Effectiveness of an In-Situ Permeable Reactive Barrier in Removing Strontium-90 from Groundwater – 15418

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ABSTRACT

An in-situ permeable reactive barrier (PRB) is being used to remove strontium-90 from groundwater along the 100-N Area shoreline at the U.S. Department of Energy Hanford Site in southeastern Washington. The PRB was formed by emplacing apatite, a calcium phosphate mineral, in the subsurface sediments via injection of calcium-citrate and sodium-phosphate solution into the aquifer through a network of vertical wells. The relatively slow biodegradation of citrate allowed sufficient time for the injected solution to disperse in the PRB treatment zone as the free calcium and phosphate combined to form apatite. Substitution of strontium for calcium in the apatite crystal structure is thermodynamically favorable. As groundwater flows through the PRB toward the Columbia River, strontium-90 is sequestered into the apatite crystal matrix. The sequestered strontium-90 undergoes radioactive decay in place within the PRB.

Groundwater monitoring wells installed between the PRB and the Columbia River are used to monitor the PRB effectiveness. The concentration of strontium-90 in the monitoring wells following apatite emplacement are compared to the pre-injection concentrations. The performance goal of the PRB is to reduce the concentration of strontium-90 in groundwater down gradient of the PRB by 90 percent, compared to the pre-injection concentrations. Groundwater samples in Fall 2013 show the percent reduction in strontium-90 concentrations ranged from 71 to 98 percent in eleven of the twelve monitoring wells. The data indicate that the PRB is effective in reducing the flux of strontium-90 toward the Columbia River and is thereby instrumental in protection of the Columbia River.

INTRODUCTION

Groundwater at the 100-N Area of the U.S. Department of Energy Hanford Site in southeastern Washington (Figure 1) is contaminated with strontium-90. The strontium-90 contamination resulted from liquid waste discharged to disposal sites near the Columbia River during operation of the N Reactor. The N Reactor, which operated from 1964 to 1986, was a dual-purpose reactor that produced plutonium for defense purposes and steam for commercial electrical power generation. Groundwater monitoring results indicate groundwater strontium-90 concentrations along the shoreline range from below the 8 pCi/L drinking water standard to 2,000 pCi/L/, with localized regions inland where strontium-90 concentrations are as high as 15,000 pCi/L. The strontium-90 groundwater plume at 100-N is depicted in Figure 2. Activities to reduce the flux of strontium-90 to the Columbia River have been underway since the early 1990s. However, strontium-90 adsorbed on vadose zone and aquifer sediments beneath the liquid waste disposal sites and on sediment along the groundwater flow path extending to the river shoreline remains a continuing source of strontium-90 contamination to groundwater. Since 2006, an in situ PRB has been successful in reducing the flux of strontium-90 contamination from groundwater into the river.

