In-Situ Uranium Stabilization Through Polyphosphate Injection: Pilot-Scale Treatability Test at the 300 Area, Hanford Site - 8187

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ABSTRACT

This paper describes the pilot-scale treatability test that was conducted to evaluate the efficacy of using a polyphosphate injection approach to treat uranium-contaminated groundwater in situ within the 300 Area aquifer at the Hanford Site in Richland, Washington. Primary test objectives were to assess 1) direct treatment of available uranium contributing to the groundwater plume through precipitation of the uranyl-phosphate mineral autunite, and 2) emplacement of secondary-treatment capacity via precipitation of the calcium-phosphate mineral apatite, which acts as a long-term sorbent for uranium. Based on an injection design analysis that incorporated results from both bench-scale testing and site-specific characterization activities, a three-phase injection approach was selected for field-scale testing. This approach consisted of 1) an initial polyphosphate injection to facilitate direct treatment of aqueous uranium in the pore space, 2) a second phase consisting of a calcium chloride injection to provide an available calcium source for the creation of apatite, and 3) a subsequent polyphosphate injection to supply a phosphate source for the formation of apatite. The total-solution volume injected during this field test was approximately 3.8 million L (1 million gal). Results from this investigation will be used to identify implementation challenges and investigate the technology's ability to meet remedial objectives. In addition, data from this test will provide valuable information for designing a full-scale remedial action for uranium in groundwater beneath the 300 Area of the Hanford Site, and a detailed understanding of the fundamental underpinnings necessary to evaluate the efficacy and potential for utilization of the polyphosphate technology at other sites with varying geochemical and hydrodynamic conditions.

INTRODUCTION

The 1996 record of decision (ROD) for the 300-FF-5 Operable Unit stipulated an interim action program of natural attenuation processes accompanied by increased groundwater monitoring. The remedial action objective of the ROD was reduction of groundwater uranium to the U.S. Environmental Protection Agency maximum contaminant level concentration of 30 µg/L. Despite the cessation of uranium releases and the removal of shallow vadose zone source materials, the goal of less than 30 µg/L has not been achieved within the anticipated 10-year time period. Because the remedial action objectives of the 1996 ROD were not met, a Phase III Feasibility Study was initiated in 2005 to identify and evaluate remedial alternatives that will accelerate monitored natural attenuation of the uranium plume.

For fiscal year 2006, the U.S. Congress authorized $10 million dollars to the Hanford Site for "…analyzing contaminant migration to the Columbia River, and for the introduction of new technology approaches to solving contamination migration issues." These funds are administered through the U.S. Department of Energy's Office of Environmental Management (EM-22). After a peer review and selection process, nine projects were selected to meet the objectives of the appropriation. As part of this effort, Pacific Northwest National Laboratory (PNNL) performed bench- and field-scale treatability testing designed to evaluate the efficacy of using polyphosphate injections to reduce uranium concentrations in the groundwater to meet drinking water standards (30 µg/L). This technology works by forming uranyl- and calcium-phosphate minerals (autunite and apatite) in the aquifer that directly sequester the existing aqueous uranium in autunite minerals and precipitates apatite minerals for sorption and long-term treatment of uranium migrating into the treatment zone, thus reducing current and future

aqueous uranium concentrations. Polyphosphate injection was selected for testing based on technology screening as part of the 300-FF-5 Phase III Feasibility Study for treatment of uranium in the 300 Area.

A groundwater plume containing uranium from past-practice discharges of liquid waste associated with nuclear fuel-fabrication activities has persisted beneath the 300 Area for many years. This plume originated from a combination of purposeful discharges of wastewater to cribs, trenches, and ponds, along with some accidental leaks and spills during nuclear fuel-fabrication activities, and is identified as the 300-FF-5 Operable Unit. Elevated uranium concentrations are transported through the high-conductivity sandy gravels of the Hanford formation and enter the nearby Columbia River shoreline and the riparian and river biota through seeps. In the current conceptual site model [1, 2], researchers assume that resupply of the plume is occurring, with continuing release coming primarily from the deep vadose zone beneath waste sites and the zone of water table fluctuations.

Comparison of uranium concentrations in groundwater at high- and low-river stage conditions provides some insight as to the distribution of uranium contamination in the deep vadose zone. During high-water conditions, elevated uranium concentrations are observed in localized areas that can be attributed to past-disposal operations. These increases in uranium concentration are most likely associated with contamination remaining in the deep vadose zone and zone of water table fluctuations associated with changes in Columbia River stages. The polyphosphate treatability test site is located near one of the two delineated deep vadose sources. The persistence of this plume is enigmatic for several reasons, including 1) discharges containing uranium-bearing effluent to ground disposal sites ended in the mid-1980s; 2) contaminated soil associated with these waste sites was removed during the 1990s, with backfilling complete by early 2004; and 3) the aquifer is comprised of highly transmissive fluvial sediment, suggesting rapid movement of groundwater.

This paper provides a preliminary status of pilot-scale treatability test activities for the polyphosphate technology, which is currently ongoing. Topics include brief descriptions of the technology and field test site; associated characterization activities that were performed, including a large-scale tracer injection and drift test; a discussion of the field-scale injection design analysis approach; a description of test operations; and a discussion of performance assessment monitoring data collected to date. Although only a preliminary assessment of the ability of the technology to meet remedial objectives is presented in this paper, available test results do provide valuable insight into implementation challenges at this site and will form the basis for designing additional bench- and field-scale testing as required to develop an injection approach that meets site remedial objectives.

