounds were selected for investigation as possible components of the polyphosphate amendment formulation (Table I). Selection of the amendment sources was based on the solubility, hydrolysis rate, and amount of phosphorus and/or calcium provided by the respective compounds.

**Table I.** Possible Sources and Associated Solubility for Polyphosphate Amendment

Phosphate Source	Formula	Ca Source	P Conc (ppm)	Ca Conc (ppm)
Sodium Orthophosphate	$\text{Na}_3\text{PO}_4 \cdot n\text{H}_2\text{O}$	$\text{CaCl}_2$	500, 1000, 1500, 2000, 2500	0, 1000, 1500
Sodium Pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7 \cdot n\text{H}_2\text{O}$	$\text{CaCl}_2$	500, 1000, 1500, 2000, 2500	0, 1000, 1500
Sodium Tripolyphosphate	$\text{Na}_5\text{P}_3\text{O}_{10} \cdot n\text{H}_2\text{O}$	$\text{CaCl}_2$	500, 1000, 1500, 2000, 2500	0, 1000, 1500
Sodium Trimetaphosphate	$(\text{NaPO}_3)_3 \cdot n\text{H}_2\text{O}$	$\text{CaCl}_2$	500, 1000, 1500, 2000, 2500	0, 1000, 1500
Sodium Hexametaphosphate	$(\text{NaPO}_3)_6 \cdot n\text{H}_2\text{O}$	$\text{CaCl}_2$	500, 1000, 1500, 2000, 2500	0, 1000, 1500
Calcium Dihydrogen Phosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$	–	500, 1000, 1500	–
Calcium Hydrogen Phosphate	$\text{CaHPO}_4 \cdot n\text{H}_2\text{O}$	–	500, 1000, 1500	–
Calcium Pyrophosphate	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot n\text{H}_2\text{O}$	–	500, 1000, 1500	–
Calcium Hypophosphite	$\text{Ca}(\text{H}_2\text{PO}_2)_2 \cdot n\text{H}_2\text{O}$	–	500, 1000, 1500	–

Heterogeneous batch experiments were conducted using a solid-to-solution ratio of 1 to 100. All experiments were conducted in Hanford groundwater and in the presence of 300 Area sediments for one week at room temperature. The uranium concentrations used in these experiments (10 to 1000 ppb) were selected to represent the range of concentrations measured within the Hanford 300 Area aquifer. Aqueous concentrations were monitored by inductively coupled plasma-mass and optical emission spectrometries (ICP-MS and ICP-OES).

### Polyphosphate Amendment Formulation Emplacement and Efficacy

Site-specific tests were conducted to optimize the formation of apatite based on environmental parameters, including pH and carbonate concentration. Saturated column experiments were conducted to quantify 1) polyphosphate treatment efficiency - the amount of polyphosphate required to treat a pore volume of uranium contaminated groundwater, and 2) polyphosphate treatment emplacement efficiency - evaluate the mixing problem (i.e., effective contact or tendency for the reagent to push contaminated groundwater ahead of the treatment volume).

The use of multi-length polyphosphate chain amendments, optimized through  $^{31}\text{P}$  NMR hydrolysis and batch precipitation experiments (ortho-, pyro-, and tripolyphosphate), was evaluated to afford rapid precipitation of autunite and/or apatite without negatively impacting the hydraulic conductivity of the formation. Preliminary characterization of geologic media collected from the 300 Area indicated that the uranium concentration within the aqueous and solid matrix of the sediment cores is below the MCL for uranium. Therefore, to effectively evaluate polyphosphate amendments for uranium remediation, it was necessary to use a solution of Hanford groundwater spiked with aqueous uranium as the influent solution, with a maximum concentration in the pore fluid of 1000 ppb.

Polyvinyl chloride columns (length,  $L = 30.48$  cm; radius,  $r = 2.54$  cm; and bulk volume,  $V_b = 194.04$  to  $202.20$  cm<sup>3</sup>) were uniformly packed with saturated sediment from the 300 Area. These flow tests were conducted to evaluate 1) the concentration of total phosphorus and calcium; the ratio of ortho-, pyro-, and tripolyphosphate; 2) the molar ratio of calcium to phosphorus; 3) the pH; and 4) the injection order. This was done to optimize emplacement of the amendment and the extent of treatment, reduction in aqueous uranium concentration, and the formation of autunite and apatite. Sodium orthophosphate ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ), sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), and sodium tripolyphosphate ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ) provided the source of each respective phosphate for all phosphorus amendment formulations and calcium-chloride ( $\text{CaCl}_2$ ) as the source of calcium. The polyphosphate amendment was contained in one solution, and the calcium amendment composed a separate solution. Calcium rapidly precipitates with orthophosphate; therefore, all injections were conducted in two phases by injecting either the calcium solution

followed by the phosphorus solution or vice versa. Details regarding the amendment formulation, injection order, calcium-to-total phosphorus molar ratio, amendment pH, and concentrations are summarized in Table II.

