PNNL-SA-49954

Project Work Plan

300 Area Uranium Plume Treatability Demonstration Project: Uranium Stabilization Through Polyphosphate Injection

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1.0 Introduction

A groundwater plume containing uranium from past-practice discharges of liquid waste associated with nuclear fuel fabrication activities has persisted beneath the Hanford Site 300 Area for many years. The persistence of this plume is enigmatic for several reasons, including: (a) discharges containing uranium-bearing effluent to ground disposal sites ended in the mid-1980s; (b) contaminated soil associated with these waste sites was removed during the 1990s, with backfilling complete by early 2004; and (c) the aquifer is comprised of highly transmissive fluvial sediment, suggesting rapid movement of groundwater. Also, a water supply well located within the plume has been in operation since 1980, with no observable effect on the plume. The current conceptual site model assumes that re-supply of the plume is occurring, with continuing release from the vadose zone beneath waste sites, the capillary fringe zone, and possibly from aquifer solids, as source candidates.

A remedial investigation conducted in the early 1990s, along with an expedited response action to remove contaminated soil from the most recently used disposal site, led to a 1996 record of decision (EPA 1996) for interim remedial action that involved continued groundwater monitoring and institution controls on the use of groundwater. Characterization of natural features and processes that would lead to attenuation of the contamination is part of the interim action, which continues. A computer simulation of the plume during the initial remedial investigation led to a prediction that concentrations would decrease to drinking water standards in 3 to 10 years from 1993, assuming no re-supply of uranium to the plume. This predicted response has not been observed in monitoring well trend data.

Maximum concentrations in the plume are currently less than 250 μg/L, with mode values ranging from 30 to 90 μg/L. The plume (>30 μg/L) currently covers an area of ~0.4 km^2. Assuming a representative thickness of the contaminated layer of 3.3 m and 27% porosity, the volume of contaminated groundwater is ~350,000 m^3 and the mass of dissolved uranium is ~20 kg. The length of Columbia River shoreline impacted is ~1,500 m. Uranium removal via the water supply well is ~21 kg/yr, based on monitoring data. Reliable estimates for the net flux of uranium to the river are not yet available, but are expected soon as a product of computer simulation efforts. (Note: Although groundwater flow rates are high, net discharge to the Columbia River is tempered by bank storage effects created by river stage fluctuations.)

Over the past 4 years, several public workshops have been held to discuss remedial action alternatives and future land use options for the Hanford 300 Area:

- June 2002 and May 2003: EPA-sponsored stakeholder workshops to discuss remedial action alternatives for the 300 Area uranium plume.

- May 2004: DOE Science and Technology Program open meeting with contractors and the public – *Conceptual Model Development and Reactive Transport Modeling for the 300 Area Uranium Plume*.

- August 2004: DOE Headquarters review and discussion of 300 Area uranium plume – *Monitoring Optimization Technical Assistance Workshop.*

- May 2005: DOE-sponsored stakeholder workshop to received public input on remedial actions and future land use for the 300 Area – *300 Area End States Public Workshop*.

- October 2005: DOE-sponsored stakeholder involvement workshop – *300-FF-5 Workshop and Tour: Progress of the Limited Field Investigation Supporting the Phase III Feasibility Study*.

The initial feasibility study for this plume considered hydraulic containment, slurry wall containment, and groundwater extraction as 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 this treatability test is to evaluate the efficacy of using polyphosphate injections to treat uranium contaminated groundwater in situ. Data obtained from this study will be used to develop implementation cost estimates, identify implementation challenges, and investigate the technologies' ability to meet remedial objectives. This information will be used in the Phase III feasibility study during final evaluation of remedial alternatives.

2.0 Technology Description

Numerous proposals have been made to remediate contaminated groundwater using phosphate amendment strategies (Arey et al. 1999; Moore et al. 2001; Seaman et al. 2001; Wright et al. 1995). These proposals put forth the common idea to apply solid phase phosphate (generally hydroxyapatite) directly to the contaminated soil, surface water, or as trench fill emplaced in the pathway of migrating contaminant plumes. These strategies have merit and represent feasible technology for near-surface treatment, yet cannot accomplish remediation of pore waters that are situated in deep aquifers or under conditions such as those found in the Hanford vadose zone where plume can extend down to 90 m.

Alternative strategies employ the use of water-soluble phosphate compounds that could be injected into the plume from strategically placed wells. However, one challenge to deploying a soluble phosphate amendment into the subsurface is the unwanted rapid precipitation of phosphate phases, which occlude the injection wells and pore space within the formation. Lee et al. (1995) proposed using tribasic sodium phosphate [$Na_3(PO_4)\cdot nH_2O$, or TSP] as a chemical stabilizer for uranium and radiostrontium. However, even in relatively dilute groundwater solutions, there are enough dissolved cations to form Al-, Fe-, Ca-, Na-phosphates. Nash et al. (1993, 1994, 2000), Nash et al. (1981, 1997, 1998, 1999), and Jensen et al. (1996) attempted to circumvent this shortcoming by proposing injection of a water-soluble organophosphate compound, phytic acid, into contaminated groundwater. The key advantage of this method is that the hydrolyzation kinetics of the molecule is slow, such that release of orthophosphate is delayed, allowing the injected amending solution to disperse and mix throughout the target plume. However, Wellman et al. 2006 (in press) demonstrated rapid agglomeration of Ca-phytate occluded 30% of the

fluid-filled pore space within the formation. Rapid reduction in the hydraulic conductivity will have a significant effect on subsequently injected phytic acid 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. 2006, in press). 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. Accordingly, use of a long-chain polyphosphate compound does not result in a drastic change in hydraulic conductivity of the target aquifer.