POLYPHOSPHATE TECHNOLOGY DESCRIPTION

The use of soluble long-chain polyphosphate amendments has been demonstrated to delay the precipitation of phosphate phases [3]. Precipitation of phosphate minerals occurs when phosphate compounds degrade in water, due to hydrolysis, to yield the orthophosphate molecule (PO_4^{3-}). The rate of the hydrolysis reaction that leads to production of orthophosphate is related to the length of the polyphosphate chain.

Injection of a sodium tripolyphosphate amendment into the uranium-bearing saturated porous media has been shown to immobilize uranium through the formation of an insoluble uranyl-phosphate mineral, autunite $\{X_{1-2}[(UO_2)(PO_4)]_{2-1} \cdot nH_2O\}$, where X is any monovalent or divalent cation. Because autunite sequesters uranium in the oxidized form, U^{6+}, rather than forcing reduction to U^{4+}, the possibility of reoxidation and subsequent remobilization 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 Site

subsurface [3]. In addition to autunite, excess phosphorous can result in apatite mineral formation, providing a long-term source of treatment capacity.

Research beginning in the mid-1960s underscored the efficacy of utilizing calcium and/or lime to precipitate stable calcium-phosphate solid phases, including apatite for direct removal of phosphate [4, 5, 6, 7]. By complexing calcium and sorbing to mineral surfaces, polyphosphate compounds effectively enhance the rate of calcium phosphate precipitation by reducing competing reactions, such as the formation of calcium carbonate, and "directing" calcium to participate in reactions resulting in calcium phosphate precipitation [5].

Previous research [8, 9] demonstrated the efficacy of hydroxyapatite for reducing the aqueous uranium concentration to <0.05 μM under the pH range of 6.3 to 6.9 in the presence of carbonate. Results suggested the binding of uranium, irrespective of dissolved carbonate concentration or aqueous uranium concentration, occurred via surface complexation; long-term retention occurred 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 [10].

TEST SITE DESCRIPTION

The polyphosphate treatability test site is located within the 300 Area of the Hanford Site, at the southern end of a liquid waste disposal trench (316-5 process trenches) that is a known source of uranium contamination. The location is sufficiently far inland from the Columbia River such that transport of river water during normal high-river stage conditions does not reach the location, an impact that would complicate test result interpretations. Pressure responses associated with fluctuations in river stage are significant at this location and must be considered when analyzing water-level trends and hydraulic test response data. The site was selected due to its proximity to a known uranium source area and because of its contaminant profile; i.e., it has a moderately thick (~6.1 m [20 ft]) interval of contaminated permeable Hanford formation gravel below the water table, and because the location is impacted less by river level fluctuations than locations closer to the river. Depth-discrete uranium concentrations in groundwater samples collected during drilling of the test site injection well (399-1-23, Fig. 1) indicated values in the Hanford Site gravels ranging from ~80 μg/L in the uppermost portion of the aquifer within the zone of water table fluctuation to ~40 μg/L deeper in the profile.

A total of 16 wells were installed in support of pilot-scale field test, including one injection well (399-1-23) and 15 monitoring wells (Fig. 1). One additional monitoring well (399-1-17A) that was installed in support of the Hanford Site groundwater monitoring network was also used as a downgradient monitoring location. The uppermost unconfined aquifer beneath the polyphosphate treatability test site is composed of unconsolidated gravel-dominated sediments of the Hanford formation, which consists predominantly of coarse sandy gravel to gravel; where present, the matrix sand is composed of medium to coarse sand. The Ringold Formation that lies beneath the Hanford formation is composed of mostly gravelly silty sand to sand. The Hanford – Ringold contact boundary ranged in depth between approximately 13.1 and 15.2 m (43 and 50 ft) below ground surface (bgs). Typical depths to water range from 10.6 m (35 ft) bgs during low-river stage conditions to 9.1 m (30 ft) bgs during spring/summer high-water conditions, resulting in a nominal Hanford aquifer thickness at this location of 4.5 to 6 m (15 to 20 ft).