**Table II.** Experimental Parameters for Polyphosphate Amendment Optimization

Column No.	Amendment Source	Wt% Source	Injection Order	Ca:P <sub>total</sub>	pH	Conc., M
1	Ortho [P] <sub>aq</sub>	0.25	1	2.2	7	1.32 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				6.58 x 10 <sup>-4</sup>
	Tripoly [P] <sub>aq</sub>	0.5				8.77 x 10 <sup>-4</sup>
	Calcium		2			1.15 x 10 <sup>-2</sup>
2	Ortho [P] <sub>aq</sub>	0.25	1	2.2	7	1.97 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				9.87 x 10 <sup>-4</sup>
	Tripoly [P] <sub>aq</sub>	0.5				1.32 x 10 <sup>-3</sup>
	Calcium		2			1.74 x 10 <sup>-2</sup>
3	Ortho [P] <sub>aq</sub>	0.25	1	2.2	No adj.	1.97 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				9.87 x 10 <sup>-4</sup>
	Tripoly [P] <sub>aq</sub>	0.5				1.32 x 10 <sup>-3</sup>
	Calcium		2			1.74 x 10 <sup>-2</sup>
4	Ortho [P] <sub>aq</sub>	0.375	1	2.2	No adj.	2.63 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				1.32 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.375				1.75 x 10 <sup>-3</sup>
	Calcium		2			2.32 x 10 <sup>-2</sup>
5	Ortho [P] <sub>aq</sub>	0.25	1	1.67	No adj.	3.47 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				1.74 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.5				2.32 x 10 <sup>-3</sup>
	Calcium		2			2.32 x 10 <sup>-2</sup>
6	Ortho [P] <sub>aq</sub>	0.25	1	1.67	7	3.47 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				1.74 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.5				2.32 x 10 <sup>-3</sup>
	Calcium		2			2.32 x 10 <sup>-2</sup>
7/11	Ortho [P] <sub>aq</sub>	0.25	1	2.2	No adj./7	2.63 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				1.32 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.5				1.75 x 10 <sup>-3</sup>
	Calcium		2			2.32 x 10 <sup>-2</sup>
8/12	Ortho [P] <sub>aq</sub>	0.25	1	2.2	No adj./7	6.58 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				3.29 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.5				4.39 x 10 <sup>-3</sup>
	Calcium		2			5.79 x 10 <sup>-2</sup>

9/13	Ortho [P] <sub>aq</sub>	0.25	1	2.2	No. Adj./7	9.21 x 10 <sup>-3</sup>
	Pyro [P] <sub>aq</sub>	0.25				4.61 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.5				6.14 x 10 <sup>-3</sup>
	Calcium		2			8.10 x 10 <sup>-2</sup>
10/14	Ortho [P] <sub>aq</sub>	0.25	1	2.2	No Adj./7	1.32 x 10 <sup>-2</sup>
	Pyro [P] <sub>aq</sub>	0.25				6.58 x 10 <sup>-3</sup>
	Tripoly [P] <sub>aq</sub>	0.5				8.77 x 10 <sup>-3</sup>
	Calcium		2			1.16 x 10 <sup>-1</sup>

Following saturation and attainment of chemical equilibrium with uranium-spiked groundwater, the influent solution was changed to Hanford groundwater containing the polyphosphate amendment or calcium followed by the other respective solution. Aliquots of the effluent solutions were collected and monitored using ICP-MS and ICP-OES. Several uranium mineral phases will fluoresce under ultraviolet (UV) radiation. This property can be used to rapidly and efficiently evaluate the presence of uranium phases within large sedimentary matrices. A control column was run to confirm that no other fluorescent phases were present within the sediment or formed as a result of saturating the column with 1 ppm uranium. This indicated that fluorescence spectroscopy could be used for qualitative evaluation of uranium-phosphate mineral-phase formation. The solid-phase formations were evaluated by fluorescence spectroscopy using short wave UV radiation, 254 nm.

## RESULTS AND DISCUSSION

### Polyphosphate Hydrolysis

Analysis of the D<sub>2</sub>O/phosphate controls, which should have yielded constant peak areas over the course of the experiment [14, 15], indicated there were fluctuations in the measured areas. Accordingly, this artifact was also reflected in the analysis of the experimental results. However, the ratios of the peak areas within the standards were constant. This consistency implied the peak areas of each sample were being influenced by an analytical artifact which could be correlated to a constant determined from the D<sub>2</sub>O/phosphate controls and used to “scale” the sample peak, thus allowing a single set of standard curves to be used to calculate concentration information for each sample.

Peak areas for all phosphate species were computed and tallied. The standard curves indicated the phosphate per peak area ratio was different for each phosphate species. Therefore, ratios of the slopes of the standard curves were used to normalize all peak areas to a single concentration per peak area ratio. Each peak area was then multiplied by the number of phosphate molecules contained in the corresponding species to yield a single phosphate per peak area ratio. Peak areas were then divided by the sum of all peak areas in the sample to yield the percent total dissolved phosphate represented by each species. For tripolyphosphate, the doublet area was used instead of the triplet area because of its greater size and differentiation from other peaks.

