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Revision 0

Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit

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

U.S. DEPARTMENT OF ENERGY

Richland Operations Office

P.O. Box 550
Richland, Washington 99352

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Terms

bgs	below ground surface
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
CHPRC	CH2M HILL Plateau Remediation Company
Ci	Curies
CMS	corrective measures study
COC	contaminant of concern
DOE	U.S. Department of Energy
DQA	data quality analysis
DQO	data quality objective
DWS	Drinking Water Standard
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ERA	ecological risk assessment
FS	Feasibility Study
HEIS	Hanford Environmental Information System
ICs	institutional controls
IROD	Interim Record of Decision
ITRD	Innovative Treatment and Remediation Demonstration
LFI	limited field investigation
LWDF	liquid waste disposal facility
meq	milliequivalent
mM	millimolar
MNA	monitored natural attenuation
NPL	National Priorities List
OU	operable unit
pCi/L	picoCuries per liter
ppm	parts per million
PRB	permeable reactive barrier

QA	quality assurance
QC	quality control
QRA	qualitative risk assessment
RAO	remedial action objective
RI	remedial investigation
ROD	record of decision
S&GRP	Soil and Groundwater Remediation Project
Sr-90	Strontium-90
TAG	Technical Advisory Group
TD	total depth
TPH	total petroleum hydrocarbon
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
TTP	treatability test plan
WDOH	Washington State Department of Health

1 Introduction

This document presents a design optimization study for evaluating further expansion of the existing saturated zone apatite permeable reactive barrier (PRB) located in the 100-NR-2 Operable Unit (OU) of 100-N at the Hanford site near Richland, Washington. Figure 1 shows the location of 100-N within the Hanford site and the location of the Hanford site within Washington State. The PRB is designed to prevent subsurface strontium-90 (Sr-90) migration from the saturated zone into the Columbia River. This design optimization study describes the test methods developed to evaluate potentially improved methods for the delivery and emplacement of apatite-forming minerals in the saturated zone.

Successful implementation of this study will result in the lateral extension of the existing saturated zone apatite PRB by at least 182 m (600 ft) from the current 91 m (300-ft) length to a minimum 274 m (900-ft) length. Figure 2 shows the details of the existing barrier, including the locations of monitoring wells and aquifer tubes used to monitor performance of the barrier. This work is being performed under the *Interim Remedial Action Record of Decision for the 100-NR-1 and 100-NR-2 Operable Units, Hanford Site, Benton County, Washington* (EPA/ROD/R10-99/112) to fulfill the interim remedial action objective (RAO) of evaluating treatment technologies. In addition, this work will contribute, in part, to achieving *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) milestone M-016-110-T03 (Ecology et al., 1989a), which states that Sr-90 concentrations in the 100-NR-2 Operable Unit will achieve the default ambient water quality standard of 8 pCi/L in the hyporheic zone and river water column by 2016. This design optimization study will further evaluate the apatite PRB technology, building on work completed under the original treatability test plan (TTP), the *Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit* (DOE/RL-2005-96). The scope presented in this design optimization study was not presented in the 2006 TTP.

Following successful implementation of this design optimization study, full expansion of the saturated zone apatite PRB would not be implemented until issuance of either an amended Interim Record of Decision (IROD) or a "final" Record of Decision (ROD). Full expansion of the apatite PRB will be documented in a Remedial Design/Remedial Action Work Plan prior to implementation.

1.1 Basis for the Design Optimization Study

Efforts to reduce the flux of Sr-90 to the Columbia River from past-practice liquid waste disposal sites have been underway since the early 1990s in 100-N at the Hanford Site, shown in Figure 1. Termination of all liquid discharges to the ground by 1993 was a major step toward meeting this goal. However, Sr-90 adsorbed on aquifer and periodically re-wetted zone solids beneath the liquid waste disposal sites and extending beneath the near-shore riverbed remains as a continuing source to groundwater and the Columbia River.

The Interim Remedial Action Record of Decision (ROD) for the 100-NR-1 and 100-NR-2 OUs, (EPA/ROD/R10-99/112) recognized the limitations of pump-and-treat technology for Sr-90 remediation by requiring that alternative treatment technologies be evaluated. The need for alternative technologies was affirmed in the first *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) five-year review, which re-emphasized the need to aggressively pursue alternative remedial action technologies for the removal, mass reduction, and/or attenuation of Sr-90 from the 100-NR-2 aquifer sediments and to further reduce the net flux of Sr-90 to the river (EPA, 2001, *USDOE Hanford Site First Five Year Review Report*). Additionally, the *Hanford Site Groundwater Monitoring for Fiscal Year 2006* (PNNL-16346) recognized from the onset that groundwater pump-and-treat was unlikely to be an effective long-term treatment method because of the geochemical characteristics of Sr-90. Subsequent performance monitoring has substantiated this determination.

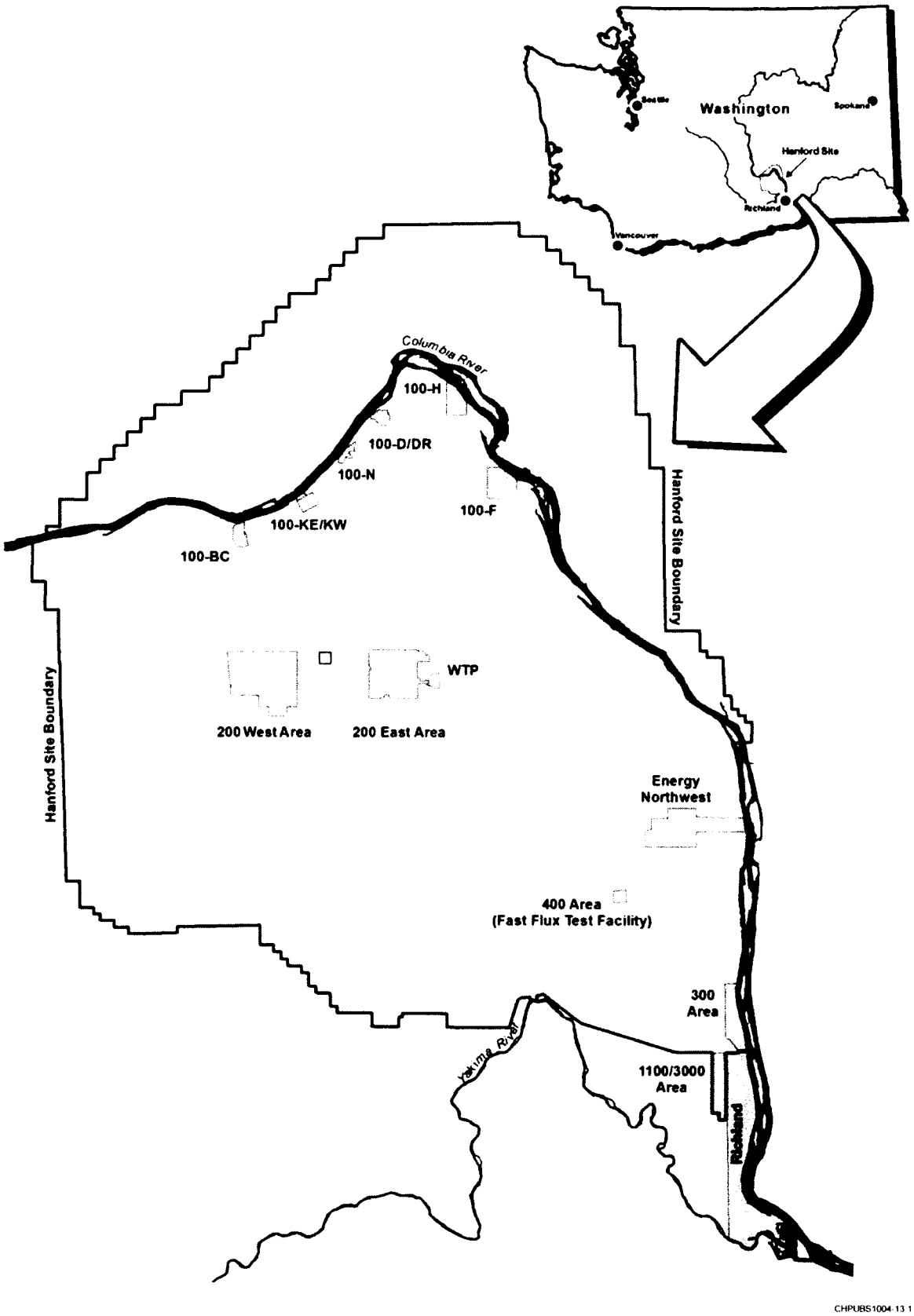


Figure 1. The Hanford Site and Washington State

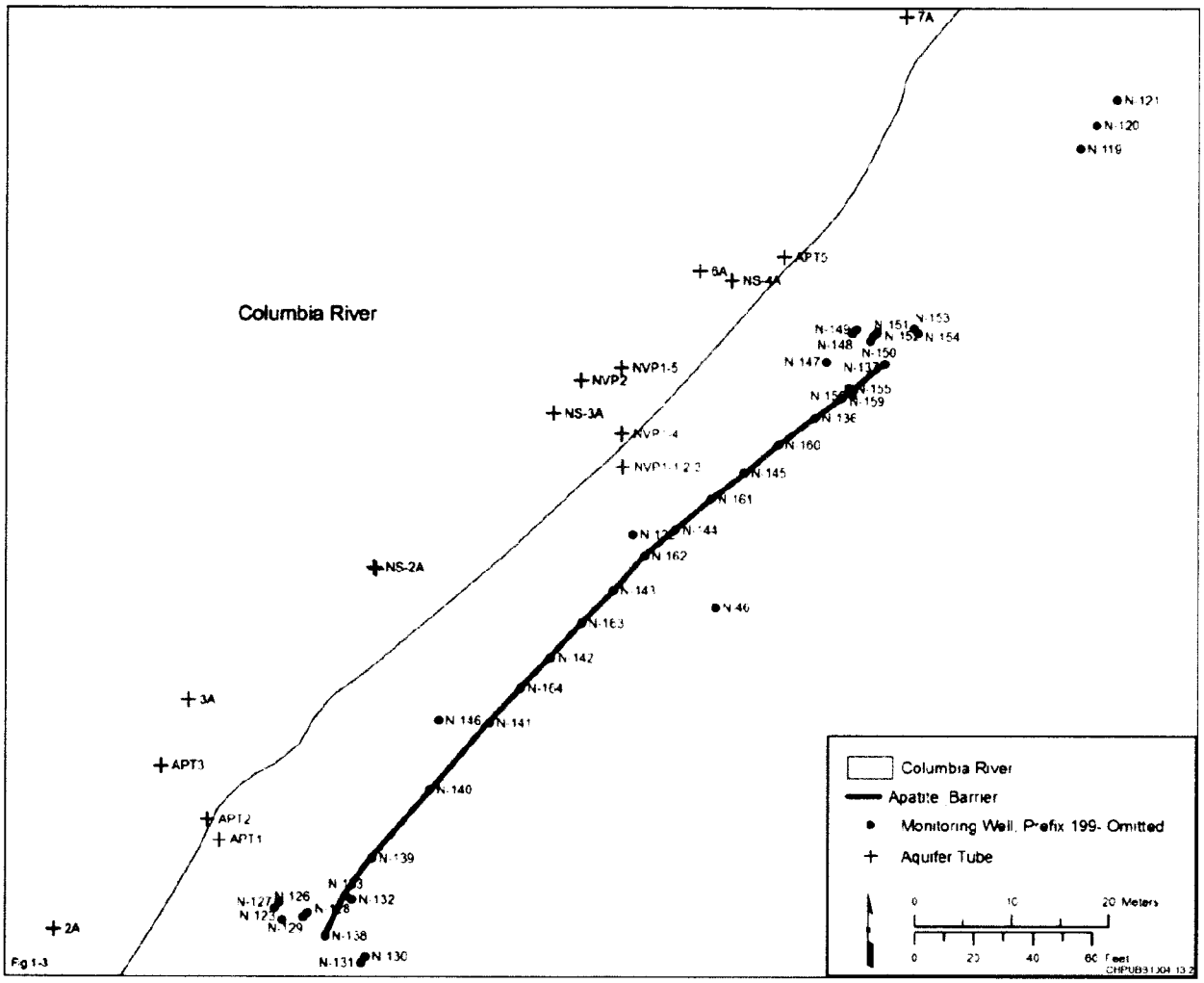


Figure 2. Detail of Existing Apatite Permeable Reactive Barrier

Following an evaluation of potential Sr-90 treatment technologies and their applicability under 100-NR-2 hydrogeologic conditions, the U.S. Department of Energy (DOE), U.S. Environmental Protection Agency (EPA) and the Washington State Department of Ecology (Ecology) agreed that the long-term strategy for groundwater remediation at 100-N should include apatite sequestration as the primary treatment technology (DOE/RL-2006-20, *The Second CERCLA Five-Year Review Report for the Hanford Site*). This agreement was based on results from an evaluation of remedial alternatives that identified the apatite PRB technology as the approach showing the greatest promise for reducing Sr-90 flux to the Columbia River at a reasonable cost.

As a result, aqueous injection (i.e., the introduction of apatite-forming chemicals into the subsurface through standard injection wells), was selected as the preferred technology and selected for treatability testing. The generalized approach for developing an in situ remedial technology for the sequestration of Sr-90 in groundwater through the formation of calcium-phosphate mineral phases (i.e., apatite) was initially documented in the original TTP (DOE/RL-2005-96). The following text reports activities completed to date in support of the original TTP (DOE/RL-2005-96):

- Laboratory-scale studies were performed to demonstrate in situ apatite formation and Sr-90 sequestration proof-of-principle, characterize the apatite formation and Sr-90 sequestration

mechanisms important to development of a pilot field-scale test design, and optimize calcium-citrate-phosphate amendment formulation to achieve site remedial objectives. Bench-scale development work is documented in PNNL-16891, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO4 Solution Injection and Sr-90 Immobilization in 100-N Sediments,* and in PNNL-SA-70033, *100-NR-2 Apatite Treatability Test FY09 Status: High Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization.*

- Two pilot-scale field tests of the technology were conducted, one at each end of the initial 91 m (300-ft) long PRB section, to characterize field-scale geohydrologic/geochemical conditions and assess the upscaling of laboratory results to actual field site conditions. Results from these pilot tests were used to refine the injection design for the remaining injection wells used to emplace the initial 91 m (300-ft) PRB section (Figure 2). These testing activities are reported in PNNL-17429, *Interim Report: 100-NR-2 Apatite Treatability Test: Low-Concentration Calcium-Citrate-Phosphate Solution Injection for In Situ Strontium-90 Immobilization.*

- Initial treatment of the 91 m (300-ft) long PRB section was performed using a low-concentration formulation and injection operation design that was based on the previous laboratory and pilot field-scale test results. The low-concentration calcium-citrate-phosphate amendment formulation was designed to emplace a small amount of treatment capacity (i.e., apatite formation) while minimizing any short-term increase in dissolved-phase Sr-90 concentration associated with injection of relatively high ionic strength solutions. A detailed description of these PRB emplacement operations, including performance assessment monitoring results through November 2007, are also provided in PNNL-17429.