In order to evaluate the efficacy of long-chain polyphosphate for in-situ immobilization of uranium, a series of laboratory tests have been conducted at conditions expected within the 300 Area Hanford aquifer. Sediment columns were prepared using Hanford sediments and saturated using Hanford groundwater spiked with 10^{-6} M uranium. Injection of a sodium tripolyphosphate amendment into the uranium-bearing saturated porous media demonstrated immobilization of uranium occurs due to formation of an insoluble uranyl phosphate mineral, autunite $\{X_{1-2}[(UO_2)(PO_4)]_{2-1}\bullet nH_2O\}$, where X is any monovalent or divalent cation. Because autunite sequesters uranium in the oxidized form, U^{6+}, rather than forcing reduction to U^{4+}, the possibility of re-oxidation and subsequent re-mobilization of uranium is negated. Release of uranium from the autunite structure may only occur through dissolution of the autunite structure. Extensive testing demonstrates the very low solubility and slow dissolution kinetics of autunite under conditions relevant to the Hanford subsurface (Wellman et al. 2006).

In addition to autunite, excess phosphorous may result in apatite mineral formation, providing a long-term source of treatment capacity. Uranium transport studies were conducted in columns packed with uranium contaminated sediment from the 300 Area. Columns were leached with respective solutions of (1) Hanford groundwater, (2) Hanford groundwater spiked with 1,500 ppm sodium tripolyphosphate, (3) Hanford groundwater spiked with 2,500 ppm sodium tripolyphosphate, and (4) Hanford groundwater spiked with 3,500 ppm sodium tripolyphosphate. Results indicate that injection of a polyphosphate solution reduces the aqueous uranium concentration to near the drinking water standards (30 ppb) after 8–12 pore volumes, depending on the concentration of phosphorus in the amendment solution, of solution have been displaced through the column.

3.0 Project Scope

The following work elements will form the scientific basis for the proposed treatability study of in situ uranium stabilization through the injection of a polyphosphate amendment. Additional technical detail is provided in Appendix A.

3.1 Task 1: Project Management

Subtask 1a – Project Support. Plan, organize, and provide top-level guidance and direction for overall project performance. Also provide project-level cost and schedule control, tracking, and reporting. Coordinate the Columbia River Protection Supplemental Technologies Project work scope

with DOE, Richland Operations, the Groundwater Remediation and Closure Assessment Project and the Office of River Protection, including participation in planning, peer reviews, and periodic project meetings.

Subtask 1b – Planning and Test Plan Preparation. This work element consists of reviewing available site hydrogeologic and geochemical data, refining the site conceptual model, developing both a laboratory-scale experimental approach and a field-scale treatability testing approach, and preparing planning documents. An experimental plan will be prepared at the beginning of the project to cover bench-scale laboratory testing. Once preliminary bench-scale testing results and site-specific characterization data are available, a field test plan will be prepared. Each plan will provide a description of planned testing activities, sampling and analysis methods, and data quality requirements.

3.2 Task 2: Bench-Scale Laboratory Testing

Bench-scale tests will be conducted using small- and intermediate-scale column experiments. Technical issues that will be evaluated include the use of multi-length polyphosphate chains and their hydrolysis rates, kinetics of autunite and apatite formation, and long-term immobilization of uranium by apatite. All experiments will be conducted with sediments from the 300 Area to make certain testing conditions are representative of the remediation area. The following sections provide a description of laboratory testing and anticipated results; scientific justification for the proposed testing is provided in Appendix A.

- ***Polyphosphate Hydrolysis Experiments***. The speciation of inorganic phosphate and its chemical affinity for other species in solution can be readily assessed using phosphorus nuclear magnetic resonance (^{31}P NMR). The chemical shift of the ^{31}P nucleus is impacted by pH, electrolyte concentration, and temperature. ^{31}P NMR will be conducted to elucidate the effect of sedimentary cations on the hydrolysis of polyphosphates. The samples will be analyzed using the 300 MHz NMR spectrumeter to quantify the degradation of long-chain polyphosphates and the formation of orthophosphate. Homogeneous, mono-cation batch tests will be conducted to quantify the effect of ubiquitous aqueous components (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, Al^{3+}, and Fe^{3+}) on the degradation of polyphosphate chains. Additionally, controlled heterogeneous batch tests will be conducted between the polyphosphate solutions and pure sedimentary components (i.e., $Al(OH)_3$, CaOH, $CaCl_2$, $Fe(OH)_3$, $FeCl_3$, quartz sand, and hydroxylapatite) to evaluate the effects of heterogeneous media on polyphosphate degradation. Finally, series of batch tests will be conducted in Hanford groundwater, in the presence and absence of Hanford sediment, to quantify degradation under site-specific, field conditions.