Results from hydraulic tests conducted at the field test site indicate that hydraulic conductivity in the Hanford formation is up to three orders of magnitude higher than that in the underlying Ringold Formation, which acts as a lower bounding aquitard at this location and effectively isolates treatability test injection operations to the high-permeability Hanford formation.
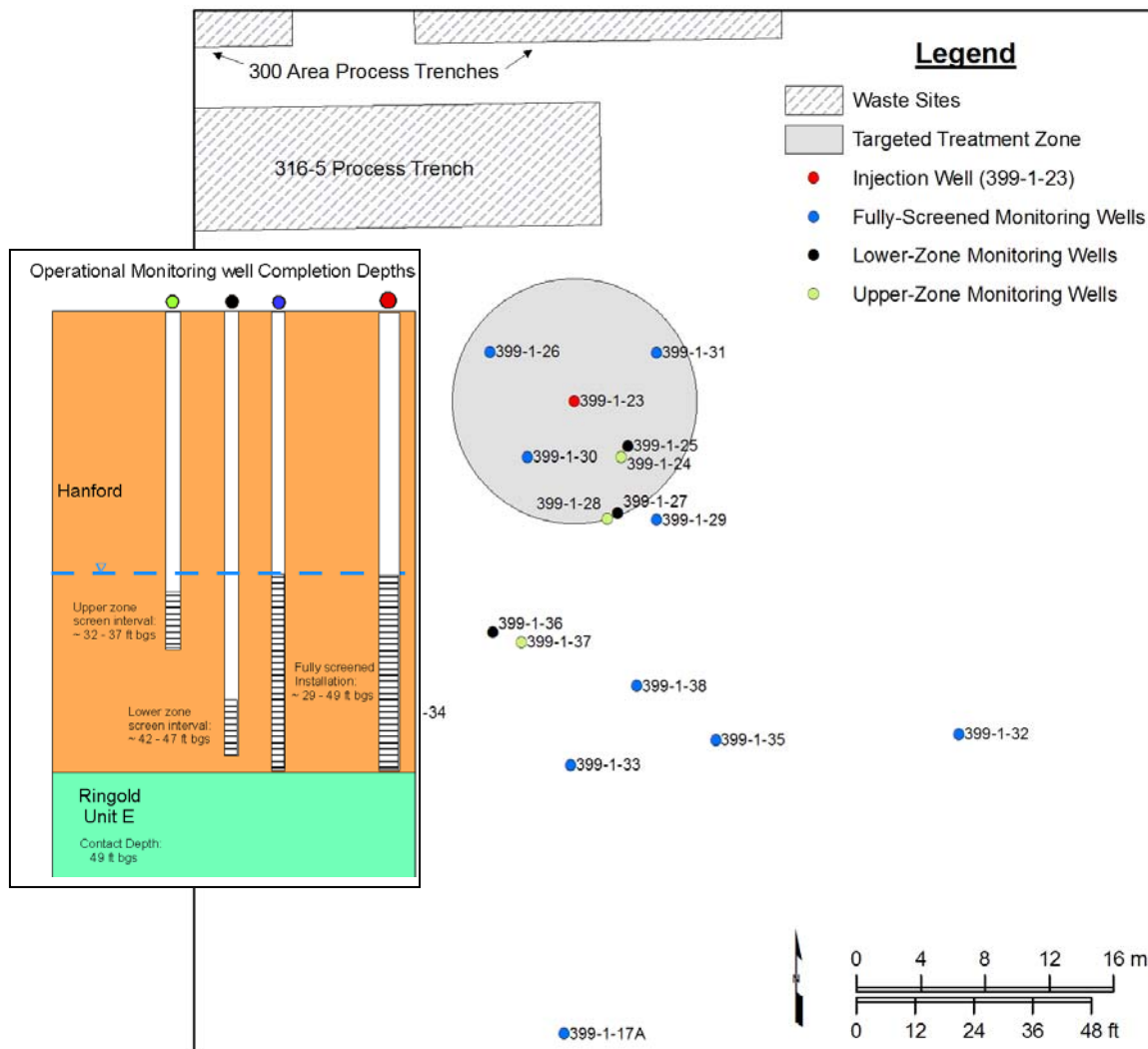
Fig. 1. Well location map and generalized construction diagram for the treatability test injection and monitoring well network.

During installation of the injection well (399-1-23), depth-discrete slug withdrawal tests were conducted throughout the underlying Ringold Formation, resulting in hydraulic conductivity estimates ranging from 0.69 to 2.16 m (2.3 to 7.1 ft) per day [11]. Pressure-buildup data collected during a 11.9-hour tracer injection test, which was conducted at a constant rate and was analyzed using the same analytical techniques for analyzing constant rate discharge tests (i.e., pumping tests), was used to provide local-scale estimates of hydraulic properties for the Hanford formation at this site. Based on Neuman type-curve analyses of this pressure buildup data, hydraulic conductivity was estimated at ~2,800 m (9,300 ft) per day [12].

Tracer Injection and Drift Test

A tracer injection test was conducted at the polyphosphate treatability test site on December 13, 2006 [12]. The objective of the tracer test was to 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. Results from the tracer test provided information on

the effective porosity of the aquifer, expected arrival times at the monitoring wells, and polyphosphate solution volume requirements for the targeted treatment zone thickness and radial extent.

The tracer test was conducted by injecting a solution containing a conservative, nonreactive bromide (Br) tracer into the central injection well (399-1-23, as shown in Fig. 1). Bromide concentration in the tracer solution was held constant at 87 mg/L during the injection. Bromide was measured in the injection stream and the surrounding monitoring wells to determine the arrival times and spatial extent of the tracer plume. The injection stream was maintained at a constant rate of 757 L (200 gal) per minute throughout the test duration for 11.9 hours (714 minutes), yielding a total injection volume of 541,300 L (143,000 gal). In addition to the collection of aqueous samples, downhole Ion Selective Electrode (ISE) probes continuously monitored bromide concentrations in the wells during the test. A total of 256 aqueous samples were collected from the injection stream and surrounding monitoring wells and were analyzed in the field laboratory trailer for bromide using an ISE probe. Specific conductance (SpC), dissolved oxygen (DO), pH, oxidation-reduction potential (ORP), and temperature were also measured using an in-line electrode in the sampling manifold. The ion chromatography (IC) analyses were conducted on each of the 256 archive samples at an offsite laboratory as an additional method of measuring bromide concentration.