- Sediment core samples collected following the initial low-concentration treatments were analyzed for apatite content and compared with the apatite formation design target for this initial treatment. Although the apatite contents were small, they were sufficient to demonstrate that phosphate mineral phases had been formed. The overlap zone between adjacent wells received an average treatment of 110 percent of the targeted apatite content within the Hanford formation and 30 percent treatment within the Ringold Formation (PNNL-18303, *Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of a Ca-Citrate-Phosphate Solution*).

- Preliminary results of the high-concentration injections were reported in an interim report (PNNL-SA-70033). The Ringold apatite content data, in addition to formulation arrival responses observed in available Ringold Formation monitoring wells, support the decision to install Ringold-only injection wells that were used during subsequent high-concentration treatments. The *Hanford 100N Area In Situ Apatite and Phosphate Emplacement by Groundwater and Jet Injection: Geochemical and Physical Core Analysis* (PNNL-19524, Draft 2010) presents a preliminary evaluation based on sediment core samples collected in November 2009 (more than a year after the high-concentration injections). The results indicate that the phosphate precipitation was relatively uniform up to 4.8 m (15.7 ft) from the injection well. The sediment cores indicated an average treatment of 100 percent of the targeted apatite content within the Hanford formation and 50 percent treatment within the Ringold Formation.

- Jet injections of phosphate, pre-formed apatite, and phosphate combined with pre-formed apatite were conducted in 2009, upgradient of the existing apatite PRB within the moderate Sr-90 plume. The solutions were injected into the vadose zone and unconfined aquifer. Preliminary results indicate that jet injection is a viable technology for emplacement of phosphate and pre-formed apatite in the vadose zone, with injected chemicals meeting the injection target goal within 1.2 m (4 ft) of the injection point. The results of the jet injection demonstration will be documented in a final test report scheduled for completion in FY 2010.

Based on the information and experience gained from performance of the work discussed previously, enhancements have been identified to improve on the delivery and emplacement of apatite-forming chemicals within the formation to produce an effective PRB. This design optimization study has been prepared to aid in the deployment and evaluation of these enhancements and demonstrate the effectiveness of this technology such that it can be optimized for full implementation prior to the Final ROD necessary to meet the Tri-Party Agreement Milestone M-016-110-T03 (Ecology et al., 1989a) of reducing Sr-90 flux to the Columbia River to 8pCi/L by 2016. Reduction of Sr-90 flux will be achieved through sequestration of Sr-90 in the PRB. The groundwater Sr-90 concentrations decreased by 90 percent in the existing barrier as a result of previous injections within two years as demonstrated through ongoing performance monitoring (PNNL-SA-70033). With time, Sr-90 concentrations should decrease further as more Sr-90 is incorporated into the apatite structure. This technology, if successful, could be implemented as a full remedial action under an amended Interim ROD or a Final ROD for the site.

This design optimization study provides a detailed discussion of test objectives and outlines the technical approach for development of field-scale deployment to optimize the installation of an apatite PRB through well injections, which may result in a beneficial extension of the PRB to an overall minimum length of 274 m (900 ft) as shown in Figure 3.

Note: The 1301-N LWDF has been backfilled since this photo was taken. Adapted from PNNL-17429.

Figure 3. Test Site Location Aerial Photo in 2003

This document is organized as follows:

- Section 1: Introduction
- Section 2: Treatment Technology Description
- Section 3: Test Objectives

- Section 4: Experimental Design
- Section 5: Equipment and Materials
- Section 6: Sampling and Analysis
- Section 7: Data Management
- Section 8: Data Analysis and Interpretations
- Section 9: Health and Safety
- Section 10: Residuals Management
- Section 11: Reports
- Section 12: Schedule
- Section 13: References

1.2 Background

The Hanford Site is located in southeastern Washington State near Richland, Washington. The 100 Area is located along the Columbia River and includes nine DOE nuclear reactors previously used for plutonium production, one of which is the 100-N Reactor (Figure 1).

Operation of the 100-N nuclear reactor required the disposal of bleed and feed cooling water from the reactor's primary cooling loop, the spent fuel storage basins, and other reactor-related sources. Two crib and trench liquid waste disposal facilities (LWDFs) were constructed to receive these waste streams, and disposal consisted of percolation into the soil. Figure 4 shows the locations of these LWDFs in relation to the rest of the 100-N site and Columbia River shoreline. The first LWDF (116-N-1/1301-N) was constructed in 1963, about 244 m (800 ft) from the river. Liquid discharges to this facility primarily contained radioactive fission and activation products, including cobalt (Co)-60, cesium (Cs)-137, Sr-90, and tritium. Minor amounts of hazardous wastes such as sodium dichromate, phosphoric acid, lead, and cadmium were also part of the waste stream. When Sr-90 was detected at the shoreline, a second LWDF (116-N-3/1325-N) was constructed farther inland (1983), and disposal at the first LWDF was eventually terminated. Discharges to the 116-N-3 LWDF ceased in 1991.

The *Integrated 100 Area Remedial Investigation/Feasibility Study Work Plan, Addendum 5: 100-N Decision Unit* (DOE/RL-2008-46-ADD5) presents a more complete history of the groundwater contamination at 100-N. In summary, as a result of wastewater disposal practices, soils beneath the LWDFs were contaminated from the surface sediments to the unconfined aquifer. A portion of the contaminants migrated to the Columbia River via groundwater. To address contamination, 100-N was divided into two OUs. The 100-NR-1 OU contains all the source waste sites located within the main industrial area around the 100-N Reactor and the Hanford Generating Plant, and includes the surface sediments and subsurface sediments associated with the LWDFs. Remedial activities are ongoing to address the contamination in this unit. 100-NR-2 contains the contaminated groundwater and aquifer beneath the 100-NR-1 OU.

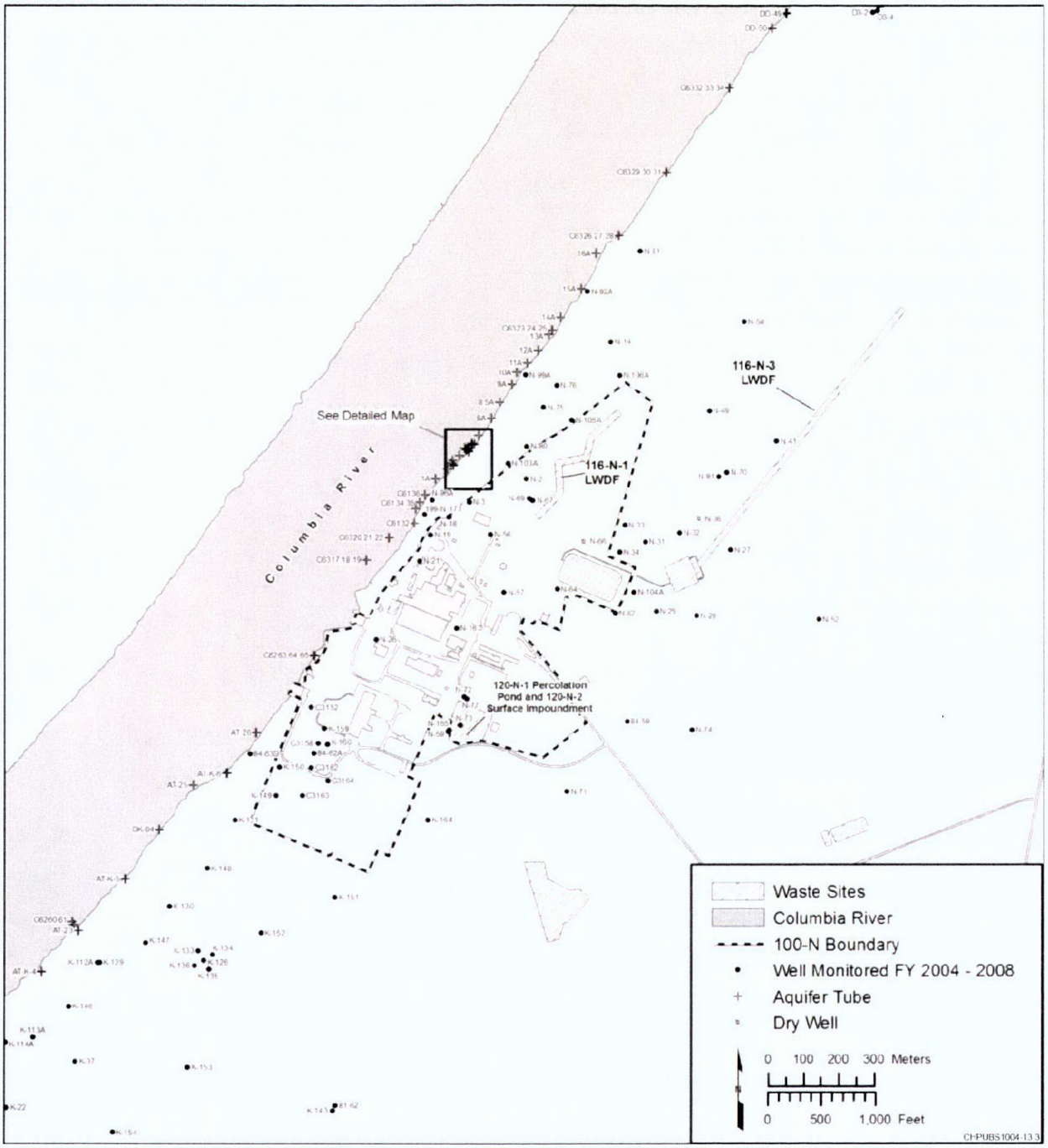


Figure 4. 100-N Area Groundwater Monitoring Wells

1.3 Site Hydrogeology

Stratigraphic units of significance in 100-N include the Elephant Mountain Basalt, Ringold Formation and the Hanford formation. Figure 5 shows that the unconfined aquifer at 100-N near the shoreline is composed of gravels and sands of the Ringold Formation and Hanford formation. The Ringold Formation is composed of several lithologic facies; of most interest at 100-N is the Ringold Unit E, which primarily forms the unconfined aquifer beneath the Hanford formation, and the Ringold Upper Mud Unit. The base

of the unconfined aquifer is defined by the top of the Ringold Upper Mud, which is considered an aquitard rather than an impermeable unit.

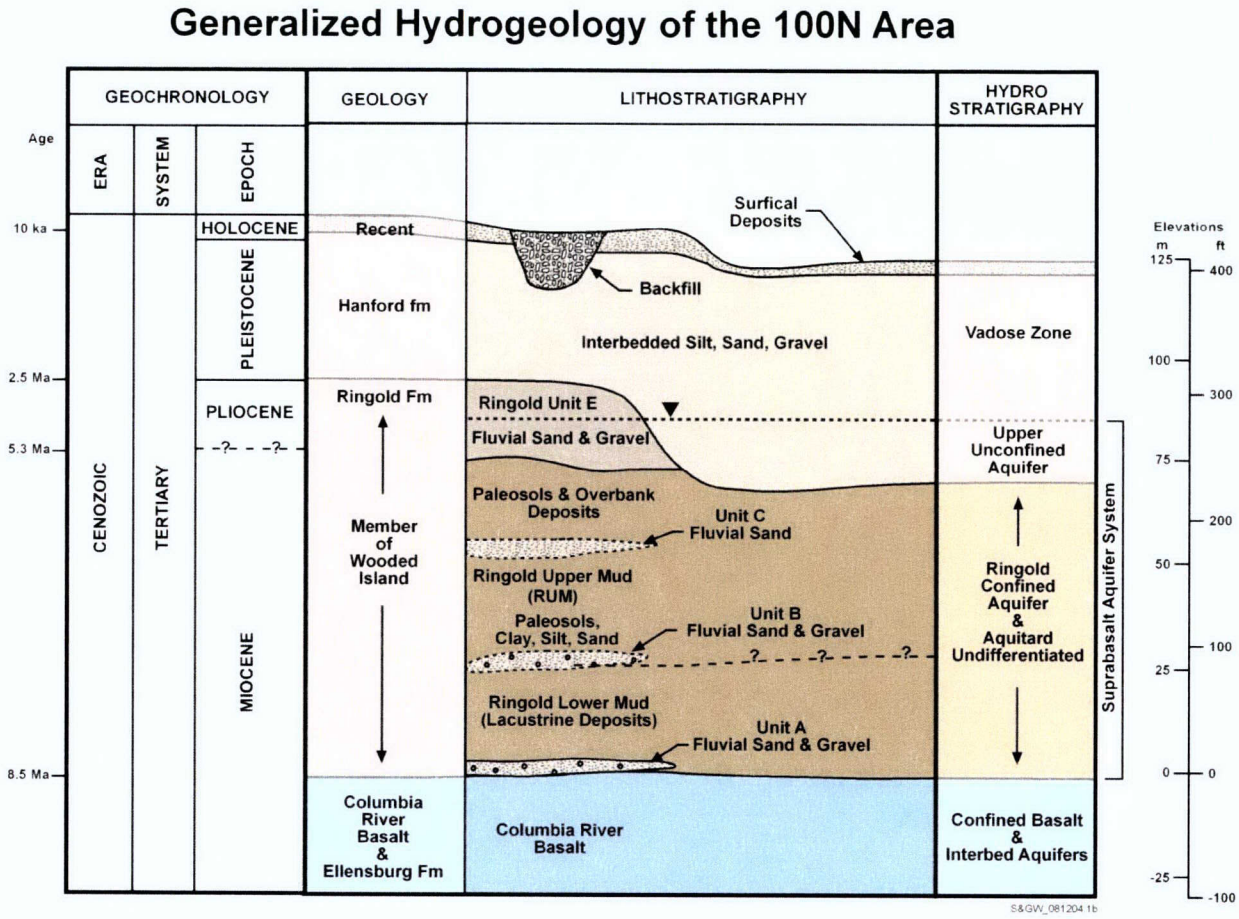


Figure 5. Generalized Geologic Stratigraphic Section of 100-N

The uppermost Ringold stratum at 100-N is Unit E, consisting of variably cemented pebble to cobble gravel with a fine- to coarse-grained sand matrix. Sand and silt interbeds also may be present. Unit E primarily forms the unconfined aquifer in 100-N and is approximately 12 to 15 m (39 to 49 ft) thick. The base of the aquifer is situated at the contact between the Ringold Unit E and the confined underlying, much less transmissive, silty strata referred to locally as the Ringold Upper Mud, approximately 60 m (197 ft) thick.