- ***Autunite and Apatite Formation Experiments***. Formation of autunite and apatite will be evaluated under conditions relevant to the 300 Area aquifer. The columns will be composed of 300 Area sediment and will be saturated with Hanford groundwater to ensure chemical equilibrium. Based on the results of ^{31}P NMR experiments, polyphosphate chain-length(s) will be optimally selected to afford rapid precipitation of autunite without negatively impacting the hydraulic conductivity of the formation. Polyphosphate hydrolysis and the release of orthophosphate will be monitored in the pore water via scanning laser Raman spectroscopy. Aqueous concentrations will be monitored via inductively coupled plasma – mass spectrometry (ICP-MS) and inductively coupled plasma – optical emission spectrometry (ICP-OES).

– ***Autunite Formation Experiments***. A series of saturated column experiments to quantify:

1. Formation rate of autunite 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 and impacts of subsurface heterogeneities (i.e., effective contact or tendency for the reagent to push contaminated groundwater ahead of the treatment volume)

Saturated column experiments will be conducted by saturating the sediment with Hanford groundwater; following saturation and attainment of chemical equilibrium, the influent solution will be changed to a solution of Hanford groundwater spiked with aqueous uranium. The uranium concentration in the pore fluid will be equal to the concentration determined during limited field investigation (LFI) characterization. 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 ^{31}P NMR hydrolysis results experiments. 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. 2006), in conjunction with aqueous uranium concentration data will provide an indirect means to evaluate the formation rate of autunite.

– ***Apatite Formation Experiments***. The formation rate and quantity of apatite formed per pore volume of treatment will be quantified based on optimal polyphosphate formulation. Similar to autunite formation experiments, saturated column experiments will be conducted by saturating the sediment with Hanford groundwater; following saturation and attainment of chemical equilibrium, the influent solution will be changed to Hanford groundwater containing the polyphosphate amendment chosen based on the results of ^{31}P NMR hydrolysis experiments. 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 concentration and formulation, flow rate, and secondary injection of calcium.

- ***Immobilization of Uranium via Apatite***. Both batch and column tests will be conducted to determine the mechanism and evaluate the effectiveness of uranium retention via apatite. Uranium sorption isotherms 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. Desorption isotherms will subsequently be conducted to quantify the rate of uranium release. A second set of batch experiments will be conducted to evaluate the transformation of sorbed uranium into uranyl-phosphate minerals. Apatite will be placed in solutions of uranium-spiked Hanford groundwater over the pH range of 6.0–8.0. At predetermined sampling intervals the solid phases will be examined via x-ray absorption fine structure spectroscopy (XAFS) and scanning electron microscopy (SEM) to determine the mechanisms of uranium binding to apatite and the rate transformation and/or incorporation of uranium into secondary minerals.

  Apatite barriers will be incorporated into a series of column experiments to evaluate the efficacy of apatite at varying concentrations to sequester uranium under realistic dynamic conditions.

Uranium-spiked Hanford groundwater will be injected into the columns. Following immobilization of the uranium on the apatite barrier, Hanford groundwater will be injected into the column. Effluent concentration will be monitored via ICP-MS. Once steady state is established, the influent flow rate will be progressively increased until a decrease in the uranium concentration is observed. The flow rate where the change is observed will define the cross-over point between desorption and dissolution kinetics controlled release. Conducting a similar procedure for various apatite contents will provide a basis to extrapolate the laboratory-derived data to make estimates of barrier performance at the field scale and determine whether the injection design should tend toward a large, low concentration treatment zone emplaced at each injection point, or smaller, higher concentration treatment zones (which would require a larger number of injection wells for full-scale deployment).

- ***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, then followed by injection of fresh Hanford groundwater into the column. The effluent composition will be chemically analyzed with ICP-OES. Flow rates through the column will be adjusted to ensure $Da >> 10$. Because of the downstream equilibrium condition (Bryant 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 Damköhler number 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.

- ***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.

3.3 Task 3: Pilot-Scale Treatability Test

This work element includes installation of test site monitoring wells and associated site specific characterization, injection design analysis, test systems design and setup, and the pilot-scale field test. The injection design analysis will incorporate results from the laboratory experimentation and available site characterization data. The field test will be conducted at one of four LFI well locations installed in support of the 300-FF-5 feasibility study. Additional wells installed by this project will be used for operational and performance monitoring purposes.

- ***Collection of Site-Specific Characterization Data***. Data collected during the LFI will be used to refine the hydrogeologic and geochemical conceptual model and select the most appropriate site for a field-scale demonstration of polyphosphate treatment. Data collected during this investigation will include geologic logging, geophysical logging, and depth discrete characterization of sediment physical properties, hydraulic properties, aqueous uranium concentration, and uranium concentrations sorbed to the sediment. Once data from the LFI drilling campaign has been evaluated, a site will be selected for the polyphosphate treatability study and operational monitoring wells will be installed. It is anticipated that up to five monitoring wells will be installed within the radial extent of the initial treatment zone and an additional three to five monitoring wells will be installed to monitor downgradient transport of the polyphosphate amended zone.

  Following installation of the monitoring well network, several hydrogeologic characterization methods will be used to obtain additional site-specific information. These tests include hydraulic testing to obtain formation hydraulic properties, electromagnetic borehole flowmeter (EBF) testing to assess the vertical distribution of horizontal hydraulic conductivity (i.e., vertical heterogeneities), and a conservative tracer injection test. The tracer test will be used to further evaluate formation heterogeneities, to assess the downgradient transport of the tracer plume (i.e., aquifer transport properties), to refine the polyphosphate injection design, and to test operational procedures.

