CHPRC-00067-FP
Revision 0

An Innovative Approach for Constructing an In-Situ Barrier for Strontium-90 at the Hanford Site, Washington

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management
Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-08RL14788

CH2MHILL
Plateau Remediation Company

P.O. Box 1600
Richland, Washington 99352

CHPRC-00067-FP
Revision 0

An Innovative Approach for Constructing an In-Situ Barrier for Strontium-90 at the Hanford Site, Washington

K. M. Thompson
Department of Energy - Richland Operations Office

R. J. Fabre
Fluor Hanford, Inc.

V. R. Vermeul
J. E. Szecsody
R. J. Fellows
M. D. Williams
J. S. Fruchter
Pacific Northwest National Laboratory

Date Published
December 2008

To Be Presented at
Waste Management Conference 2009

WM Symposia, Inc.
Phoenix, AZ

March 1-5, 2009

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-08RL14788

CH2MHILL
Plateau Remediation Company

P.O. Box 1600
Richland, Washington

J. D. Aardal 12/08/2008
Release Approval Date

Approved for Public Release;
Further Dissemination Unlimited

LEGAL DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This document is available to the U.S. Department of Energy and its contractors, in paper from the Office of Scientific and Technical Information (OSTI). It is available for sale to the public from the National Technical Information Service (NTIS).

This report has been reproduced from the best available copy. Available in paper copy.

Printed in the United States of America

An Innovative Approach for Constructing an In-Situ Barrier for Strontium-90 at the Hanford Site, Washington - 9325

K.M. Thompson
U.S. Department of Energy, Richland Operations Office
P.O. Box 550, Richland, WA 99352

R. J. Fabre
Fluor Hanford Incorporated,
P.O. Box 1000, Richland, WA 99352

V.R. Vermeul, J.E. Szecsody, R.J. Fellows, M.D. Williams and J.S. Fruchter
Pacific Northwest National Laboratory
P.O. Box 999, Richland, WA 99354

ABSTRACT

Efforts to reduce the flux of Sr-90 to the Columbia River from Hanford Site 100-N Area past-practice liquid waste disposal sites have been underway since the early 1990s. Termination of all liquid discharges to the ground in 1993 was a major step toward meeting this goal. However, Sr-90 adsorbed on aquifer solids beneath liquid waste disposal sites and extending beneath the near-shore riverbed remains a continuing contaminant source to groundwater and the Columbia River. The initial pump-and-treat system proved to be ineffective as a long-term solution because of the geochemical characteristics of Sr-90. Following an evaluation of potential Sr-90 treatment technologies and their applicability under 100-NR-2 Operable Unit hydrogeologic conditions, the U.S. Department of Energy and the Washington State Department of Ecology agreed to evaluate apatite sequestration as the primary remedial technology, combined with a secondary polishing step utilizing phytoextraction if necessary. Aqueous injection was initiated in July 2005 to assess the efficacy of in-situ apatite along the 100 m of shoreline where Sr-90 concentrations are highest. The remedial technology is being developed by Pacific Northwest National Laboratory. CH2M Hill Plateau Remediation Company is implementing this technology in the field with support from PNNL.

INTRODUCTION

Strontium-90 discharge from former liquid waste disposal sites at the 100-N Area, located at the Hanford Site in Richland, Washington, has resulted in Sr-90 release to groundwater, the Columbia River, and biota along the river bank. Efforts to reduce the flux of Sr-90 to the Columbia River from the 100-N Area past-practice liquid waste disposal sites have been underway since the early 1990s. Termination of all liquid discharges to the ground in 1993 was a major step toward meeting this goal. However, Sr-90 adsorbed on aquifer solids beneath liquid waste disposal sites and extending beneath the near-shore riverbed remains a continuing contaminant source to groundwater and the Columbia River. The initial pump-and-treat system used proved to be ineffective as a long-term solution because of the geochemical characteristics of Sr-90. Following an evaluation of potential Sr-90 treatment technologies and their applicability under 100-NR-2 Operable Unit hydrogeologic conditions, the U.S. Department of

Energy and the Washington State Department of Ecology agreed to evaluate apatite sequestration as the primary remedial technology, combined with a secondary polishing step using phytoextraction if necessary. Apatite $[Ca_6(PO_4)_{10}(OH)_2]$ is emplaced in vadose and saturated zones by the infiltration and injection of a Ca-citrate-PO4 solution (Fig. 1).