The uppermost stratigraphic unit in 100-N is the Hanford formation, which consists of uncemented and clast-supported pebble, cobble, and boulder gravel with minor sand and silt interbeds. The matrix in the gravel is composed mostly of coarse-grained sand, and an open-framework texture is common. For most of 100-N, the Hanford formation extends from ground surface to just above the water table, 5.8 to 24.5 m (19 to 77 ft) in thickness. However, channels of Hanford gravels extend below the water table.

The Hanford formation is more transmissive (3 to 10 times) than the underlying Ringold Unit E. However, due to geologic heterogeneity, the hydraulic conductivity in both units is highly variable. Typical values of 15 and 182 meters per day (m/d) (19 and 597 feet/day [ft/d]) have been used for modeling purposes for the Ringold Formation and Hanford formation, respectively (HydroGeoLogic, Inc., 2001, *Strontium-90 Transport in the Near River Environment at the 100-N Area*). Figure 5 provides a generalized geologic stratigraphy of 100-N. Figure 6 depicts a cross section of the Hanford and Upper

Ringold Units in the near-river environment. As illustrated in Figure 6, the aquifer extends into the Columbia River channel and the high river stage rises into the Hanford formation.

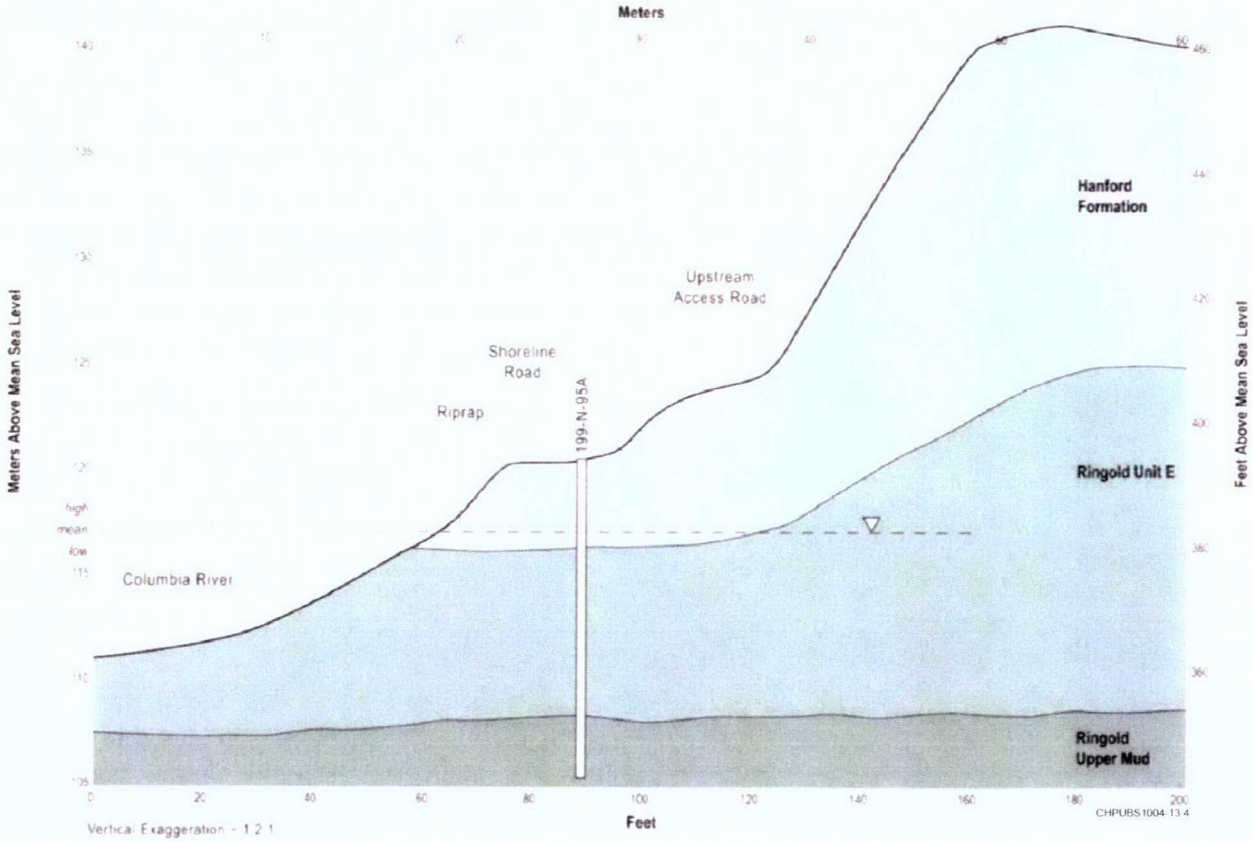


Figure 6. Site Geologic Model in Cross Section

Site-specific hydrogeologic characterization data were gathered during the installation of injection and monitoring wells for previous treatability tests. In addition, two pilot test sites located at the upstream and downstream ends of the PRB section, 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. Figure 7 shows the locations of these pilot test sites in relation to the existing barrier. Figure 8 shows the details of monitoring and injection well locations and depths at the first pilot test site. Figure 9 shows the details of monitoring and injection well locations and depths and the locations of aquifer tubes adjacent to the second pilot test site. Comparison of test results from these two locations indicate that permeability contrast between the Hanford formation and Ringold Formation is significantly less over the upstream one-third of the barrier. The estimated hydraulic conductivity for the Hanford formation and Ringold Formation over the upstream portion of the barrier is 12 and 10 m/day (39 and 32 ft/day), respectively (PNNL-17429). By contrast, hydraulic conductivity for the Hanford and Ringold Formations over the downstream portion of the barrier was estimated at 29 and 9 m/day (95 and 29 ft/day), respectively. Based on previous injections, temporary groundwater mounding has been observed, which indicates the injections have overcome the localized variability in hydraulic conductivity. One of the objectives of the design optimization study is to evaluate injection into each of these formations separately. The actual injection volumes will potentially be adjusted based upon field observations during injections.

Geologic characterization data collected during well installation were used to develop a detailed geologic cross section along the 100-N shoreline. Figure 10 shows the vertical Sr-90 profiles along this cross

section. Figure 11 shows the vertical Sr-90 profiles through the existing PRB. Because the texture of the sediments between the upper stratigraphic units (Ringold Unit E, Hanford formation, and backfill) is so similar (i.e., sandy gravel), distinguishing between these units is sometimes uncertain. Furthermore, the boundaries between these units are not always discrete, but instead often grade into one another as a result of the sediment reworking and mixing during deposition. Although the actual formation contact depths remain somewhat uncertain, the geologic cross sections depicted in Figures 10 and 11 represent the working model for the site.

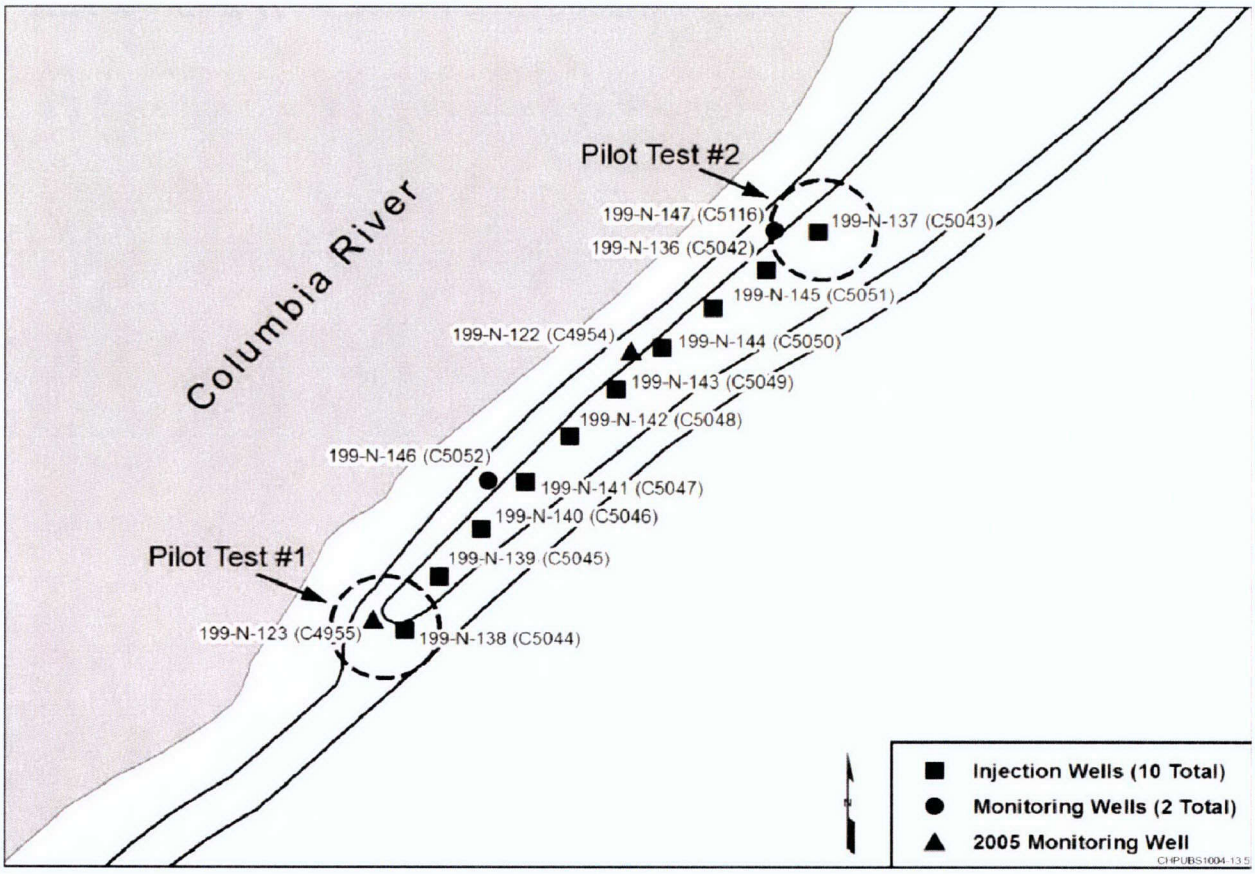
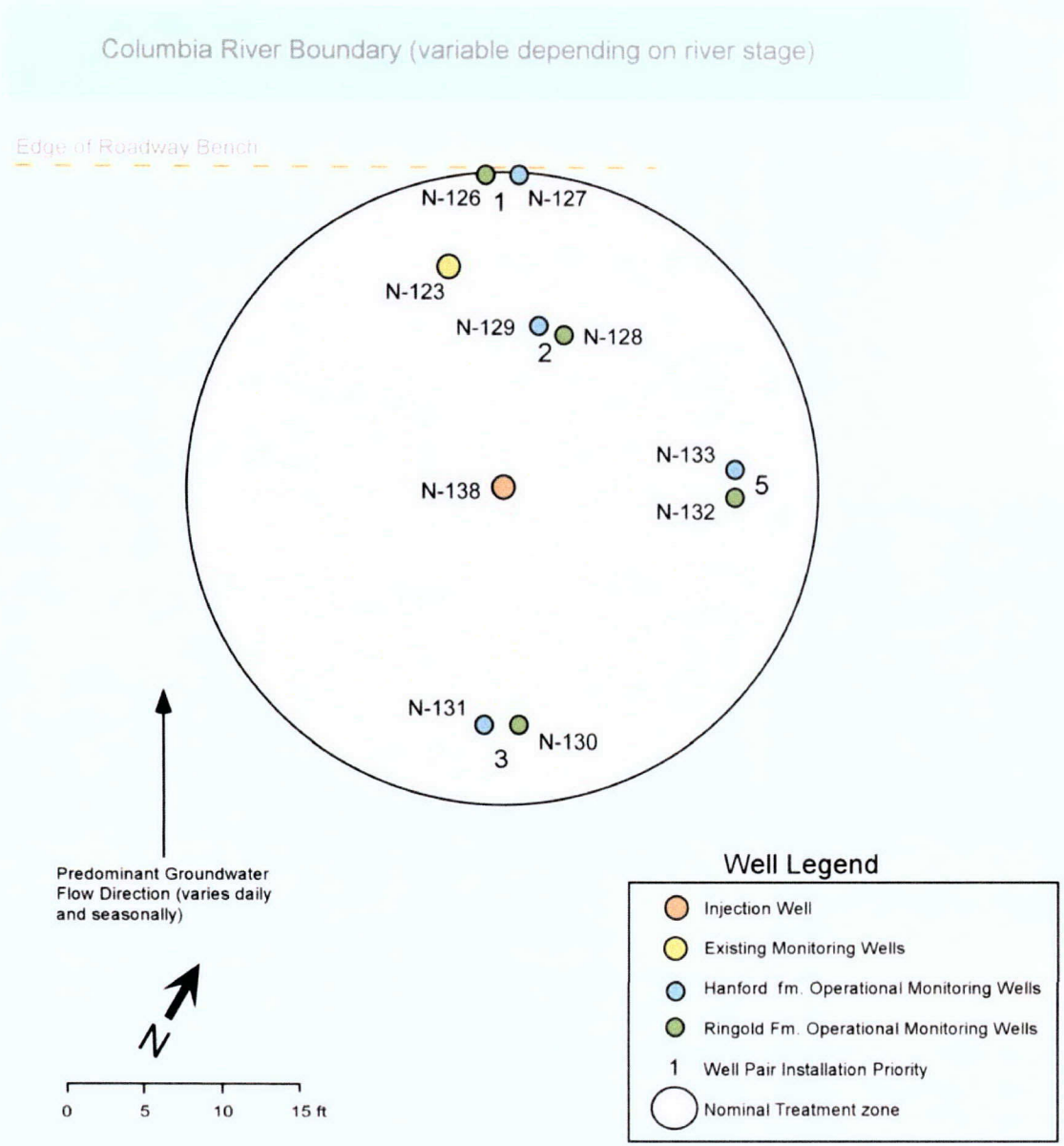