- ***Injection Design Analysis***. A groundwater flow and transport model, which is being developed to support the 300-FF-5 feasibility study, will provide a basis for developing a refined model of flow and transport at the scale of the proposed treatability test. This design tool will incorporate both bench-scale experimental results and site-specific characterization data and will be used to evaluate the various geohydrologic, geochemical, and polyphosphate reaction mechanisms that control emplacement of a polyphosphate amended treatment zone. The model will be used to design both the tracer and polyphosphate injection strategies.

- ***Polyphosphate Injection at Selected Pilot Test Site Location***. Based on bench-scale experimental results and subsequent treatment zone emplacement design analyses, a pilot-scale field test of the technology will be conducted at the selected location. Operational parameters (volumes, rates, concentrations), constituents/field parameters monitored, and sampling frequency will be determined based on the implementation approach selected and the scale of the field treatment. Monitoring data collected during the polyphosphate injection test will be used to assess the areal extent of treatment and determine where performance assessment samples are collected.

3.4 Task 4: Performance Assessment Sampling

Boreholes will be drilled and sediment samples collected for laboratory analysis treatment effectiveness. In addition, groundwater samples will be collected and analyzed to evaluate treatment performance.

- ***Post Treatment Column Studies***. Column studies will be conducted on sediment cores extracted from the remediation area following treatment to quantify the efficacy of the polyphosphate amendment for the immobilization of uranium. ICP-MS, ICP-OES, and ion chromatography (IC) will be used for quantifiable aqueous cation and anion analyses.

- ***Sediment Analyses***. Sediments will be characterized to determine basic chemical characteristics of the sediments as well as the forms or "species" of uranium present. Major elements in the sediments, including total uranium will be measured by x-ray fluorescence (XRF), fluorescence will be utilized to identify uranium minerals which will be collected via mechanical separation, x-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) will be utilized to identify precipitated uranium phases. The semi-selective chemical extraction technique (Tessier et al. 1979, with modifications) will be used to determine the percentage of uranium present in the extractable phases of water soluble, cation-exchangeable, carbonate solid bearing compounds; amorphous oxides; organic matter; crystalline Fe[III] oxides; and strong acid leachable compounds. The residual uranium content in the remaining bulk sediment will be measured by XRF.

- ***Groundwater Analyses***. ICP-MS, ICP-OES, and IC will be used for quantifiable aqueous cation and anion analyses before, during, and following deployment of the polyphosphate amendment. This will allow changes in aqueous concentrations, and speciation, due to amendment implementation to be tracked and correlated with the formation of solid phases within the sediment.

- ***Post-Treatment Hydraulic Testing***. Hydraulic tests will be conducted following emplacement of the treatment zone and compared with pre-treatments values to assess the impact of treatment on aquifer hydraulic properties. Specifically, pre- and post-treatment hydraulic responses will be compared to determine whether any degree of aquifer plugging occurred.

3.5 Task 5: Data Analysis and Reporting

This work element consists of managing, compiling, and evaluating all of the data generated during the treatability studies and preparing a treatability test report. The final report will cover activities ranging from basic laboratory development work through the field-scale demonstration of the technology. Findings presented in the report will form the basis for an evaluation of this technology for full-scale implementation during the feasibility study.

4.0 Assumptions

The following assumptions pertain to this scope of work:

- No project-specific Quality Assurance Plan (QAP) will be required; work will be conducted under the Groundwater Performance Assessment Project QAP.

- Procurement of drilling services will be conducted by the site remediation contractor, Fluor Hanford, Inc.

- Fluor Hanford, Inc. will provide both drilling and coring services for the project according to the proposed schedule.

- Investigation derived waste disposal services will be provided by Fluor Hanford, Inc.

- This treatability study will focus on uranium sequestration in the saturated zone and will not address emplacement or performance issues associated with treatment of any vadose source areas.
- The schedule shown in this proposal will be approved by the DOE and the appropriate regulatory agencies.
- The project will start on or before May 15, 2006.