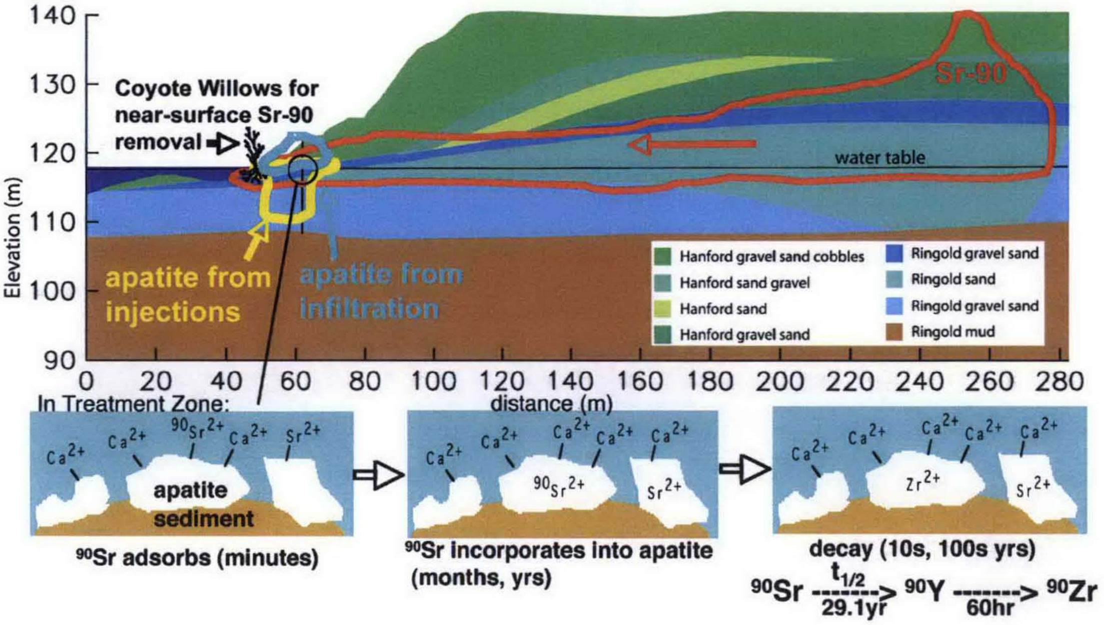

Fig. 1. Conceptual cross section of the Hanford Site 100-N Area Sr-90 contamination spread (red) in Hanford and Ringold Formations, and zone of apatite emplacement by well injection (yellow) and infiltration (light blue). Coyote willow placement also shown.

Upon biodegradation of the citrate in the solution, the slow release of calcium from the Ca-citrate complex results in the formation of apatite. Strontium-90 first adsorbs on and is then incorporated into the precipitated apatite over time [1, 2]. Laboratory studies were conducted to develop both an injection and infiltration strategy to result in apatite precipitate in Sr-90 contaminated zones. Aqueous injection was initiated in July 2005 to assess the efficacy of in-situ apatite along the 100 m of shoreline where Sr-90 concentrations are highest. The remedial technology is being developed by Pacific Northwest National Laboratory (PNNL). The CH2M Hill Plateau Remediation Company (CHPRC) is performing the field implementation with support from PNNL.

In addition to apatite emplacement, phytoextraction is being tested as a polishing step for the sediment along the 100-N Area shoreline (Fig. 1). The proposed technology is based on the use of a native phreatophytic plant species, Coyote willow (*Salix exigua*), to extract Sr-90 from the vadose zone soil and aquifer sediments (phytoextraction) and filter Sr-90 (rhizofiltration) from the shallow groundwater along the riparian zone of the Columbia River. Strontium can act as a nutritional analog for calcium, which can account for 0.1 to > 5.0% of a plant's dry weight.

To date, low- and high-concentration Ca-citrate-PO4 solution has been injected in 16 wells in the 100-N Area at the Hanford Site. Aqueous monitoring, as well as sediment coring, has been conducted to evaluate the performance of the injections. Large laboratory experiments have been used to develop the Ca-citrate-PO4 solution infiltration and field-scale experiments have been conducted to evaluate Coyote willow phytoextraction. Design of the integration of these three treatments in the zone that has the highest Sr-90 contamination at the 100-N Area river shoreline is currently in progress.