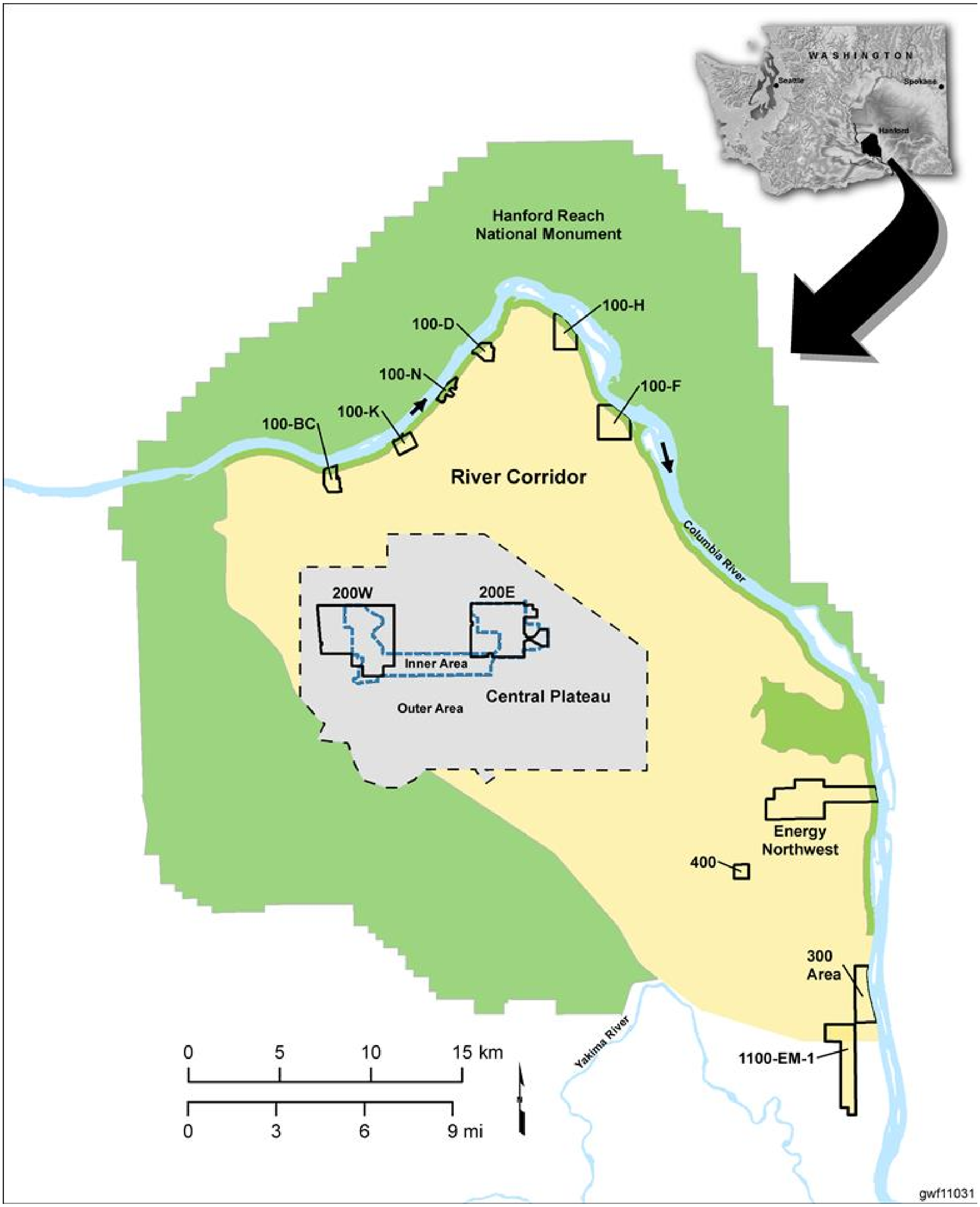


Fig. 1. U.S. Department of Energy Hanford Site. The 100-N Area is located on the northern portion of the site along the Columbia River.

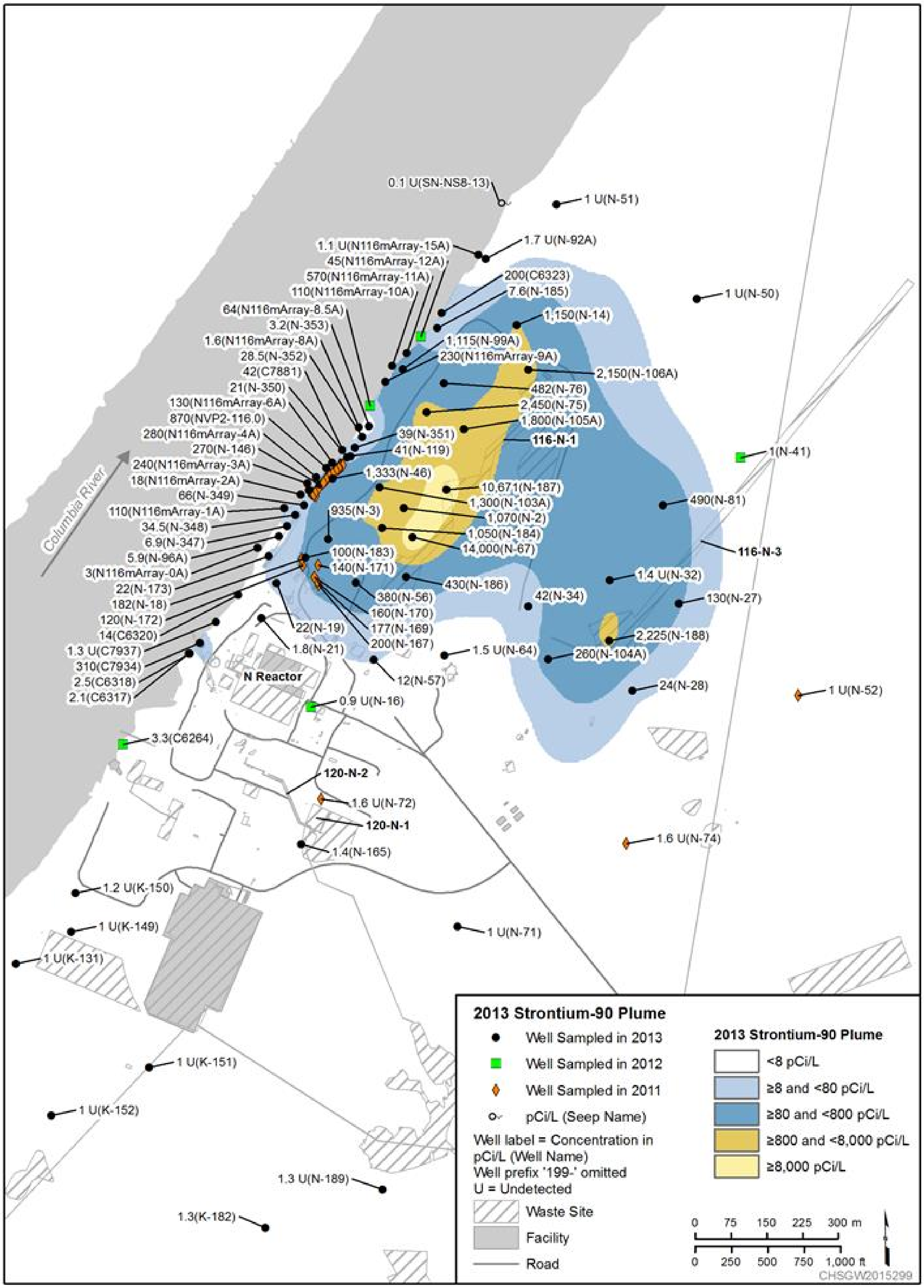


Fig. 2. Strontium-90 Groundwater Contamination Plume at 100-N.