5.0 Schedule

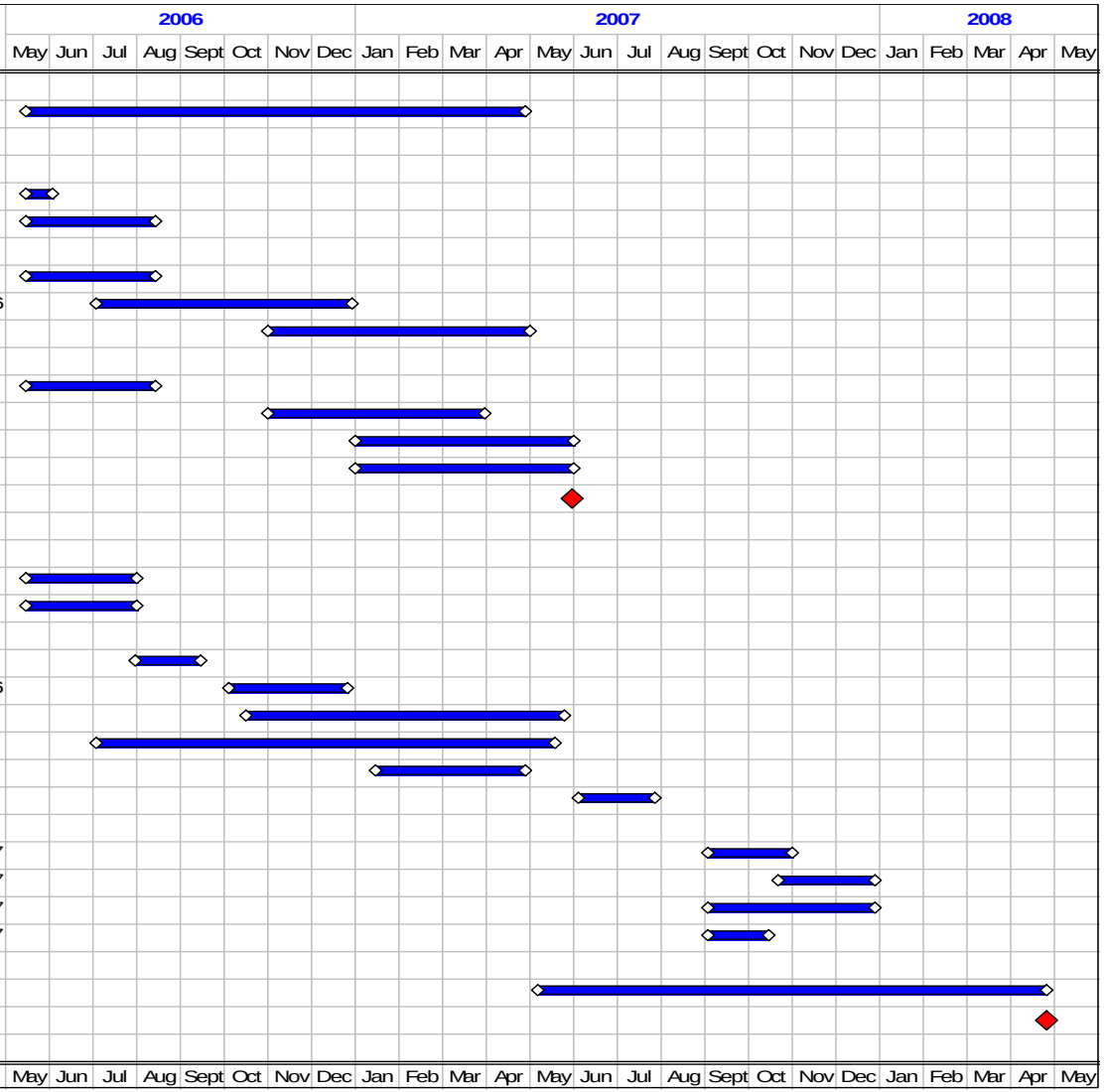
A detailed schedule for the polyphosphate treatability test is shown in Table 1, and a depiction of how the treatability test fits into the 300-FF-5 feasibility study is provided on Plate 1 attached to this plan.

6.0 Budget

Total costs for this plan is estimated to be approximately $1.7 million.

Table 1. Schedule for the Polyphosphate Treatability Test

Activity Name	Start Date	Finish Date
Polyphosphate Treatability Test		
Project Planning	5/15/06	4/27/07
Bench Scale Testing		
Experimental Plan Preparation	5/15/06	6/2/06
Polyphosphate Hydrolysis Experiments	5/15/06	8/14/06
Autunite and Apatite Formation		
Batch studies (rate & quantity)	5/15/06	8/14/06
Column Studies (rate, dist., trt. capacity)	7/3/06	12/29/06
Emplacement Efficiency	11/1/06	4/30/07
Immobilization of Uranium via Apatite		
Batch studies (Kd adsorption & retention)	5/15/06	8/14/06
Column Studies (treatment efficiency)	11/1/06	3/30/07
Apatite Barrier Longevity	1/1/07	5/31/07
Polyphosphate Phys. Property Optimization	1/1/07	5/31/07
Interim Report on Bench Scale Testing	5/31/07	
Pilot Scale Field Testing		
Drilling Planning	5/15/06	7/31/06
Char. Plan (drilling, hyd & tracer testing)	5/15/06	7/31/06
Collect Site Specific Char. data		
Monitoring Well Installation	7/31/06	9/14/06
Hydraulic / Tracer Testing	10/4/06	12/26/06
Test Systems Design and Setup	10/16/06	5/25/07
Injection Design Analysis	7/3/06	5/18/07
Field Test Plan Preparation	1/15/07	4/27/07
Polyphosphate Injection Test	6/4/07	7/27/07
Performance Assessment Sampling		
Post treatment core sample collection	9/3/07	10/31/07
PA Core Sample Analysis	10/22/07	12/28/07
PA Groundwater Analysis	9/3/07	12/28/07
Post-treatment Hydraulic Testing	9/3/07	10/15/07
Data Analysis and Reporting	5/6/07	4/25/08
Final Report	4/25/08	



7.0 References

Arey JS, JC Seaman, and PM Bertsch. 1999. "Immobilization of Uranium in Contaminated Sediments by Hydroxyapatite Addition." *Environmental Science and Technology* 33:337-342.

Bryant SL, RS Schechter, and LW Lake. 1987. "Mineral Sequences in Precipitation Dissolution Waves." *AIChE J*. 33(8):1271-1287.

EPA. 1996. *Record of Decision for the USDOE Hanford 300-FF-1 and 300-FF-5 Operable Units Remedial Actions*. EPA/ROD/R10-96/143, U.S. Environmental Protection Agency, Region 10, Seattle, Washington.