For wells located within a radial distance of 8.8 m (29 ft), 50% bromide concentration arrival times (t_{50}) ranged from 16 to 310 minutes (Table I).

Table I. Bromide Tracer Injection Arrival Times and Porosity Results for Targeted Injection Volume Monitoring Wells

Well Name	Well Screen Zone	Radial Distance (ft)	50% Tracer Arrival (min)	Average Velocity (ft/day)	Estimated Effective Porosity
399-1-23	Full	0	-	-	-
399-1-24	Upper	14.9	124	170	0.32
399-1-25	Lower	14.4	39	530	0.11
399-1-26	Full	19.9	111	260	0.16
399-1-27	Lower	24.5	na	-	-
399-1-28	Upper	24.9	216	170	0.20
399-1-29	Full	29.6	310	140	0.20
399-1-30	Full	14.8	16	1300	nc
399-1-31	Full	19.6	90	316	0.13
-	-	-	-	-	Average = 0.19
nc = Not calculated due to uncharacteristic response. na = 50% arrival not observed.					

These results indicate a general correlation between tracer arrival time and radial distance from the injection well, with a few notable outliers that provide some insight as to the level of heterogeneity present at this site.

The tracer arrival times were used to estimate the effective porosity of the aquifer according to the following equation:

$$n = \frac{t_{50} \cdot Q_{tot}}{\pi \cdot r^2 \cdot L \cdot 7.48}$$

(Eq. 1)

where n =   effective porosity
         t_{50} =   50% Br⁻ concentration arrival time (minutes)
         Q_{tot} =   total injection rate (200 gpm)
         r =   radial distance from the injection well (feet)
         L =   aquifer thickness (15 feet).

Effective porosities were calculated for each of the eight monitoring wells within the targeted injection volume, except for the two extreme outlier wells. Values range from 11 to 32% for the different wells, with an average effective porosity of 19%. This value is consistent with porosity estimates based on physical property analysis of core samples collected form the site [11].

In addition to monitoring wells located within the injection pore volume, two additional monitoring wells were monitored downgradient from the injection well beyond the radial extent of the targeted injection volume; wells 399-1-32 (Fig. 1) and 399-1-7 are located 32 and 188 m (104 and 617 ft)from the injection well, respectively. By combining the results from the bromide tracer drift with water level measurements and the resulting hydraulic gradient calculations, it is possible to estimate hydraulic conductivity (K) according to Darcy's Law:

$$v = \frac{K}{n} \cdot \frac{dh}{dx}$$

(Eq. 2)

$$K = \frac{v \cdot n}{\frac{dh}{dx}}$$

where K =   hydraulic conductivity (ft/day)
         v =   groundwater velocity based on the tracer arrival time (ft/day)
         n =   average effective porosity from the tracer arrival times (19% from above)
         dh/dx =   time-weighted average hydraulic gradient during tracer drift (ft/ft).

The tracer arrival curve for well 399-1-32 (Fig. 2) shows an early arrival response ahead of the main peak arrival, indicating the presence of formational heterogeneities that result in a faster flow path between the injection well and this location that could not be explained by transport through a homogeneous porous media.

For this reason, hydraulic conductivities were estimated for both the interpreted preferential flow path, resulting in an early tracer arrival and the bulk porous media attributed to transport of the main plume body. For the main tracer plume arrival at well 399-1-32, the groundwater velocity was estimated at ~15 m (50 ft) per day during tracer drift, based on a distance of 31.69 m (104 ft) and a tracer transport duration of ~3,000 minutes.
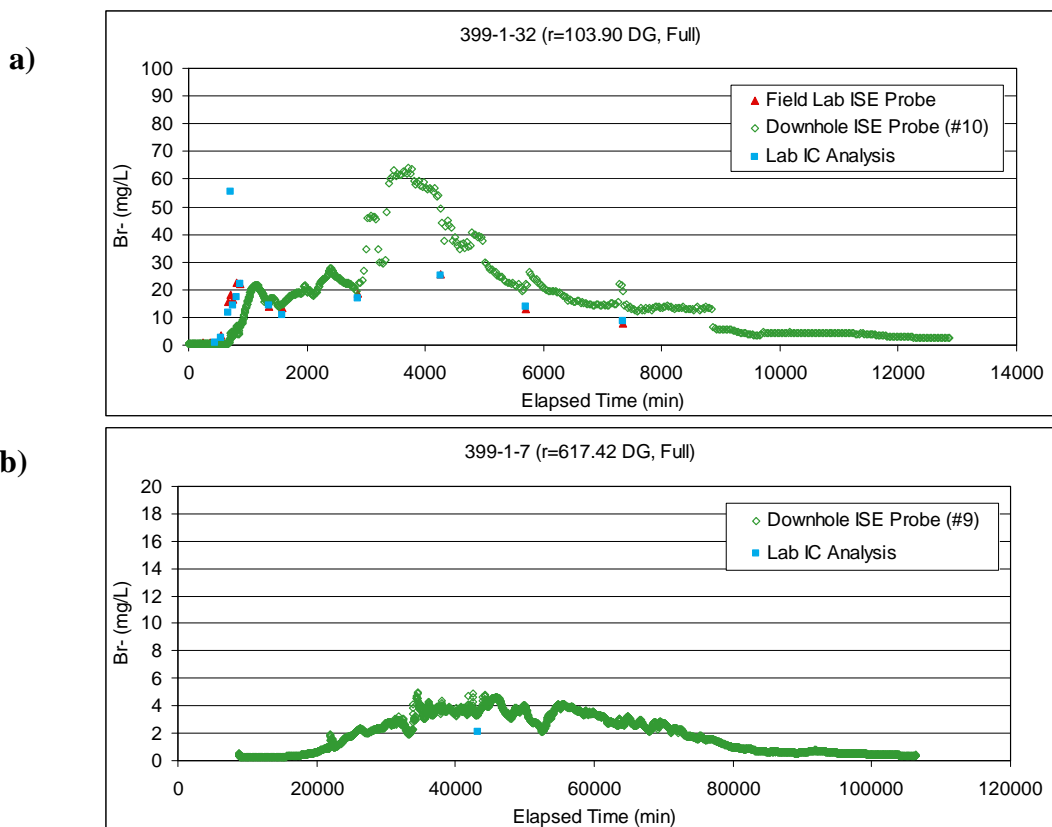
a)