Fig 4 shows the <sup>31</sup>P NMR spectra of 0.2 M tripolyphosphate and 0.2 M pyrophosphate in carbonate buffered D<sub>2</sub>O. Tripolyphosphate spectra shows three distinct signals at ~-3 ppm, -4.7 ppm, and ~-18 ppm. The resonant signal at -3 ppm (doublet) and -18 ppm (triplet) represent tripolyphosphate, whereas the single peak observed at -4.7 ppm represents the degradation reaction product pyrophosphate. Tripolyphosphate degrades to pyro- and orthophosphate as shown in Equation (1); once formed pyrophosphate can undergo further hydrolysis to orthophosphate, Equation (2).



Prior to conducting the homogeneous- and heterogeneous-degradation experiments, a series of <sup>31</sup>P NMR experiments were conducted with known amounts of tripolyphosphate. The results from these experiments provided

the required information to develop a linear relationship between the concentration of tripolyphosphate and integrated peak area. Equation (3) is based on the spectra obtained for the tripolyphosphate doublet, and the results of a linear regression are shown in Fig. 5.

$$P\text{ Conc.} = \frac{\text{Integrated Peak Area}}{(2.94 \times 10^6)} \quad (\text{Eq. 3})$$

The resulting regression coefficient is  $(2.94 \pm 0.20) \times 10^6$  with a  $R^2 = 0.99$ . A similar technique was used for developing equations to quantify the degradation products, pyro- and orthophosphate.

Results from homogeneous  $^{31}\text{P}$  NMR experiments suggest the presence of aqueous cations;  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mg}^{2+}$  do not have a significant effect on the rate of tripolyphosphate hydrolysis at the cation concentrations used for these experiments (Fig. 6). These results are consistent with the findings of an independent homogeneous experiment conducted with Hanford Site groundwater, in which the groundwater had no catalytic effect on tripolyphosphate degradation (Fig. 6). Also shown in Fig. 6 are the results collected for the heterogeneous experiments conducted with naturally occurring mineral  $\text{FeOOH}$  as well as with native Hanford sediments. The percentages for the heterogeneous experiments were the only statistically significant deviations in the phosphate. These results suggest the presence of  $\text{FeOOH}$ . Native Hanford Site sediment had a measurable catalytic effect on the hydrolysis of sodium tripolyphosphate, evident by a 12% and 24% decrease in the tripolyphosphate concentration, respectively.

### Polyphosphate Amendment Formulation

Research beginning in the mid-1960s underscored the efficacy of using calcium and/or lime to precipitate stable calcium-phosphate solid phases, including apatite, for direct removal of phosphate [16, 1, 17, 18]. By complexing calcium and sorbing to mineral surfaces, polyphosphate compounds effectively enhance the rate of calcium-phosphate precipitation by reducing competing reactions, such as the formation of calcium-carbonate, and it “directs” the calcium to participate in reactions resulting in calcium-phosphate precipitation [16].

Static tests were conducted based on the minimum amendment concentration as defined by previously conducted, preliminary column tests, which indicated a 1000 ppm sodium tripolyphosphate solution would reduce the aqueous concentration of uranium to near the MCL in ~12 pore volumes [19]. This established the initial upper limit for the concentration of phosphorus at 1000 ppm. Additionally, lower concentrations of 100, 250, and 500 ppm were investigated to ensure that the amendment did not contain excessive phosphorus that may not be used in remediation efforts. Results of batch tests suggested that a concentration of 1000 ppm was required to remove more than 50% of the aqueous uranium.

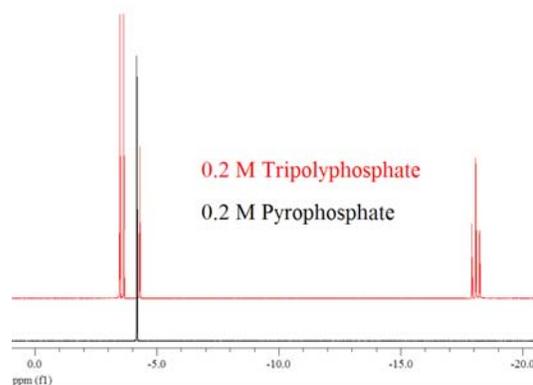


Fig 4. A  $^{31}\text{P}$  NMR Spectrum of a Buffered Aqueous Solution of 0.2 M Pyro- and Tripoly-Phosphate Solutions. A single peak is displayed in the pyrophosphate spectra at -4.2 ppm, whereas the tripolyphosphate spectra show three signals: 1) the tripolyphosphate triplet (~ -18 ppm), 2) the tripolyphosphate doublet (~ -3 ppm), and 3) the pyrophosphate degradation compound (~ -4.7 ppm).

