
**Pacific Northwest
National Laboratory**

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**Experimental Plan:
Uranium Stabilization Through
Polyphosphate Injection**

**300 Area Uranium Plume Treatability
Demonstration Project**

D. M. Wellman
J. S. Fruchter
V. R. Vermuel

September 2006

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830



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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

This experimental plan describes a laboratory-testing program to be performed at Pacific Northwest National Laboratory (PNNL) in support of the 300-FF-5 feasibility study. The objective of the proposed treatability test is to evaluate the efficacy of using polyphosphate injections to treat uranium contaminated groundwater in situ. This study will be used to

- Investigate the technology's ability to meet remedial objectives
- Identify implementation challenges
- Develop implementation cost estimates

These activities will be conducted in parallel with the site characterization plan and limited field investigation results, which will more accurately define the vertical extent of uranium in the vadose zone and in the capillary fringe zone laterally throughout the plume. The experimental plan will establish the viability of the method and, along with results from the Site Characterization Plan, provide the means for determining how best to implement the technology in the field. Results of the experimental plan, site characterization plan and limited field investigation will be integrated to design the field-scale treatability test based on site-specific information for polyphosphate remediation of the 300 Area uranium plume within the feasibility study time frame at an overall cost savings.

Acronyms

DIW	deionized water
DOE	U. S. Department of Energy
EDS	energy dispersive spectroscopy
EPA	U. S. Environmental Protection Agency
FY	fiscal year
HASQARD	Hanford Analytical Services Quality Assurance Requirements Documents
ICP-OES	inductively coupled plasma-optical emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
MCL	maximum concentration limit [in groundwater reports, MCL = maximum contaminant level]
M&TE	materials and test equipment
ORP	Office of River Protection
PA	performance assessment
PFA	<i>perfluoroalkoxide</i>
PNNL	Pacific Northwest National Laboratory
³¹ P NMR	phosphorus nuclear magnetic resonance
QA	quality assurance
QAPD	quality assurance program documents
RA	risk assessment
ROD	record of decision
SBMS	Standards-Based Management System
SEM	scanning electron microscope
SPFT	single-pass flow through
THAM	<i>tris hydroxymethyl aminomethane</i>
XRD	x-ray diffraction

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1.0 Introduction

This experimental plan covers work elements associated with laboratory optimization of the polyphosphate amendment formulation to treat aqueous uranium within the 300 Area. Polyphosphate treatment shows promise for reducing the concentration of dissolved uranium in a plume that has persisted beneath the 300 Area for some time. The polyphosphate technology was selected for further testing during the 300-FF-5 Phase III Feasibility Study technology screening process. An initial feasibility study (DOE 1995) for the 300-FF-5 uranium plume considered hydraulic containment, slurry wall containment, and groundwater extraction as potential remedial action technologies. None were selected for interim action, and reduction of contamination levels by natural processes was considered a viable alternative while source removal actions continued.

Subsequent planning for a Phase III feasibility study focused on methods that would reduce the concentration of uranium in the aquifer, including multiple methods to immobilize uranium using chemical-based technologies. Based on this initial technology screening, the polyphosphate technology was identified as the best candidate for further evaluation and selected for treatability testing. The objective of the polyphosphate treatability test is to evaluate the efficacy of using polyphosphate injections to reduce uranium concentrations in groundwater to meet drinking water standards (30 µg/L) in situ. The work elements described in this experimental plan pertain to integration of site-specific characterization data with laboratory testing to optimize the polyphosphate amendment for implementation of a field-scale demonstration of the technology.

Data collected during the 300-FF-5 limited field investigation are being used to refine the hydrogeologic and geochemical conceptual model for the uranium plume that is the target of the treatability test. Information developed under several research investigations into the geochemistry of uranium in the 300 Area (Serne et al. 2002; Zachara et al. 2005) has also contributed significantly to refining the conceptual site model for uranium contamination. These results have been used to select an appropriate site for a field-scale demonstration of the polyphosphate treatment technology. Well 399-1-23, which was installed as part of the limited field investigation, has been identified as the preferred location for a field-scale demonstration of the technology. During this experimental effort, the formulation of the polyphosphate amendment will be optimized to work within the subsurface based on the geochemistry and hydrology of the area.

2.0 Background

This section provides background information on the 300 Area uranium plume and selection of polyphosphate remediation technology for further site-specific evaluation and treatability testing. In 1996, a record of decision (EPA 1996) identified the following interim actions for remediation of the uranium contaminant plume beneath the site:

- Continued groundwater monitoring to determine how contaminant conditions may change with time.
- Institutional controls to limit the use of groundwater.

Interim action results have determined that uranium concentrations in the groundwater plume have been generally declining, but still persist at concentrations above the drinking water standard (remediation goal). Therefore, re-evaluation of the remedy for uranium contamination is necessary because the rate of decrease in uranium concentrations is significantly different than the rate of decrease expected and used as a basis for the remedy selection in the current record of decision.

During the 300-FF-5 Phase III Feasibility Study technology screening process, polyphosphate treatment judged to be the most promising among five other active remedial technologies for uranium at this site for reducing the concentration of dissolved uranium. Polyphosphate technology was selected for further testing.

2.1 300 Area Uranium Plume

The 300-FF-5 Operable Unit, a groundwater operable unit, includes the water and solids that constitute the aquifer. The 300-FF-5 Operable Unit, located in the southeast portion of the Hanford Site, includes groundwater affected by contaminants released from waste sites in three geographic sub-regions of the operable unit: the 300 Area, 618-11 burial ground, and 316-4 cribs/618-10 burial ground (Figure 1).

Facilities in the 300 Area of the Hanford Site were primarily involved with fabrication of nuclear fuel for plutonium production, which included some research and development activities, during the period spanning the startup of Hanford reactors in 1944 through the late 1980s (Young and Fruchter 1991). The range of activities produced a wide variety of waste streams that contained chemical and radiological constituents (Gerber 1992; DeFord et al. 1994). Since the early 1990s, extensive remediation of liquid waste disposal sites and solid waste burial grounds has taken place. As of March 2004, most liquid waste disposal sites, which are located in the north half of the 300 Area, have been excavated, backfilled, and the ground surface 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 yet taken place.

Groundwater beneath the 300 Area and the two outlying geographic sub-regions (618-11 burial ground and 316-4 cribs/618-10 burial ground) contain contaminants from past-practice disposal activities at concentrations that exceed the U.S. Environmental Protection Agency (EPA) standards for drinking water supplies. Uranium is the most prominent waste constituent remaining in the environment, and it has persisted in waste sites and groundwater during the years following the shutdown of most fuel fabrication activities and cessation of liquid effluent disposal to the ground. Uranium in soluble form is of concern for chemical toxicity, as well as for radiological exposure, although the concentrations in groundwater for chemical toxicity are lower than those associated with exceeding radiological dose standards. Specific criteria on the toxicity to freshwater aquatic organisms are not currently established, so by default, the criteria for the protection of aquatic organisms are the same as those applied for protection of human health.

