

## **Infiltration and Injection of a Ca-Citrate-PO<sub>4</sub> Solution to Form Apatite InSitu for Sr-90 Remediation at the Hanford 100N Area – An Update**

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### **ABSTRACT**

Sr-90 present in groundwater and the vadose zone at the Hanford 100N area due to past waste disposal practices has reached the nearby Columbia River, as evidenced by Sr-90 concentrations in near river wells and aquifer tubes and near shore sediments. Sr-90 is currently being remediated by adsorption onto apatite, followed by incorporation of the Sr-90 into the apatite structure. If the Sr-90 can remain immobilized for 300 years (~ten 29.1-yr half-lives of Sr-90 decay), it will have decayed below regulatory limits to Y-90 and to stable Zr-90. Apatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] is being precipitated in situ into saturated zone sediments by injection of an aqueous solution of Ca-citrate and Na-phosphate through a series of 16 wells. In the vadose zone, solution infiltration was evaluated in 2-D laboratory experiments and solution high pressure jetting was evaluated in a small field scale test. For the treatability study, field scale demonstration of the technology was implemented through injection of a low-concentration, apatite-forming solution, followed by high concentration solution injections as required to emplace sufficient treatment capacity to meet treatability test objectives. Analysis of field cores collected after the high concentration injections indicates that targeted apatite contents were achieved and that 40% of the Sr-90 was incorporated in the apatite structure, 50% is adsorbed to the apatite surface, and 10% is adsorbed to sediment minerals. Because Sr-90 adsorption to apatite is 55 times stronger than Sr-90 adsorption to sediment, the fraction of mobile Sr-90 has decreased by ~90%. Field aqueous Sr-90 monitoring in four compliance monitoring wells over a year following the high concentration injections indicates 84% to 95% decrease in Sr-90 concentrations (relative to the low and high end of the baseline range, respectively), which is consistent with the core results.

### **INTRODUCTION**

**Sr-90 Contamination in Near River Sediments.** Sr-90 present in groundwater and the vadose zone at the Hanford 100N area due to past waste disposal practices has reached the nearby Columbia River, as evidenced by Sr-90 in the river and near shore sediments. Two crib and trench liquid waste disposal facilities (LWDFs) were constructed to receive these waste streams, and disposal consisted of percolation into the soil. The first LWDF (1301-N, Figure 1a) was constructed in 1963, about 244 meters (800 feet) from the river. Liquid discharges to this facility contained radioactive fission and activation products, including cobalt-60, cesium-137, strontium-90, and tritium. When Sr-90 was detected at the shoreline, disposal at the first LWDF was terminated and a second crib and trench (1325N LWDF) was constructed further inland in 1983. Discharges to 1325-N ceased in 1993.

The Sr-90 contamination distribution in sediments reflects the hydrodynamics in the 100-N Area. Sr-90 has leached from surface disposal trenches through the variable thickness vadose zone to groundwater and moved toward the Columbia River. Due to diurnal and seasonal changes (2 – 3 meters) in river stage associated with dam operations, the saturated zone thickness changes and flow reversals do occur (i.e., movement of river water into the aquifer). The result on Sr-90 is a smearing of the plume vertically and horizontally. The unconfined aquifer in this portion of the 100-N Area are comprised of sediments (gravel with sand/silt) of the Ringold unit E and overlying Hanford formation (15- to 20-ft contact depth). The Hanford formation is generally more conductive (Ksat 12 to 29 m/day) compared to the underlying Ringold unit E (9 to 10 m/day). The Ringold E unit is bounded by the underlying silty Ringold upper mud, which acts as an aquitard. Groundwater flows primarily in a north-northwesterly direction most of the year and discharges to the Columbia River. The groundwater gradient varies from 0.0005 to



Figure 1. Hanford, Wa 100N area: a) picture of disposal trench, and b) map of remediation wells.

0.003 ft/ft. Near the LWDF facilities, average groundwater velocities are estimated to be between 0.1 and 2 ft/day, with 1 ft/day average.

**Apatite Remediation of Sr-90.** Sr-90 is currently being remediated by adsorption onto apatite (55 times stronger than Sr-90 adsorption to sediment), followed by incorporation of the Sr-90 into the apatite structure. Because of strong Sr-90 adsorption by ion exchange to sediments (retardation factor ~125), about 1% of the Sr-90 is in groundwater and 99% on sediments. If the Sr-90 can remain immobilized for 300 years (~ten 29.1 yr half-lives of Sr-90 decay), it will have decayed to Y-90 and to stable Zr-90. Apatite minerals sequester elements into their molecular structures via isomorphous substitution, whereby elements of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the hexagonal crystal structure [1]. Apatite has been used for remediation of other metals including U [2], lead [3], Pu [4], and Np [5].

Apatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] is being precipitated in situ in the saturated zone by injection of a aqueous solution of Ca-citrate and Na-phosphate [6] through a series of 16 injection wells screened in the Ringold and Hanford formations (Figure 1b). Laboratory experiments have also demonstrated that infiltration of the Ca-citrate and Na-phosphate solution will precipitate apatite in unsaturated sediments [7], and a small field demonstrate site is currently being set up to evaluate the technology. Although laboratory experiments have demonstrated that Sr-90 is slowly incorporated into apatite over time, field cores taken after low-concentration and high-concentration injections are being used in this study to evaluate the mass of apatite precipitate, and the distribution of Sr-90 adsorbed on the sediment, adsorbed on apatite, and incorporated in the apatite structure.

Development of the final injection approach for full-scale deployment of the apatite permeable reactive barrier technology will consider the following design criteria: 1) emplacement of sufficient apatite to meet long-term remedial objectives, 2) limit permeability reduction by emplacing only the apatite content needed to meet remedial objectives, 3) limit short-term increases in  $^{90}\text{Sr}$  concentration associated with the injection of high ionic strength solutions, and 4) implementation cost.

#### **FIELD INJECTIONS AND LABORATORY ANALYSIS**

**Apatite Mass Needed for Sr-90 Remediation.** Two factors control the amount of apatite needed to sequester  $^{90}\text{Sr}$  in the Hanford 100-N Area. First, from a mass balance standpoint, a specific amount of apatite is needed that will remove all strontium and  $^{90}\text{Sr}$  from groundwater over the next 300 years (i.e., 10 half lives of  $^{90}\text{Sr}$  decay, half-life 29.1 years). This calculation is dependent on the crystal substitution of strontium for calcium in apatite. If 10% substitution is assumed, then 1.7 mg of apatite is sufficient to sequester strontium and  $^{90}\text{Sr}$  from the estimated 3300 pore volumes of water that will flow through an apatite-laden zone. This calculation assumes an average groundwater flow rate of 0.3 m/day (1 ft/day) and a 10-m (32-ft) apatite PRB thickness. The second factor that controls the amount of apatite needed to sequester  $^{90}\text{Sr}$  is the rate of incorporation. This permeable reactive barrier concept, which relies on emplacement of apatite solids in the aquifer, is viable only if the natural groundwater flux rate of strontium and  $^{90}\text{Sr}$  ( $1.36 \times 10^{-6}$  mmol strontium/day/cm<sup>2</sup>) is slower than the removal rate of strontium and  $^{90}\text{Sr}$  by apatite. If the groundwater flow rate is too high, even highly sorbing Sr and  $^{90}\text{Sr}$  could advect through the apatite-laden zone more quickly than it is removed. One way to mitigate these impacts would be to emplace excess apatite in the treatment zone (i.e., greater than the amount needed based on the mass balance calculation above), which will result in removal of  $^{90}\text{Sr}$  at an increased rate.

**Injection Strategy to Minimize Initial Sr-90 Mobilization.** A number of different injection strategies were previously evaluated [8, 9] for providing sufficient apatite formation while minimizing initial Sr-90 mobilization. These included: 1) sequential injection of low then high concentration Ca-citrate- $\text{PO}_4$  and 2) injection of a Ca-poor formulation of Ca-citrate- $\text{PO}_4$  solution. Sequential injection of a low concentration solution precipitates a small apatite concentration, which incorporates most of the Sr-90 in the injection zone. After sufficient time (~year), a subsequent high concentration Ca-

citrate-PO<sub>4</sub> solution can then be injected to build up the apatite mass with significantly less Sr-90 mobilization.

The original calcium-citrate-phosphate amendment formulation was based on the stoichiometric ratio of Ca:PO<sub>4</sub> in apatite (5:3), and a Ca:citrate ratio of 1:2.5 to form the aqueous Ca-citrate complex [6, 10]. Therefore, the initial Ca-citrate-PO<sub>4</sub> formulation contained the ratios of 4 mM Ca, 10 mM citrate, and 2.4 mM PO<sub>4</sub>. Early laboratory experiments with this formulation (and higher concentrations) did successfully precipitate apatite, but left considerable excess Ca in solution because there is a significant quantity of adsorbed Ca<sup>2+</sup> on sediment minerals (by ion exchange) that exchanges off the surface during solution injection [8]. Injection of any calcium-poor (i.e., less Ca than the 5:3 ratio of Ca:PO<sub>4</sub>) will utilize some Ca<sup>2+</sup> from the sediment, as well as Sr and Sr-90, which chemically behave similarly to calcium. Overuse of calcium-poor Ca-citrate-PO<sub>4</sub> solutions would eventually deplete the sediment Ca<sup>2+</sup> content, and the phosphate would have to drift downgradient in the aquifer to a zone with some available calcium for precipitation to occur. The final low concentration apatite amendment formulation designed to minimize the initial <sup>90</sup>Sr peak was a Ca-citrate-PO<sub>4</sub> solution with a 1: 2.5:10 ratio [8], which is 75% depleted in the calcium needed to form apatite (i.e., 75% of the calcium used in apatite formation is desorbed from aquifer sediments).