Jensen MP, K Nash, JW Morse, EH Appelman, and MA Schmidt. 1996. *Immobilization of Actinides in Geomedia by Phosphate Precipitation*. ACS Symposium Series #651, p. 272-285.

Lee SY, CW Francis, ME Timpson, and MP Elless. 1995. *Radionuclide Containment in Soil by Phosphate Treatment.* Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Moore RC, C Sanchez, J Schelling, J Jones, DR Anderson, F Salas, D Lucero, and K Holt. 2001. *Bench-Scale Testing of In-Situ Formation of Apatite in Hanford Soils for Sorption of Uranium and Technetium*. Sandia National Laboratories, Albuquerque, New Mexico.

Nash K. 1993. "Stability and Stoichiometry of Uranyl Phosphonate Coordination Compounds in Acid Aqueous Solutions." *Radiochimica Acta* 61:147-154.

Nash K. 1994. "Actinide Phosphonate Complexes in Aqueous Solutions." *Journal of Alloys and Compounds* 213/214:300-304.

Nash K. 2000. *Organophosphorous Reagents in Actinide Separations: Unique Tools for Production, Cleanup and Disposal*. Argonne National Laboratory, Argonne, Illinois.

Nash K, S Fried, AM Friedman, and JC Sullivan. 1981. "Redox Behavior, Complexing, and Adsorption of Hexavalent Actinides by Humic Acid and Selected Clays. *Environmental Science and Technology* 15(7):834-837.

Nash K. MP Jensen, and MA Schmidt. 1997. "Actinide Immobilization in the Subsurface Environment by In-Situ Treatment with a Hydrolytically Unstable Organophosphorous Complexant: Uranyl Uptake by Calcium Phytate." *Actinides* 97.

Nash K, EJ Jensen, and MA Schmidt. 1998. "In-Situ Actinide Immobilization of Actinides for Groundwater Cleanup: Laboratory Demonstration with Soil from the Fernald Environmental Management Project." In WW Schultz and NJ Lombardo (eds.), *Science and Technology for Disposal of Radioactive Tank Wastes*, p. 507-518, Plenum Press, New York.

Nash K, LR Morse, MP Jensen, EH Appelman, MA Schmidt, S Friedrich, M Redko, and JJ Hines. 1999. *Water-Soluble Organophosphorous Reagents for Mineralization of Heavy Metals*. Argonne National Laboratory, Argonne, Illinois.

Seaman JC, JS Arey, and PM Bertsch. 2001. "Immobilization of Nickel and Other Metals in Contaminated Sediments by Hydroxyapatite Addition." *Journal of Environmental Quality* 30:460-469.

Tessier et al. 1979

Wellman DM, JP Icenhower, AP Gamerdinger, and SW Forrester. 2006. "Effects of pH, Temperature, and Aqueous Organic Material on the Dissolution Kinetics of Meta-Autunite Minerals, $(Na, Ca)_{2-1}[(UO_2)(PO_4)]_2\ 3H_2O$." *American Mineralogist* 91:143-158.

Wellman DM, JP Icenhower, and AT Owen. 2006, in press. "Comparative Analysis of Soluble Phosphate Amendments for the Remediation of Heavy Metal Contaminants: Effect on Sediment Hydraulic Conductivity." *Environmental Chemistry*.

Wright J, LM Peurrung, TE Moody, JL Conca, X Chen, PP Didzerekis, and E Wyse. 1995. *In Situ Immobilization of Heavy Metals in Apatite Mineral Formulations*. Pacific Northwest Laboratory, Richland, Washington.

Appendix A

Scientific Basis for Proposed Laboratory Testing

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Scientific Basis for Proposed Laboratory Testing

A.1 Use of Multi-Length Polyphosphate Chains

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:

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

where k_+ = the rate constant
A = frequency factor (also called the Arrhenius constant)
R = gas constant
T = temperature (in Kelvin).

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

A.2 Kinetics of Autunite and/or 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:

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

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

However, heterogeneous nucleation on foreign or heterogeneous surfaces lowers the interfacial energy, *A*. Equation A.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:

$$B(t) = kN(t) = kN_{\circ} \exp(-kt) \tag{A.3}$$

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 rate should be fastest at early times and will diminish exponentially.

These equations are relevant to 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 polyphosphate.

A.3 Sequestration of Uranium by Apatite

In order to evaluate the effectiveness of an apatite barrier for immobilizing uranium in the subsurface, it is necessary to understand: (1) the mechanism by which the barrier immobilizes uranium (i.e., sorption vs. precipitation of uranium-phosphate minerals), and (2) how long the barrier will remain efficacious in immobilizing uranium.

Arey et al. (1999) conducted a series of batch tests to evaluate the ability of hydroxyapatite to immobilize uranium in sediments of varying organic carbon contents. Results of this investigation indicate the presence of apatite lowered aqueous uranium concentrations to values near the drinking water standard (30 ppb). Furthermore, sorbed uranium was secondarily sequestered in Al/Fe phosphate phases over the pH range of 4.0–4.5. Fuller et al. (2002, 2003) demonstrated the immobilization of uranium on apatite occurs initially by surface complexation with further transformation of sorbed uranium into chernikovite, hydrogen autunite, in the absence of dissolved carbonate over the pH range of 6.3–6.9. Immobilization of uranium on the apatite surface via surface complexation or alternative sorption reaction is a readily reversible process with the infiltration of groundwater. However, sequestration of uranium in a secondary mineral phase requires dissolution of the solid phase in order to re-release uranium into the subsurface. To evaluate the efficacy of an apatite barrier for the long-term sequestration of uranium, it is necessary to understand the mechanism of retention under conditions relevant to the 300 Area subsurface.