The uranium plume is just upstream of the City of Richland municipal water supply intake on the Columbia River. In addition elevated uranium concentrations enter the river along the shoreline and enter the riparian and river biota through seeps. The 1996 record of decision (ROD) for the 300-FF-5 Operable Unit (EPA 1996) stipulated an interim action program of natural attenuation process

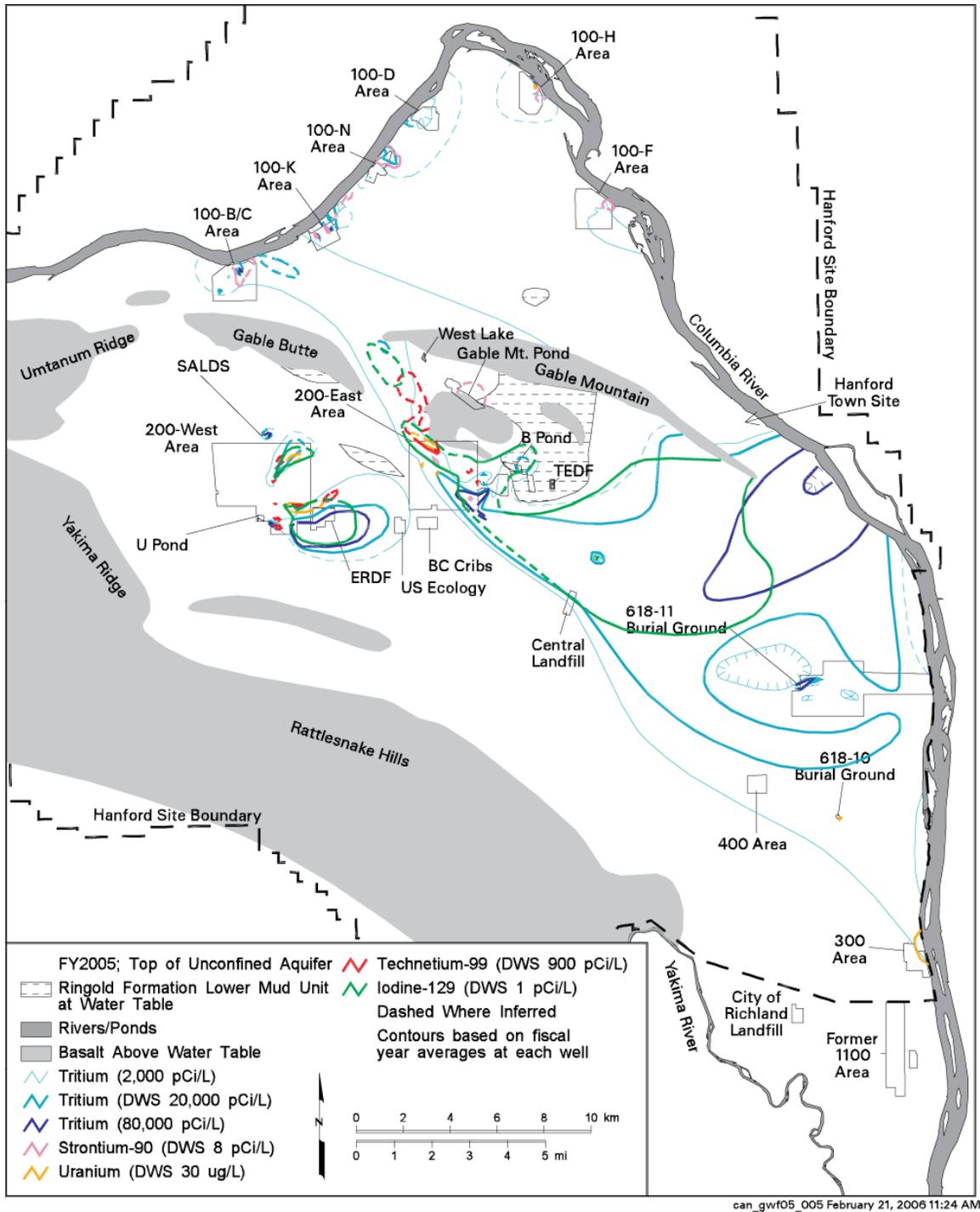


Figure 1. Map of the Hanford Site

accompanied by increased groundwater monitoring. The remedial action objective of the ROD is reduction of groundwater uranium to the EPA maximum contaminant level (MCL). The EPA's MCL in groundwater for drinking water supplies is currently 30 µg/L uranium, measured as total uranium in the water sample. During the remedial investigation in the early 1990s and the development of the initial ROD, the proposed standard for uranium was 20 µg/L.

Despite the cessation of uranium releases and the removal of shallow vadose zone source materials, the second five-year review of the ROD will state that as of 2006, dissolved uranium concentration below the cleanup criteria established by the ROD have not been achieved within the anticipated 10-year time period. A Phase III feasibility study was begun in 2005 to identify and evaluate remedial alternatives that will accelerate monitored natural attenuation of the uranium plume. Polyphosphate application is judged to be the most promising among five other active remedial technologies for uranium at this site. Presently focused application of polyphosphate is proposed in source or "hot spot" areas that would significantly reduce the inventory of available uranium that contributes to the groundwater plume (Figure 2).

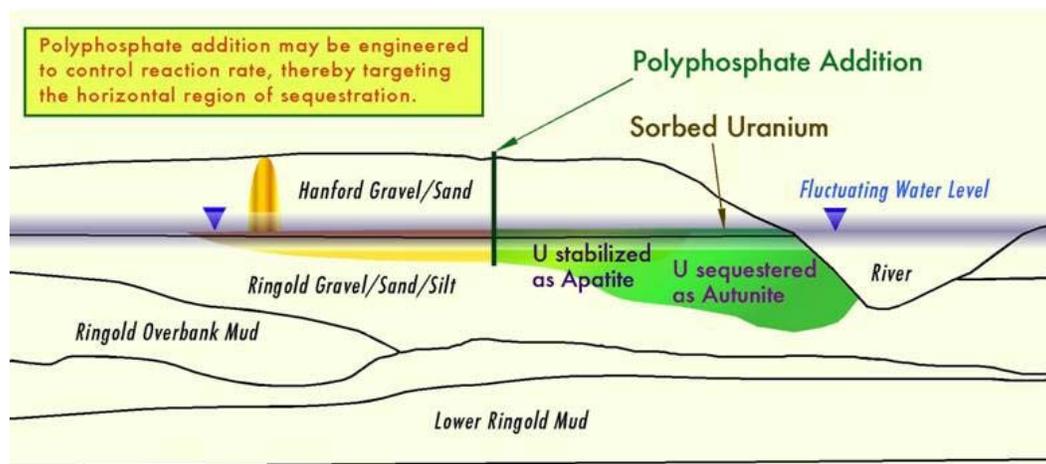


Figure 2. Schematic Depicting the 300-FF-5 Operable Unit Geology and Proposed Treatability Test of Polyphosphate to Sequester Uranium