The decrease in the short-term peak aqueous strontium concentrations, and concentrations at 30 days, was substantial as the formulation was changed from a Ca-citrate-PO<sub>4</sub> ratio of 4:10:2.4 to 1:2.5:10. With the original formulation (2.4 mM PO<sub>4</sub>, ionic strength 96 mM), the peak strontium concentration was 10x that of the initial groundwater concentration, and the strontium concentration did not decrease by 30 days. With the calcium-poor formulation at 4 times the amount of phosphate (10 mM PO<sub>4</sub>, ionic strength = 65 mM), the initial strontium peak aqueous concentration was 3.3 times that in groundwater, and by 30 days, this had decreased to 0.4 times that of groundwater.

**Field Injections for In Situ Precipitation of Apatite.** To emplace sufficient mass of apatite in the near river sediments in the Hanford 100N area, a series of injection wells were installed parallel to the river (Figure 1b). A sequential injection strategy was used in which a low concentration Ca-citrate-PO<sub>4</sub> solution (1 mM, 2.5mM, 10 mM) was initially injected, which was followed by a high concentration Ca-citrate-PO<sub>4</sub> solution (3.6 mM, 9 mM, 40 mM) injection approximately 1 year later. Low concentration injection volumes in 10 wells screened in both the Hanford and Ringold formations, were 60,000 gallons for each formation. All injection operations were conducted during high river stage conditions to treat as high in the Hanford formation as possible, as described in detail elsewhere [9]. High concentration injections were conducted in the 10 fully screened wells and in 6 addition wells screened only in the Ringold formation.

**Vadose Zone Treatment.** Depending on the river stage, some of the vadose zone sediments can be treated with water-saturated injections, although there is a short time window for this treatment because the river stage is generally high for only a short duration in the late spring. Two other methods for treating vadose zone sediments were considered: a) infiltration of the solution, b) high pressure injection of the solution into

unsaturated sediments. Solution infiltration was evaluated in small to large 2-D laboratory studies [7] and is will be tested at a small field scale site. High pressure solution injection was tested at a small field scale site, and core samples are being taken to evaluate the delivery of phosphate.

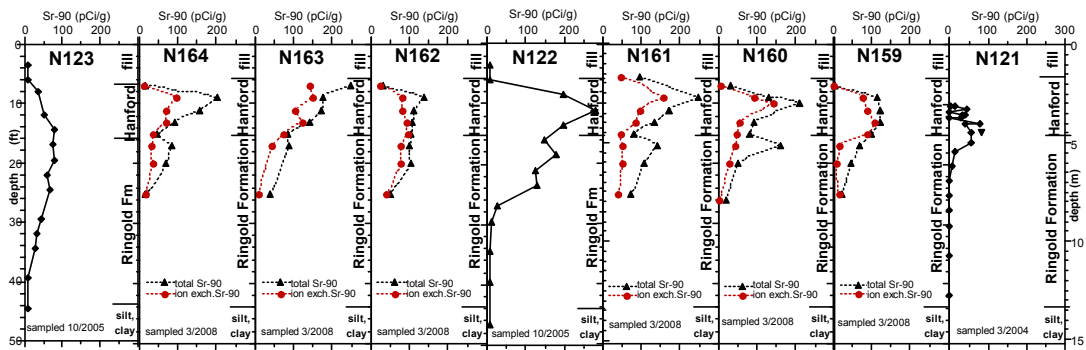
**Analysis of Field Cores.** Chemical extractions were conducted from sediments at selected depths in six wells drilled in March 2008 (i.e., post low-concentration injections) and in October 2009 (post high-concentration injections). Apatite was measured in the core samples by an acid extraction with 0.5M HNO<sub>3</sub> for 15 minutes, and aqueous analysis of the total phosphate. Experiments spiking untreated sediment with differing masses of apatite showed that this method to dissolve most (86%) of the apatite with a minimum of excess phosphate from sediment minerals. A series of sediment samples taken from 11 wells prior to any Ca-citrate-PO<sub>4</sub> injections were used to measure the background phosphate (i.e., phosphate dissolved by the acid extraction from natural sediment minerals [7]). Two additional chemical extractions were also conducted to measure the ion exchangeable Sr-90 (0.5M Mg(NO<sub>3</sub>)<sub>2</sub> extraction for 1 hour) and an acid extraction to dissolve the apatite to measure the Sr-90 incorporated into the apatite structure 0.5M HNO<sub>3</sub> for 15 minutes. Ion exchangeable and acid extraction of Sr-90 from subsurface sediments prior to any Ca-citrate-PO<sub>4</sub> injections [9, 11] show that ~90% of the Sr-90 is held on sediments by ion exchange, and is easily removed with the high ionic strength solution even after decades of contact time. The remaining 10% of the Sr-90 is hypothesized to be incorporated into carbonates. Electron microprobe analysis of laboratory and field sediments was used to identify crystalline apatite in the sediment [10], and fraction of Sr-90 substitution in the apatite crystals [7].