Figure 7. Existing Apatite Permeable Reactive Barrier Treatment Area



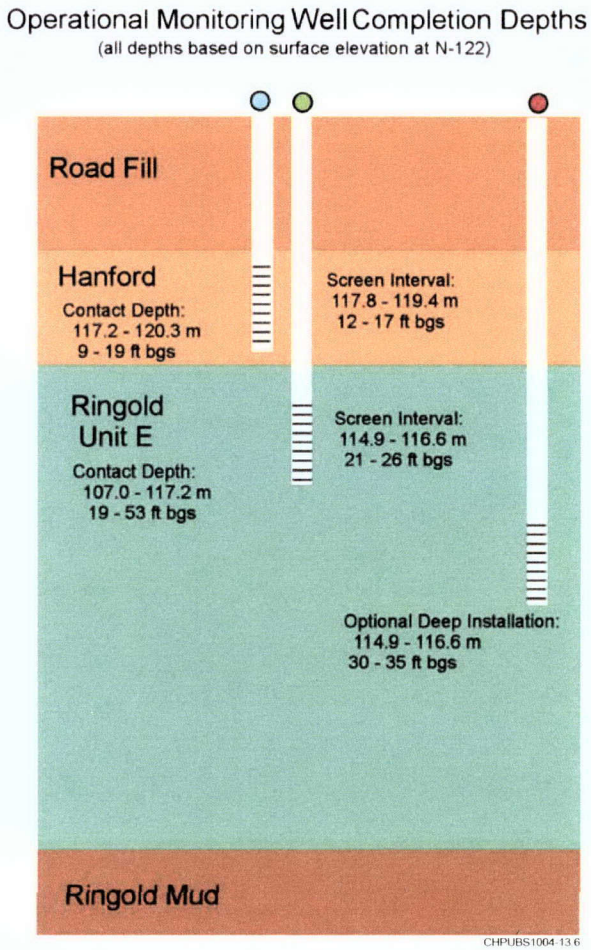
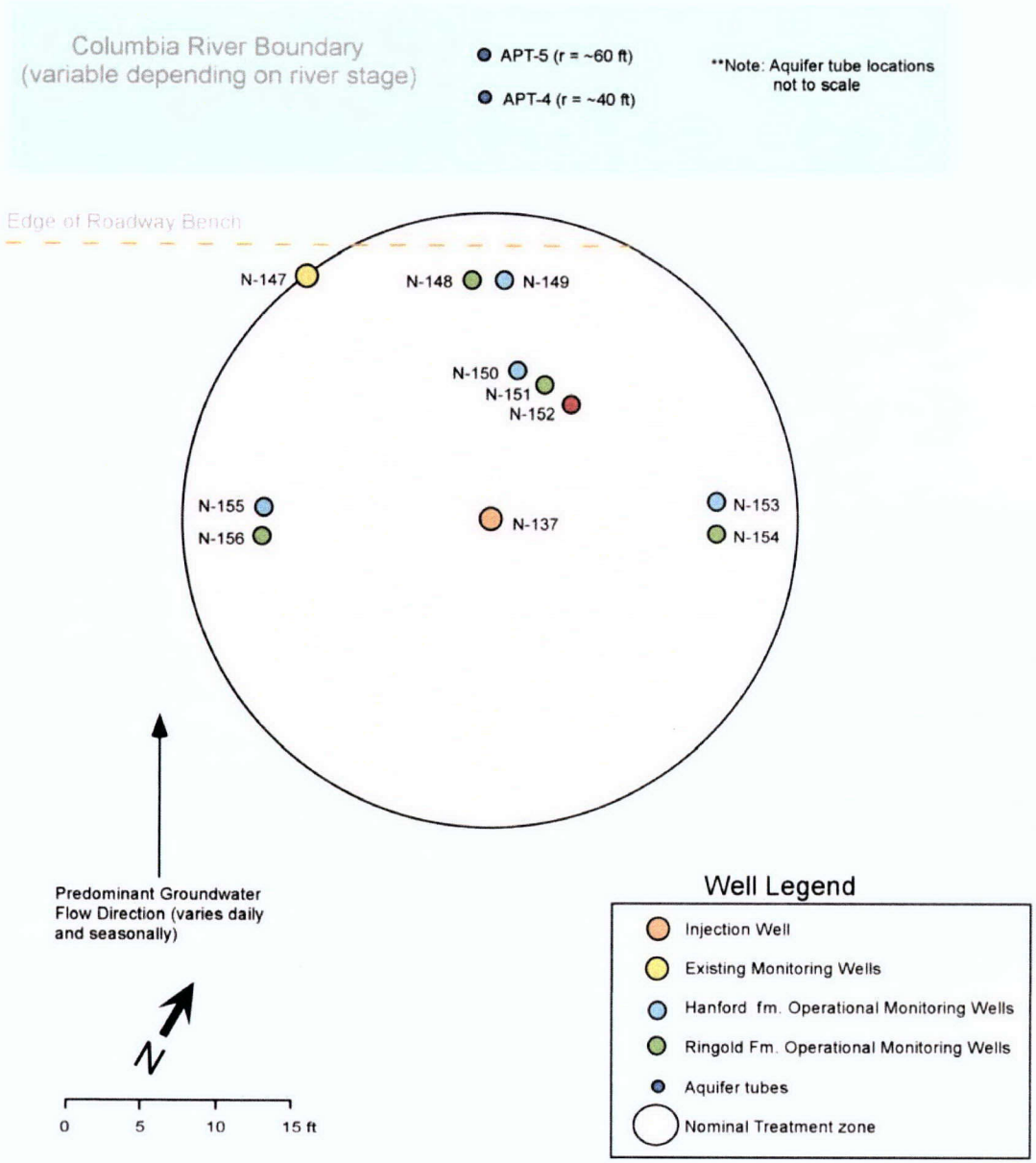


Figure 8. Pilot Test Location 1



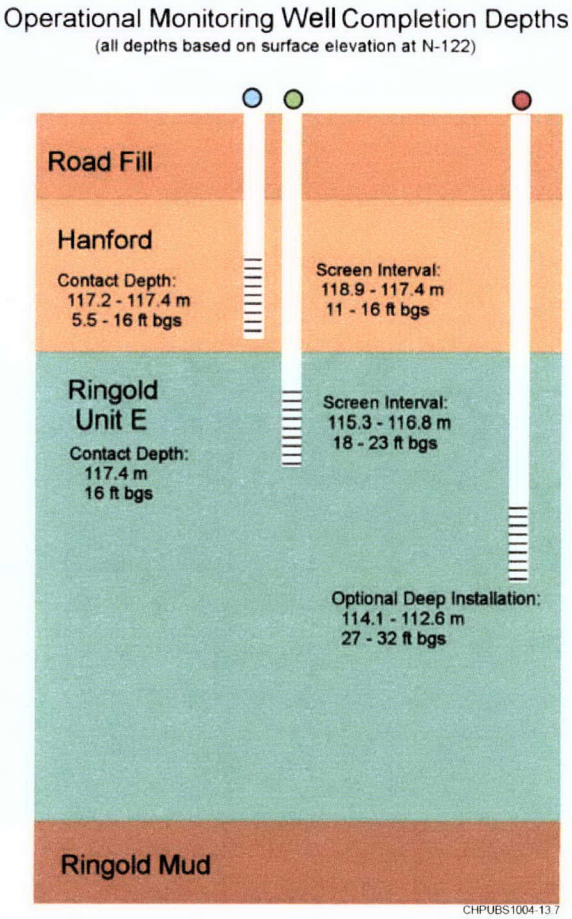


Figure 9. Pilot Test Location 2

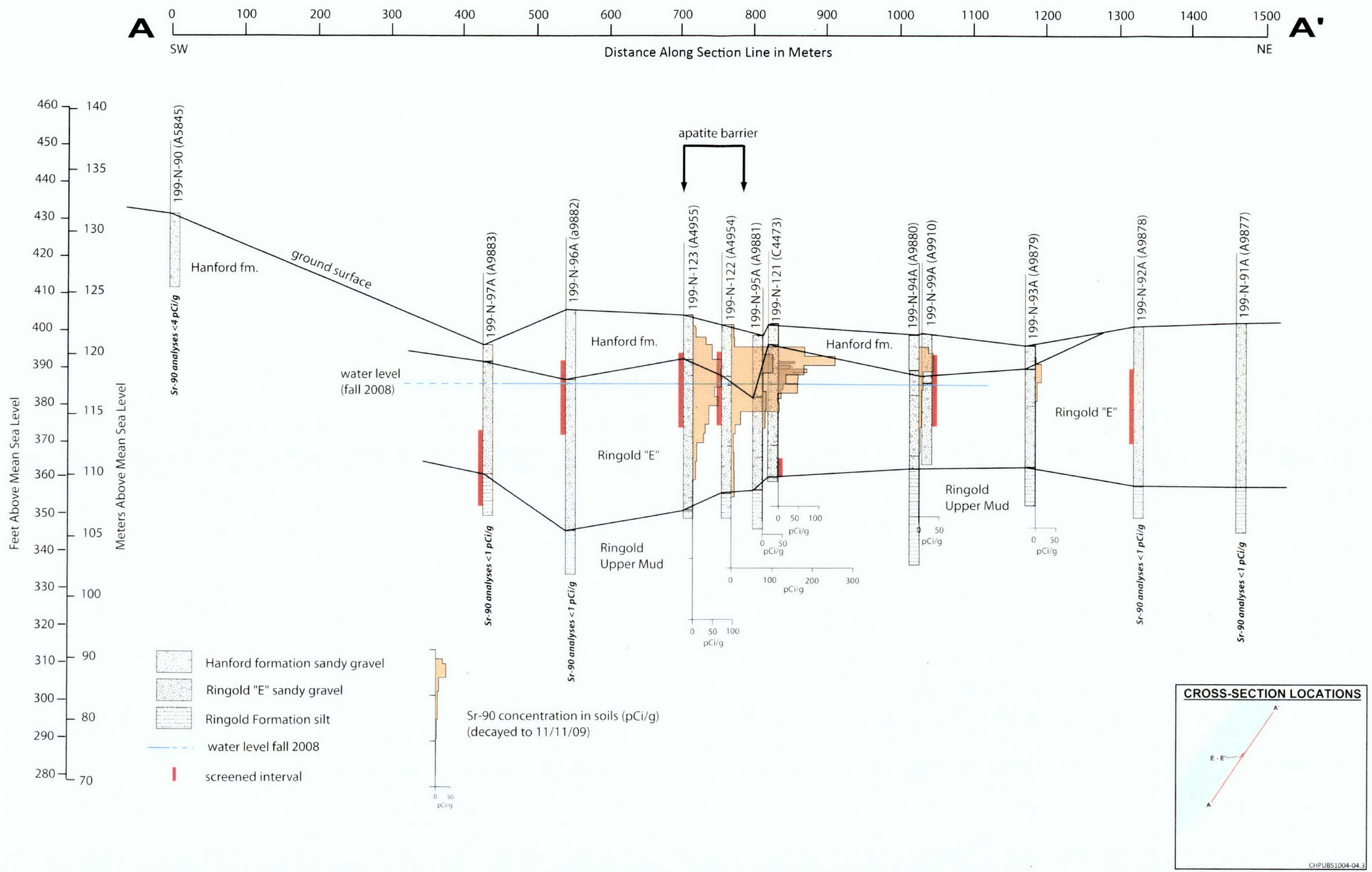


Figure 10. Geologic Cross Section with Vertical Strontium-90 Profiles

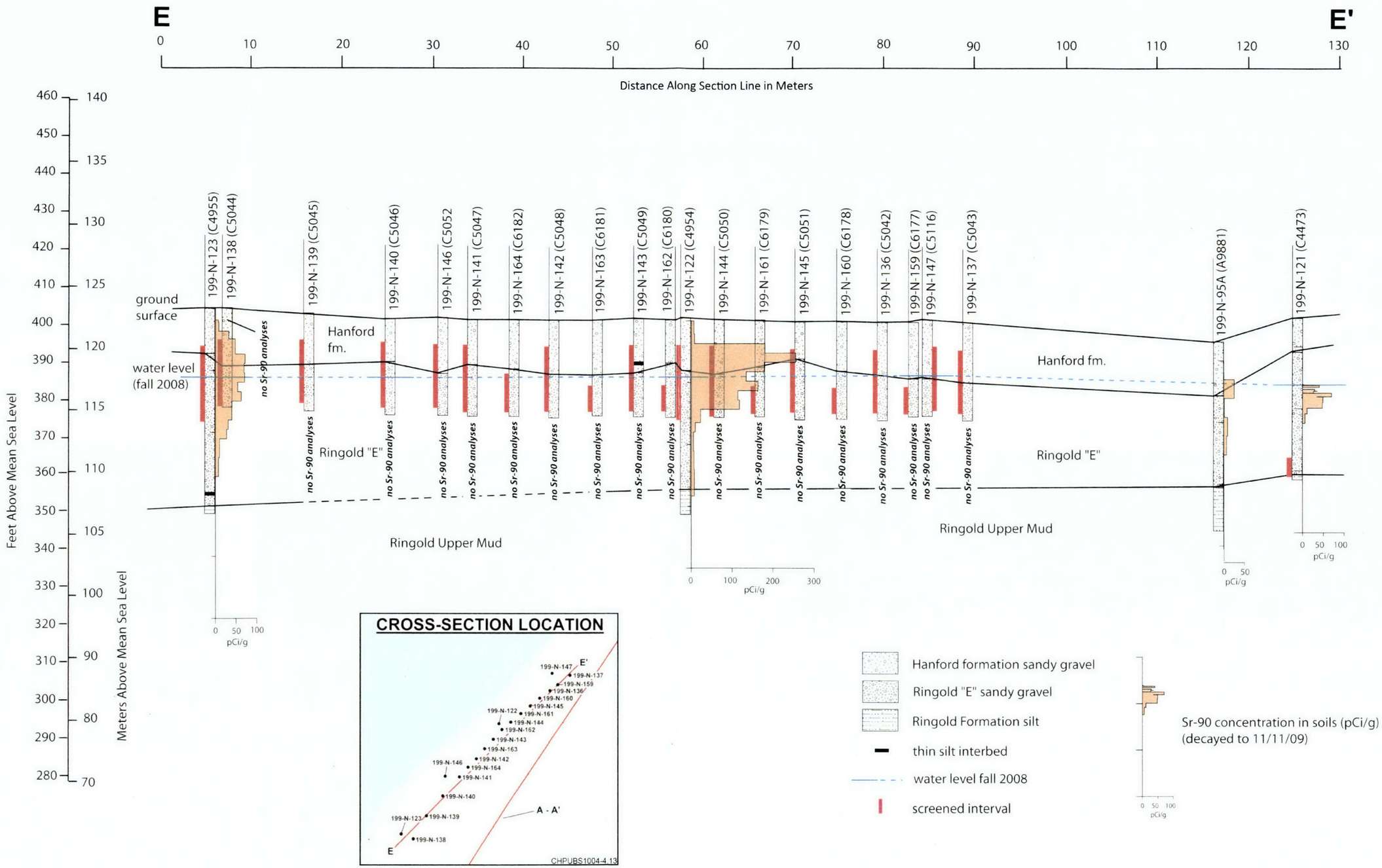


Figure 11. Geologic-Cross Section Through Existing Permeable Reactive Barrier with Vertical Strontium-90 Profiles

Groundwater flows primarily in a north-northwesterly direction most of the year and discharges to the Columbia River, as shown in Figure 12, although flow is reversed (river water flow into the aquifer) for short periods under high river stage. The groundwater gradient varies from 0.0005 to 0.003 m/m. Near the LWDF facilities, average groundwater velocities are estimated to be between 0.03 and 0.6 m/d (0.1 and 2 ft/d), where 0.3 m/d (1 ft/d) is generally considered as typical. However, groundwater flows near the river are significantly influenced by both the diurnal (daily) and seasonal variability in Columbia River stage.