BACKGROUND

Strontium-90 is difficult to remove from the groundwater because it sorbs strongly to sediment. Following an evaluation of potential strontium-90 treatment technologies and their applicability under the site hydrogeologic conditions, sequestration of strontium-90 using a PRB was selected as the primary treatment for groundwater remediation at the 100-N Area (Figure 3). The treatment technology used at the 100-N Area was developed and tested by Pacific Northwest National Laboratory using an approach that included laboratory bench-scale experiments, an initial pilot-scale field test, and the emplacement and evaluation of a 91-meter-long treatability-test-scale PRB [1]. The initial PRB was then extended to a total length of 311 meters by CH2MHILL Plateau Remediation Company and its contractors.

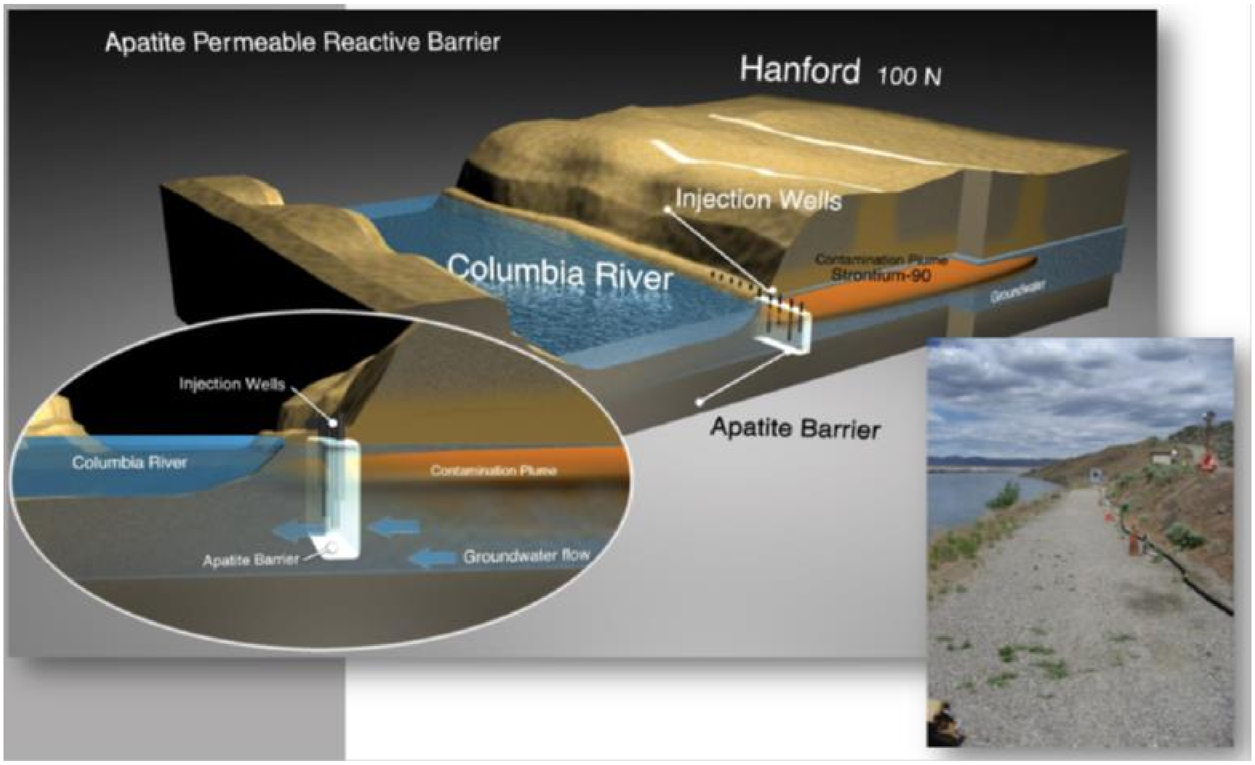


Fig. 3. 100-N Permeable Reactive Barrier.

PRB INSTALLATION

The PRB to sequester strontium-90 was implemented by injecting a calcium-citrate complex and sodium-phosphate solution into the unconfined aquifer through a linear network of vertical wells installed parallel to the Columbia River down gradient of the strontium-90 groundwater contaminant plume (i.e., the PRB well network). The citrate kept the calcium in solution while the injected solution migrated from the injection point. The relatively slow biodegradation of citrate (half-life of 50 hours) allowed sufficient time for the injected solution to disperse in the PRB treatment zone as the free calcium and phosphate combined to form apatite [$Ca_{10}(PO4)_6(OH)_2$] and co-precipitate strontium-90 in the treatment zone; amorphous apatite forms within a week and then crystalline apatite forms within a few weeks [2]. The citrate also desorbed calcium from the sediment, thereby reducing the amount of calcium needed in the injection solution.