2.2 Polyphosphate Remediation Technology

Numerous proposals have been made to sequester uranium, in situ, with solid phase hydroxyapatite (Arey et al. 1999; Conca 1996; Gauglitz and Holterdorf 1992; Moore et al. 2001; Seaman et al. 2001; Wright et al. 1995), and water-soluble phosphate compounds, such as tribasic sodium phosphate $[\text{Na}_3(\text{PO}_4) \cdot n\text{H}_2\text{O}]$ (Lee et al. (1995) or phytic acid (Jensen 1996; Nash et al. 1998a, 1998b, 1999), that could be injected into contaminant plumes from strategically placed wells, as a chemical stabilizer for uranium and other radionuclides and heavy metals. The advantages of soluble amendments is they allow for treatment of plumes situated deep within the subsurface and act to sequester uranium by precipitating insoluble uranium minerals rather than by reversible sorption mechanisms. However, Wellman et al. (2006a) demonstrated that compounds including tribasic sodium phosphate and phytic acid result in the rapid formation of phosphate phases. Formation of these phases occludes ~30% of the fluid-filled pore space within the sedimentary formation. Rapid reduction in the hydraulic conductivity will have a significant effect on subsequently injected amendment solutions, the targeted groundwater plume, or both, by deflecting flow from the natural path.

Conversely, the use of soluble long-chain polyphosphate materials have been demonstrated to delay the precipitation of phosphate phases (Wellman et al. 2006a) (Figure 3). Precipitation of phosphate minerals occurs when phosphate compounds degrade in water, due to hydrolysis, to yield the orthophosphate molecule (PO_4^{3-}). The longer the polyphosphate chain, the slower the hydrolysis reaction that leads to orthophosphate production (Figure 4). Accordingly, use of a long-chain polyphosphate compound does not result in a drastic change in hydraulic conductivity of the target aquifer.

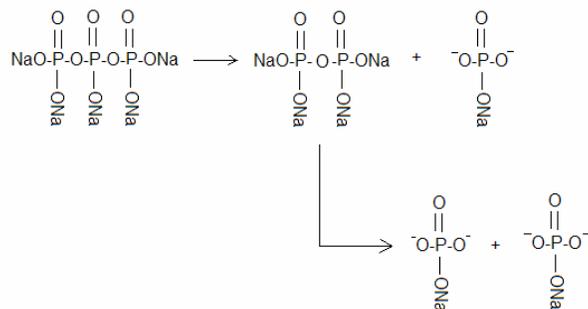


Figure 3. Schematic Depicting the Step-Wise Hydrolysis of Sodium Tripolyphosphate

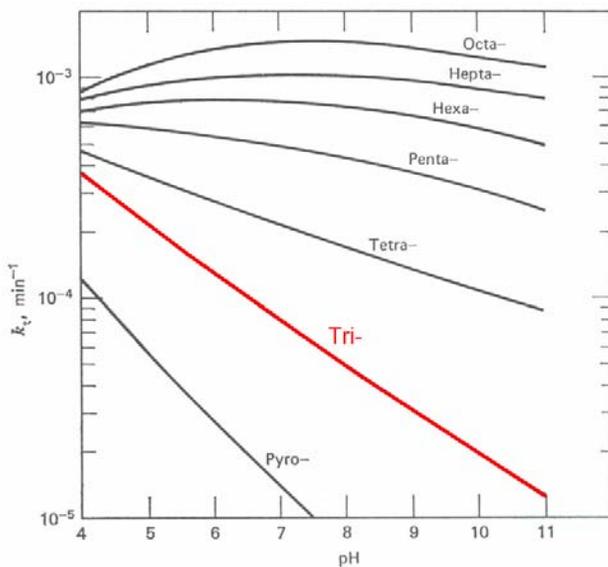


Figure 4. Hydrolysis Rate of Polyphosphate Molecules as a Function of pH

A critical component of the treatability test will be to evaluate the use of multi-length polyphosphate amendment formulations, the hydrolysis rates of polyphosphates, kinetics of autunite and apatite formation, and long-term immobilization of uranium by apatite. The purpose of this test plan is to delineate the laboratory testing to be performed in fiscal years (FY) 2006 – 2007 on sediments from the 300 Area aquifer to provide site specific information evaluating the polyphosphate addition and determining how best to implement the technology in the field.

3.0 Objectives

This experimental plan describes a laboratory testing program to be performed at Pacific Northwest National Laboratory (PNNL) in support of the in support of the 300-FF-5 feasibility study. The objective of the proposed treatability test is to evaluate the efficacy of using polyphosphate injections to treat uranium contaminated groundwater in situ. This study will be used to evaluate the use of multi-length polyphosphate amendment formulations, the hydrolysis rates of polyphosphates, kinetics of autunite and apatite formation, and long-term immobilization of uranium by apatite.

These activities will be conducted in parallel with a limited field investigation, which is currently underway to more accurately define the vertical extent of uranium in the vadose zone, capillary fringe zone, and laterally throughout the plume. The treatability test will establish the viability of the method and, along with characterization data from the limited field investigation, will provide the means to determine how best to implement the technology in the field. By conducting the treatability work in parallel with the ongoing limited field investigation, the resulting feasibility study will provide, site-specific information for evaluating polyphosphate addition and selecting a suitable remediation strategy for the uranium plume within the feasibility study time frame at an overall cost savings

4.0 Laboratory Testing

4.1 Polyphosphate Hydrolysis Experiments

A long-chain polyphosphate molecule is required to forestall hydrolysis of the polyphosphate molecule. However, a balance between the rate of polyphosphate degradation, groundwater flow rate, autunite/apatite precipitation, and injection rate must be met in order to optimize the remediation strategy. Thus, a clear understanding of polyphosphate hydrolysis kinetics is necessary to select the best chain or mix of polyphosphate chain lengths in order to directly precipitate autunite for immediate mitigation of aqueous uranium concentrations, and further precipitate apatite to control the long-term release of uranium from the sedimentary source.

In a homogeneous environment, the release of the orthophosphate molecule is dependent upon both the chain length and the pH of the solution; as the length of the phosphate chain increases, the hydrolysis rate decreases (Shen and Morgan 1973). However, surface-mediated processes affect reaction rates in heterogeneous systems by lowering the activation energy, E_a , of the system, as expressed in the Arrhenius equation:

$$\log k_+ = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where k_+ = the rate constant
 A = the frequency factor (also called the Arrhenius constant)
 R = the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
 T = the temperature (K).

Therefore, it is essential to quantify the hydrolysis rates of long-chain phosphates in porous media before a remediation strategy can be effectively implemented.