399-1-32 (r=103.90 DG, Full)

Legend:
- Field Lab ISE Probe
- Downhole ISE Probe (#10)
- Lab IC Analysis

y-axis: Br- (mg/L), 0 to 100
x-axis: Elapsed Time (min), 0 to 14000

b)

399-1-7 (r=617.42 DG, Full)

Legend:
- Downhole ISE Probe (#9)
- Lab IC Analysis

y-axis: Br- (mg/L), 0 to 20
x-axis: Elapsed Time (min), 0 to 120000

Fig. 2. Breakthrough curves showing bromide concentrations through time for downgradient wells a) 399-1-32 and b) 399-1-7.

The tracer drift duration was defined as the time period between the end of the test when the tracer plume was centered over the injection well (t = 714 minutes) and the arrival time of the center of mass at 399-1-32 (t = ~3,700 minutes). The time-weighted average gradient during tracer transport between the injection well and well 399-1-32, as determined from water-level measurements, was ~6.5E-4 ft/ft. The estimated hydraulic conductivity using these parameters is about 4,300 m (14,000 ft) per day.

The fast-path hydraulic conductivity was calculated using the same equation used for the main tracer plume, but with some notable differences in the sources of the parameter values. Because the fast-path tracer arrival at well 399-1-32 occurred during the injection test phase, the transport duration was defined as the time between the beginning of the injection test (t = 0) and the 50% early tracer concentration arrival time at well 399-1-32 (t = ~930). The calculated groundwater velocity estimate based on this arrival time and the radial distance to the injection well is ~49 m (160 ft) per day. Using this groundwater velocity and the observed gradient conditions over the test interval, hydraulic conductivity for this interpreted preferential flow path was estimated at 6,100 m (20,000 ft) per day, or ~40% higher than that estimated based on transport of the bulk tracer plume.

The breakthrough curve for well 399-1-7, the more distant downgradient monitoring well (radial distance of 188 m [617 ft]), shows a more dispersed tracer plume arrival (Fig. 2). The first arrival of the tracer occurred after ~12 days (17,280 minutes) and steadily increased in concentration to a maximum of about 5 mg/L around the 30-day (43,200 minutes) mark. Although first arrival of the tracer plume at this location is generally consistent with the 15 m (50 ft) per day velocity calculated from the well 399-1-32 tracer arrival data (i.e., 188 m [617 ft] in 12 days or ~15 m [50 ft] per day), the dispersed nature of this

arrival response and the variability in groundwater velocity and flow direction over the relatively long travel path preclude a quantitative velocity or hydraulic conductivity estimate using these data.

Results from the bromide tracer injection and drift test provide valuable information for design of the polyphosphate treatability test. For example, the 541,313 L (143,000 gal) injected during the tracer test appears to be a suitable volume to create a 9-m (30-ft) diameter pore volume. The test results also suggest that formational heterogeneities exist that affect groundwater transport within and downgradient of the targeted treatment zone, but when taken in composite, the average porosity estimate of 19%, calculated using the arrival times in wells located within the injection pore volume is consistent with other reported porosity values [11]. Lastly, the equipment and sampling methods used in the tracer test were successful at capturing arrival responses and should be suitable for operation and monitoring of the polyphosphate injection.

This simplified approach for evaluation of tracer injection and drift data provides for a quantitative estimate of treatability test-scale transport properties and variability in those properties, and forms the basis for a more technically rigorous evaluation based on local-scale flow and transport modeling [12]. Results from both of these analyses were used to develop a field-scale injection design.

INJECTION DESIGN ANALYSIS

The objective of the injection design analysis was to determine injection volumes, rates, and sampling requirements for the treatability test. This analysis was based on the results of bench-scale studies, the tracer injection and drift test, and the use of analytic and numerical models [12]. The injection volumes, which are based on the observed arrival of conservative species during the tracer injection test, have been increased to account for increased aquifer thickness during spring high-river stage conditions. These volumes were also increased to account for retardation associated with the reactive species used for the polyphosphate treatability test, as determined based on bench-scale laboratory tests.