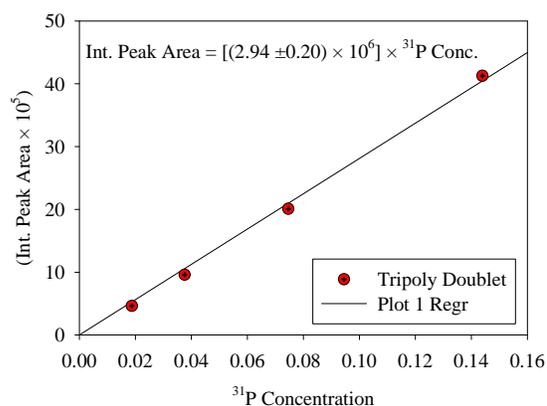


Fig. 5. A  $^{31}\text{P}$  NMR Spectrum Integrated Peak Area as a Function of a Known Aqueous Concentration of Tripolyphosphate. These results are based on the tripolyphosphate doublet, and were used to develop a linear equation that could be used to quantify the amount of tripolyphosphate at a given time.

Solubility limitations for calcium-phosphate sources prevented calcium dihydrogen phosphate, calcium hydrogen phosphate, and calcium pyrophosphate from serving as a sufficient source of phosphate or calcium to be included in the amendment formulation. Although, calcium hypophosphite provides a sufficient source of calcium and phosphorus, rather than forming discrete precipitates it produced fine floccules. The formation of fine floccules as a result of phytic acid remediation was previously shown to provide sorption sites for uranium [20, 21, 22, 23, 24]. However, in open-framework, highly conductive subsurface environments fine floccules may be highly mobile. Alternatively, it has also been shown that rapid flocculation, due to heterogeneous nucleation, in regions of moderate- to low-hydraulic conductivity, may occlude pore space [9]. Either of these results would be detrimental and, therefore, calcium hypophosphite was eliminated from further consideration. Similar effects and concerns eliminated sodium trimetaphosphate from further consideration.

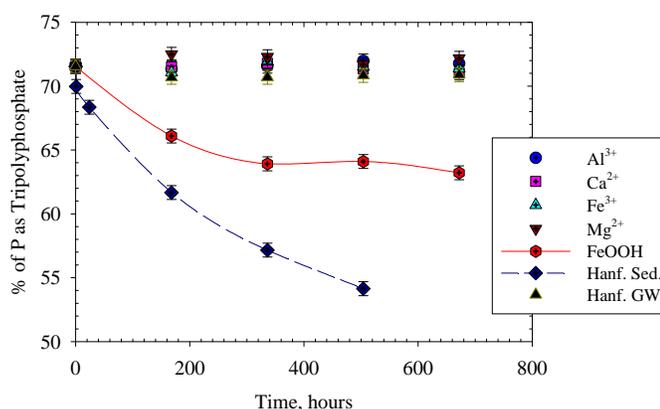


Fig. 6. Percentage of Phosphorus as Tripolyphosphate as a Function of Time for Homogeneous Experiments Conducted with Aqueous Cations, Al<sup>3+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, and Hanford Site Groundwater; and Heterogeneous Experiments Conducted with Solids, FeOOH, and Hanford Site Sediment

The objective of static tests was to identify the calcium-to-phosphorus molar ratio for maximum removal from the aqueous phase. The mechanisms of removal may include sorption and precipitation; however, no attempt was made to discern the degree of removal based on these respective mechanisms. Greater than 90% removal of calcium and phosphorus from solution was achieved in the presence of sodium orthophosphate, sodium pyrophosphate, and sodium tripolyphosphate, respectively, with calcium-chloride as the calcium source [11]. The optimum molar ratio of calcium to phosphorus for sodium orthophosphate and sodium pyrophosphate is 1.5; whereas, the optimum calcium-to-phosphorus molar ratio for sodium tripolyphosphate is ~2.4. Moreover, removal of uranium from all solutions was both rapid (<2 min) and complete (~100%), indicating the formation of limited solubility compounds, such as autunite and/or uranium-bearing apatite. Sodium hexametaphosphate was eliminated from further consideration due to lower precipitation percentages and effects on the sedimentary matrix. These data suggested that it is possible to remove and sequester uranium from 300 Area aquifer using aqueous polyphosphate and calcium sources.

### Polyphosphate Amendment Formulation Emplacement and Efficacy

Visual inspection of sediment removed from columns 1 through 4 (Table II), after application of the associated amendment formulations, indicated the formation of fluorescent green precipitates under shortwave (254-nm) UV radiation. A control column demonstrated that no phases were present or formed within the sedimentary matrix upon application of the polyphosphate amendment in the absence of uranium. Thus, the formation of fluorescent green precipitates was used as a means of qualitative identification of uranium-phosphate phases (Fig. 7). Qualitatively, the precipitate appeared to be within or coating ~50% of the sediment particles. Analysis of effluent-solution samples by ICP-MS from columns 1 through 4 demonstrated ~50% reduction in the aqueous-uranium concentration. This suggested that to treat 100% of the aqueous uranium, a higher concentration of phosphorus and calcium in the amendment formulation was necessary. Comparison of columns 2 and 3 suggested there was little effect of pH in reducing the aqueous-uranium concentration; however, precipitation of calcium-phosphate was more significant under pH conditions ~7.