Fluctuations in river stage resulting from seasonal variations and daily operations of Priest Rapids Dam, located 29 km (18 mi) upstream of 100-N have a significant impact on groundwater flow direction, hydraulic gradient, and groundwater levels near the river. The volume of water moving in and out of the unconfined aquifer on both a daily and seasonal basis is an order of magnitude greater than groundwater flowing as a result of the regional hydraulic gradient. In addition, with the changing direction of groundwater flow, pore water velocities near the river may exceed 10 m/d (32.8 ft/d) (HydroGeoLogic, Inc., 1999, *Groundwater-River Interaction in the Near River Environment at the 100-N Area*). During the high river stage, river water moves into the bank and mixes with groundwater. The zone of mixing is restricted to within tens-of-meters of the shoreline. During low river stage, this bank storage water drains back into the river and may be observed as springs along the riverbank. Springs, seeps, and subsurface discharge along the Columbia River bank are the primary pathway of 100-N groundwater contaminants to the Columbia River. Additional details on the extent of seasonal and daily changes in river stage at the site from Priest Rapids Dam discharge is reported in the 2008 interim report (PNNL-17429).

1.4 Nature and Extent of Strontium-90 Contamination

Groundwater at 100-N has been contaminated with various radionuclides and non-ionic and ionic constituents. Of primary concern are the presence of Sr-90 in the groundwater and the discharge of Sr-90 to the Columbia River via groundwater. Strontium-90 may bioaccumulate in plants and animals as a result of its chemical similarity to calcium. With a half-life of 29.1 years, it will take approximately 300 years for the Sr-90 inventory present in the subsurface at 100-N to decay to activities below the 8 picoCuries per liter (pCi/L) drinking water standard.

The zone of Sr-90-contaminated soils resulting from 30 years of wastewater discharge to the LWDFs includes the portions of the vadose zone that were saturated during discharge operations, and the underlying aquifer, which extends out to the Columbia River. Figure 13 shows a conceptual model of the site, including the location of the Sr-90 plume in the underlying aquifer and its relation to the LWDFs. During operations, a groundwater mound approximately 6 m (20 ft) high was created. Not only was the water table raised into the generally more transmissive Hanford sediments, but steeper hydraulic gradients were created, increasing the groundwater flow rate toward the river.

While the 100-N Reactor was operating, the volume of effluent discharged into the LWDFs caused extensive seepage of contaminated groundwater along the riverbank. Figure 14 shows the area of the riverbank that experienced seepage related to LWDF use, in relation to the location of LWDF 116-N-1/1301N. Since that time, the number of springs and seeps has decreased in proportion to the decrease in artificial recharge caused by the wastewater disposal. The seepage contained high levels of radionuclides, which posed a risk to humans and aquatic biota. To mitigate the risk of radiological exposure, large basalt boulders were placed along the shoreline as riprap in 1984. Along with the riprap steel casings, referred to as "seep wells," were installed to provide sampling access to the seepage. Figure 15 shows the locations of these seep wells and the nearby seepage spots in relation to both LWDFs. The seep wells have been sampled annually in the past to satisfy near-field environmental monitoring requirements.

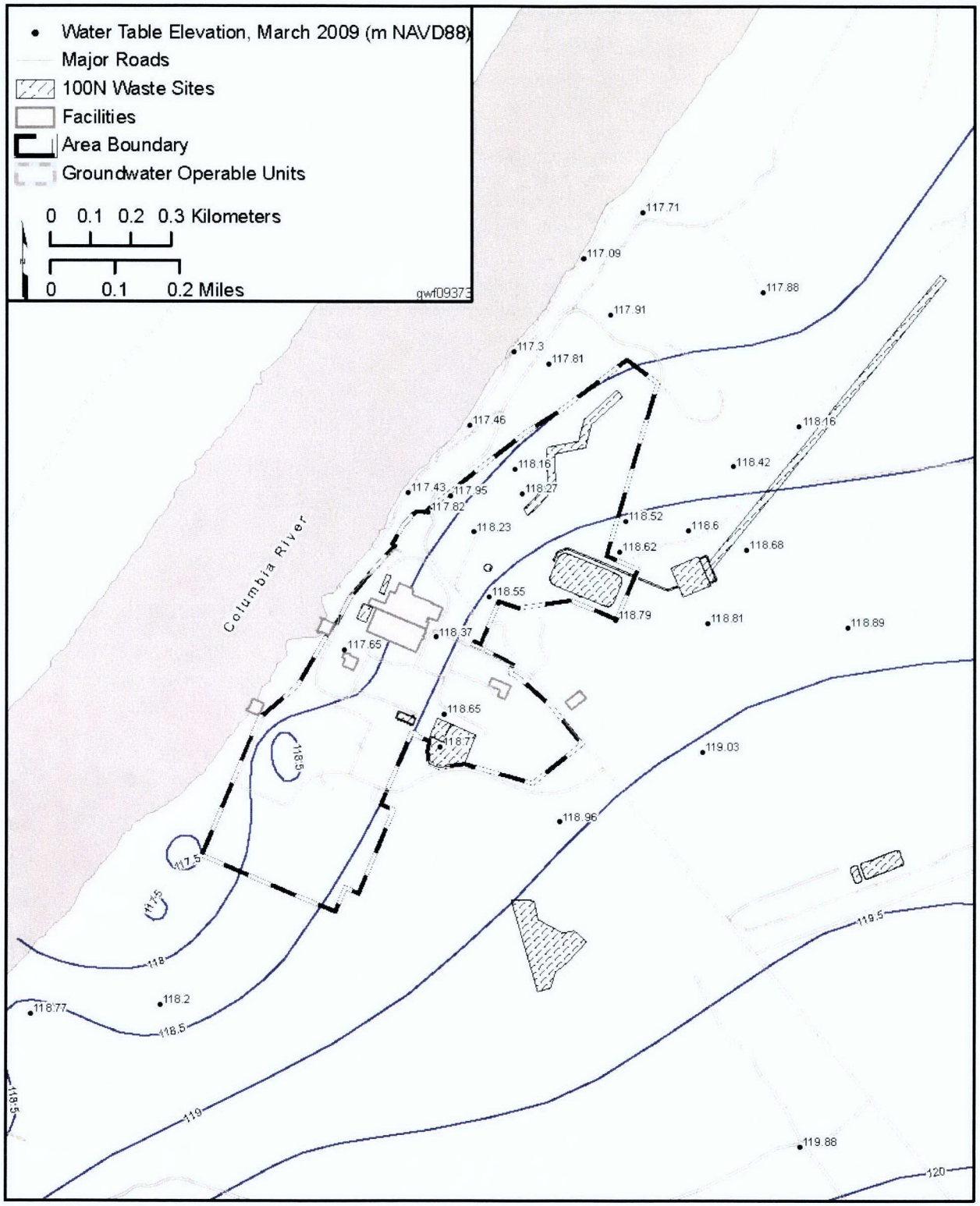


Figure 12. Groundwater Contour Map (March 2009)

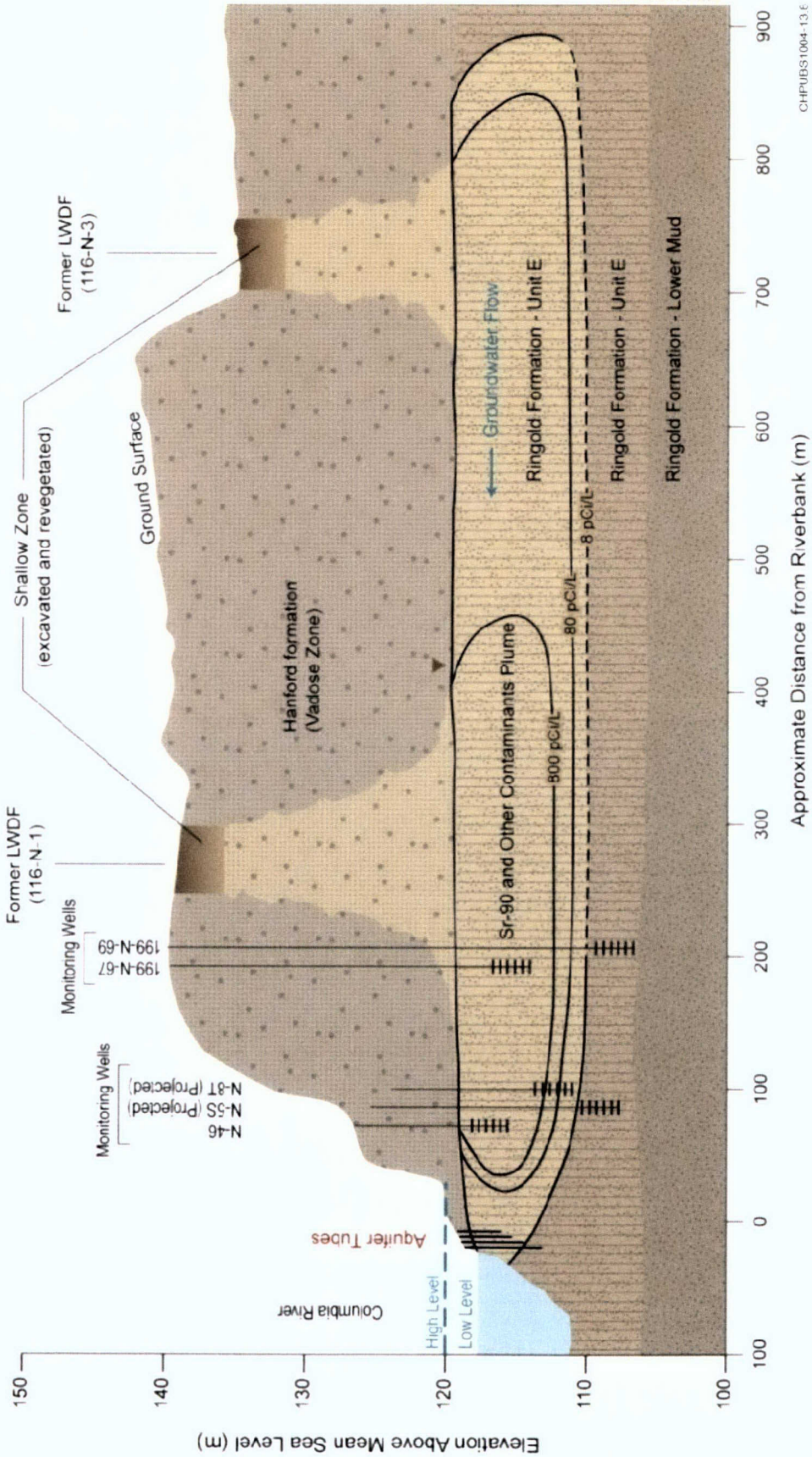


Figure 13. Conceptual Site Model for 100-NR-1/NR-2 Operable Units

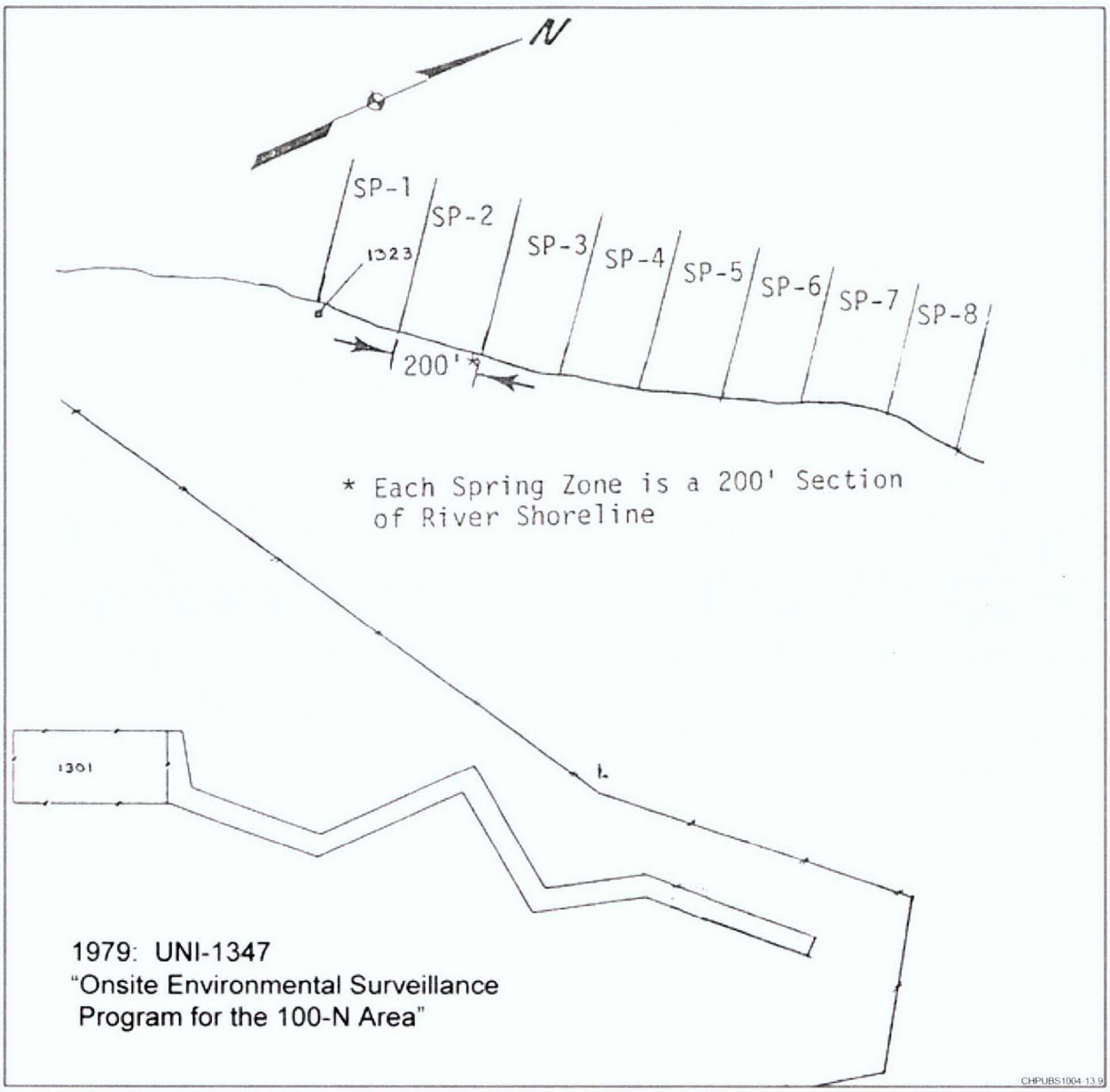


Figure 14. Areas of Riverbank Springs at 100-N During Operations (Prior to Seep Well Installation)