## RESULTS AND DISCUSSION

**Sr-90 Mass Distribution Prior to Injections.** With 99%+ of the Sr-90 adsorbed to sediments (primarily by ion exchange) and < 1% aqueous, the total Sr-90 in 100N sediment cores varied with depth and laterally (Table 1, Figure 2) due to infiltration of the Sr-90 from trenches, and redistribution over time from to groundwater flow and river stage change. Data from nine wells show highest Sr-90 concentration in the center wells and lower Sr-90 at west and east ends, which is consistent with groundwater monitoring results. The trend with depth shows the highest Sr-90 mass in the Hanford formation (Table 1). Because the water table varies, the mass of Sr-90 in this zone of water table fluctuation varies

**Table 1.** Total Sr-90 in sediments (pCi/g).

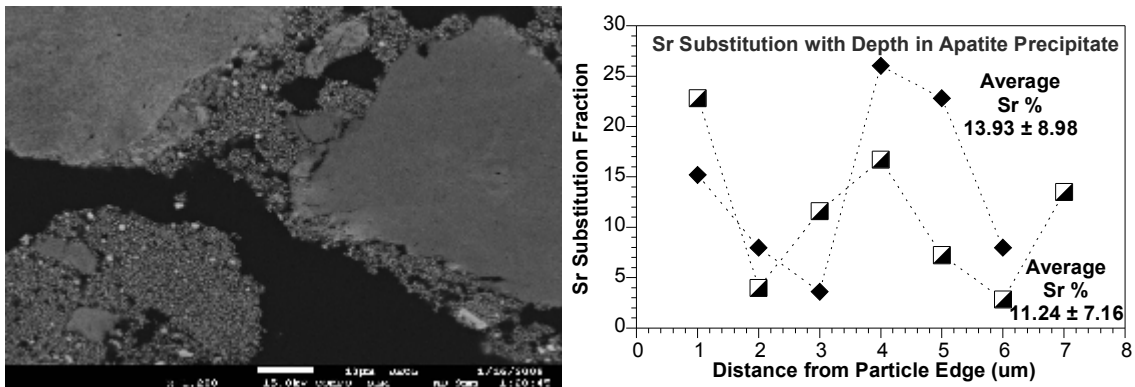
well	fill, 7' Sr-90 (pCi/g)	Hanford Fm Sr-90 range (pCi/g)	Ringold Fm Sr-90 range (pCi/g)	maximum Sr-90 (pCi/g)	depth (ft)
N-123	9.1	35.9 - 78.7	59.3 - 75.9	78.7	14.5
N-139	—	44.6 - 58.4	41.0	58.4	12
N-140	—	67.8	--	67.8	12
N-164	14.4	46.0 - 201.3	67.6 - 81.7	201.3	9
N-142	—	127.3	--	127.3	7-14*
N-163	—	85.2 - 248.6	39.6 - 88.5	248.6	7
N-143	—	169.0	--	169.0	14
N-162	29.6	88.6 - 135.4	46.9 - 101.6	135.4	9
N-122	8.7	196 - 280	6.0 - 179	280.0	11
N-144	—	63.0 - 87.1	42.3 - 65.0	87.1	12
N-161	95.0	79.1 - 246.7	71.2 - 140.4	246.7	9
N-160	31.4	79.6 - 207.8	19.5 - 159.2	207.8	10
N-136	—	229.0	--	229.0	12
N-159	1.85	97.7 - 122.1	22.1 - 66.9	122.1	11
N-121	—	0 - 79.7	0 - 55.9	79.7	13.25
mean:	23.7±26.0	104.9±68.1	55.4±47.7	*composite	
# points	11	55	44		



**Figure 2.** Total and ion exchangeable Sr-90 after low concentration injections.

from 30 to 70% (i.e., a significant mass is above the water table during a majority of the year). The maximum Sr-90 concentration is mainly located at the fill/Hanford formation interface (7-9' depth, Table 1), with a few deeper maximum values in the 15 boreholes. This could be caused by the water saturation during the operational period at 100-N Area, when discharge to the trenches was occurring, which was significantly higher than current conditions.