The injection volume for a conservative species at the polyphosphate treatability test site was estimated based on the results of the bromide tracer test and adjusted volumetrically to account for the higher river stage conditions expected for the polyphosphate injection in June 2007. The targeted treatment volume was defined as reaching 90% or greater concentrations at a 7.62-m (25-ft) radial distance from the injection well. The tracer arrival data presented in Table I show there is significant variability in the tracer arrival due to heterogeneities at the site. In addition to this tabular comparison, results of an analytic solution for advection and dispersion for wells around an injection well at different radial distances [13] were used to assess tracer arrivals. This analytic solution assumes a homogeneous, isotropic aquifer with constant thickness. Comparisons with the analytic solution were used to show the relative differences between the measured tracer arrivals and the expected response assuming homogeneous conditions. This approach allowed for the wells to be categorized as fast or slow relative to this measure.

Based on these comparisons, most of the wells southeast of the injection well had slower tracer arrivals than wells in other directions. Well 399-1-30, to the southwest of the injection well, had a very rapid arrival indicating preferential flow in that direction. Wells to the northeast and northwest had similar arrivals to the average expected at the site. Using the comparison to the analytic solution for well 399-1-29, it appears that the tracer response at this well is influenced by multiple layers within the screened zone as seen by an initial early tracer arrival to about 50% of the tracer injection concentration followed by a slow increase during the rest of the injection period. This response may be associated with the same higher conductivity feature that results in early arrival at lower zone monitoring well 399-1-25.

Tracer arrival data for each monitoring well was evaluated to determine what injection volume was required to meet the design criteria of 90% or greater concentration arrival. These volumes were then scaled based on cylindrical geometry to calculate the volume required to achieve this 90% arrival at a 7.62-m (25-ft) radial distance. Using this scaling approach, the average volume requirement from all wells at the site was ~331,000 L (87,400 gal) for water table conditions encountered during the December 2006 tracer test. Adjusting for the 25% increase in aquifer thickness expected due to increased river stage in June 2007 resulted in a pore volume estimate of 414,000 L (109,000 gal) for the same 7.6-m (25-ft) radial extent.

Chemical requirements for the polyphosphate treatability test were based on 1) bench-scale experiments designed to determine reactive species retardation and rate information, and 2) the determination of the fluid-volume requirements (based on the tracer test) for treatment of a specified volume in the subsurface. Based on this evaluation, a field-scale injection approach was developed that was composed of three separate injection phases. The first phase consisted of injecting a polyphosphate amendment for sequestration of aqueous uranium in phosphate mineral phases (i.e., autunite); the second phase consisted of injecting a calcium-chloride solution for supplementing the existing calcium in the aquifer for apatite formation; and the third phase consisted of another polyphosphate injection (same composition as the first injection) for providing phosphate for apatite formation. This approach relied on bench-scale results that showed both calcium and phosphate species would sorb to formation sediments, helping to facilitate mixing between these two required components for apatite formation. The injection volumes for the first and third injections were scaled up to a total volume of 990,300 L (262,000 gal) based on the retardation factor of ~2.4 for the polyphosphate amendment determined in laboratory experiments using site sediments. The injection volume for the calcium-chloride solution in the second phase was scaled up to 1,980,000 L (523,000 gal) based on a retardation factor of 4.8. The injection rate was specified at 757 L (200 gal) per minute, the same rate used during the tracer injection test.

Table II presents the pilot-scale treatability test amendment formulation.

Table II. Pilot-Scale Field Test Amendment Formulation

Injection	Amendment	Formula	CAS #	Formula Wt (g/mol)	Solubility, g/L 23°C H_2O	Conc. (g/L)	Conc. (M)
1	Sodium phosphate, monobasic	NaH_2PO_4	7558-80-7	119.98	29.63	0.59	4.94×10^{-3}
	Sodium pyrophosphate	$Na_4P_2O_7$	7722-88-5	265.9	32.81	0.66	2.47×10^{-3}
	Sodium tripolyphosphate	$Na_5P_3O_{10}$	7758-29-4	367.86	60.40	1.21	3.29×10^{-3}
	Sodium bromide	NaBr	-	102.90	--	0.103	1.00×10^{-3}
2	Calcium chloride	$CaCl_2$	10043-52-4	110.98	800	3.41	3.07×10^{-2}
3	Sodium phosphate, monobasic	NaH_2PO_4	7558-80-7	119.98	29.63	0.59	4.94×10^{-3}
	Sodium pyrophosphate	$Na_4P_2O_7$	7722-88-5	265.9	32.81	0.66	2.47×10^{-3}
	Sodium tripolyphosphate	$Na_5P_3O_{10}$	7758-29-4	367.86	60.40	1.21	3.29×10^{-3}
	Sodium bromide	NaBr	-	102.90	-	0.103	1.00×10^{-3}

The solubility values listed were experimentally analyzed in tap water and filtered through a 0.45-μm filter at room temperature. Moreover, the values are not independent solubility values; rather, they are the maximum solubility within the total polyphosphate formulation. Results of batch and column tests that demonstrated optimum performance was achieved using a formulation to which the contribution of phosphorus is 25% orthophosphate, 25% pyrophosphate, and 50% tripolyphosphate. The mixture of the various components of the polyphosphate solution was used to achieve a solution pH of ~7.

The amendment solution was prepared by mixing in order the sodium orthophosphate, sodium pyrophosphate, and sodium tripolyphosphate to achieve a pH of 7 and prevent degradation of polymerized phosphate molecules during preparation of the remedy solution.