BACKGROUND

Strontium-90 Contamination in the 100-N Area, Hanford Site

Stronitium-90 is found primarily adsorbed to sediments by ion exchange (99% adsorbed, <1% in groundwater) in the upper portion of the unconfined aquifer and lower vadose zone (Fig. 1). Although primarily adsorbed, significant Sr-90 can be easily mobilized by seasonal river stage increases, and by plumes of higher-ionic strength groundwater so it is still considered a high mobility risk. The lower part of the unconfined aquifer in the 100-N Area consists of Ringold Formation sandy gravel, which is overlain by more permeable (approximately 3x) Hanford formation sandy gravel (Fig. 1). A series of 10 wells screened in both formations along a 100-m-long section of shoreline have received injections of a Ca-citrate-PO4 solution to treat Sr-90 primarily in the water-saturated Ringold Formation sediments. An additional six wells are screened in the underlying Ringold Formation to increase injection efficiency.

EXPERIMENTAL METHODS

Ca-citrate-PO4 Solution Reactivity with Sediments

The viability of using Ca-citrate-PO4 solutions to form apatite in situ in water-saturated zones has been demonstrated through previous research and field demonstration [3, 4, 5]. This remediation technology relies upon the Ca-citrate-PO4 solution forming apatite precipitate [$Ca_6(PO_4)_{10}(OH)_2$], which incorporates some Sr-90 during initial precipitation and additionally slowly incorporates Sr-90 by solid phase substitution for calcium. Strontium substitution occurs because strontium-apatite is thermodynamically more stable than calcium-apatite. After the Sr-90 is in the apatite structure, Sr-90 will decay to Y-90 (29.1 yr half-life) and then Zr-90 (64.1 hr half-life) without the potential for migration into the Columbia River. Injection of a Ca-citrate-PO4 solution into saturated sediment results in biodegradation of the citrate within a few days in both oxic and anoxic environments. The degradation produces low-molecular weight organic acids (acetate and formate) and finally CO_2 [2, 4]. Upon citrate biodegradation, the slow release of calcium from the calcium-citrate complex results in the formation of apatite. Some Sr-90 in the injection zone (30% to 70%) is incorporated into apatite during the initial precipitation phase (i.e., within days), although the majority of Sr-90 incorporation is from the adsorption of Sr-90 onto the apatite surface, followed by slow solid-phase substitution of strontium for calcium in the apatite structure [6, 7]. Two factors that control the viability of this technology in a specific field site are as follows: a) sufficient apatite needs to be emplaced to incorporate strontium and Sr-90 for 300 years (approximately10 half-lives of Sr-90 decay); and b) the rate of incorporation needs to exceed the natural groundwater strontium flux [4].

Because injection of the Ca-citrate-PO4 solution (or any solution of higher-ionic strength than groundwater) into the subsurface does result in some desorption of Sr-90, an injection strategy was developed to inject sufficient PO4 to sequester Sr-90 for 300 years while minimizing the initial Sr-90 desorption. This strategy is to inject a low concentration solution (10 mM PO4), which results in an initial < 5% desorption of Sr-90, but also sufficient apatite mass to sequester 50% to 70% of the Sr-90 in the injected zone after 6 months. Then, a high concentration solution (40 mM to 60 mM PO4) can be injected and because significant Sr-90 mass is already incorporated into apatite in the injection zone, there is less initial Sr-90 desorption. In addition to this sequential low- then high-concentration injection strategy, the composition of the injection solution was modified to minimize the initial strontium desorption. Initially, the composition of the injection solution contained a stoichiometric ratio of calcium to PO4 to form apatite (i.e., 4 mM calcium, 10 mM citrate, and 2.4 mM PO4 [5]. The citrate is needed in excess (2.5x at pH 7.5) to complex the injected calcium. Because Hanford Site subsurface sediments contain significant calcium (77% of ion exchange sites are calcium) and the water is Ca-CO3 saturated, the final injection formulation (1 mM calcium, 2.5 mM citrate, 10 mM PO4) was calcium-poor to utilize calcium (and Sr-90) desorbing from sediments.

Ca-Citrate-PO4 Solution Field Injection Strategy

The objectives of the field treatability testing are to address the following: a) will apatite precipitate in the target zone; b) does the apatite result in reducing Sr-90 in groundwater; and c) given a fixed well spacing of 10 m, what is the optimal injection volume per well for installation of a 100-m barrier wall.