A.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. Ignoring diffusion and dispersion processes, the rate of release of component *i* per unit cross-sectional area is:

$$J_i = U_r \times C_i \tag{A.4}$$

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

Integrating Equation A.4 over time,

$$m(t) = A_c \int_0^t U_r C_i dt \tag{A.5}$$

where $m(t)$ = mass of component *i* having exited the barrier at time *t*
A_c = 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_l) is

$$t_l = \frac{m_{o,i}}{A_c U_r C_i} \tag{A.6}$$

where $m_{o,i}$ is 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 A.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 Damköhler number 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

$$Da = \frac{\theta A_m k_o}{U_r C_i^* A_c} \tag{A.7}$$

where θ = volumetric water content
A_m = phosphate mineral surface area
k_o = dissolution rate constant
C_i^* = 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 Damköhler number can be used 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 A.7 or an alternative correlation is needed before extrapolation to field conditions and evaluation of the phosphate barrier lifetime could be scientifically justified.

A.5 References

Arey JS, JC Seaman, and PM Bertsch. 1999. "Immobilization of Uranium in Contaminated Sediments by Hydroxyapatite Addition." *Environmental Science and Technology* 33:337-342.

Avrami M. 1939. "Kinetics of Phase Change, I." *Journal of Chemistry and Physics* 7:1103-1112.

Avrami M. 1940. "Kinetics of Phase Change, II." *Journal of Chemistry and Physics* 8:212-224.

Fuller CC, JR Bargar, and JA Davis. 2003. "Molecular-Scale Characterization of Uranium Sorption by Bone Apatite Materials for a Permeable Reactive Barrier Demonstration." *Environmental Science and Technology* 37:4642-4649.

Fuller CC, JR Bargar, JA Davis, and MJ Piana. 2002. "Mechanisms of Uranium Interactions with Hydroxyapatite: Implication for Groundwater Remediation." *Environmental Science and Technology* 36:158-165.

Shen CY and FW Morgan. 1973. "Hydrolysis of Phosphorous Compounds." In *Ed. Environmental Phosphorous Handbook*, EJ Griffith, A Beeton, JM Spencer, and DT Mitchell (eds.), p. 241, John Wiley & Sons, New York.

Appendix B

Response to Summary Comments from Supplemental Columbia River Activities Peer Review

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B.1 Summary Evaluation

The panel generally supports this proposal with some recommendations and uncertainties that should be addressed. Identified issues and concerns are related to the method of injection and influence of subsurface heterogeneity, longevity of the polyphosphate apatite barrier, approaches to laboratory experiments, geochemical impacts resulting from the injection, and long-term monitoring of the uranium plume. The proposal provides for a combination of laboratory and field investigations that should provide the data required to evaluate the likelihood of successful deployment.

B.2 Technical Issues for Consideration

1. *A more detailed description of how polyphosphate will be injected and dispersed, including impacts of subsurface heterogeneity.*

   Response: The field-scale injection design will be based on results from laboratory-scale studies and site-specific characterization data from the selected field treatability test site. The field test will be designed to assess the impacts of field-scale heterogeneities at the pilot field scale and provide the information needed to evaluate the impact of subsurface heterogeneities on full-scale deployment of the technology.

2. *Include more detailed discussion of alternative methods to mitigate uranium movement.*

   Response: The subject proposal provides a detailed discussion of the polyphosphate technology, which was selected for treatability through a screening process that will be documented in detail in the 300-FF-5 Phase III feasibility study. Text was added to the introduction of this work plan that describes this process. Evaluation of alternative technologies for uranium remediation that were proposed by the peer review panel is not within the scope of this proposal and, thus, will not be performed. Additional proposed technologies could be evaluated under separate U.S. Department of Energy (DOE) EM-21 funded projects. The use of push-pull testing will be evaluated during injection design analysis. This type of testing approach may be used to gain additional characterization data. However, its usefulness will depend on the relationship between groundwater velocity and reaction kinetics of the selected polyphosphate formulation.

3. *The concentration of phosphate resulting from the injection as a potential a risk to near-term water quality.*

   Response: Water quality impacts will be evaluated.