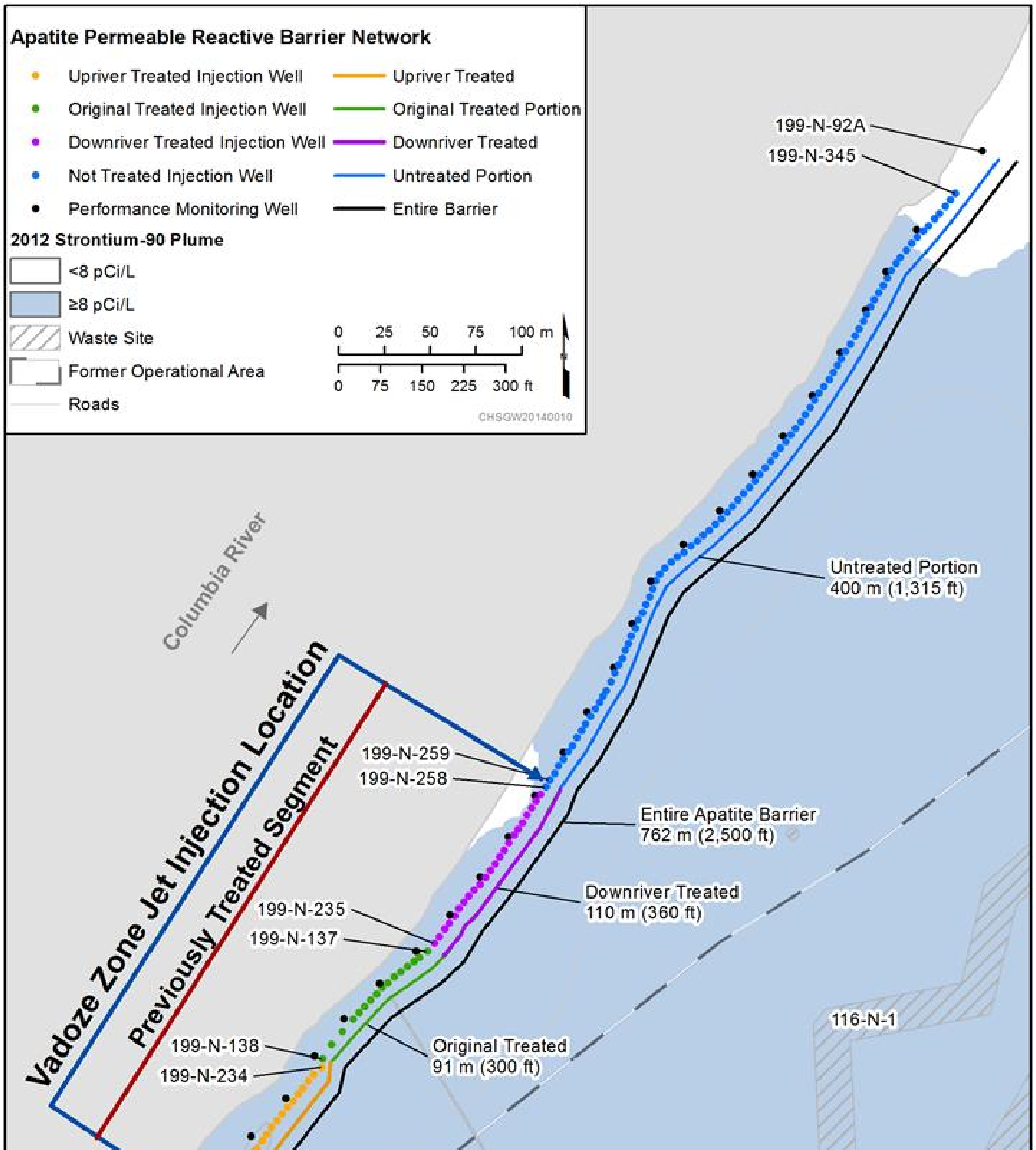
Strontium-90 migrating with groundwater into the treatment zone adsorbs on the apatite surface within minutes, and the apatite recrystallizes with permanent strontium-90 substitution for calcium within months to years [3] (Figure 4). The strontium-90 in groundwater is sequestered within the apatite PRB as contaminant-laden groundwater flows through the PRB. The strontium-90 sequestered in the apatite PRB undergoes radioactive decay (half-life 29.1 years) in place. The apatite PRB is designed to sequester strontium-90 for approximately 300 years and mitigate movement of strontium-90 toward the river. During this time period, strontium-90 in the plume and PRB will radioactively decay to below the drinking water standard.

Fig. 4. Strontium Substitution for Calcium in Apatite Matrix.

An initial 91-meter-long PRB was created from 2006 through 2008 by injection of apatite-forming solutions into 16 wells spaced between 4 to 9 meters apart. This apatite PRB, installed along the Columbia River shoreline as a treatability test, was designed to remediate the highest concentration strontium-90 contaminated groundwater flowing toward the river. Based on the laboratory and field-scale treatability tests, the composition of the apatite-forming solution was optimized to minimize the number of injection operations required; minimize the short-term increases in strontium-90 and some metals concentrations associated with injection of high ionic strength solutions; and keep injection formulations well below solubility limits to reduce the potential for operational challenges associated with solution stability [4].

During 2009 and 2010, the PRB well network was extended along the river shoreline by adding 146 injection wells. In September 2011, 48 of the 146 wells in the extended well network were injected with apatite-forming solution in two segments, one upriver and one downriver of the original PRB, creating an apatite PRB approximately 311 meters long [5]. Future injections into the remaining extended network wells will create a PRB with a total length of approximately 762 meters, capable of intercepting the entire strontium-90 groundwater plume along the river. Figure 5 shows the planned length of the PRB and the portions of the PRB that have thus far been treated.