**Laboratory Measurement of Sr-90 Incorporation Into Apatite.** Electron microprobe analysis of the Sr substitution in apatite precipitate formed with the low concentration solution showed that after 1.3 years, there was 16.1% substitution of strontium for calcium in microcrystalline (20-40 micron particles composed of < 1 micron crystals) apatite, and 9.1% substitution of strontium for calcium in crystalline apatite (20-40 micron, single crystal [7]). An image of the microcrystalline apatite (Figure 3a, speckled) and crystalline apatite (solid grey) shows that both occur from Ca-citrate-PO<sub>4</sub> solution injection into sediment. At field scale, the emplaced apatite is expected to continue substitution of Sr for Ca for hundreds of years. It is possible that this high Sr substitution at short (<1 year) time scales would decrease if the morphology of the apatite precipitate varied with depth or diffusion is not controlling the substitution rate. The electron microprobe was used to confirm that the Sr substitution in apatite was diffusion controlled by measuring the Sr substitution with depth in single apatite crystals. For this



**Figure 3.** Electron microprobe picture of apatite precipitate (a), and Sr fraction substitution (b).

analysis, a Sr-substituted apatite from an experiment running for 1.3 years was used. The Sr substitution for Ca in two different conglomerate particles did not have a trend with depth from the edge of the particle (Figure 3b), indicating substitution was occurring throughout the presumed open structure. Therefore, with the mixture of crystalline and microcrystalline apatite the precipitation in sediment was microcrystalline, and the assumption of 10% Sr substitution for Ca in the apatite structure is achievable.

Emplacement of the 1.7-mg apatite/g of sediment required to meet remedial objections will occupy some pore space in the aquifer, which has an average field porosity of 20%. Given crystal lattice dimensions of 9.3 Å by 6.89 Å (assume a cylinder of dimensions  $7.5 \times 10^{-21} \text{ cm}^3/\text{atom}$ ), the 1.7 mg apatite/g sediment would occupy 13.6% of the pore space, so some degree of permeability decrease is expected.

**Sr-90 Mass and Apatite Distribution after Low Concentration Injections.** Phosphate concentration measured in the 100N sediment samples taken in March of 2008 at specific depths (7', 9', 11', 13', 15', 17', 20', 25') in six new wells (N159, N160, N161, N162, N163, N164, on Figure 1b). These wells are spaced 15 feet laterally from the fully screened injection wells, within the overlap zone between two adjacent wells. Assuming full concentration PO<sub>4</sub> overlap at these locations and a low concentration Ca-citrate-PO<sub>4</sub> formulation (10 mM PO<sub>4</sub>), an average 0.136 mg PO<sub>4</sub>/g sediment (0.34 mg apatite/g of sediment) would be expected to form. Therefore, at this 15 ft lateral distance, measured values were 75% of the design target, which indicates relatively good lateral coverage.

Phosphate extractions clearly showed evidence of the phosphate injections, with PO<sub>4</sub> (in mg PO<sub>4</sub>/g sediment, adjusted to account for pre-treatment PO<sub>4</sub> content based on analyses of pre-treatment sediment samples) averaging  $0.102 \pm 0.133 \text{ mg/g}$  over the entire depth (7 – 26 ft), or 0.150 mg/g in the Hanford Formation and 0.041 mg/g in the Ringold Formation [7, 12]. Phosphate profiles with depth in all six wells (55 points) clearly showed a much greater proportion of treatment in the Hanford Formation (Table 1), likely due to the larger injection volumes

**Table 2.** Average PO<sub>4</sub> in 100N sediments after low concentration injections.

depth (ft)	formation	sample date	PO <sub>4</sub> (mg/g)
4-6	fill	3-2008	0.000
7-9	Hanford	3-2008	$0.134 \pm 0.156$
10-12	Hanford	3-2008	$0.136 \pm 0.122$
13-15	Hanford	3-2008	$0.179 \pm 0.158$
16-18	Ringold	3-2008	$0.059 \pm 0.092$
19-21	Ringold	3-2008	$0.030 \pm 0.034$
21-26	Ringold	3-2008	$0.033 \pm 0.093$

that would be proportioned to this higher permeability formation during treatment in the fully screened wells. Barrier injection operations completed by the spring of 2008 using the low concentration formulation (10 mM PO<sub>4</sub>) were designed to emplace 0.136 mg PO<sub>4</sub>/g sediment. Therefore, PO<sub>4</sub> extraction data from post-treatment core samples indicates that, at a radial distance of ~15 feet from adjacent injection wells, the Hanford Formation received an average treatment of 110% and Ringold Formation an average treatment of 30% of the targeted apatite content.