POLYPHOSPHATE INJECTION TEST

The pilot-scale polyphosphate treatability test was conducted on June 11-15, 2007. As indicated above, the injection design specified that the test be conducted in three separate phases. The first phase consisted of a 965,000 L (255,000 gal) injection of polyphosphate solution, followed by a second phase consisting of 2,200,000 L (580,000 gal) of calcium-chloride solution. The third phase consisted of another 927,000 L (245,000 gal) injection of polyphosphate solution. All injection phases were conducted at a constant rate of 757 L (200 gal) per minute, for a total test duration of 3.8 days. Solute concentrations were held constant during each phase of the injection and analytes of interest were measured in the injection stream and the surrounding monitoring wells to determine arrival times at each location and assess the overall extent of treatment. Parameters monitored during the test include major cations by Inductively Coupled Plasma – Optical Emission Spectrometry, trace metals by ICP-Mass Spectrometry, anions by IC, and a full suite of field-measurable parameters including SpC, pH, DO, ORP, temperature, and both Br- and Cl-concentration by ion-selective electrode. During the field experiment, approximately 1,000 aqueous samples were collected and submitted for laboratory determination of anion and major cation concentrations.

As indicated previously, only a preliminary assessment of the technology's ability to meet remedial objectives is presented in this paper; collection and assessment of performance data is still ongoing. However, available test results do provide valuable insight into implementation challenges at this site. The biggest challenges to implementation of the polyphosphate technology identified during this field-scale demonstration are the extremely high-permeability nature of the Hanford formation, formation heterogeneities that result in even higher-flow velocities over some flow paths, and the inability of bench-scale column experiments to make accurate predictions of sorption for the various phosphate compounds and calcium under the complex hydrogeologic conditions encountered at the field scale.

Fig. 3 shows a plot of reactive (Ca and PO_4) and conservative (Br and Cl) species for the injection well, along with comparable plots for two monitoring wells.

In the monitoring well plots, observed concentration have been normalized to the injection concentration of each analyte. As shown in the plot for well 399-1-26, only limited overlap between Ca and PO_4 occurred during the transition between injection phases at this location, indicating the potential for apatite formation is low. This response illustrates the limited retardation of the reactive species observed under field conditions. Also shown is a plot for well 399-1-38 where, although still limited, more overlap between Ca and PO_4 occurs during the second and third phases of the injection test.
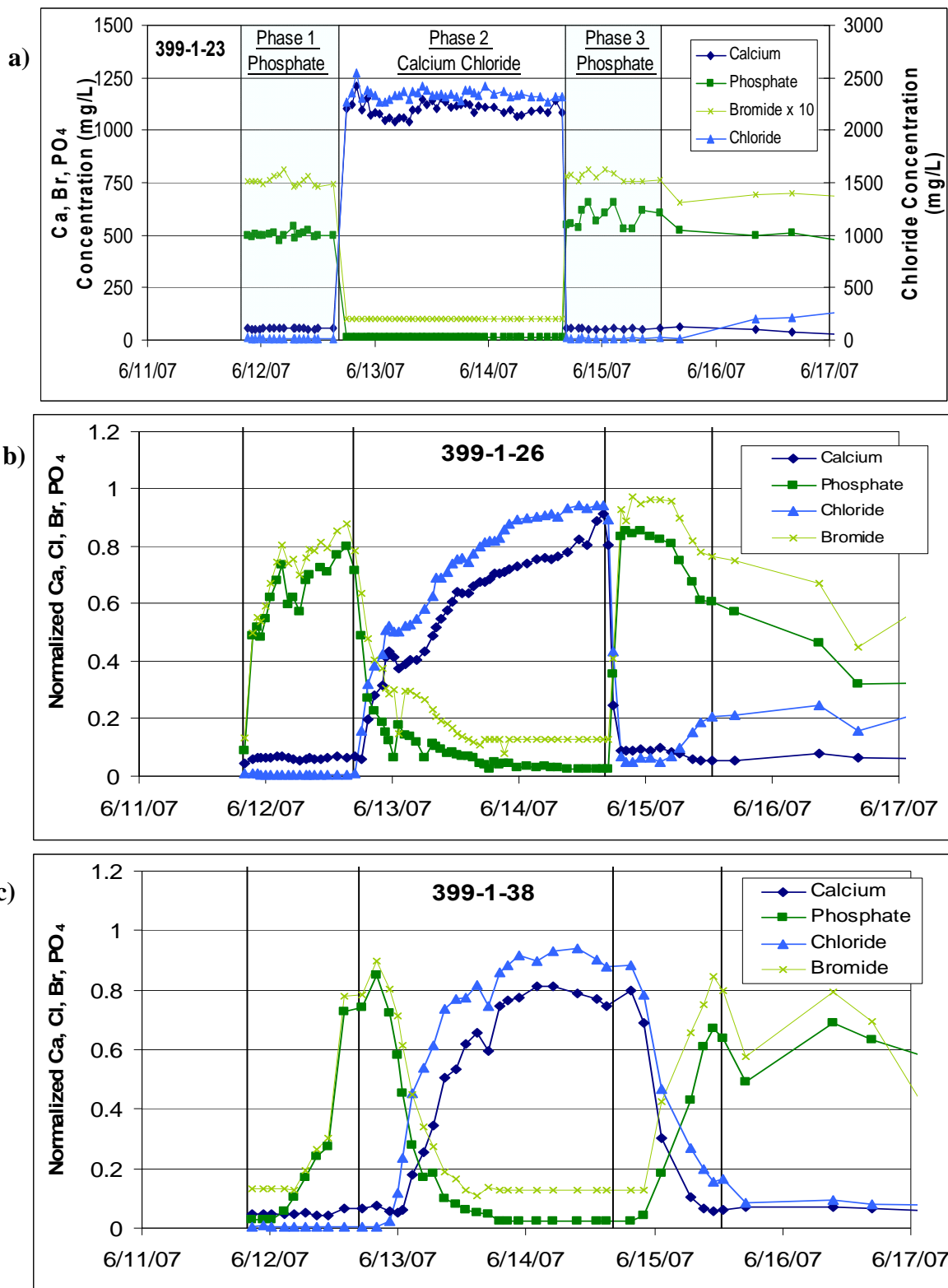
Fig. 3. Injection concentrations (a) and normalized arrival concentrations for PO$_4$, Br, Ca, and Cl at two monitoring well locations (b and c).