An injection system was designed and used for the 2011 PRB expansion. The system included two chemical mixing and injection skids, each of which could inject apatite forming solutions into six wells simultaneously. Each skid contained equipment for blending the calcium-citrate and phosphate chemical solutions with river water at controlled ratios and flow rates and injecting the mixed solution into injection wells (Figure 6).



	Total Wells	Monitoring Wells	Injection Wells	Injection Completed	Remain to be Injected	Injection Year
Original Barrier	20	4	16	16	0	2008
Upriver Expansion	41	6	35	24	11	2011
Downriver Expansion	130	19	111	24	87	2011
Expansion Total	171	25	146	48	98	Future Planning
Overall Total	191	29	162	162		

Note:
Basis for 2500 ft. APB.
Amended Record of Decision for 100-NR-1 and NR-2 Operable Units, Hanford Site – 100 Area, Benton County, Washington – September 2010 (which is the first regulatory requirement to expand the barrier length to 2,500 feet)

Fig. 5. Apatite Permeable Reactive Barrier Network.

Fig. 6. Apatite Chemical Injection Skid Setup.

PRB PERFORMANCE MONITORING

Performance monitoring wells installed down gradient of the PRB, between the PRB injection wells and the Columbia River, are used to monitor the effectiveness of the PRB to sequester strontium-90. Groundwater samples were collected from these wells prior to injection of the up gradient PRB wells. Groundwater monitoring of the treated portion of the apatite PRB is conducted twice a year, once during low river stage in the fall (September) and once during high river stage (June). The concentrations of strontium-90 in the groundwater performance monitoring samples are compared to the pre-injection concentrations to evaluate performance of the PRB. The performance goal of the PRB is to reduce the concentration of strontium-90 in groundwater down gradient of the PRB by 90 percent compared to the pre-injection concentrations.

Figure 7 shows the location of the performance monitoring wells down gradient of the PRB. In 2013, groundwater samples were collected from performance monitoring wells during high river stage in May and during low river stage in September. A comparison of 2013 data to baseline conditions is shown in Table I, identifying the monitoring well, the baseline strontium-90 concentration for comparison based on pre-injection concentrations, strontium-90 concentrations measured at the monitoring wells in 2013, and percent strontium-90 reduction compared to baseline concentrations.

Strontium-90 concentrations are typically higher in groundwater samples collected in the Fall because of lower river levels associated with seasonal river flows. This seasonal low river flow period provides the most representative groundwater flow conditions toward the river. Groundwater flow gradients to the river are steeper in the Fall and groundwater samples from monitoring well locations would have less dilution from river water. Groundwater samples in Fall 2013 show the percent reduction in strontium-90 concentrations ranged from 71 to 98 percent in eleven of the twelve wells, whereas the Spring 2013 comparison show an 81 to 98 percent reduction to pre-injection concentrations. At the twelfth well (199-N-347 in Table I), the pre-injection concentration was already below the drinking water standard of 8 pCi/L and reduction to concentrations is not expected to be of the same magnitude.

TABLE I. PRB performance monitoring wells

Monitoring Well	Strontium-90 Concentration (pCi/L)			Percent Reduction in Strontium-90 (Baseline to Fall 2013)[b]	
	Pre-injection Baseline[a]	Spring 2013	Fall 2013	Spring	Fall
Upriver Apatite Permeable Reactive Barrier (Treated 2011)					
199-N-96A	37.9	2.3	5.9	94	84
199-N-347	7[c]	8.5	5.8	-21	17
199-N-348	1,800	28	41	98	98
199-N-349	230	27	66	88	71
Central (Original) Apatite Permeable Reactive Barrier (Treated 2006-2008)					
199-N-122	4,630	390	560	92	88
199-N-146	985	180	270	82	73
199-N-147	1,842	150	120	92	93
199-N-123	1,180	110	140	81	88
Downriver Apatite Permeable Reactive Barrier (Treated 2011)					
199-N-350	240	13	29	94	88
199-N-351	350	32	46	91	87
199-N-352	580	26	31	96	95
199-N-353	83	3.5	2.8	97	97

a. Pre-injection baseline concentrations for the upriver and downriver PRB monitoring wells area based on samples collected in 2010. Pre-injection baseline concentrations for the central PRB monitoring wells are from Table 4.1 in PNNL-19572, *100-NR-2 Apatite Treatability Test: High-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization*.

b. The percent reduction in strontium-90 concentration is calculated as ([pre-injection value] – [2013 value] / [pre-injection value]) × 100.

c. Strontium-90 is a beta emitter. Gross-beta concentrations are approximately two times the strontium-90 concentrations. The strontium-90 concentration was 1.1 pCi/L (U). The gross beta concentration, 14 pCi/L, was divided by two to approximate the strontium-90 concentration of 7 pCi/L.