The speciation of inorganic phosphate and its chemical affinity for other species in solution can be readily assessed with phosphorus-31 nuclear magnetic resonance (^{31}P NMR). Controlled ^{31}P NMR will be conducted to quantify the kinetic degradation rate of tripoly- and pyrophosphate molecules under conditions present within the Hanford 300 Area subsurface. The effect of aqueous cations and sedimentary components on the hydrolysis of polyphosphates will be evaluated over the pH range from 6 to 8 at $T = 23^\circ\text{C}$.

Table 1. Experimental Conditions for the Quantification of the Homogeneous Degradation of Polyphosphate in the Presence of Aqueous Cations

Aqueous Component	Concentrations, mg/L	Matrix
HCO_3^-	Sat.	
Ca^{2+}	59	Sat. HCO_3^-
Mg^{2+}	15	Sat. HCO_3^-
Na^+	26	Sat. HCO_3^-
Fe^{3+}	0.22	Sat. HCO_3^-

Table 2. Experimental Conditions for the Quantification of the Heterogeneous Degradation of Polyphosphate in the Presence of Sedimentary Material

Sedimentary Material	Matrix
$\text{Fe}(\text{OH})_3$	Sat. HCO_3^-
Quartz	Sat. HCO_3^-
300 Area Sediment	Sat. HCO_3^-

4.2 Autunite and Apatite Formation

In homogeneous systems the precipitating phase first forms stable nuclei and then grows via crystallization to macroscopic size. The nucleation rate can be expressed as:

$$B = \beta \exp\left(\frac{-A}{\ln^2 s}\right) \quad (2)$$

where B = the rate
 β = the frequency factor
 A = a parameter that depends on interfacial energy
 s = the degree of supersaturation of the solution.

However, heterogeneous nucleation on foreign or heterogeneous surfaces lowers the interfacial energy, A . Equation (3) can be used to understand the increase in precipitation rates due to heterogeneous nucleation (Avrami 1939, 1940). The rate of heterogeneous nucleation can be expressed as:

$$B(t) = kN(t) = kN_o \exp(-kt) \quad (3)$$

in which the nucleation rate as a function of time, $B(t)$, is equivalent to the product of a constant times the nucleation density as a function of time, $kN(t)$, and is equal to the product of a constant, k , the number of heterogeneous germ nuclei, N_o , and exponentially to the negative product of the constant, k , and time, t . Note the degree of supersaturation of the solution is still important, and is accounted for in the parameter k . The nucleation rate is directly proportional to the number of nucleation sites available, a number that should be large for a solution percolating through porous media. This equation also suggests that nucleation rates should be fastest at early times and will diminish exponentially.

These equations are relevant to the understanding of surface-mediated catalysis of autunite and apatite precipitation kinetics. Rapid initial rates are critical for the successful deployment of a soluble polyphosphate amendment. The above equations imply that catalysis of polyphosphate hydrolysis and solid phase precipitation should be immediate after orthophosphate contacts porous media. Furthermore, it highlights the importance of quantifying kinetic precipitation data for systems in more realistic column experiments containing actual 300 Area sediments coupled with knowledge regarding the degradation of proposed polyphosphates (Table 3).

Table 3. Proposed Phosphate Sources for Polyphosphate Amendment

Phosphate Source	Formula
Sodium Orthophosphate	$\text{Na}_3\text{PO}_4 \cdot n\text{H}_2\text{O}$
Sodium Pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7 \cdot n\text{H}_2\text{O}$
Sodium Tripolyphosphate	$\text{Na}_5\text{P}_3\text{O}_{10} \cdot n\text{H}_2\text{O}$
Sodium Trimetaphosphate	$(\text{NaPO}_3)_3 \cdot n\text{H}_2\text{O}$
Sodium Hexametaphosphate	$(\text{NaPO}_3)_6 \cdot n\text{H}_2\text{O}$
Calcium Dihydrogen Phosphate	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$
Calcium Hydrogen Phosphate	$\text{CaHPO}_4 \cdot n\text{H}_2\text{O}$
Calcium Pyrophosphate	$\text{Ca}_2\text{P}_2\text{O}_7 \cdot n\text{H}_2\text{O}$
Calcium Hypophosphite	$\text{Ca}(\text{H}_2\text{PO}_2)_2 \cdot n\text{H}_2\text{O}$

4.2.1 Batch Experiments

Formation of autunite and/or apatite will be evaluated under conditions relevant to the 300 Area aquifer. Series of batch and saturated column experiments will be conducted to quantify:

1. Formation rate of autunite/apatite for various polyphosphate formulations.
2. Polyphosphate treatment efficiency – amount of polyphosphate required to treat a pore volume of uranium contaminated groundwater.

3. Polyphosphate treatment emplacement efficiency - evaluate mixing problem (i.e., effective contact or tendency for the reagent to push contaminated groundwater ahead of the treatment volume).

Prior to conducting tests with 300 Area sediment cores, batch experiments will be conducted over a range of polyphosphate sources and concentrations to identify the required conditions to obtain maximum precipitation of autunite and/or apatite (Table 4). The thermodynamic geochemical code EQ3NR (Wolery 1992) was utilized to assess the necessary concentration of phosphorus to precipitate hydroxylapatite and autunite given the minimum and maximum saturation state measured within the aquifer. Thermodynamic databases from numerous literature sources were used to update the computer code (Alwan and Williams 1980; Chen et al. 1999; Finch 1997; Grenthe et al. 1992; Kalmykov and Choppin 2000; Langmuir 1978; Nguyen et al. 1992; O'Hare et al. 1976, 1988; Sergeyeva et al. 1972; Vochten 1990). It is important to note that because of the complex chemistry of uranium, there is significant debate within the literature regarding the stoichiometry and the thermodynamic values assigned to aqueous uranium species and secondary mineral phases. As such, the geochemical calculations are based on current knowledge, but may have significant uncertainty associated with them. Batch experiments will evaluate the potential composition of the polyphosphate amendment based on the extreme (i.e. maximum and minimum) concentration range measured within the 300 Area aquifer. The use of multi-length polyphosphate chain amendments will be evaluated to afford rapid precipitation of autunite and/or apatite. All experiments will be conducted in Hanford groundwater and in the presence of 300 Area sediments. Aqueous concentrations will be monitored via inductively couple plasma–mass spectrometry (ICP-MS) and inductively couple plasma–optical emission spectrometry (ICP-OES); solid phase formation will be evaluated with X-ray diffraction (XRD).