Sr-90 was also measured in cores taken after low-concentration injections (3/2008) to measure the total Sr-90 (black triangles, Figure 2) and ion exchangeable Sr-90 (red circles, Figure 2). For all boreholes, the total Sr-90 averaged  $105 \pm 68 \text{ pCi/g}$  in the Hanford

formation ( $n = 55$ ),  $55.4 \pm 44.7$  pCi/g in the Ringold formation ( $n = 44$ ), and  $23.7 \pm 26$  pCi/g in the fill. The average depth of the highest Sr-90 concentration in each well was 11.1 ft depth. 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  $\text{PO}_4$ ) averaged  $61.2 \pm 22.4\%$ . Untreated sediments from the 13' depth of N-122 showed 86.7% ion exchangeable Sr-90 (2005 results), so 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 100N sediment may have been incorporated into apatite and is not slowly migrating in groundwater.

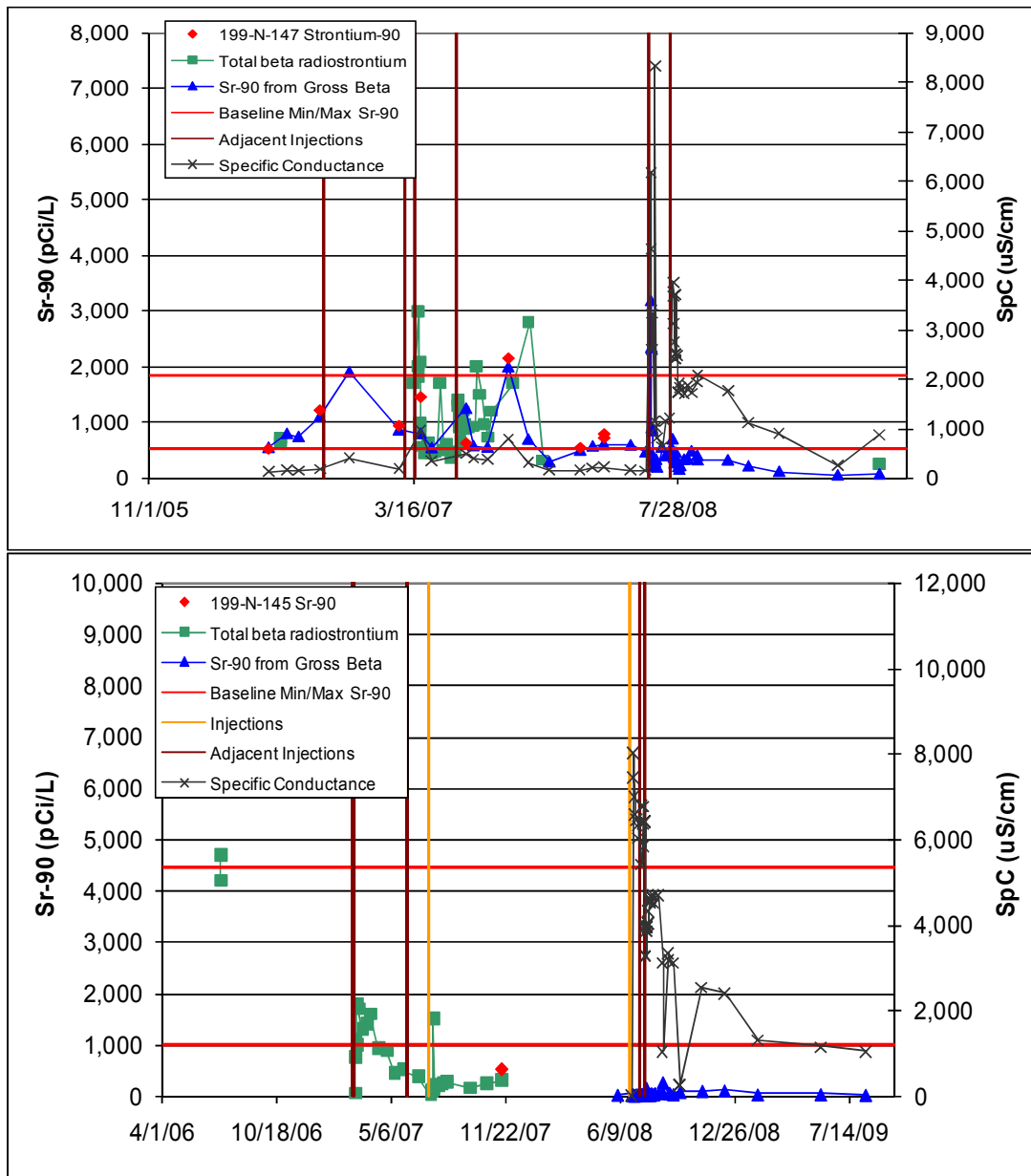
**Sr-90 Mass and Apatite Distribution after High Concentration Injections.** Three boreholes were drilled at different radial distance from injection well N-137 to collect cores for apatite and Sr-90 analysis. The target apatite concentration (1.7 mg apatite/g of sediment) corresponds to a pore volume amendment of 90 mM of phosphate precipitated in sediment with no retardation, or 45 mM phosphate precipitated with a retardation of 2.0. Laboratory and field Ca-citrate- $\text{PO}_4$  injections have demonstrated that phosphate retardation is in the range of 1.6 to 2.4, and dependent on the injection rate (i.e., due to slow  $\text{PO}_4$  removal from solution by adsorption and precipitation). Given the 10 mM  $\text{PO}_4$  and 40 mM  $\text{PO}_4$  injections in 100N wells, an average apatite loading of 1.9 mg apatite/g of sediment (0.608 mg  $\text{PO}_4$ /g) is expected. There may be higher concentrations near the injection wells and lower concentrations at greater distance from the injection wells.