Two pilot test sites at the east and west ends of the barrier, which are equipped with extensive monitoring well networks, were used for the initial injections to develop the injection design for the remaining portions of the barrier. Based on a comparison of hydraulic and transport response data at the two pilot test sites, it was determined that the apparent permeability contrast between the Hanford and Ringold Formations was significantly less over the upstream portion of the barrier, allowing for treatment of the entire Hanford/Ringold screened interval with a single injection operation at high-river stage. Because of a larger contrast over the downstream portion of the barrier, wells screened only across the contaminated portion of the Ringold Formation will be installed prior to future injections to provide for better treatment efficiency and coverage. Analysis of the operational and early monitoring results of the pilot tests were used to modify the injection solution composition, injection volumes, and operational parameters. A tracer injection test and the first pilot-scale apatite injection test were conducted at the upstream end of the barrier in spring 2006 during high-river stage conditions. A second pilot-scale test was conducted at the downstream end of the barrier in September 2006 during low-river stage conditions.

Design specifications for the barrier installation are that the chemical concentrations should be at least 50% of injection concentration 6 m from each injection well. This is considered a sufficient radial extent of treatment to provide overlap of treatment between injection wells. While monitoring points were not installed between injection wells outside the pilot test sites, monitoring was conducted in adjacent injection wells during treatment operations. Because no monitoring wells were available at a 6-m radial distance to assess the extent of treatment, arrival data from adjacent injection wells (9 m spacing) were used as an indicator. To account for the increase in radial distance to this monitoring point, the phosphate concentration metric for arrival at adjacent injection wells was reduced 20% to 30% of the injection concentration (from 50% at a 6-m distance).

The river stage during the barrier injection was an important parameter in the depth interval treated and the efficiency of treatment. River stage along this section of the Columbia River is controlled by the rate of discharge at Priest Rapids Dam, located approximately 30 km upstream of the 100-N Area. Initially, it was hypothesized that conducting injections during low-river stage would provide treatment of the Ringold Formation, while injections during high-river stage would allow for targeting Hanford formation treatment.

Evaluation of Field Injections

Short-term (days to months) increases in strontium and Sr-90 were expected during the low concentration Ca-citrate-phosphate field injection tests, which were designed based on bench-scale laboratory studies with the low concentration formulation and sediments from the 100-N Area. The observed increases in Sr-90 concentration are a result of the higher ionic strength of the solution and increases in calcium concentration resulting from this process. Concentrations are expected to decline over time (months, years) as Sr-90 is incorporated through initial precipitation and adsorption/slow incorporation into the apatite, and as the reagent plume dissipates. Elevated Sr-90 concentrations are monitored with specific conductance values to correlate the elevated Sr-90 concentrations with residual high-ionic strength injection solutions. Compliance monitoring wells and river tubes are located outside the primary treatment zone, and therefore are expected to take additional time for Sr-90 concentrations to decline to treatment zone levels.

Given the strong Sr-90 adsorption to sediment (aqueous fraction is approximately 1%), Sr-90 extraction from sediment cores was also used to evaluate Ca-citrate-PO4 injection performance. The performance assessment approach used in this study is based on measurements of a) ion exchangeable Sr-90; b) acid-extractable Sr-90; and c) acid-extractable PO_4 from field-treated sediment samples. Samples were taken at 30-cm intervals (3 to 8 m, 120 samples) in spring 2008 when six additional wells were installed in the Ringold Formation. The Sr-90 in sediment (pretreatment) averages 86.7% ion exchangeable, with the balance of Sr-90 aqueous or held in other phases such as carbonates. Ion-exchangeable extractions post-treatment were expected to decrease over time as Sr-90 is incorporated into apatite. The fraction of Sr-90 held by ion exchange in each core (using acid-extractable Sr-90 as the total Sr-90 for that core) is needed, as there is considerable spatial variability of the Sr-90 contamination.