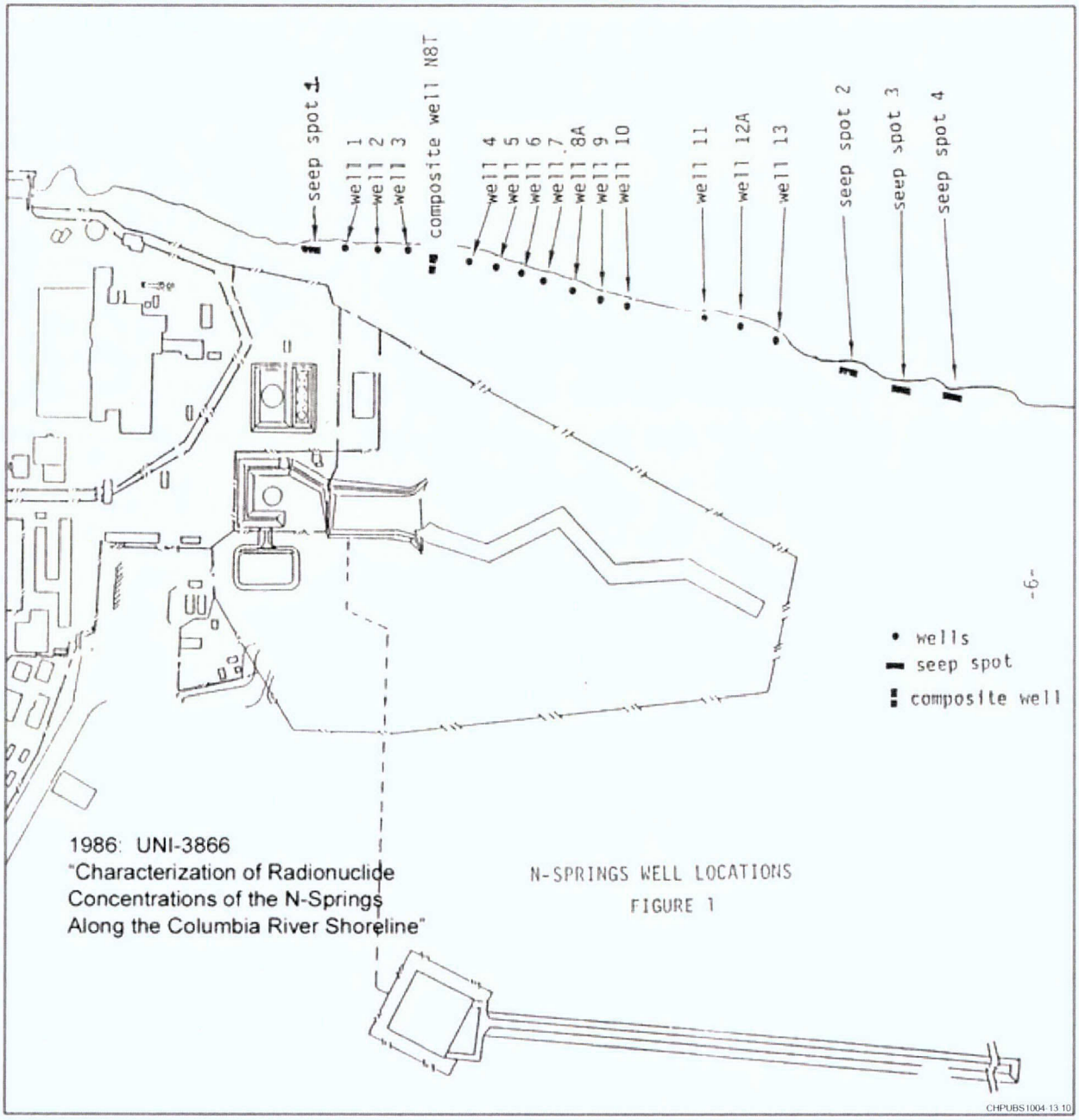


Figure 15. Locations of Seep Wells and Seepage Spots Along the 100-N Shoreline

N-Springs data from 1985 to 1991 showed significantly higher concentrations of Sr-90 in seep wells NS-2, NS-3, and NS-4 compared to the adjacent springs upstream and downstream (BHI-00185, *Technical Reevaluation of the N-Springs Barrier Wall*). Well NS-3 and the neighboring monitoring wells 199-N-46 and 199-N-8T have currently and historically shown the highest Sr-90 concentrations along the shoreline, with concentrations as high as 15,000 pCi/L observed at Well 199-N-46 in 2001 (Innovative Treatment and Remediation Demonstration [ITRD] Program, 2001, *Hanford 100-N Area Remediation Options Evaluation Summary Report*; DOE/RL-2004-21, *Calendar Year 2003 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit [OU] Pump & Treat Operations*). Recent clam data collected for the ecological risk assessment (ERA) show that the highest concentrations of Sr-90 in clams were observed along approximately 91 m (300 ft) of riverbank that encompass NS-1, NS-2, NS-3, and NS-4. The previous N-Springs data, recent aquifer tube data, groundwater data, and clam data (DOE/RL-2006-26, Rev. 1, Reissue, *Aquatic and Riparian Receptor Impact Information for the 100-NR-2 Groundwater Operable Unit*) all indicate that treating the 91 m (300 ft) of shoreline near Well 199-N-46 will address the highest concentration portion, if not the majority, of the near-shore Sr-90 contamination. The targeted length of shoreline under the existing PRB is between approximately NS-1 and NS-4. This design optimization study will potentially extend the PRB to treat a larger area up- and downstream of the area with the highest concentrations.

In 1995, the Sr-90 groundwater plume extended approximately 400 m (1,300 ft) along the length of the river between the 1,000 pCi/L contours, and approximately 800 m (2,600 ft) between the 8 pCi/L (the drinking water standard) contours (HydroGeoLogic, Inc., 1999). The highest concentrations along the shoreline were observed between Wells 199-N-94 and 199-N-46. An area of "preferential flow" was identified in BHI-00185 that encompasses Wells 199-N-94, 199-N-95, and 199-N-46. The 199-N prefix for monitoring wells refers to a grid location (199) and reactor area (N). Because of an erosional feature in the Ringold Unit, the Hanford formation dips below the water table at this location, forming a more transmissive flow path between the disposal crib and the Columbia River. Wastewater appears to have concentrated along this route, resulting in higher concentrations in this area than would be predicted based on regional groundwater flow direction.

A 2003 report indicated that the majority of the 1,500 Ci of Sr-90 remaining in the unsaturated and saturated zones in 100-N is present in the vadose zone above the aquifer (DOE/RL-2004-21). An estimated 72 Ci of Sr-90 are contained in the saturated zone soils, approximately 0.8 Ci is in the groundwater, and 1,427 Ci are in the vadose zone. Data from soil borings collected along the riverbank indicate that Sr-90 concentrations in soil reach a maximum concentration near the mean water table elevation and then decrease with depth (BHI-00185). This vertical contaminant distribution is also reflected in depth-discrete groundwater concentration data. Most of the Sr-90 contamination is found in the Hanford formation, with roughly a third of the mass in the upper portion of the lower Ringold E (Figure 16) (PNNL-18303). Sr-90 concentrations in the Ringold E decrease with depth. Because Sr-90 has a much greater affinity for sediment than water (high K_d), its rate of transport in groundwater to the river is considerably slower than the actual groundwater flow rate. The relative velocity of Sr-90 to groundwater is approximately 1:100. Under current conditions, approximately 0.14 to 0.19 Ci are released to the Columbia River from 100-N annually (ITRD, 2001).

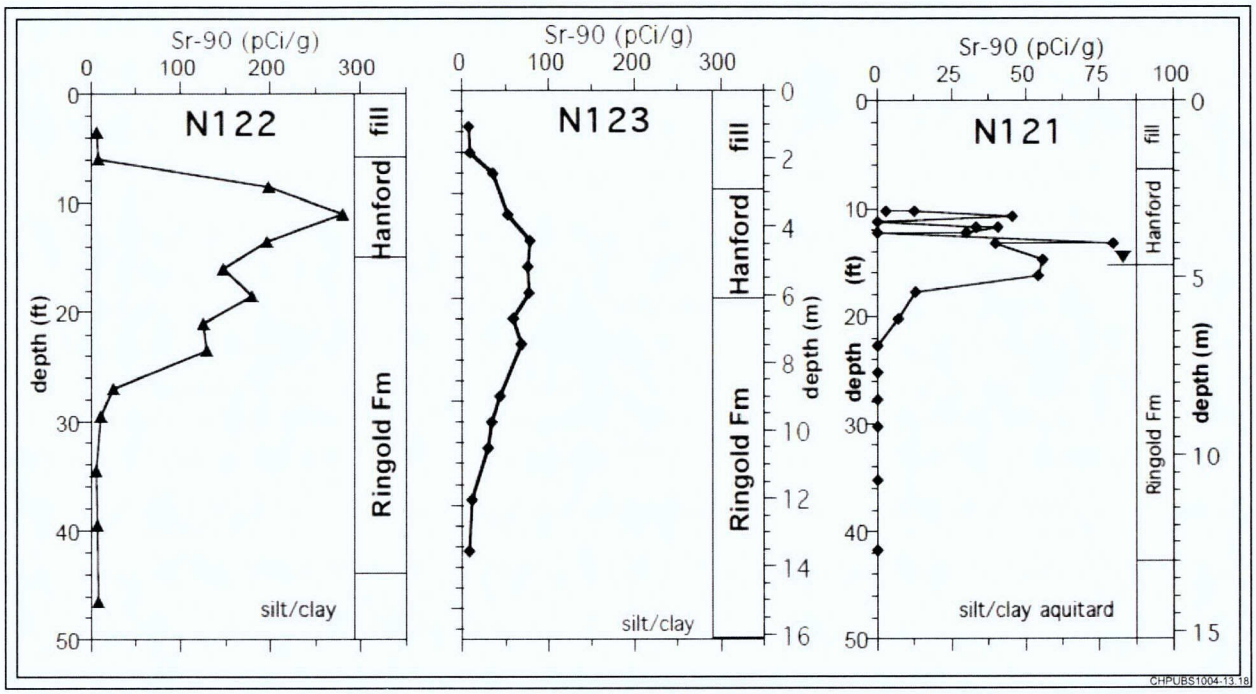


Figure 16. Sr-90 Contamination in Subsurface Sediments

The Sr-90 concentrations in groundwater along the Columbia River at 100-N show significant temporal variability based on measurements from aquifer tubes and compliance monitoring wells installed prior to the apatite treatability test. Additionally, as discussed previously, there is a general spatial trend in Sr-90 concentrations in the aquifer along the river, with the highest concentrations existing over the central/ downstream portion of the 91 m (300-ft) long apatite PRB section, and concentrations decreasing from this high in both the upstream and downstream directions are shown in Figure 17.

Sr-90 has not been detected in the river water column as monitored by river aquifer tubes; however, recent pore water characterization activities, performed under the *Remedial Investigation Work Plan for Hanford Site Releases to the Columbia River* (DOE/RL-2008-11), indicate Sr-90 entering the river near the 100-N outfall and spillway. The three-phase groundwater upwelling sampling and analysis under DOE/RL-2008-11 is complete; the additional sampling activities are being implemented for estimating the impacts of 100-N contamination on the Columbia River. These data will provide insight regarding contaminant levels potentially entering the river through the hyporheic zone and groundwater/river mixing ratios within the biotic zone (upper approximately 30 cm [12 in.] of substrate). This work is being performed under the *Sampling and Analysis Plan for the 100-NR-2 Operable Unit River Pore Water Investigation* (DOE/RL-2010-69).