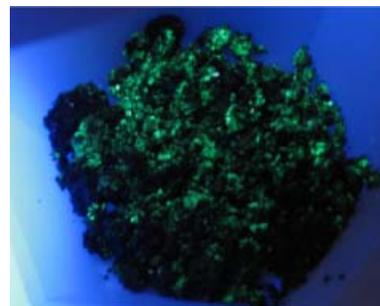


Fig. 7. Representative Photo of Sediment Sectioned from the Effluent End of Column 1, Illustrating the Visual Identification of Uranium-Phosphate under Shortwave UV Radiation.

Column 4 highlighted the significance of the complex relationship between ortho-, pyro-, and tripolyphosphate. Although the concentration of aqueous uranium decreased ~50%, the formation of calcium-phosphate was restricted to a discrete region within the sediment matrix (Fig. 8).

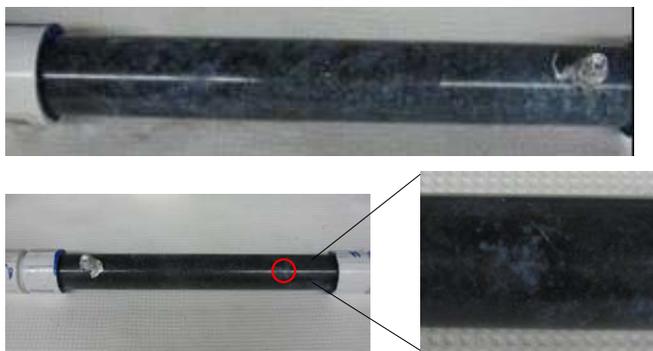


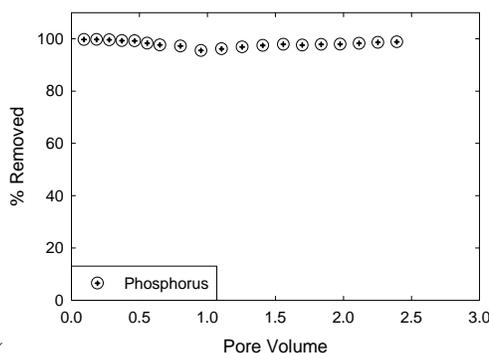
Fig. 8. Photo Showing Disperse Precipitation of Calcium-Phosphate Throughout Column 1 (top) and Discrete Precipitation of Calcium-Phosphate Within Column 4 (bottom)

Columns 5 and 6 (Ca:P molar ratio = 1.67), in comparison to columns 2 and 3 (Ca:P molar ratio = 2.2), illustrated the significance of the calcium-to-phosphorus molar ratio. Qualitatively, the Ca:P molar ratio of 2.2 (columns 2 and 3) afforded more precipitation than a Ca:P molar ratio of 1.67 (columns 5 and 6). The latter gave no visual indication of calcium-phosphate precipitation. Although batch testing indicated the optimal Ca:P molar ratio for removal of calcium and phosphorus in the presence of both ortho- and pyrophosphate was ~1.5, columns 1 through 4 illustrate the significance of the Ca:P ratio of 2.4 indicated by tripolyphosphate batch testing.

The calcium and phosphorus formulations were conducted in duplicate, with columns 7 through 10 at the unadjusted pH (pH 7.0), and columns 11 through 14 at the adjusted pH with a Ca:P molar ratio = 2.2 for all columns. For these experiments, the concentration of calcium varied from  $2.32 \times 10^{-2}$  M to  $1.16 \times 10^{-1}$  M, and phosphorus concentrations ranged from  $1.05 \times 10^{-2}$  M to  $5.26 \times 10^{-2}$  M. Precipitation of calcium-phosphate in columns 7 through 10 was limited, eliminating consideration of non-adjusted amendment solutions. Alternatively, the degree of calcium phosphate precipitation increased using the same amendment formulation adjusted to pH ~7 (columns 11 through 14). In columns 11 and 12, the concentration of aqueous uranium in the effluent solution increased over the first 0.5 to 1 pore volumes during remedy injection to concentrations between 1.2 to 3 times the influent uranium concentration (Fig. 9a, b). However, increasing the concentration of phosphorus and calcium in the amendment formulation (column 14) precluded this phenomenon. Additionally, the concentration of aqueous uranium in column 14 was reduced to below the MCL (30  $\mu$ g/L) within 0.5 to 1 pore volumes of treatment, and remained well below 30  $\mu$ g/L for the remainder of the experiment (Fig. 9d).

Columns 15 through 18 used the optimum formulations identified through previous tests (columns 13 and 14) as well as two additional formulations that contained equivalent total phosphorus concentrations, but maintained total calcium-to-phosphorus ratios of 1.9 (columns 17 and 18). The order of injection was altered for all columns (15 through 18) such that calcium was injected prior to phosphorus. Qualitative visual inspection of the columns following treatment suggested the most complete distribution within the column and removal of uranium occurred in column 16, using a calcium-to-phosphorus molar ratio of 1.9, pH 7.0 (Fig. 10).