Phosphate was analyzed in 45 samples at different depth (15 in each of 3 boreholes) using the  $< 4$  mm grain size fraction, and in 18 samples at different depth (6 in each borehole) using the full grain size fraction. Average phosphate for three boreholes (both Hanford and Ringold formations) was  $0.415 \pm 0.232$  mg  $\text{PO}_4$ /g of sediment, or 68% of the target of 0.608 mg  $\text{PO}_4$ /g of sediment (equivalent to 1.9 mg apatite/g). The Hanford formation received an average of  $0.559 \pm 0.253$  mg  $\text{PO}_4$ /g (92% of target) and the Ringold formation received an average of  $0.268 \pm 0.113$  mg  $\text{PO}_4$ /g (44% of target). The fill received a minor amount of phosphate (average  $0.203 \pm 0.17$  mg  $\text{PO}_4$ /g). These reported values are based on extraction from the whole grain size distribution (1.0 to 2.0 kg per sample). Phosphate extractions on the  $< 4$  mm grain size averaged 17% lower (normalized to the  $\text{PO}_4$  in the whole grain size distribution). There was variability between boreholes, which are located at different distance from the injection well N-137.

Sr-90 measurement in cores taken after the high-concentration injections showed an average of 50.6% ion exchangeable Sr-90 (Hanford and Ringold Formations), and 39.4% Sr-90 incorporation into apatite by 1 year. It is expected that additional Sr-90 will be incorporated into apatite in the following years. Given that Sr-90 adsorption to apatite ( $K_d = 1375$  mL/g,  $R_f = 6800$ ) is 55 times stronger than to sediment ( $K_d = 25$  mL/g,  $R_f = 125$ ), there was a slight increase in Sr-90 adsorption with the addition of the small amount of apatite. A multicomponent ion exchange simulation showed that the 8.3% of the ion exchangeable Sr-90 is sorbed to apatite and 91% is sorbed to sediment, with a slight overall increase in total sorption.



**Sr-90 Aqueous Monitoring after High Concentration Injections.** Additional apatite was emplaced in the 100N near river sediments by high concentration Ca-citrate-PO<sub>4</sub> injections in 2008. These injections consisted of 120,000 gallons into each of 4 upstream wells and 60,000 gallons into 12 wells on the downstream portion of the barrier (Figure 1b). Injection wells that are screened only in the Ringold Formation were installed between the fully-screened injection wells on the downstream portion of the barrier to provide better vertical reagent coverage due to the larger contrast in permeability between the Hanford and Ringold formations. Sr-90 aqueous data is indicative of the effect of apatite emplacement, although cores taken a year after the high concentration injections are currently being analyzed for Sr-90 substitution in the apatite (similar to Figure 2) for confirmation. Short-term increases in <sup>90</sup>Sr concentration associated with the injection of



**Figure 4.** Field data of aqueous Sr-90 concentration before and after low- and high-concentration injections for: a) compliance well N-147, and b) injection well N-145 [12].

high ionic strength solutions (Figure 4, vertical lines at 7/2008) during the high concentration treatments were generally comparable or less than that observed during the initial low concentration treatment (Figure 4, vertical lines at 3/2007). Horizontal red lines indicate the range of aqueous Sr-90 that occurs prior to any injections (i.e., baseline minimum and maximum). There is considerable variability in these Sr-90 values due to seasonal change in the near-river water level, which accesses a different fraction of sediment vertically, which has a different mass of adsorbed Sr-90.