4.2.2 Column Experiments

The formation rate and quantity of apatite formed per pore volume of treatment will be quantified based on polyphosphate formulation optimized through ³¹P NMR hydrolysis and batch precipitation experiments. The use of multi-length polyphosphate chain amendments will be evaluated to afford rapid precipitation of autunite and/or apatite without negatively impacting the hydraulic conductivity of the formation. The columns will be composed of 300 Area sediment and will be saturated with Hanford groundwater to ensure chemical equilibrium. Following saturation and attainment of chemical equilibrium, the influent solution will be changed to Hanford groundwater containing the polyphosphate amendment. The rate of apatite formation and quantity of apatite formed per pore volume of treatment will be quantified over a range of conditions that include variations in polyphosphate amendment concentration, density, and viscosity, injection rate, flow rate, and mixing rate. If the physical properties of the selected amendment preclude effective implementation, the concentration of the formulation will be optimized to allow for implementation and the resulting effect on treatment (i.e. additional pore volumes of amendment injection) will be quantified. Aqueous concentrations will be monitored via ICP-MS and ICP-OES.

The formation rate and quantity of autunite formed will be evaluated utilizing sedimentary cores from the 300 Area. Preliminary characterization results indicate the uranium concentration within the aqueous and solid matrix of the sediment cores is below the MCL for uranium. As such, in order to effectively evaluate polyphosphate amendments for uranium remediation, it will be necessary to conduct parallel tests which use 1) Hanford groundwater, and 2) a solution of Hanford groundwater spiked with aqueous uranium as the influent solution. The uranium concentration in the pore fluid will be equal to the

Table 4. Experimental Batch Conditions for Polyphosphate Amendment Optimization

Phosphate Source	Phosphorus Conc. (ppm)	Calcium Source	Calcium Conc. (ppm)	Uranium Conc. (µg/L)		Precipitate
				10	1000	
Sodium Orthophosphate	1000			10	1000	Autunite
					0.00	Apatite
Sodium Pyrophosphate	1000			10	1000	Autunite
					0.00	Apatite
Sodium Tripolyphosphate	1000			10	1000	Autunite
					0.00	Apatite
Sodium Orthophosphate	500			10	1000	Autunite
					0.00	Apatite
Sodium Pyrophosphate	500			10	1000	Autunite
					0.00	Apatite
Sodium Tripolyphosphate	500			10	1000	Autunite
					0.00	Apatite
Sodium Trimetaphosphate	1000			10	1000	Autunite
					0.00	Apatite
Sodium Trimetaphosphate	500			10	1000	Autunite
					0.00	Apatite
					0.00	Apatite
Sodium Hexametaphosphate	1000			10	1000	Autunite
					0.00	Apatite
Sodium Hexametaphosphate	500			10	1000	Autunite
					0.00	Apatite
					0.00	Apatite
Calcium Hypophosphite	1000			10	1000	Autunite
					0.00	Apatite
Calcium Hypophosphite	500			10	1000	Autunite
					0.00	Apatite
Calcium Hypophosphite	250			10	1000	Autunite
					0.00	Apatite
Calcium Hydrogen Phosphate	100 (solubility limited)			10	1000	Autunite
					0.00	Apatite
Sodium Orthophosphate	1000	Calcium Chloride	500	10	1000	Autunite
					0.00	Apatite
Sodium Orthophosphate	500	Calcium Chloride	500	10	1000	Autunite
					0.00	Apatite
Sodium Pyrophosphate	1000	Calcium Chloride	500	10	1000	Autunite
					0.00	Apatite
Sodium Pyrophosphate	500	Calcium Chloride	500	10	1000	Autunite
					0.00	Apatite

Table 4. (contd)

Phosphate Source	Phosphorus Conc. (ppm)	Calcium Source	Calcium Conc. (ppm)	Uranium Conc. (µg/L)		Precipitate
				10	1000	
Sodium Tripolyphosphate	1000	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
Sodium Tripolyphosphate	500	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
Sodium Trimetaphosphate	1000	Calcium Hypophosphite	500	10	1000	Autunite
				0.00		Apatite
Sodium Trimetaphosphate	1000	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
				0.00		
Sodium Trimetaphosphate	500	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
Sodium Hexametaphosphate	1000	Calcium Hypophosphite	500	10	1000	Autunite
				0.00		Apatite
Sodium Hexametaphosphate	1000	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
				0.00		
Sodium Hexametaphosphate	500	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
Calcium Hypophosphite	1000	Calcium Chloride	1000	10	1000	Autunite
				0.00		Apatite
Calcium Hypophosphite	1000	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
Calcium Hypophosphite	500	Calcium Chloride	1000	10	1000	Autunite
				0.00		Apatite
Calcium Hypophosphite	500	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite
Calcium Hypophosphite	250	Calcium Chloride	1000	10	1000	Autunite
				0.00		Apatite
Calcium Hypophosphite	250	Calcium Chloride	500	10	1000	Autunite
				0.00		Apatite

maximum concentration measured within the 300 Area. This will allow the efficacy of the polyphosphate amendment to be evaluated under minimum and maximum uranium concentrations. Following saturation and attainment of chemical equilibrium with uranium-spiked groundwater, the influent solution will be changed to Hanford groundwater containing the polyphosphate amendment chosen based on ³¹P NMR hydrolysis results experiments. Aqueous concentrations will be monitored via ICP-MS and ICP-OES. Fluorescence and scanning laser Raman spectroscopy will be utilized to monitor the in-situ

formation of autunite. The results of previous work regarding the stability of autunite (Wellman et al. 2006b), in conjunction with aqueous uranium concentration data will provide an indirect means to evaluate the formation rate of autunite.

4.3 Immobilization of Uranium via Apatite

Fuller et al. (2003, 2002) evaluated the speciation of uranium sequestered with hydroxyapatite under the pH range of 6.3 to 6.9. Hydroxyapatite was effective at reducing the aqueous uranium concentration to $<0.05 \mu\text{M}$. Surface complexation was identified to be the dominate mechanism of retention versus direct precipitation of chernikovite, hydrogen autunite, at $[\text{U}] < 5800 \text{ ppm}$. However, long-term retention occurs through the transformation of sorbed apatite to chernikovite. Similar evidence for the long-term retention of uranium via initial sorption and subsequent transformation to uranium mineral phases of low solubility has been observed down gradient of the uranium ore deposit at Koongarra, Australia (Murakami et al. 1997). However, in order to evaluate the effectiveness of an apatite barrier for immobilizing uranium under high flow conditions, in the subsurface, it is necessary to understand: 1) the rate at which the barrier immobilizes uranium, 2) how long the barrier will remain efficacious in immobilizing uranium, and 3) the long-term retention of uranium via the barrier. Thankur et al. (2005) recently quantified the kinetics, loading, and retention of uranium on hydroxyapatite at pH 8. The results of this investigation illustrated the efficacy of hydroxyapatite for the sorption and retention of uranium. However, the sorption reaches a maximum at pH 8; whereas, the pH of the 300 Area ranges from 6 – 7 depending on the level of the river and degree of mixing within the aquifer. Therefore, the kinetics, loading, and retention of uranium on hydroxyapatite under the pH range of 6 – 7 must be quantified in order to evaluate the efficacy of apatite as a long-term sequestrant for uranium within the 300 Area aquifer.