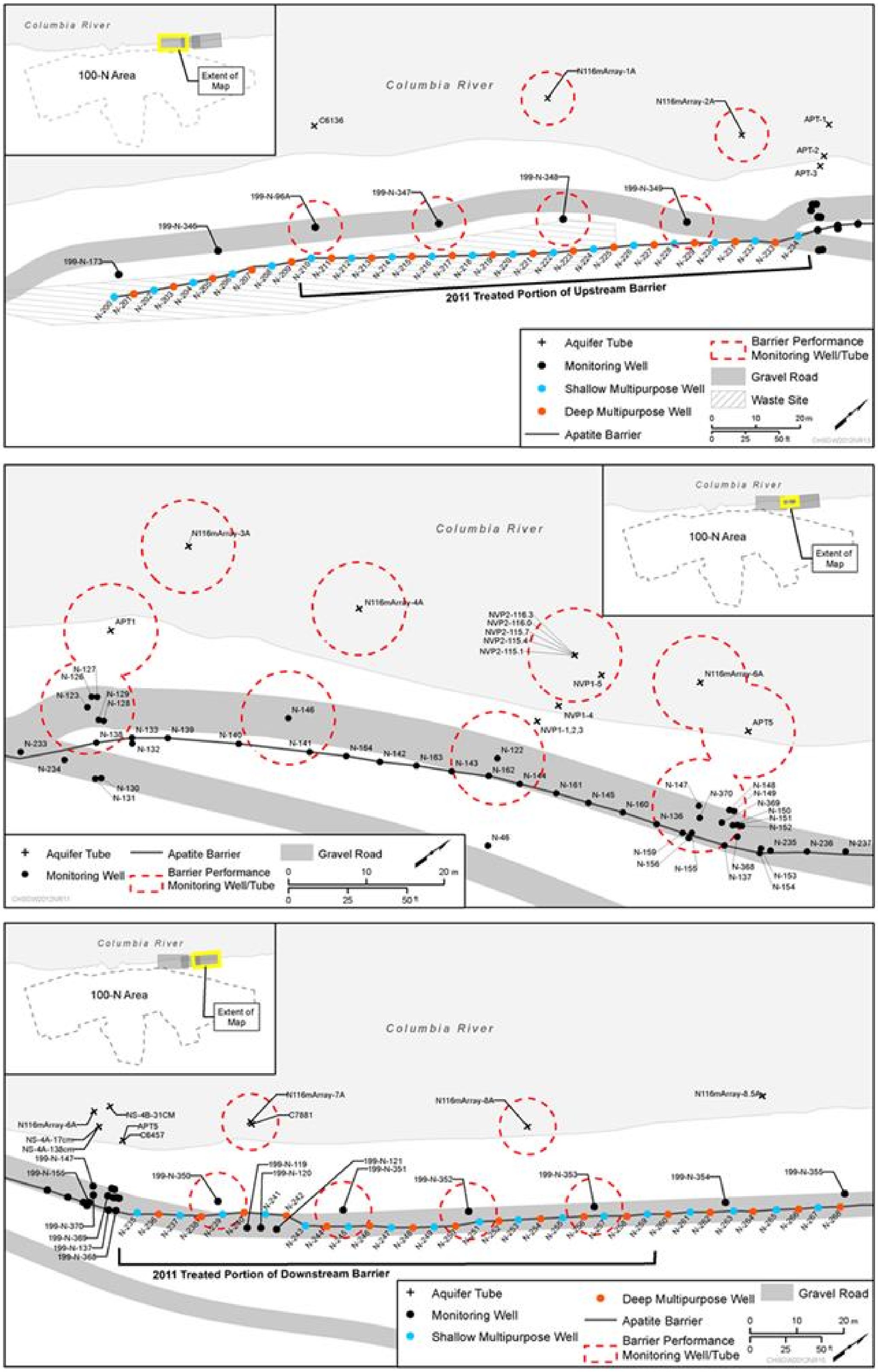


Fig. 7. Permeable Reactive Barrier Performance Monitoring Wells.

The central segment of the PRB has been in place the longest (since 2008). Figure 8 plots the percent reduction in strontium-90 concentrations observed in this portion of the PRB. Figure 8 shows the strontium-90 concentrations were still considerably lower in the performance monitoring wells along the central segment of the PRB than before the injections started in 2006. Following completion of the apatite injections in 2008, strontium-90 concentrations declined in the performance monitoring wells (Figure 8). The wells showed temporary, higher strontium-90 concentrations immediately following the injections of the apatite solution, which had a higher ionic strength than groundwater and temporarily mobilized cations and anions, causing their concentrations in groundwater to increase. Strontium-90 concentrations in performance monitoring Well 99-N-123, which are near the upriver end of the central PRB segment, temporarily increased again following injections into the nearby upriver and downriver PRB extension wells in 2011. The elevated concentrations observed during the 2008 and 2011 injections are shown in Figure 8 by spikes in the monitoring well trends that go off scale. These temporary elevated concentrations declined by the next sample interval. The 2013 data indicate that the strontium-90 concentrations in groundwater have been reduced by approximately 90 percent in three of the four performance monitoring wells (Table I). The percent reduction in strontium-90 concentrations in Fall 2013 ranged from 73 percent (Well 199-N-146) to 93 percent (Well 199-N-147).