Based on the lack of separation between the reactive and conservative species in each injection phase (i.e., PO_4/Br and Ca/Cl), it is clear that the retardation factors of 2.4 and 4.8 for the polyphosphate and calcium-chloride solutions, respectively, as determined from bench-scale column experiments using only the small-size fraction of sediments, are not representative of field-scale conditions. Larger-scale laboratory column experiments that incorporate the large-size fraction of the sediment, instead of just scaling small-size fraction estimates to account for the volume contained in the large-size fraction, along with experiments over a larger range of pore water velocities are needed to develop a more effective injection strategy.

Fig. 4 shows preliminary uranium stabilization performance data for the same two monitoring wells whose amendment arrival responses are presented in Fig. 3.
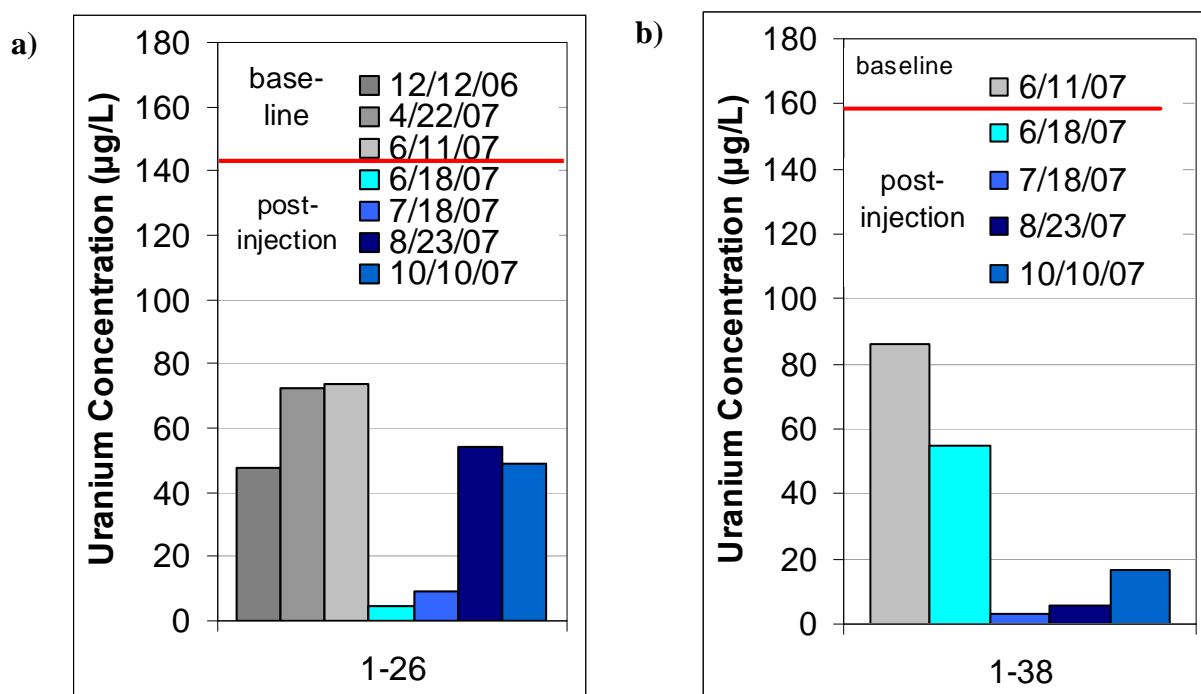

Fig. 4. Preliminary uranium stabilization performance monitoring data for monitoring wells (a) 399-1-26 and (b) 399-1-38.

The initial performance results looked promising with respect to reductions in uranium concentration, with concentrations in most monitoring wells located within a radial distance of 23 m (75 ft) reduced to well below drinking water standards (as indicated in both examples provided in Fig. 4). However, evidence for the emplacement of a substantial amount of long-term treatment capacity (i.e., apatite formation) was less definitive. Uranium concentration rebound observed at some monitoring locations (e.g., well 399-1-26, which is located on the upgradient side of the treatment zone and would be expected to break through first) indicates that apatite formation may be small relative to the design target. This performance response is consistent with the Ca/PO_4 arrival data presented above. Longer-term uranium stabilization performance monitoring is ongoing. Data from this pilot-scale treatability test, along with supplemental bench-and intermediate-scale laboratory testing, will form the basis for designing a modified injection approach that meets site remedial objectives.

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