Batch tests will be conducted to quantify the effectiveness of uranium retention via apatite. Batch uranium sequestration tests will be conducted over a narrow pH range comparable to that expect within the 300 Area, pH 6.0 – 8.0, to quantify the retention of uranium on apatite as a function of pH. The K_d (mL/g), defined as the concentration of a contaminant in the solid divided by the concentration of the contaminant in the fluid, is determined from ICP-OES analysis of the sample aliquots. We will use the American Society of Testing Materials (ASTM D 4319-93, Reapproved 2001) standard test methodology for determining K_d values and the maximum loading capacity of uranium with apatite. The ICP-MS will be conducted according to standard technical procedures developed by PNNL.

Desorption isotherms will subsequently be conducted to quantify the long-term retention of uranium with apatite. We will use the American Society of Testing Materials (ASTM D 4793-93, Reapproved 2004) standard test methodology for sequential batch extraction. The ICP-MS will be conducted according to standard technical procedures developed by PNNL.

4.4 Apatite Barrier Longevity

The Hanford subsurface does not contain sufficient naturally occurring phosphate to support precipitation of phosphate minerals such as apatite. An artificially created apatite barrier will be in a state of thermodynamic disequilibrium. Consequently, it is necessary to understand the processes that will determine how long an apatite barrier will function. To evaluate these processes, apatite will be precipitated in uncontaminated Hanford sediment; subsequently, uncontaminated Hanford groundwater

will be displaced through the column to quantify the longevity of the apatite barrier. The effluent composition will be chemically analyzed with ICP-OES. Flow rates through the column will be adjusted to ensure a Damköhler number (Da) $\gg 10$. Because of the downstream equilibrium condition (Bryant et al. 1987), effluent exiting the column should reflect equilibrium with respect to the phosphate minerals formed in the barrier. This will be verified by comparing the effluent chemical composition with predictions using the solubility product for apatite. Once steady-state is established, the influent flow rate will be progressively increased until a decrease in the phosphorus concentration is observed. The flow rate where the change is observed will define the cross-over point between solubility and dissolution kinetics controlled release, or the critical Damköhler number. By conducting a similar procedure for the different conditions of barrier formation (i.e. pH), A_m and the critical Da will be correlated with the conditions of barrier formation. This will provide a basis for extrapolating the laboratory-derived data to make scientifically defensible predictions of barrier lifetime at field conditions. Ignoring diffusion and dispersion processes, the rate of release of component i per unit cross-sectional area is:

$$J_i = U_r \times C_i \quad (4)$$

where J_i = mass flux of component i
 U_r = average flow rate through the barrier
 C_i = the concentration of component i .

Integrating Equation (4) over time,

$$m(t) = A_c \int_0^t U_r C_i dt \quad (5)$$

where $m(t)$ = the mass of component i having exited the barrier at time t
 A_c = the cross-sectional area of the porous medium normal to the direction of flow.

If we assume that U_r and C_i are non-time varying functions, then barrier lifetime (t_i) is

$$t_i = \frac{m_{o,i}}{A_c U_r C_i} \quad (6)$$

where $m_{o,i}$ = the initial mass of component i precipitated as a phosphate mineral in the soil.

Assuming perfect mixing, $m_{o,i}$ can be determined for a given A_c . Thus, the only unknown in Equation (6) is C_i , which will be determined either by the dissolution kinetics of apatite, or by the rate of mass transport through the barrier.

The Da provides a basis to assess when equilibrium solubility will control mass transfer rates versus the dissolution kinetics of a solid phase. It is given by the ratio of hydraulic residence time to mass transfer reaction time

$$Da = \frac{\theta A_m k_o}{U_r C_i^* A_c} \quad (7)$$

where θ = volumetric water content
 A_m = the phosphate mineral surface area
 k_o = the dissolution rate constant
 C_i^* = the solubility-limited concentration of component i .

A value of Da greater than about 10 indicates that mass transfer rate will be solubility controlled.

In theory, the Da can be utilized to extrapolate data from laboratory experiments run at higher temperature and much faster flow rate than exist in the field to field-equivalent conditions. However, the implied relationship among the variables has rarely been experimentally verified and never for a phosphate barrier of the type proposed here. Validation of equation (7) or an alternative correlation is needed before extrapolation to field conditions and evaluation of the phosphate barrier lifetime could be scientifically justified.

4.4.1 Single-Pass Flow-Through (SPFT) Test Methods

Evaluation of each the kinetic rate parameters for the dissolution of apatite will be done with the single-pass flow-through (SPFT) test method. The SPFT apparatus also provides for experimental flexibility so that each of the kinetic test parameters can be isolated and quantitatively determined. Temperature, flow rate, solution composition, and sample mass and size can all be manipulated to assure accurate rate determinations. See McGrail et al. (2000) for a detailed description of the SPFT system.

In general, the SPFT system consists of a programmable pump that transports solutions from an influent reservoir via Teflon lines. Solution is transferred into 60 mL capacity *perfluoroalkoxide* (PFA) reactors (Savillex). The reactors are situated within constant temperature ovens, whose temperature is controlled to $\pm 2^\circ\text{C}$ by tested and calibrated thermocouples. The powdered specimen rests at the bottom of the reactor and influent and effluent solutions enter and exit, respectively, from fluid transfer lines that protrude through two separate ports at the top of the reactor. The residence time of aqueous solutions in the reactor varies with the flow rate, which is adjusted in accordance with the needs of the experiment. The effluent line carries solution to collection vials that are positioned outside the oven.

Effluent solution is collected continuously and aliquots of the fluid sample are retained for both pH measurement and analysis of dissolved element concentrations by either ICP-MS or ICP-OES. Solutions earmarked for analysis by ICP-MS or ICP-OES methods are preserved in reagent grade nitric acid. Concentrations of aqueous Ca and P quantify the dissolution rates as a function of pH and temperature. Blank solution samples will be collected and used to establish the concentration of background analytes, before the sample specimens are added to the reactor. The blank samples will be treated in exactly the same manner as the cells with the metal samples.