4. *Evaluate impacts to subsurface geochemistry as a result of the polyphosphate injection.*

   Response: Most impacts identified by the peer review panel will be evaluated, although some are not within the scope of this treatability study:

   - Geochemical impacts on microbial populations are not currently within the scope of this study and no aseptically handled samples were collected during the limited field investigation (LFI) that are providing sediments for the proposed laboratory experiments

   - The potential for colloidal migration of uranium will be evaluated during laboratory testing

   - The potential for phosphate to disperse clay minerals, affecting permeability is not directly addressed within the scope of this study; however, indirect evaluation of this will be accomplished during laboratory column tests

   - Precipitation of phosphate minerals will be evaluated as noted within the current work plan via laser Raman spectroscopy and x-ray diffraction (XRD)

   - The impacts of mineral weathering and associated release of uranium have, in part, been previously addressed by Wellman et al. (2006); furthermore, the weathering of apatite will be evaluated during the course of this investigation

   - Sorption of uranium and potential impacts of pH will be evaluated as outlined within the work plan

   - The use of polyphosphate "blends" will be evaluated as outlined above in the work plan via nuclear magnetic resonance (^{31}P NMR) results and subsequent column testing

   - Long-term evaluation of apatite barrier natural analogues is not currently within the scope of this project

5. *The proposed approach for the column experiments uses uranium-spiked clean sediment, rather than uranium-contaminated sediment. It is unclear whether the spiked uranium sediment can adequately mimic uranium-contaminated sediment. Consider batch studies as an alternative to column studies, to evaluate the mass transfer and sorption of uranium. In addition, column experiments should include post-mortem analysis.*

   Response: Column experiments will be conducted on 300 Area sediments, both clean and uranium contaminated, to evaluate the ability of polyphosphate amendments to treat uranium-laden pore fluids, as well as uranium associated with the sedimentary matrix. Additionally, as outlined within the work plan, batch tests will complement column testing to evaluate the sorption of uranium to solid phases. Sedimentary and aqueous phase analyses will be conducted in-line during testing as well as post-mortem.

6. *Impacts of the water level at different river stages in the approaches for various experiments.*

   Response: The injection design analysis for the pilot-scale field test will consider the effects of river stage variability.

7. *Use of store and release covers for infiltration in the case of a precipitation event.*

   Response: A well injection approach will be used distribute polyphosphate in the aquifer. No surface infiltration will be performed during this treatability study.

8. *Evaluate the possible economy-of-scale benefits from testing both the injection of polyphosphate and calcium-citrate-polyphosphate apatite solution for addressing the strontium-90 plume in the Hanford 100-N Area and the uranium plume in the Hanford 300 Area.*

   Response: Because both of these technologies are in an early stage of development and require technology specific testing, there is likely little economy of scale benefit associated with combining these projects. Given that the technologies being proposed for the 100-N Area strontium-90 plume and the 300 Area uranium plume are similar, results from each treatability study can be evaluated to determine the advantages and disadvantages of each and whether a given technology is better suited to the hydrogeologic and geochemical conditions present at the two sites.

9. *Potential stakeholder concerns about the longevity of the polyphosphate apatite barrier and long-term stewardship of the Hanford Site.*

   Response: The formation of apatite and associated treatment longevity will be evaluated.

10. *The DOE Richland Operations Office should perform a Natural Resource Damage Assessment, since in-situ treatment of uranium leaves a possible continuing source of uranium in the Hanford subsurface.*

    Response: DOE response required.

B.3 Implementation Strategy

11. *Budgeted costs, sequencing, and timing are generally appropriate for the level of work.*

    Response: None required.

12. *Provide more detail about the development of the field project. A test plot should be large enough and include sufficient number of monitoring wells to determine the efficacy of the process.*

    Response: Additional detail regarding the pilot-scale field test was not provided because the design for this field test is not yet well developed. Results from the proposed laboratory testing and site-specific characterization data will be used to develop this design. Once preliminary bench-scale testing results and site-specific characterization data are available, a field test plan will be prepared that will contain the additional requested detail.

13. *Since 40% of the budgeted cost is for drilling wells for injecting polyphosphate, consider using boreholes and existing wells to significantly reduce costs.*

    Response: Proposed budget does include the used of existing wells. We would prefer not to spend this much of the budget on drilling, but drilling costs this high are not uncommon for technology development projects on the Hanford Site.

14. *There may be additional unforeseen costs, such as inadequate well placement or additional drilling, during the transition to the field test.*

    Response: Attempts were made to include all likely costs in the proposal, but it is agreed that there is always the potential for unforeseen cost.

15. *The pilot test plan should include a discussion of spatial scales and time.*

    Response: The field test plan will include this discussion.

16. *Full-scale implementation will require additional testing and design to address outstanding technical issues, such as the impact of subsurface heterogeneity.*

    Response: It is likely that additional field-scale testing will be required following the pilot-scale injection before the technology is ready for full-scale deployment. Results from the pilot-scale injection would be used to design a larger scale field treatability test.

17. *In-situ stabilization of uranium should include long-term monitoring of uranium concentrations, including coring to ensure available uranium is sequestered within autunite in oxidized form.*

    Response: Aqueous monitoring and coring are included in the proposal.

18. *Provide evidence that this technology can be implemented and operated cost effectively. Currently, this approach is just a proof-of-principle test.*

    Response: The proposed pilot-scale treatability test will provide initial information on implementability and cost effectiveness; but as indicated in peer review comment 16, additional testing will likely be required before the technology is ready for full-scale deployment.

19. *Consider combining polyphosphate injection with the apatite infiltration in the Hanford 100-N Area, and perform concurrent laboratory tests for uranium and strontium-90.*

    Response: See response to comment 8.

B.3 References

Wellman DM, JP Icenhower, AP Gamerdinger, and SW Forrester. 2006. "Effects of pH, Temperature, and Aqueous Organic Material on the Dissolution Kinetics of Meta-Autunite Minerals, $(Na, Ca)_{2-1}[(UO_2)(PO_4)]_2\ 3H_2O$." *American Mineralogist* 91:143-158.