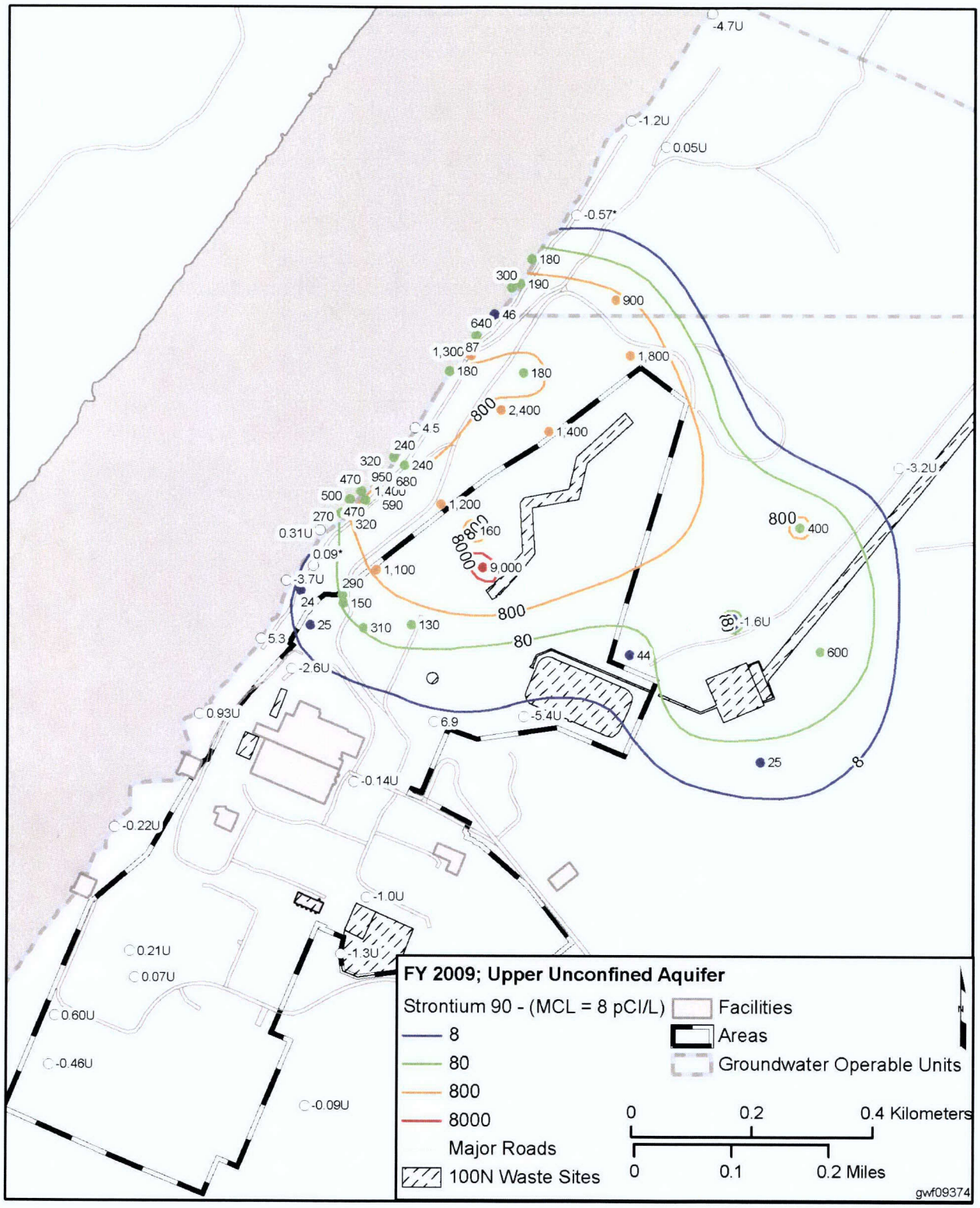


Figure 17. Strontium-90 in 100-N (2009), Upper Part of Unconfined Aquifer

1.5 Remediation History

The following text discusses the remediation history studies to date.

1.5.1 National Priorities List/Corrective Measures Study

The 100-N area of the Hanford Site was placed on the National Priorities List (NPL) in 1989 (40 CFR 300, "National Oil and Hazardous Substances Pollution Contingency Plan," Appendix B, "National Priorities List"), the same year DOE, EPA, and Ecology signed the Tri-Party Agreement, which established the procedural framework and schedule for the remedial response actions at the Hanford site (Ecology et al., 1989a). In 1994, the *Limited Field Investigation Report for the 100-NR-2 Operable Unit: Hanford Site, Richland, Washington* (LFI) (DOE/RL-93-81) was published and, based on the data presented, a qualitative risk assessment (QRA) was conducted. The QRA indicated that groundwater contaminants in the 100-NR-2 OU exceeded human health risk levels, prompting an Expedited Response Action to address Sr-90 in groundwater. In 1995, a pump-and-treat system was installed as an interim measure to control the movement of Sr-90 to the Columbia River.

A corrective measures study (CMS) (DOE/RL-95-111, *Corrective Measures Study for the 100-NR-1 and 100-NR-2 Operable Units*), conducted to support the selection of remedial alternatives to address contamination at the 100-NR-1 and 100-NR-2 OUs, determined that sufficient information was not available to decide a final groundwater remedy. Four alternatives were proposed for consideration as interim remedies (No Action, Institutional Controls, Hydraulic Controls, and Pump-and-Treat). Pump-and-treat was retained as the selected interim remedy because it was expected to provide a hydraulic barrier, while removing Sr-90 from extracted groundwater, and did not preclude any potential final remedies.

The results from the CMS and the Tri-Parties' preference for interim remedial action were summarized in the *Proposed Plan for Final Remedial Actions at the 100-NR-1 Source Sites Operable Unit and Interim Remedial Action at the 100-NR-2 Groundwater Operable Unit* (DOE/RL-96-102), which was made available to the public in March 1998. In September 1999, DOE, Ecology, and EPA signed the Interim Action ROD for the 100-NR-2 OU (EPA/ROD/R10-99/112).

1.5.2 Expedited Response Action

In response to a regulatory Action Memorandum, dated September 23, 1994 (Butler and Smith, 1994, "Action Memorandum: N-Springs Expedited Response Action Cleanup Plan, U.S. Department of Energy Hanford Site, Richland, WA"), an expedited response action to address Sr-90 groundwater contamination was implemented at N-Springs. The Action Memorandum required the installation and operation of a 189 L/min (50 gpm) pump-and-treat system and the construction of a grouted-hinge sheet pile wall at the river's edge by September 1995.

In March 1995, Ecology and EPA concurred with DOE that installing the sheet pile wall could not be achieved in the manner specified. Ecology and EPA subsequently directed DOE to proceed with installing a pump-and-treat system as an expedited response action. The 100-NR-2 OU pump-and-treat system was completed by August 1995 and was in full operation by September 1995, meeting the Tri-Party Agreement Milestone M-16-12D (Ecology et al., 1989a). Based on recommendations in the *N Springs Expedited Response Action Performance Evaluation Report* (DOE/RL-95-110), the system was upgraded to operate at 227 L/min (60 gpm) beginning on December 17, 1996.

1.5.3 Interim Action Record of Decision

The RAO specific to groundwater and surface water protection for the 100-NR-2 OU described in the Interim Action ROD included the following requirements:

- Protect the Columbia River from adverse impacts from the 100-NR-2 groundwater so designated beneficial uses of the Columbia River are maintained. Protect associated potential human and ecological receptors using the river from exposure to radioactive and nonradioactive contaminants present in the unconfined aquifer. Protection will be achieved by limiting exposure pathways, reducing or removing contaminant sources, controlling groundwater movement, or reducing concentrations of contaminants in the unconfined aquifer.
- Protect the unconfined aquifer by implementing remedial actions that reduce concentrations of radioactive and nonradioactive contaminants present in the unconfined aquifer.
- Obtain information to evaluate technologies for Sr-90 removal and evaluate ecological receptor impacts from contaminated groundwater (by October 2004).
- Prevent destruction of sensitive wildlife habitat. Minimize the disruption of cultural resources and wildlife habitat in general and prevent adverse impacts to cultural resources and threatened or endangered species.

The following actions were taken to fulfill the requirements of the Interim Action ROD:

- The pump-and-treat system was operated continuously from 1995 to 2006, when it was placed in standby by Tri-Party Agreement change request M-16-06-01 approved by DOE, EPA, and Ecology (Ecology et al., 1989a). Groundwater monitoring has been conducted as approved by Ecology, and annual reports summarizing the monitoring data have been submitted each year since the beginning of operations in 1995.
- Under the ITRD Program, the Technical Advisory Group (TAG) for 100-N completed a remedial options evaluation that included stabilization by phosphate injection (ITRD, 2001) in November 2001.
- *Strontium-90 at the Hanford Site and its Ecological Implications* (PNNL-13127) was submitted to DOE in May 2000. This report presented an assessment of the potential for ecological impacts to salmon embryos.
- An Ecological Risk Assessment was conducted in accordance with an approved sampling and analysis plan (DOE/RL-2006-26, Rev. 0). A comment draft report was submitted to Ecology on October 31, 2005. The final draft was issued in 2009 (DOE/RL-2006-26, Rev. 1, Reissue).
- A letter report, *Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit,* was submitted to DOE in October 2004 by Fluor/CH2M HILL (FH-0403540, "Transmittal of the Draft Letter Report, Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit"). This letter report and related public workshop comments (December 2004), together with the ITRD Report, contribute to the technology evaluation requirement specified in the Interim Action ROD.
- To field test a promising test treatment technology, a TTP was submitted to DOE in March 2006 (DOE/RL-2005-96). This TTP initiated implementation of an apatite PRB covering 91 m (300 ft) of the highest concentrations along the shoreline. In addition to the TTP, three separate addenda to the TTP have been submitted, each outlining additional testing to evaluate apatite emplacement methods or treatment areas. The first describes injection of a high-concentration aqueous solution to follow the initial low-concentration injection. Second is a plan for infiltration of aqueous solution into the vadose zone along the 100-N shoreline. The third investigates jet injection of various solutions.

1.5.4 Pump-and-Treat Performance

Installed in 1995, the pump-and-treat system at 100-N used four extraction wells, a treatment skid (using clinoptilolite), and two injection wells. The system operated from September 1995 through March 2006, removing approximately 1.8 Ci of Sr-90 from the aquifer. The 0.2 Ci removed each year by the pump-and-treat system was estimated to be 10 times less than the amount removed by natural radioactive decay (DOE/RL-2004-21). Although the pump-and-treat system may have met the objective of reducing the flow of groundwater (and non-adsorbing co-contaminants) in the Sr-90 plume area to the river, it did not meet the objective of reducing Sr-90 concentrations in aquifer pore fluid at the shoreline or in the stream bank storage zone. Based on the pump-and-treat system's limited effectiveness in removing Sr-90 from within these zones and the need for ambient conditions to test the PRB, DOE, Ecology, and EPA approval placed the system in a standby mode in March 2006 (M-16-06-01).

1.6 Evaluation of Strontium-90 Treatment Technologies

The following discussion describes the evaluation of the Sr-90 treatment technologies.

1.6.1 Innovative Treatment and Remediation Demonstration Report

As required by the Interim Action ROD, DOE conducted a comprehensive review of Sr-90 treatment technologies to complement the existing interim remedial actions. This review was commissioned under DOE's ITRD program and culminated with ITRD, 2001. Based on the evaluation presented in this document, the TAG recommended that monitored natural attenuation (MNA), soil flushing, phytoremediation, stabilization by phosphate injection, impermeable barriers (sheet pile and cryogenic), and treatment barriers (clinoptilolite) be evaluated further for Sr-90 remediation. Subsequent evaluations and field trials led to the elimination of soil flushing and sheet pile barriers as viable technologies for the 100-NR-2 OU.

1.6.2 Letter Report 2004

Submitted to DOE in October 2004, the letter report evaluated the most promising treatment alternatives and proposed a path forward for selecting and testing alternatives (FH-0403540). Alternatives evaluated included PRBs, impermeable barriers, MNA, and phytoremediation. At that time, the final length of the barrier wall was assumed to be about 600 m (2,000 ft).

Four PRB technologies were considered: vertical hydrofracture, aqueous injection, air injection, and trenching. These technologies, with the exception of aqueous injection, emplace some form of mineral apatite into the subsurface to sequester Sr-90. In aqueous injection, apatite precursors are introduced as dissolved chemicals into the aquifer via injection wells, and apatite precipitates in a treatment zone surrounding the point of injection.

Impermeable barriers reduce Sr-90 entering the river by increasing the groundwater flow path to allow time for the Sr-90 to decay. Alternatives included a slurry wall via trenching and a bentonite grout curtain installed via hydrofracture. MNA allows for the natural decrease of Sr-90 concentrations over time, and phytoremediation uses plants to extract Sr-90 from the root zone on the riverbank.

One of the outcomes of the technology screening presented in the letter report was the decision that barrier walls constructed via trenching are not feasible along the shoreline. The letter report also reiterated the conclusion from the ITRD (ITRD, 2001) that MNA may be appropriate for portions of the plume far from the river, but will not limit current discharges of Sr-90 to the river. Phytoremediation was retained for consideration in conjunction with a barrier, but is not regarded as a standalone solution for the near-shore area.

The remaining technologies (aqueous injection PRB, air injection PRB, hydrofracture PRB, and hydrofracture grout curtain) were evaluated based on effectiveness, implementability, reduction of

near-shore contamination, public acceptance, risk, and cost. Overall, these technologies compared closely, and a single approach was not clearly identified. However, because aqueous injection has the potential to treat the sediments at the shoreline, the letter report recommended that it be the first technology to test in the field.

1.6.3 Treatability Test Plan 2006

Following the presentation of the letter report (FH-040350), a TTP was written to address the path forward for field testing Sr-90 sequestration using apatite. Several methods were evaluated for apatite emplacement into the subsurface, including pneumatic injections of solid apatite and vertical hydrofracture for apatite emplacement. Ultimately, aqueous injections of apatite precursors were carried forward because of an increased treatment zone around the injection point and the prospect of treating a larger area of the near-shore aquifer.

The 2006 TTP outlined field testing to be conducted in two separate phases: an initial field pilot test at two locations on either end of the barrier, followed by installation and treatment of a sufficient number of wells to create a 91 m (300 ft) PRB. The pilot tests were to be located at the east and west ends of the barrier because of the extensive monitoring networks at those locations, as shown in Figures 7 and 8. The objectives of the pilot test phase were to address the following objectives:

- Will apatite precipitate in the target zone?
- Does the apatite result in decreasing Sr-90 concentration in groundwater?
- Given a fixed spacing of 9 m (30 ft), what is the optimal injection volume per well for installation of a 91 m (300 ft) barrier wall?

The pilot testing and PRB emplacement were conducted in 2006 and 2007. The objectives of the low-concentration injections were to stabilize the Sr-90 in the subsurface before a high-concentration injection. The low-concentration solution injected consisted primarily of calcium chloride, trisodium citrate, and sodium phosphate. Analyzing the results from the two pilot tests led to modifying the injection solution concentration, injection volumes, and operational parameters. The first pilot test was conducted in spring 2006 during high-river stage conditions. A second pilot test was conducted during low-river stage conditions. The associated location of the pilot test (which end of the barrier), well construction, and river stage during the injection were important parameters in determining the depth interval treated and the treatment efficiency. During this phase of the testing, injection wells were screened across both the Hanford and the upper portion of the Ringold Formation to target the highest concentrations of Sr-90 the 2008 interim report (PNNL-17429).

Temporary increases in groundwater Sr-90 concentrations were expected as a result of the low-concentration injection. The observed increases were an artifact of injecting a high ionic strength solution into the aquifer and increasing calcium concentrations. Monitoring results from the first pilot test injection showed an average increase in Sr-90 concentrations of 8.4 times the average baseline concentrations. Based on the results of the first pilot test, the injection solution was modified with calcium and citrate concentrations 2.5 times lower. This resulted in an average peak in Sr-90 that was 3.8 times that of the average baseline concentration. The injection formulation was again revised for the barrier injection wells in 2007. This solution had lower calcium and citrate concentrations, as well as an approximately four-fold increase in phosphate. A more complete summary of the low-concentration injection can be found in PNNL-17429.