However, with the exception of column 17, quantitative analysis of effluent uranium concentrations indicates that concentrations do not decline as rapidly as those measured in the previous set of columns, 11 through 14, wherein



phosphorus was injected first, followed by calcium (

Fig. 11. Representative Plot Depicting the Removal of Phosphorus by Sorption and Precipitation Reactions.

Fig. 12). Additionally, the efficacy and long-term performance of columns 15 through 18 is less than that of columns 11 through 14 where, uranium concentrations remained well below 30  $\mu\text{g/L}$ . The aqueous concentration of uranium measured in the effluent solutions collected from columns 15 through 18 declined to below 30  $\mu\text{g/L}$ , but then exhibited a number of fluctuations above and below the MCL for the remainder of the experiment. It is hypothesized that these fluctuations can be attributed to the initial formation of precursor calcium-uranate phases, which are more soluble than uranium-phosphate phases. Upon injection of the polyphosphate solution, the calcium-uranate phases likely undergo rapid dissolution to release soluble uranium that re-precipitates as a uranium-phosphate phase. Although both injection schemes ultimately result in formation of uranium-phosphate, precipitation and dissolution of calcium-uranate phases may afford undesirable fluctuations in uranium concentration above 30  $\mu\text{g/L}$ .

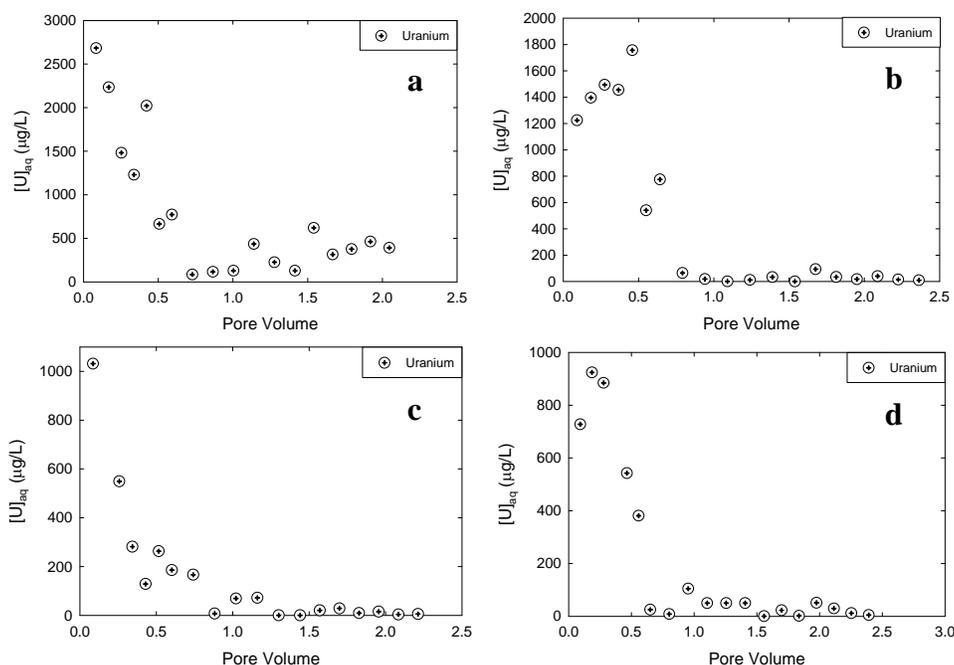
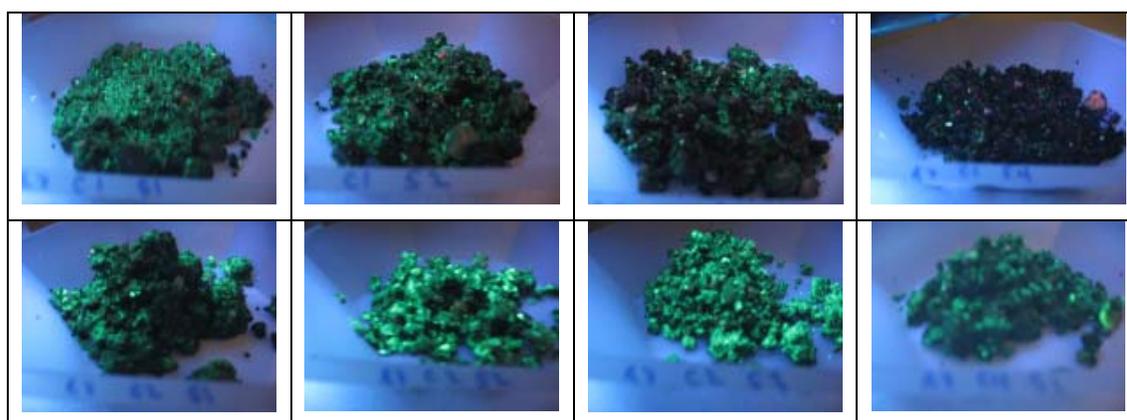


Fig. 9. Graphs Depicting Aqueous-Uranium Concentrations from Columns Saturated with 1,000  $\mu\text{g/L}$  Uranium as a Function of the Number of Pore Volumes of Polyphosphate Remedy Displaced Through Columns a) 11, b) 12, c) 13, and d) 14 (Table II).