Ca-citrate-PO4 Solution Laboratory Infiltration Studies

Laboratory studies were initiated to develop an efficient means to emplace apatite in vadose zone sediments in the Hanford Site 100-N Area due to the significant amount of Sr-90 mass in these unsaturated sediments. Earlier studies demonstrated that infiltration of the Ca-citrate-PO_4 solution into unsaturated sediment does result in citrate biodegradation and formation of apatite [8]. In addition, some Sr-90 is incorporated into apatite during initial precipitation and additional Sr-90 is slowly incorporated into apatite (half-life 5.5 to 16 months). Current studies use 2-D infiltration systems from 0.5 m to 2.4 m in height for the purpose of quantifying how to emplace apatite precipitate at specific depth ranges. Of the approximately 5 m of the vadose zone in the 100-N Area, Sr-90 contamination is generally located in the lower half (Fig. 2). In addition, it is hypothesized that higher Sr-90 concentrations are in low-K discontinuous lenses due to higher residual water content. Therefore, these infiltration studies are focused on optimizing the infiltration rate and solution concentration to result in most of apatite to precipitate in the lower half of the unsaturated system and within low-K lenses.

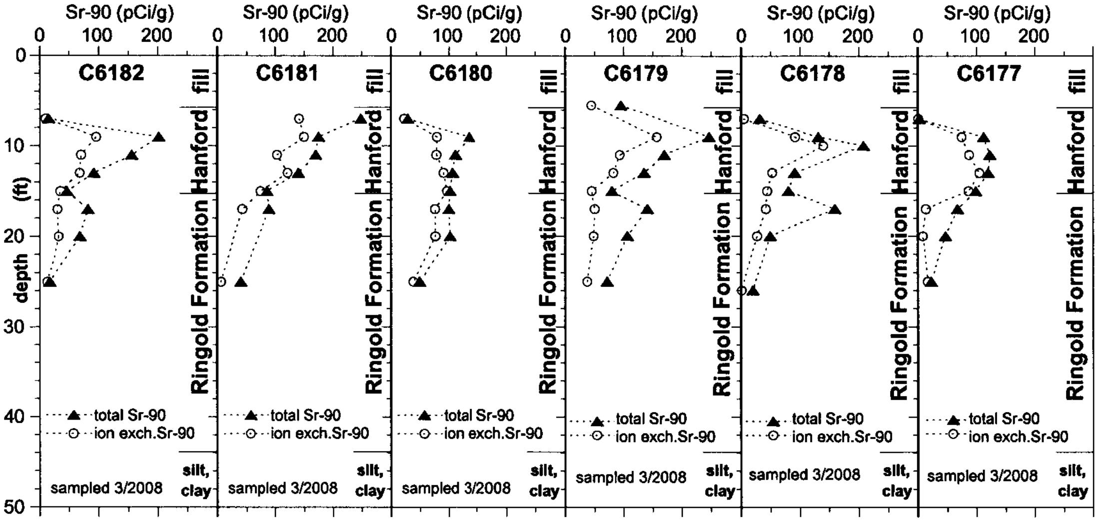

Fig. 2. Total and ion exchangeable Sr-90 (pCi/g) in sediments after low-concentration Ca-citrate-PO4 injections. Well locations are in Figure 3a.

Phytoextraction of Sr-90 with Coyote Willows (*Salix exigua*)

Phytoremediation/phytoextraction is a managed, remediation technology in which plants or integrated plant/rhizosphere systems are employed to extract and/or sequester soil contaminants [9]. The system is a polishing step directed at extracting Sr-90 from the vadose and saturated zone associated with the Columbia River riparian zone. Strontium is a nutritional analogue of calcium in plants and is assimilated by plant roots at the same rate. The phytoextraction rate (plant accumulation) of Sr-90 is directly related to the ratio of soil porewater (calcium/strontium) encountered by the roots [10]. A field treatability study employing a native phreatophyte species was initiated in March 2007 along the Columbia River shoreline at 100-K West at the Hanford Site. Sixty Coyote willow trees were planted in an enclosed compound to assess the growth (biomass increase) of the plants under Hanford Site conditions.

RESULTS AND DISCUSSION

Low Concentration Ca-citrate-PO4 Solution Injection

The Hanford Site 100-N Area injections in the 10 barrier wells screened in the Hanford and Ringold Formations (Fig. 3a) were conducted during two phases–the first in February to March 2007, which was supposed to target low-river stage conditions but resulted in both low- and high-river stage conditions, and a second phase in June to July 2007 during high-river stage conditions.