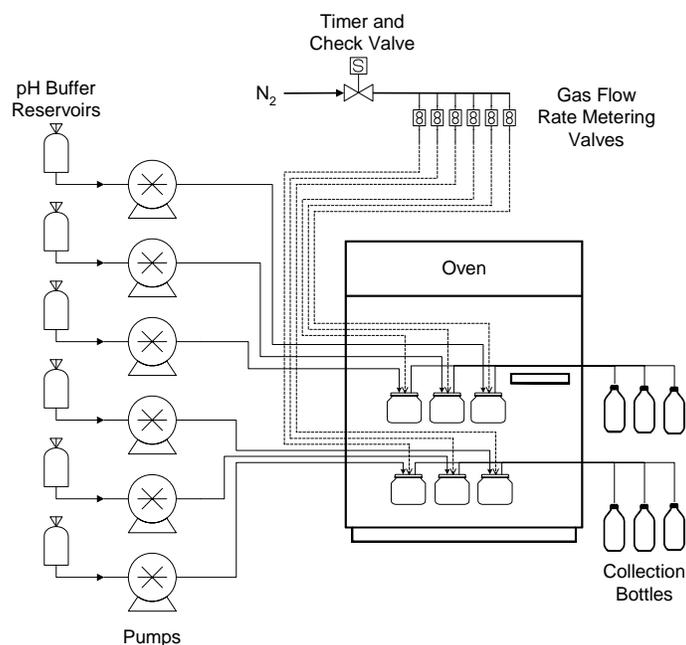


Figure 5. Schematic of the Single-Pass Flow-Through (SPFT) Apparatus

4.4.1.1 Material Preparation

The hydroxyapatite sample used in this study will be prepared by sieving into the desired size fractions with ASTM standard sieves (ASTM 2001). After being sized the samples will be washed in deionized water (DIW), sonicated in DIW, and rinsed in ethanol to remove any fine-grained adherence. Each sample will then be dried in a 90°C oven.

4.4.1.2 Buffer Solutions

The solutions that will be used to control the pH during the SPFT experiments are summarized in Table 5. Table 5 also contains a summary of the in-situ pH values computed at each test temperature using EQ3NR (Wolery 1992). It is important to take into account the change in pH that occurs at different temperatures when computing dissolution rates from SPFT data as the in-situ pH can vary by as much as 1.5 pH units over the temperature range from 23° to 90°C. These solutions will be prepared by adding small amounts of the organic *tris hydroxymethyl aminomethane* (THAM) buffer to DIW and adjusting the solution to the desired pH value using 15.8M HNO₃ or 1M LiOH. The THAM buffer range is between pH 7 to 10; therefore the alkaline solutions, pH range 11 and 12, will be prepared by adding of LiOH and LiCl to DIW and adjusting the solution to the desired pH value using 15.8M HNO₃ or 1M LiOH.

Table 5. Composition of Solutions Used in Single-Pass Flow-Through Experiments. Solution pH values above 23°C were calculated with EQ3NR Code V7.2b database.

Solution	Composition	pH @			
		23°C	40°C	70°C	90°C
1	0.05 M THAM + 0.047 M HNO ₃	7.01	6.57	5.91	5.55
2	0.05 M THAM + 0.02 M HNO ₃	8.32	7.90	7.25	6.89
3	0.05 M THAM + 0.0041 M HNO ₃	8.99	8.67	8.08	7.72
4	0.05 M THAM + 0.003 M LiOH	9.99	9.55	8.88	8.52
5	0.0107 M LiOH + 0.010 M LiCl	11.00	10.89	10.43	10.06
6	0.0207 M LiOH + 0.010 M LiCl	12.02	11.74	11.08	10.70

THAM = *Tris* hydroxymethyl aminomethane buffer.

4.4.1.3 Rate Calculations and Uncertainty

Dissolution rates, based on steady-state concentrations of elements in the effluent, are normalized to the amount of the element present in the sample by the following formula:

$$r_i = \frac{(C_i - \bar{C}_{i,b})q}{f_i S} \quad (8)$$

where r_i = the normalized dissolution rate for element i ($\text{g m}^{-2} \text{d}^{-1}$)
 C_i = the concentration of the element i in the effluent (g L^{-1})
 $\bar{C}_{i,b}$ = the average background concentration of the element of interest (g L^{-1})
 q = the flow rate (L d^{-1})
 f_i = the mass fraction of the element in the metal (dimensionless)
 S = the surface area of the sample (m^2).

The surface area will be determined using two techniques: (1) N₂-adsorption BET (Brunauer et al. 1938) and (2) calculated geometric surface area (McGrail et al. 1997). Depending on the results of each surface area analysis and the evaluation of SEM images (to determine if a large amount of micro-porosity exists) the more appropriate measure of the specific surface area will be chosen. The value of f_i can be calculated from the chemical composition of the sample. Flow rates are determined by gravimetric analysis of the fluid collected in each effluent collection vessel upon sampling. The background concentration of the element of interest is determined, as previously discussed, by analyses of the starting input solution and the three blank solutions. Typically, background concentrations of elements are below their respective detection threshold. The detection threshold of any element is defined here as the lowest calibration standard that can be determined reproducibly during an analytical run within 10%. In cases where the analyte is below the detection threshold, the background concentration of the element is set at the value of the detection threshold.

Determining the experimental uncertainty of the dissolution rate takes into account uncertainties of each parameter in Equation (8). For uncorrelated random errors, the standard deviation of a function $f(x_1, x_2, \dots, x_n)$ is given by:

$$\sigma_f = \sqrt{\sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2} \quad (9)$$

where σ_f = the standard deviation of the function f
 x_i = parameter i
 σ_i = the standard deviation of parameter i .

Substituting (8) into (9) results in:

$$\sigma_{r_i} = \sqrt{\left(\frac{q}{f_i S} \right)^2 (\sigma_{C_i}^2 + \sigma_{\bar{C}_{i,b}}^2) + \left(\frac{C_i - \bar{C}_{i,b}}{f_i S} \right)^2 \sigma_q^2 + \left(\frac{(C_i - \bar{C}_{i,b})q}{f_i^2 S} \right)^2 \sigma_{f_i}^2 + \left(\frac{(C_i - \bar{C}_{i,b})q}{f_i S^2} \right)^2 \sigma_S^2} \quad (10)$$

Equation (10) can also be expressed in terms of the relative error, $\hat{\sigma}_{r_i} = \sigma_{r_i} / r_i$, and is given by

$$\hat{\sigma}_{r_i} = \sqrt{\frac{(\hat{\sigma}_{C_i} C_i)^2 + (\hat{\sigma}_{\bar{C}_{i,b}} \bar{C}_{i,b})^2}{(C_i - \bar{C}_{i,b})^2} + \hat{\sigma}_q^2 + \hat{\sigma}_{f_i}^2 + \hat{\sigma}_S^2} \quad (11)$$

Relative errors of 10%, 10%, 5%, 3%, and 15% for C_i , $\bar{C}_{i,b}$, q , f_i , and S , respectively, are typical for measurements conducted at PNNL. But to reduce the error associated with mass fraction (f_i), the samples to be used in these experiments will be ground, homogenized, sub-sampled and analyzed at least three times to obtain a more accurate composition with a better estimate of the uncertainty. The conservative appraisal of errors assigned to the parameters in equation (11), in addition to the practice of imputing detection threshold values to background concentrations, results in typical uncertainties of approximately $\pm 35\%$ on the dissolution rate.