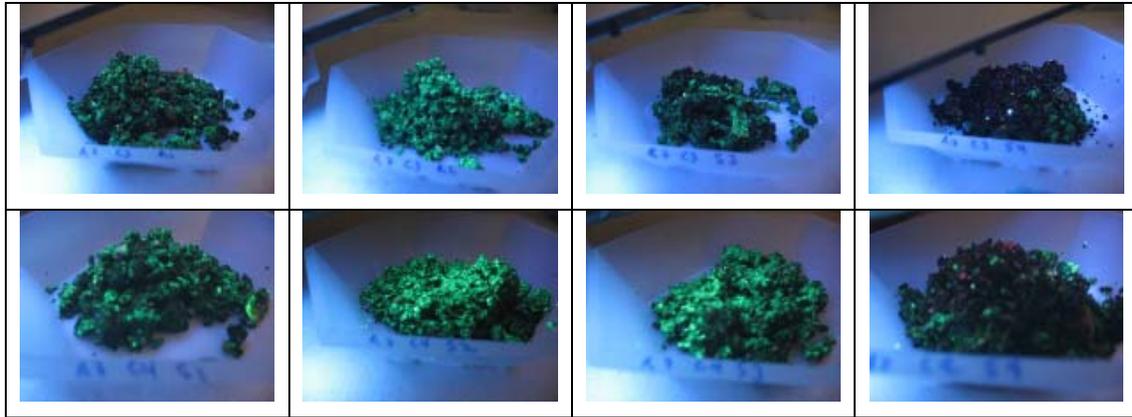


Fig. 10. Photos of Column Sections Taken under Shortwave UV Radiation. Orientation: top-down, columns 15 through 18; left to right, influent to effluent.

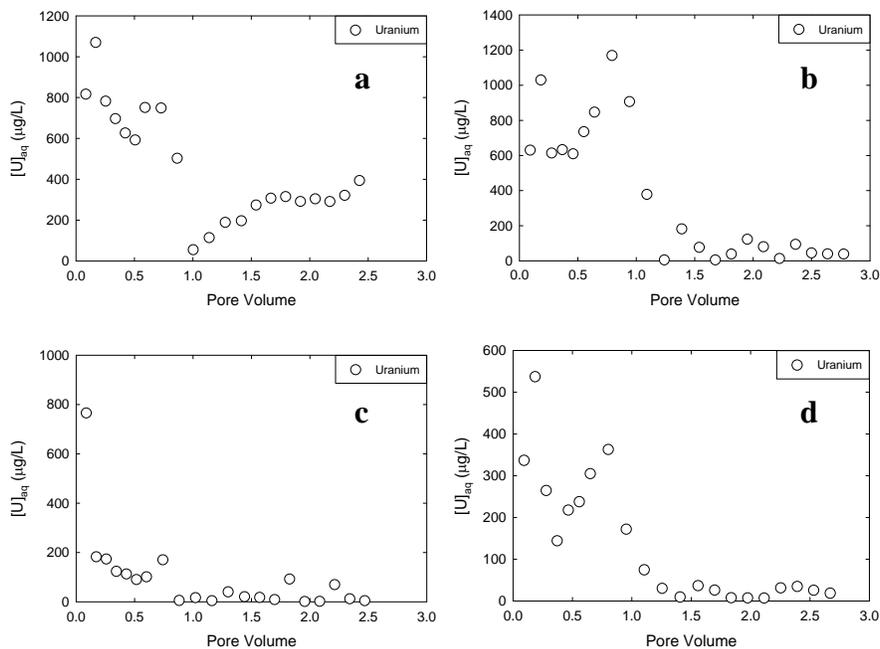


Fig. 12. Graphs Depicting Aqueous-Uranium Concentrations from Columns Saturated with 1000 µg/L Uranium as a Function of the Number of Pore Volumes of Polyphosphate Remedy Displaced Through Columns a) 15, b) 16, c) 17, and d) 18 (Table II). Remedy injection order was calcium followed by phosphorus.

Regardless of the injection order or concentration of phosphorus and calcium used in the amendment formulation, all phosphorus, including degradation products, was removed via sorption and precipitation reactions. Fig. 11 is a representative plot for the removal of phosphorus during treatment of a uranium-contaminated column with results being comparable for all column tests conducted. Effluent concentrations of phosphorus are at or below background groundwater concentrations. Thus, the potential for downgradient transport and potential migration to the river is minimal.

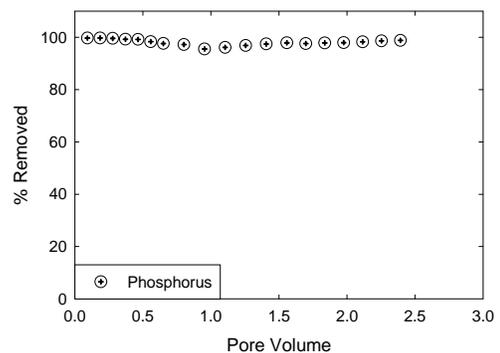


Fig. 11. Representative Plot Depicting the Removal of Phosphorus by Sorption and Precipitation Reactions.