Injection of the Ca-citrate-PO4 solution showed nearly unretarded movement of the citrate, a peak for calcium due to ion exchange, and retarded movement of phosphate (Fig. 4, at a radial distance of 3 m from the injection well). Within 5 days of the injection, citrate was biodegraded as evidenced by decreasing citrate concentration and increasing formate (degradation intermediate) concentration. As citrate is biodegraded, Ca^{2+} is no longer held in solution, and precipitates with phosphate as apatite (at this near-neutral pH range of 7.3 to 8.3).

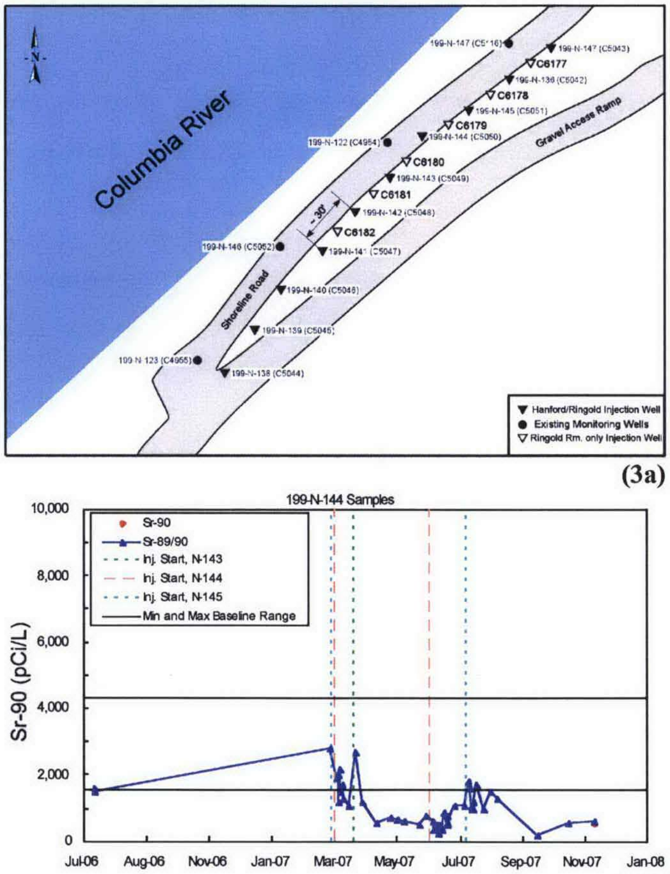

Fig. 3. Injection well location (a) and (b) Sr-90 monitoring data for well N144 after low concentration injections.

For the upstream portion of the barrier, the contrast between permeability in the Hanford and Ringold formations was sufficiently small that injections at high-river stage alone were successful in treating both the Hanford and Ringold Formation. However, for the downstream portion of the barrier, multiple injections did not provide complete treatment. High-river stage conditions provided a hydraulic barrier that contained the injection solution in the Hanford formation, allowing adequate treatment [5]. Unfortunately, it appeared that injections conducted during low-river stage were of limited success in providing adequate extent of treatment in the Ringold Formation. The large contrast in permeability between the Hanford and Ringold Formations along the downstream portion of the barrier resulted in the loss of a significant portion of the injection volume to the relatively thin saturated Hanford formation interval, associated shoreline seeps, and limited treatment of the Ringold Formation.

Based on this injection performance metric, phosphate concentrations measured in adjacent fully screened injection wells indicated generally satisfactory treatment. However, data from available Ringold Formation monitoring wells indicated treatment of the Ringold Formation over the downstream portion of the barrier (where Hanford/Ringold permeability contrast is larger) was not as effective.