4.4.1.4 Determining the Rate Dependency on Solution pH

The pH values of the solutions that will be used in these experiments will span the range from 7 to 12. The choice of this range of pH values is because solutions percolating through the disposal system are expected to be neutral to alkaline. The bulk of these solutions will be made with the organic buffer THAM and pH-adjusted with ultrapure nitric acid. Alkaline ($\text{pH} \geq 11$) solutions will be produced by addition of lithium hydroxide to DIW. The change in pH values with temperature (see Table 5) will be taken into account when computing parameters used in the reactive transport modeling. In the experiments, adjustments will be made to obtain solutions that are as close to the specified pH values as possible. By keeping the temperature and flow rate constant while varying the solution pH allows the value of η , the pH power law coefficient, to be determined. Dissolution rates over this span of pH values will also be performed over the temperature interval 23 to 90°C with hydroxyapatite.

4.4.1.5 Temperature Dependency (\bar{k}_o and E_a)

Because reactions involving dissolution of hydroxyapatite involve breaking of strong Ca-P bonds, there is a strong dependency of the dissolution rate on temperature. In the present case, the temperature of the subsurface is too cool (15°C) for direct tests because reaction rates at this temperature are slow, making the duration of the experiments impracticable. An alternative strategy is to conduct experiments at higher temperatures, where rates are faster, and then extrapolate the results down to the temperature of interest (15°C). Full temperature-dependence will be determined for hydroxyapatite over the temperature range of 23° to 90°C.

4.5 Polyphosphate Amendment Physical Property Optimization

Upon selection of the polyphosphate amendment formulation, column tests will be conducted to concurrently evaluate the amendment density, viscosity, injection rate, and mixing rate within the aquifer to determine whether the selected amendment will perform effectively. If the physical properties of the selected amendment preclude effective implementation, the concentration of the formulation will be optimized to allow for implementation and the resulting effect on treatment (i.e. additional pore volumes of amendment injection) will be quantified.

5.0 Expected Deliverables

Expected output from this experimental plan is a data package including the mechanism and extent of uranium retention with apatite, kinetic rate data for the formation of autunite and apatite from polyphosphate amendments, hydrolysis of polyphosphate amendments as measured by ^{31}P NMR, and the stability of apatite under conditions relevant to the Hanford 300 Area subsurface, that will be supplied to modelers for STORM simulations. Results from this experimental plan will be documented in a PNNL report.

6.0 Quality Assurance, ES&H, and Waste Management Requirements

6.1 Quality Assurance

The work will be conducted in accordance with the Groundwater Project Quality Assurance Plan (PNNL 2006). All instrument calibrations and materials will be traceable, test procedures and associated training activities will be documented in detail, and test methods will comply with established plans and procedures. The Standards-Based Management System (SBMS) subject area Software (PNNL 2005) is being followed for data analysis software being used to store, sort, and reduce data.

All staff members contributing to the work specified in this experimental plan will have received proper technical and quality assurance training. The specific technical procedures that will be used are:

Method	Analysis	Document Number	Procedure Title
Inductively coupled plasma-optical emission spectroscopy (ICP-OES)*	Ca, Fe, K, Mg, Mn, Na, P, S, Si	PNNL-AGG-ICP-AES*	Inductively Couple Plasma – Optical Emission Spectrometry (ICP-OES) Analysis
Inductively coupled plasma-mass spectroscopy (ICP-MS)	U	PNNL-AGG-415	Inductively Coupled Plasma Mass Spectrometric (ICP-MS) Analysis
Ion chromatography (IC)	Cl ⁻ , F ⁻ , PO ₄ ³⁻	AGG-IC-001	Determinations by Ion Chromatography (IC)
Solid-state pH electrode and meter	pH	AGG-PH-001	pH Measurement
X-ray diffraction (XRD)	Mineralogy	RPL-XRD-PIP	Operation of Scintag Pad-V X-Ray Diffractor (RGD #62)
Scanning Electron Microscopy/ Energy-Dispersive X-ray Spectrometry (SEM/EDS)	Particle morphology, size, and qualitative elemental analysis	PNL-SP-3	Scanning Electron Microscopy/Energy Dispersive Spectrometry
Particle-size distribution		PNL-MA-567, SA-3	Particle-size analysis (Pipette or hydrometer method); wet sieve analysis will be used to remove sand-size particle
Hydraulic conductivity		PNL-MA-567, SA-5	Falling head hydraulic conductivity
Water retention		UFA-SK-01	Determination of water retention as a function of water content using open-flow centrifugation techniques
Water content		PNL-MA-567, SA-7	Water content
Bulk density		PNL-MA-567, SA-8	Clod density/bulk density
Particle density		PNL-MA-567, SA-9	Determining particle density; necessary for constant head hydraulic conductivity
Column packing		WHC-IP-0635, GEL-3 Rev. 3	Moisture relationships of soils; necessary for constant head hydraulic conductivity
pH/EC		PNL-G-5-pH/EC	Measuring pH/EC of low-level radioactive solutions
Saturated column experiments		AGG-SAT-COL-001	Conducting saturated column experiments
Batch experiments		AGG-BSE-001	Batch sorption experiments
Flow-through testing		RPL-PIP-SPFT R2	Conducting flow-through experiments
Surface area		AGG-SA-001	Measuring surface area
* The document number states ICP-AES, but the instrument in use is an ICP-OES. ICP-AES and ICP-OES are equivalent and refer to the same analytical technique.			

Staff executing routine analytical procedures shall comply with Hanford Analytical Services Quality Assurance Requirements Documents (HASQARD), Volume 1: Administrative Requirements and Volume 4: Laboratory Technical Requirements, otherwise known as HASQARD (DOE 1998). Any analytical procedural deviations shall be documented in the narrative of the data report with a justification, unless these deviations result from updated versions of the procedures. All data not meeting the quality control (QC) requirements shall be properly noted and the associated QC failures will be documented and reported according to NQARD-1602. Individuals who have not completed the appropriate training will not conduct work.

6.2 Environmental Safety and Health

All precautionary measures will be taken to insure that laboratory work will be conducted in a safe manner. Safety glasses, and face shields when appropriate, will be used to protect the eyes and face. Those working with acid will be required to follow the safety practices associated with each acid they are using. Work will be performed in chemical hoods when there is potential for acid spills or the release of noxious vapors. The flow apparatus to be used for these tests is sitting in a plexiglass catch basin so that should a break or leak occur in one or more of the fluid transfer lines, the spill would be contained within the catch basin and could not overflow onto the laboratory floor.

6.3 Waste Management

Small amounts of liquid and solid wastes will be generated from the testing conducted under this Test Plan. These wastes managed in accordance with appropriate satellite accumulation in the laboratory. All regulated wastes will be properly disposed per requirements found in PNNL's SBMS Managing Waste (PNNL 2006) Subject Area procedures.

7.0 References

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