## SUMMARY AND CONCLUSIONS

### Polyphosphate Amendment

Based on the results of column transport experiments, a three-phase injection strategy was identified as an effective approach to obtain both direct treatment of the uranium contamination in groundwater (i.e., autunite formation) and secondary formation of calcium-phosphate. This will provide the long-term treatment capacity within the amended zone to address uranium solubilized and released from the deep vadose zone and capillary fringe during future high water table conditions. The three-part injection strategy consists of the following:

- Initial polyphosphate amendment injection to precipitate aqueous uranium within the treatment zone as autunite. This will prevent the formation of soluble calcium-uranate, which may re-dissolve, thereby releasing a pulse of uranium into the groundwater upon injection of the soluble polyphosphate.
- The initial polyphosphate injection is directly followed by injection of a calcium-chloride ( $\text{CaCl}_2$ ) solution to provide a sufficient calcium source for apatite formation during a subsequent polyphosphate injection. Due to the higher  $K_d$  of the  $\text{CaCl}_2$  solution, as measured on site-specific sediments, a larger injection volume will be required to reach the full radial extent of the targeted treatment zone for this component of the amendment formulation. However, this same increased retardation will help to facilitate mixing between the calcium and polyphosphate amendments during the third and final injection phase.
- The  $\text{CaCl}_2$  injections are directly followed by a final polyphosphate injection. This provides additional time-released phosphorus for lateral precipitation of calcium-phosphate as the remedy migrates downfield, and additional hydraulic driving force to achieve the maximum lateral distribution of solid-phase calcium-phosphate.

Table III presents the final polyphosphate remediation amendment formulation. Results of batch and column tests demonstrated that optimum performance is achieved using a formulation to which the contribution of phosphorus is 25% orthophosphate, 25% pyrophosphate, and 50% tripolyphosphate. Anhydrous forms of pyrophosphate and tripolyphosphate were used to maximize solubility and minimize cost. The mixture of the various components of the polyphosphate solution will be used to achieve a solution pH of  $\sim 7$ . The amendment solution will be prepared by mixing, in order, the sodium orthophosphate, sodium pyrophosphate, and sodium tripolyphosphate to achieve a pH of  $\sim 7$ , and prevent degradation of polymerized phosphate molecules during preparation of the remedy solution. The total Ca:P molar ratio is 1.9.

**Table III.** Pilot Scale Field-Test Amendment Formulation

Injection	Amendment	Formula	Formula Wt, g/mol	Density, g/cm <sup>3</sup> (25°C)	Conc., g/L	Conc., M
1	Sodium phosphate, monobasic	$\text{NaH}_2\text{PO}_4$	119.98	1.004	0.59	$4.94 \times 10^{-3}$
	Sodium pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7$	265.9		0.66	$2.47 \times 10^{-3}$
	Sodium tripolyphosphate	$\text{Na}_5\text{P}_3\text{O}_{10}$	367.86		1.21	$3.29 \times 10^{-3}$
	Sodium bromide	$\text{NaBr}$	102.90		0.103	$1.00 \times 10^{-3}$
2	Calcium chloride	$\text{CaCl}_2$	110.98	1.005	3.41	$3.07 \times 10^{-2}$
3	Sodium phosphate, monobasic	$\text{NaH}_2\text{PO}_4$	119.98	1.004	0.59	$4.94 \times 10^{-3}$
	Sodium pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7$	265.9		0.66	$2.47 \times 10^{-3}$
	Sodium tripolyphosphate	$\text{Na}_5\text{P}_3\text{O}_{10}$	367.86		1.21	$3.29 \times 10^{-3}$
	Sodium bromide	$\text{NaBr}$	102.90		0.103	$1.00 \times 10^{-3}$

### Application of Polyphosphate Remediation Technology

Polyphosphate technology has been developed for controlled application and precipitation within deep subsurface contaminant plumes. A thorough understanding of site-specific geochemical and hydrodynamic conditions enables optimization of polyphosphate technology for controlled remediation without discharging excess phosphorus into the environment, which could detrimentally impact the environment or downgradient drinking water supplies. Standard groundwater wells allow injection of polyphosphate technology deep below the ground surface, providing treatment of contaminants too deep for conventional solid-phase apatite emplacement, or rapidly precipitating soluble applications of short-chain inorganic or organic phosphate sources. The degradation kinetics of long-chain polyphosphate molecules, such as sodium tripolyphosphate, affords a time-released source of inorganic phosphate. Polyphosphate technology affords direct remediation of soluble 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 remobilization of uranium is minimal. Release of uranium from autunite may only occur through dissolution of the mineral structure. In addition to autunite, excess phosphorous can result in apatite (calcium phosphate) mineral formation, providing a long-term source of treatment capacity. A field-demonstration has been conducted within a uranium contaminated aquifer on DOE's Hanford Site in southeastern Washington State, and is the subject of a companion publication [25].

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