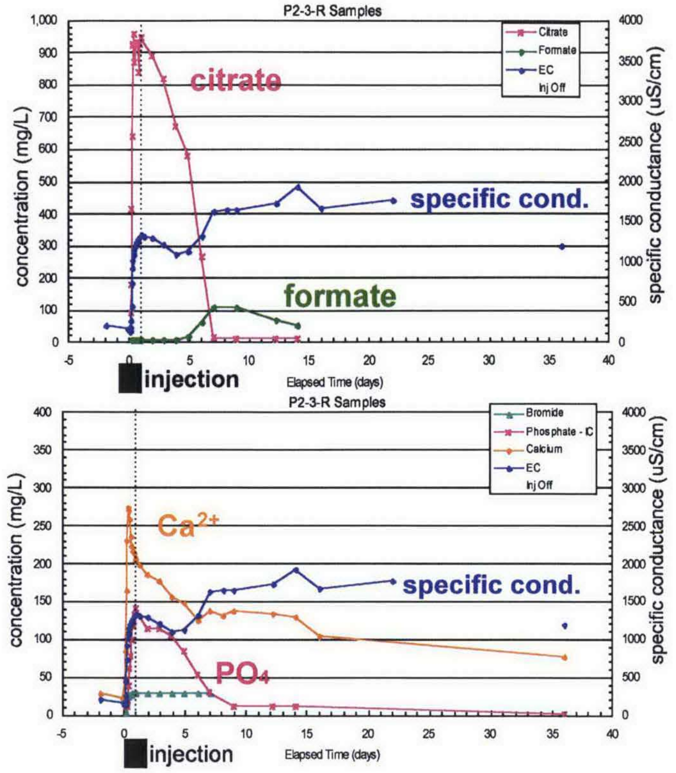

Fig. 4. Injection monitoring data for well P2-3R during second pilot test.

Strontium-90 concentrations in monitoring wells at the first pilot test site, conducted in spring 2006, showed an average increase in peak Sr-90 concentrations of 8.4 times the average baseline measurements at the site measured earlier in the year. Based on these results and additional laboratory measurements, the Ca-citrate-phosphate injection concentrations were revised with lower calcium and citrate concentrations (2.5 times) for the second pilot test, which was conducted in fall 2006. Average peak Sr-90 concentrations following the second pilot test injection were lower than the first pilot test, at 3.8 times the average baseline Sr-90 concentrations from wells at the site while still forming the same mass of apatite. The injection formulation was revised again following the second pilot test with further decreases in calcium and citrate concentrations and an approximate 4 times increase in the phosphate concentration to maximize the apatite precipitate mass and minimize the initial Sr-90 increase.

Longer-term, post-treatment Sr-90 concentrations at most injection well locations showed that levels were maintained near or below the low end of the estimated range in baseline Sr-90 concentration, indicating that the low concentration treatments likely did have an impact on aqueous Sr-90 concentrations within the treatment zone. For one well (N-144, Fig. 3b), Sr-90 concentrations increase somewhat during solution injections in adjacent wells (vertical dashed lines), but within baseline concentration range (horizontal black lines). Months after the injections, Sr-90 concentrations have decreased to below baseline concentrations.

Additional monitoring that encompasses the full extent of seasonal variability in Columbia River stages would be required to fully assess the effectiveness of the low concentration treatments. Longer-term, post-treatment Sr-90 concentrations in the compliance monitoring wells and river tubes have in general remained high relative to baseline ranges, although values had started to drop by the end of the monitoring period. Elevated Sr-90 concentrations were well correlated with elevated specific conductance values, indicating that the elevated Sr-90 concentrations are likely associated with impacts from residual high-ionic strength injection solutions. Compliance monitoring wells and river tubes are located outside the primary treatment zone and thus are expected to take additional time for Sr-90 concentrations to decline to treatment zone levels.

Evaluating Change in Sr-90 Mobility with Analysis of Cores

Phosphate extractions of 55 samples taken at 3 to 8 m depths in six cores clearly showed evidence of the phosphate injections, with PO_4 (in mg PO_4/g sediment) averaging 0.102 ± 0.133 mg/g over the entire depth. The cores in the Hanford formation averaged 0.150 mg/g and in the Ringold Formation averaged 0.041 mg/g (Table I), and generally decreased with depth. Phosphate profiles with depth in all 6 wells (55 points) clearly showed a much greater proportion of treatment in the Hanford formation, likely due to the larger injection volumes that would be proportioned to this higher permeability formation during treatment in the fully screened wells.

Table I. Depth Average PO_4 in 100-N Area Sediments in March 2008 After Low Concentration Injections

Depth (Ft)	Formation	Sample Date	PO_4 (mg/g)
4-6	Fill	3-2008	0.000
7-9	Hanford	3-2008	0.134 ± 0.156
10-12	Hanford	3-2008	0.136 ± 0.122
13-15	Hanford	3-2008	0.179 ± 0.158
16-18	Ringold	3-2008	0.059 ± 0.092
19-21	Ringold	3-2008	0.030 ± 0.034
21-26	Ringold	3-2008	0.033 ± 0.093

Barrier injection operations completed by spring 2008 using the low concentration formulation (10 mM PO_4) were designed to emplace 0.136 mg PO_4/g sediment, or 0.34 mg apatite/g of sediment. Therefore, PO_4 extraction data from post-treatment core samples indicates that, at a radial distance of approximately 5 m from adjacent injection wells, the Hanford formation received an average treatment of 110% and the Ringold Formation an average treatment of 30% of the targeted apatite content.