Evaluation of the aqueous Sr-90 data from all wells indicates a stepwise improvement in  $^{90}\text{Sr}$  sequestration performance between the low and high concentration injections. The average reduction in  $^{90}\text{Sr}$  concentrations at the four compliance monitoring locations was 95 % relative to the high end of the baseline range and 84% relative to the low end of the baseline range (Figure 4a shows one compliance well), indicating that the performance objective specified in the treatability test plan (90% reduction in  $^{90}\text{Sr}$  concentration) was met within one year of high concentration treatment. Treatment in most of the 16 injection wells shows even lower Sr-90 values ([12] one injection well shown in Figure 4b), due to higher fraction of apatite in that zone and some ion exchange effect. It should be noted that because of the high ionic strength of the low- and high-concentration Ca-citrate- $\text{PO}_4$  injections, there is some initial Sr-90 desorption and mobilization from near injection well sediments before apatite precipitation occurs.

Analysis of the ion exchangeable  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  in the injection zone sediments show a 47% decrease in  $\text{Ca}^{2+}$ , and a 95% decrease in  $\text{Sr}^{2+}$ , due to the apatite precipitation utilizing both cations. The greater depletion of  $\text{Sr}^{2+}$  is caused by preferential incorporation into apatite. In the next few years, upgradient groundwater (with  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and Sr-90) will invade the apatite-laden zone, and conditions will return to natural equilibrium conditions. The apatite will also continue to incorporate the Sr and Sr-90.

## CONCLUSIONS

Sr-90 contamination in the shallow aquifer and vadose zone sediments at the Hanford Site 100N area are slowly leaching into the nearby Columbia River. The original concept for field-scale deployment of the apatite permeable reactive barrier technology involved injection of an initial low-concentration, apatite-forming solution (Ca-citrate- $\text{PO}_4$ ), followed by higher concentration injections as required to emplace sufficient treatment capacity to meet remedial objectives. The low concentration injections were designed to provide a small amount of treatment capacity, thus stabilizing the  $^{90}\text{Sr}$  residing within the treatment zone, while minimizing  $^{90}\text{Sr}$  mobilization due to the injection of high ionic strength solutions. In theory, this approach would act to minimize  $^{90}\text{Sr}$  mobilization during subsequent high-concentration injections.

Analysis of sediment cores after the low-concentration injections with phosphate extractions clearly showed evidence of the phosphate injections, with  $\text{PO}_4$  (in mg  $\text{PO}_4/\text{g}$  sediment, adjusted to account for pre-treatment  $\text{PO}_4$  content based on analyses of pre-treatment sediment samples) averaging  $0.102 \pm 0.133$  mg/g over the entire depth (7 – 26 ft), or 0.150 mg/g in the Hanford Formation and 0.041 mg/g in the Ringold Formation. 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 in the Ringold and Hanford formations in the area. The contrast was lower in the upstream portion of the barrier. 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  $105 \pm 68$  pCi/g in the Hanford formation,  $55.4 \pm 44.7$  pCi/g in the Ringold formation, and  $23.7 \pm 26$  pCi/g in the fill. Untreated sediments from showed 86.7% ion exchangeable Sr-90. After the low-concentration injections, ion exchangeable Sr-90 decreased to 61.2%, or ~25% Sr-90 incorporation into apatite.

High concentration solution injections in 2008 relies more heavily on calcium naturally present in the aquifer sediments as a source for apatite formation, and contains significantly less Ca-citrate. Core analysis after the high-concentration injections showed that the Hanford formation received an average of  $0.559 \pm 0.253$  mg PO<sub>4</sub>/g (92% of target) and the Ringold formation received an average of  $0.268 \pm 0.113$  mg PO<sub>4</sub>/g (44% of target). The fill received a minor amount of phosphate (average  $0.203 \pm 0.17$  mg PO<sub>4</sub>/g). Sr-90 measurement in cores taken after the high-concentration injections showed an average of 50.6% ion exchangeable Sr-90 (Hanford and Ringold Formations), and 39.4% Sr-90 incorporation into apatite by 1 year. The mass of ion exchangeable Sr<sup>2+</sup> and Ca<sup>2+</sup> in the injection zone sediments show a 47% decrease in Ca<sup>2+</sup>, and a 95% decrease in Sr<sup>2+</sup>, due to the apatite precipitation utilizing both cations. It is expected that additional Sr-90 will be incorporated into apatite in the following years.

The average decrease in <sup>90</sup>Sr aqueous concentrations at the four down gradient compliance monitoring wells was 95 % relative to the high end of the baseline range and 84% relative to the low end of the baseline range, which is consistent with the core analysis. A stepwise improvement in <sup>90</sup>Sr sequestration performance between the low and high concentration injections was observed, with concentrations at nearly all monitoring locations well below the low end of the baseline range by one year after the high concentration treatment.

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