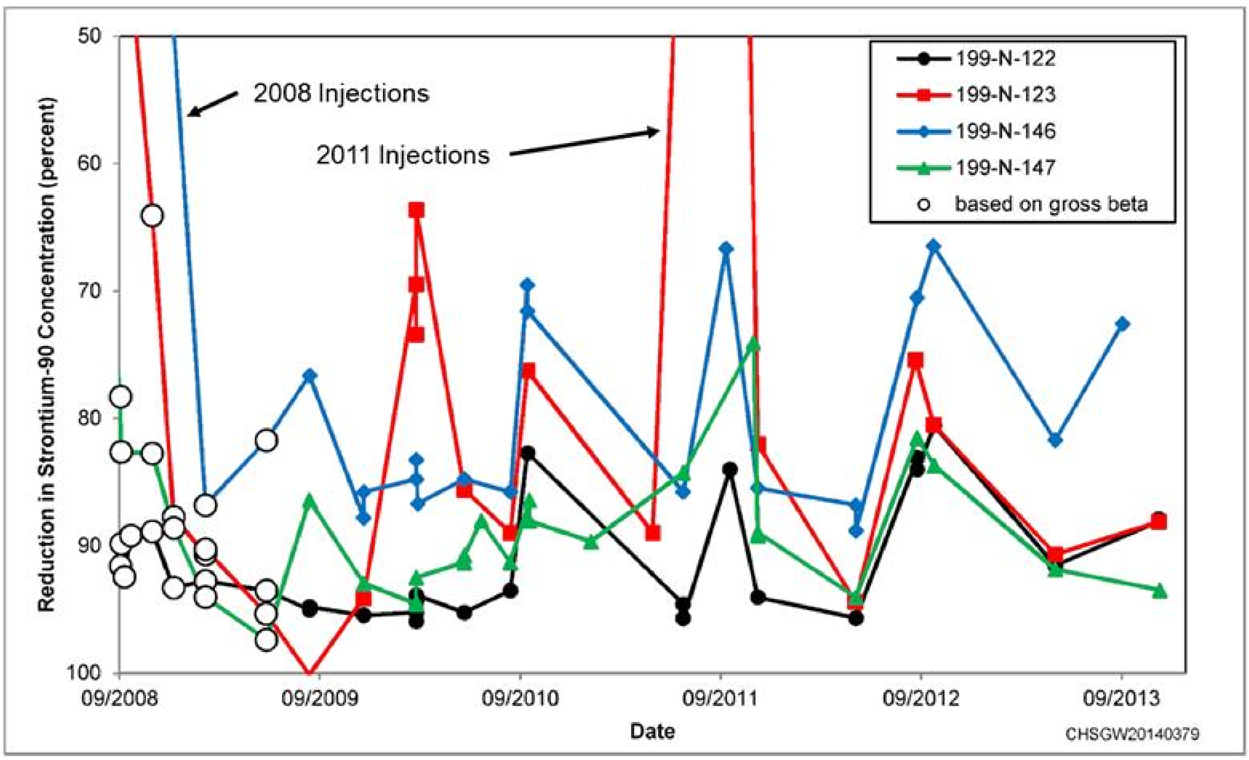


Fig. 8. Percent Strontium-90 Reduction in Central PRB Segment Monitoring Wells. Off scale trends reflect mobilization of cations and anions during injection of higher ionic strength apatite solutions.

In the performance monitoring wells along the upriver PRB extension, the percent reduction in strontium-90 concentrations in the Fall 2013 measurements (the end of the second year following the injections) ranged from 17 percent (Well 199-N-347) to 98 percent (Well 199-N-348) (Table I). The relatively low percent reduction in Well 199-N-347 reflects comparison of the low baseline strontium-90 concentration in this well (the strontium-90 concentration was nondetect, and the strontium-90 concentration estimated from gross beta was 7.0 pCi/L) to the low strontium-90 concentration measured during Fall 2013 performance monitoring (5.8 pCi/L). Figure 9 plots the percent reduction in strontium-90 concentrations observed in the upriver segment of the PRB. Because concentrations in Well 199-N-347 are below the drinking water standard, the percent reduction in strontium-90 concentrations in this well is not plotted on Figure 9.

In the performance monitoring wells along the downriver PRB extension, the percent reduction in strontium-90 concentrations in Fall 2013 ranged from 87 percent (Well 199-N-351) to 97 percent (Well 199-N-353) (Table I and Figure 10). The downriver extension intercepts higher strontium-90 groundwater concentrations than the upriver extension and indicates an initial successful PRB performance.