Aqueous monitoring during the low concentrations injections in the downstream portion of the barrier showed insufficient treatment was occurring in the Ringold Formation due to the large contrast in hydraulic conductivity between the Hanford and Ringold Formations in the area. The contrast was lower in the upstream portion of the barrier. The Ringold-only injection wells were installed in early 2008 on the downstream portion of the barrier to correct this problem for use in the high concentration injections. For all boreholes, the total Sr-90 averaged 105 ± 68 pCi/g in the Hanford formation (n = 55), 55.4 ± 44.7 pCi/g in the Ringold Formation (n = 44), and 23.7 ± 26 pCi/g in the fill.

The average depth of the highest Sr-90 concentration in each well was 3 to 4 m depth (Fig. 2). The new well data are consistent with Sr-90 distributions along the barrier length, as indicated by monitoring well and aquifer tube data and tissue concentrations in clams. The fraction Sr-90 that was ion exchangeable (of total Sr-90 in the sediment) in the treatment zone (i.e., field treatment with 10 mM PO_4) averaged 61.2 ± 22.4%. Untreated sediments from the 4-m depth of well N-122 showed 86.7% ion exchangeable Sr-90 (2005 results). Thus, the current results indicate about 25% of the Sr-90 mass (i.e., 86.7% ion exchangeable pretreatment minus 61.2% ion exchangeable post low-concentration treatment) in the 100-N Area sediment may have been incorporated into apatite and is not slowly migrating in groundwater.

The total Sr-90 vertical profiles in three of six of the Ringold-only wells (Fig. 2) show two Sr-90 peaks, which correspond to peaks in the Hanford and Ringold Formations. Because the unconfined aquifer water table averages 15-m depth (generally in the Ringold Formation), groundwater advection of Sr-90 may account for this second, deeper Sr-90 peak.

High Concentration Ca-citrate-PO4 Solution Injection

A high concentration Ca-citrate-PO_4 solution (3.6 mM calcium, 9.0 mM citrate, and 40 mM PO4) was injected into 14 Hanford and Ringold Formation wells (Fig. 3a) and 6 Ringold-only wells in the July to August 2008 time frame. Short-term Sr-90 concentrations increased as expected, as much as 10x above baseline concentrations, which was significantly less than would be expected without the previous low concentration injections. The long-term evaluation of the performance of the effect of this PO_4 injection is still in progress. To date, Sr-90 values in injection wells are below baseline concentrations, and downgradient monitoring wells still show elevated Sr-90 concentrations due to the presence of the injection solution, which is slowly migrating out of the aquifer.

Ca-citrate-PO4 Solution Infiltration

Infiltration experiments conducted in small-to-large laboratory systems quantified processes and process interactions that were needed to develop an infiltration strategy to be used in the current pilot scale infiltration study. Apatite forms under unsaturated water conditions, and the spatial distribution is controlled by the following: a) phosphate adsorption rate (hours); b) citrate biodegradation rate (10's of hours), and the infiltration rate (variable). The most efficient method to emplace apatite precipitate at depth is to promote rapid infiltration to exceed the biodegradation half-life (50 to 150 hr). This effect of apatite precipitate with depth as a function of the infiltration rate and solution concentration was developed in a series of 30 2-D laboratory infiltration experiments. Varying only the infiltration rate from very slow (Fig. 5a, 430 hr to reach 50-cm depth) to rapid (Fig. 5c, 1 hr to reach 50-cm depth) shows that there is greater precipitate at depth due to the solution not being biodegraded over the short contact time, and phosphate sorption being minimized to some extent. In these experiments, the Ca-citrate-PO_4 solution is being infiltrated in the upper-left corner of the 2-D system. For the very slow infiltration rate (Fig. 5a), citrate biodegradation is occurring very near the infiltration point. While rapid infiltration results in the solution penetration to depth, there is insufficient time for lateral spread of the solution due to capillary forces (Fig. 5c).