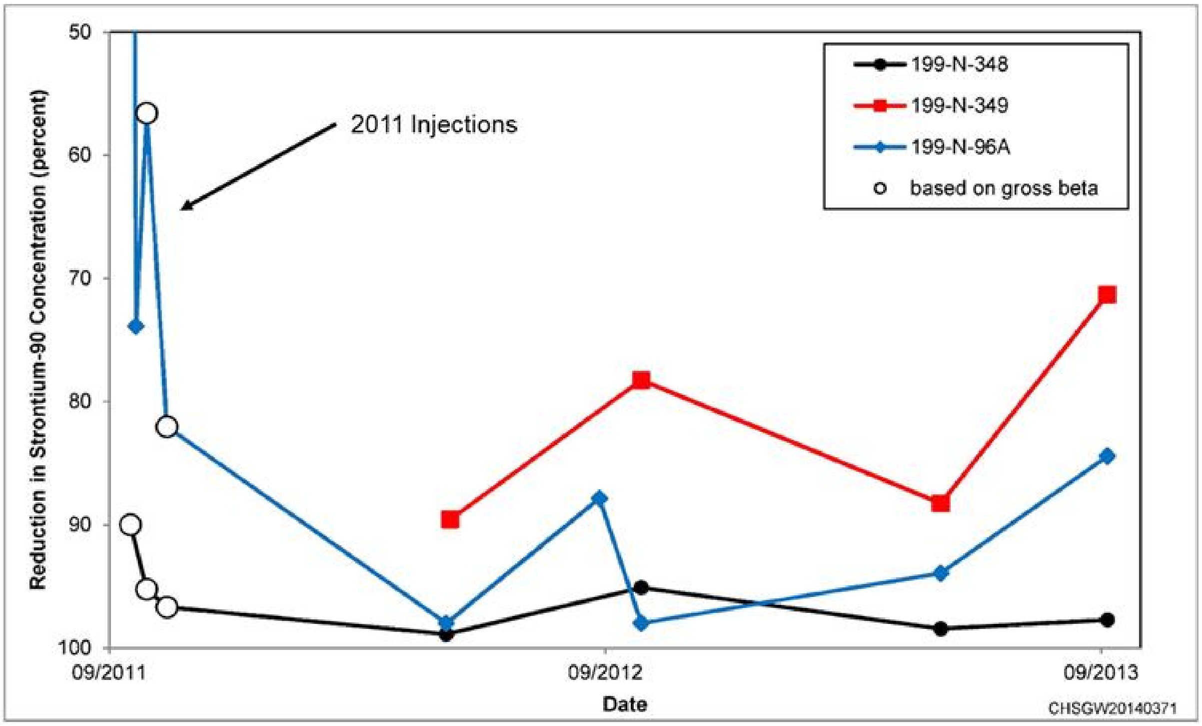


Fig. 9. Percent Strontium-90 Reduction in Upriver PRB Segment Monitoring Wells. Off scale trends reflect mobilization of cations and anions during injection of higher ionic strength apatite solutions.

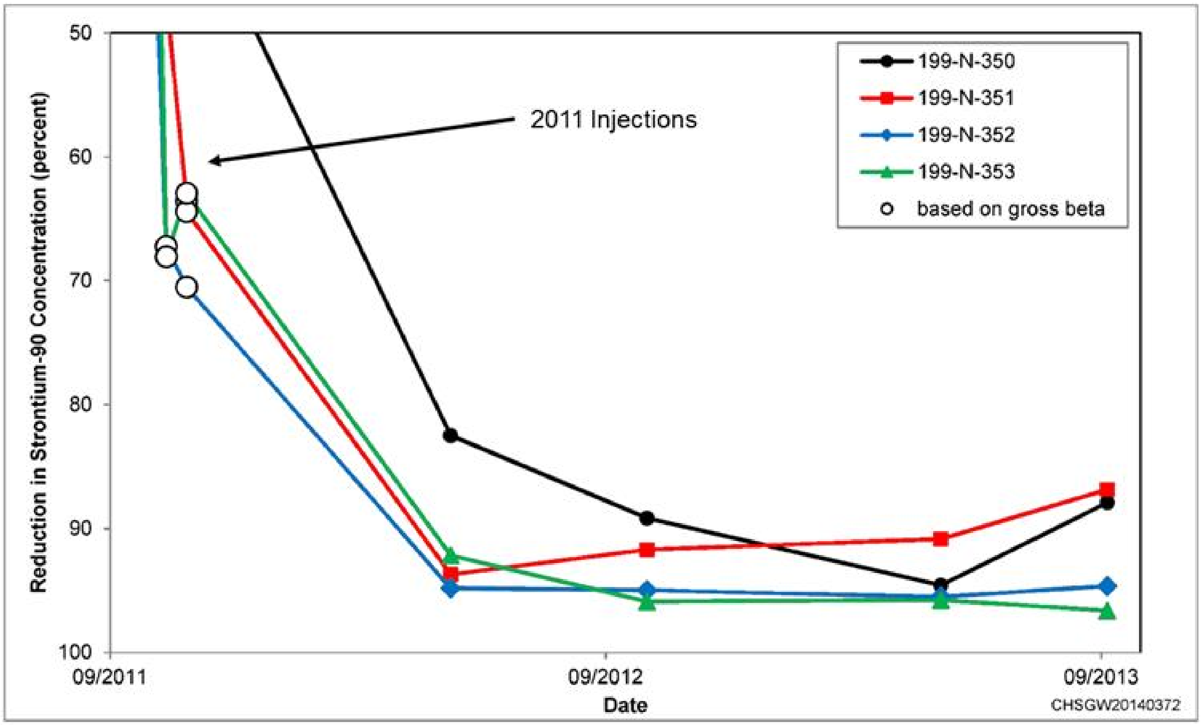


Fig. 10. Percent Strontium-90 Reduction in Downriver PRB Segment Monitoring Wells. Off scale trends reflect mobilization of cations and anions during injection of higher ionic strength apatite solutions.

CONCLUSIONS

The data indicate that the PRB is effective in mitigating the migration of strontium-90 toward the Columbia River and is thereby instrumental in protection of the Columbia River. The methods and results of implementing the apatite PRB may be applicable to other groundwater cleanup projects.

Groundwater monitoring down gradient of the PRB provides a measure for evaluating barrier effectiveness. Ongoing monitoring will determine the continued PRB effectiveness or identify regions where re-injections may need to be considered to improve PRB performance.

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