The objectives of the original TTP were not fully met during the initial low-concentration injections. Injection of a high-concentration solution, which is addressed in Addendum 1 of that TTP, was required to meet the first two objectives of the TTP. The third objective of determining injection volumes for

a fixed 9.1 m (30-ft) injection well spacing was met based on formulation arrival responses observed in neighboring wells.

1.6.3.1 Treatability Test Plan Addendum 1

TTP Addendum 1 (DOE/RL-2005-96-ADD1, *Treatability Test Plan Addendum for 100-NR-2 Groundwater Operable Unit*), issued in April 2008, described the plan for conducting high-concentration injections of apatite-forming chemicals at the 100-N treatability test site. The pilot test sites used for the initial low-concentration injections were used for the high-concentration apatite injection to assess the side effects of the process prior to continuing with the remaining barrier well injections.

The primary objective of the high-concentration injection was to maximize the amount of apatite formation, providing long-term treatment, while limiting the temporary increase in Sr-90 caused by the injection solution. The high-concentration injection solution was approximately four times the final low-concentration injection solution of 1 millimolar (mM) $CaCl_2$, 2.5 mM citrate, and 10 mM phosphate, used for barrier emplacement in 2007. The final high-concentration solution was determined in the laboratory prior to field implementation and documented in an injection-specific field test instruction.

Following the high-concentration injection, all the objectives from the TTP (Section 1.5.2) were met. Apatite formation was confirmed in the target zone through collection of soil cores one year after the initial low-concentration injection. Decreases in Sr-90 groundwater concentrations have been indicated by performance assessment monitoring results following the low-concentration and high-concentration treatments. Short-term increases in Sr-90 concentrations associated with the injection of high-ionic-strength solutions during the high-concentration treatments were comparable to or less than those observed during the initial low-concentration treatment. The full data record indicates a stepwise improvement in Sr-90 sequestration performance between the low- and high-concentration injections. The average decrease in Sr-90 concentrations at the four compliance monitoring locations was 95 percent relative to the high end of the baseline range and 84 percent relative to the low end of the baseline range. A treatment target of 90 percent reduction was realized at all four compliance monitoring wells (PNNL-SA-70033).

Injection volume requirements for the fixed 9.1 m (30-ft) injection well spacing, which provides for overlap between adjacent injection wells of sufficient extent to form a continuous PRB, have been determined based on formulation arrival responses observed during the low- concentration calcium-citrate-phosphate injections (PNNL-17429) and the high-concentration injection (PNNL-SA-70033). In addition to the specified injection volumes, it was determined that, due to the difference in hydraulic conductivity in the Ringold Formation and Hanford formation, installation of injection wells targeting only the lower portion of the contaminated zone (Ringold Formation) were needed to provide effective formulation coverage over the downstream section of the PRB. It was also determined that, in addition to the requirement that Hanford formation treatments be performed during the highest Columbia River stage conditions (to treat the full saturated thickness), Ringold Formation only injection wells should be treated during low Columbia River stage conditions to achieve an acceptable radial extent of treatment.

1.6.3.2 Treatability Test Plan Addendum 2

TTP Addendum 2, issued January 2009, describes preliminary field scale infiltration experiments near the apatite PRB. The purpose of this test plan was to address strategies for infiltration of aqueous solution from near-ground surface into the vadose zone and the type of monitoring equipment that could be used to monitor the infiltration front. The use of infiltration reagents will help to treat the significant amount of Sr-90 mass that is in the sediments along the shoreline at 100-NR-2 in the vadose zone. Field testing of the wells installed in 2009 is planned for Fall 2010.

Previous evaluations of the potential for infiltrating water through the roadbed fill material have indicated that compaction of these materials may severely limit infiltration rates. In this test plan, the upper 1 m (3 ft) of roadbed would be excavated to increase infiltration. Laboratory experiments were conducted to determine whether the unsaturated Hanford formation is conducive to formation of apatite through surface application of reagents (PNNL-18303).

These two-dimensional infiltration experiments showed that infiltration rate, concentration of the calcium-citrate-phosphate solution, and addition of water after solution infiltration, all affected apatite precipitation in the vadose zone. Rapid infiltration of calcium-citrate-phosphate solution resulted in apatite precipitation at greater depths, while decreasing the infiltration rate resulted in greater lateral spreading of the apatite precipitate. Infiltrating water into the vadose zone after the apatite precursor solution resulted in both improved depth of infiltration and lateral spreading of apatite precipitate. Increasing the injection concentration resulted in greater depths of apatite precipitation by decreasing the effects of phosphate adsorption onto sediment. These tests also showed that to precipitate adequate amounts of apatite, repeated cycles of infiltration with time between to allow for water drainage was necessary. The most effective method for emplacing apatite in low hydraulic conductivity soils involved repeated cycles of rapid infiltration of calcium-citrate-phosphate solution, followed by slow infiltration of water.

The most effective method found to date for emplacing apatite in high hydraulic conductivity regions was air/surfactant injection where the calcium-citrate-phosphate was present in a foam. This study showed that while it is difficult to emplace apatite accurately in the vadose zone because of the infiltration rate control required, it is possible to use this method to sequester Sr-90 in the subsurface.

1.6.3.3 Treatability Test Plan Addendum 3

TTP Addendum 3, issued in September 2009, described the plan for conducting a preliminary field-scale demonstration upstream of the current apatite PRB treatability test site. The demonstration was conducted to evaluate potential strategies for jet injection of three different media: a phosphate-only solution, pre-formed apatite, and the same phosphate solution and pre-formed apatite. The field-scale demonstration was conducted upstream of the existing apatite PRB and downstream of the total petroleum hydrocarbon (TPH) wells.

The objective of the jet injection pilot-scale demonstration was twofold: to evaluate the ability of different technologies to deliver material/chemical solutions into the vadose zone and upper unconfined aquifer within three distinct treatment zones in the 100-N shoreline; and to evaluate the ability of the method to install a PRB in the vadose zone containing a specific amount of apatite (4 mg apatite/g sediment).

Results from collected sediment cores indicate that jet injection is a viable method for emplacement of phosphate and pre-formed apatite in the vadose zone. These cores also show that jet injection is a viable method for installing a PRB in the vadose zone at a target concentration of 3.4 mg apatite per gram of sediment (1.1 mg phosphate per gram of sediment). In each of the test areas, apatite concentrations met or exceeded these values in all cases but one.

1.6.4 Proposed Plan 2010

A proposed plan (DOE/RL-2009-54, *Proposed Plan for Amendment of 100-NR-1/NR-2 Interim Action Record of Decision*) has been drafted to propose an amendment to the Interim Action ROD for 100-NR-1/2 (EPA/ROD/R10-99/112). This draft proposed plan specifically addresses the use of aqueous apatite injection as a remedial alternative for treatment of the soil and groundwater in 100-N. The proposed plan was based on agreement by DOE and Ecology (DOE/RL-2006-20), that the long-term strategy for groundwater Sr-90 remediation at 100-N should include apatite sequestration as the primary treatment technology to be tested (Ecology et al., 1989a, Tri-Party Agreement Milestone M-016-14B).

The proposed plan considered no action and four other alternatives, and evaluated them against the nine CERCLA criteria. The proposed alternatives included MNA with institutional controls (ICs), resume pump-and-treat operations, impermeable barrier, and an apatite PRB. Based on existing information and the evaluation presented in the draft proposed plan, Alternative 4—apatite PRB—is identified as the proposed preferred alternative for Sr-90 interim remedial action at the 100-NR-1/NR-2 OU. If this proposed plan is approved, the apatite PRB alternative may be implemented through an amendment to the Interim Action ROD for the 100-NR-2 OU.

1.6.5 Remedial Investigation/Feasibility Study Work Plan

A remedial investigation/feasibility study (RI/FS) work plan for the entire 100 Area was written in 2008 and approved in 2010 (DOE/RL-2008-46, *Integrated 100 Area Remedial Investigation/Feasibility Study Work Plan)* outlining the overall process for developing and completing an RI/FS, proposed plan, and final ROD at the separate 100 Areas. Separate addendums were prepared for each of the 100 Areas. The 100-N area is addressed in a draft DOE/RL-2008-46-ADD5. This addendum identifies the data gaps or uncertainties in the 100-NR-1 and 100-NR-2 OUs and the specific data needs required to reduce or eliminate the associated uncertainty.

2 Treatment Technology Description

This section describes the characteristics of apatite in general and the properties that make it amenable as a sequestering agent for Sr-90. Additionally, it describes the different forms of apatite, the different injection solutions, and the mass of apatite needed in 100-N.

2.1 General Characteristics of Apatite

Apatite [$Ca_{10}(PO_4)_6(OH)_2$] is a natural calcium phosphate mineral occurring primarily in the Earth's crust as phosphate rock. It is also a primary component in the teeth and bones of animals. Apatite minerals sequester elements into their molecular structures via isomorphic substitution, whereby elements of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the hexagonal crystal structure. Figure 18 shows cationic and anionic substitutions that commonly occur in the apatite structure. Because of the extensive substitution into the general apatite structure, more than 350 apatite minerals have been identified (Moelo et al., 2000, "Lulzacite, $Sr_2Fe^{2+}(Fe^{2+},Mg)_2Al_{-4}(PO_4)_4(OH)_{10}$, a New Strontium Phosphate"). Apatite minerals are very stable with very low solubility in pH neutral to alkaline water (Wright et al., 2004, "PIMS Using Apatite II™: How It Works To Remediate Soil and Water"). The solubility product (K_{sp}) of hydroxyapatite is about 10^{-44}, while quartz crystal, which is considered the most stable mineral in the weathering environment, has a K_{sp} of 10^{-4} (Geochem Software, Inc., 1994, *Mac MINTEQ-A2: Aqueous Geochemistry for the Macintosh*). Strontiapatite, $Sr_{10}(PO_4)_6(OH)_2$, which is formed by the complete substitution of calcium by strontium (or Sr-90), has a K_{sp} of about 10^{-51}, another 10^7 times less soluble than hydroxyapatite (Verbeeck et al., 1977, "Solubility and Solution Behaviour of Strontium Hydroxyapatite"). The substitution of strontium for calcium in the crystal structure is thermodynamically favorable, and will proceed provided the two elements coexist.

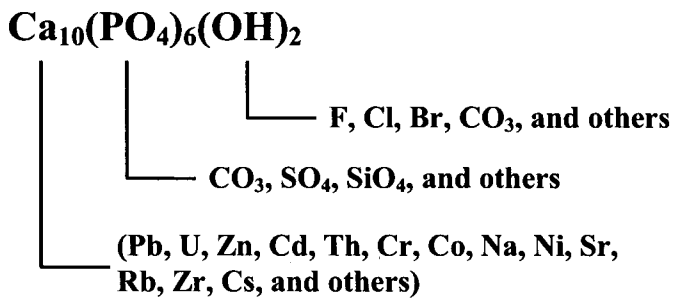


Figure 18. Cationic and Anionic Substitution in Apatite

Apatite can remove soluble strontium and Sr-90 from groundwater both during and after its formation. Removal can occur via precipitation of strontium in solution with phosphate anions (time scale of days), adsorption to the apatite surface (adsorption of Sr-90 to apatite is ~55 times stronger than to Hanford sediment), and slow substitution into the apatite structure (time scale of months to years). Precipitation directly from solution, or homogeneous nucleation, generally occurs only at very high metal concentrations; that is, greater than 10 parts per million (ppm). However, apatite will act as a seed crystal for the precipitation of metal phosphates at much lower concentrations (Ma et al., 1993, "In Situ Lead Immobilization by Apatite"). The apatite itself serves as a small but sufficient source of phosphate to solution, and with low concentrations of cations such as strontium or calcium, heterogeneous nucleation occurs on the surface of the apatite seed crystal (Lower et al., 1998, "Aqueous Lead Sorption by Hydroxylapatite: Applications of Atomic Force Microscopy to Dissolution, Nucleation, and Growth Studies"). Over time, the precipitated metals are sequestered into the apatite crystal matrix.

Although the rate of metal incorporation into the apatite crystal lattice can be relatively slow (on the order of months to years), the precipitation reaction is nearly instantaneous on the molecular scale. Initially, the precipitate formed is amorphous apatite; over time, however, it will transform into a more stable apatite crystal.

Note that stable strontium and other competing cations in groundwater, especially the divalent transition metals (e.g., cadmium, zinc, iron, lead, and manganese), can also be incorporated in the apatite structure. The average concentrations of stable strontium and competing cations present in groundwater will dictate the mass of apatite needed for long-term sequestration. Recent experiments measuring strontium incorporation in apatite from a solution containing only calcium and strontium, as compared to a solution containing calcium and strontium in groundwater (containing all transition metals), found no difference in the strontium uptake mass (PNNL-16891).

The effect of competing cation concentrations is to reduce the in situ apatite longevity for a given mass loading. To achieve a desired longevity (e.g., a 300-year period during which most of the Sr-90 will have decayed), loading must be increased to account for the competing cation effect.

Nitrate (as Nitrogen) concentrations do exceed the drinking water standards (DWS) (45 mg/L) beneath a portion of 100-N, although nitrate concentrations along the river are below the DWS. Sources for nitrate groundwater contamination potentially include both pre-Hanford (e.g., agriculture) and Hanford activities. There is no effective interaction between the apatite and nitrate (Bostick et al., 2000, "Phosphate-Induced Metal Stabilization: Use of Apatite and Bone Char for the Removal of Soluble Radionuclides in Authentic and Simulated DOE Groundwaters").

2.2 Apatite Placement in the Subsurface

Because apatite exists as solid particles, it is difficult to displace laterally from an injection point in the subsurface to any significant distance. The surrounding soil tends to filter and block the particles from propagating outward. Various high-energy emplacement techniques exist to essentially force the particles outward by displacing the surrounding media (e.g., hydrofracturing and jet injection). In contrast, aqueous injection of apatite precursors forms apatite through in situ precipitation of aqueous reactants.

Three different permutations of aqueous injection have been considered at the 100-NR-2 OU: high-concentration, low-concentration, and phosphate only. The selected approach to be evaluated for expansion of the barrier wall is the high-concentration calcium-citrate-phosphate solution. This approach was selected to evaluate the effectiveness of the high-concentration PRB formulation without sequential low- then high-concentration injection, and the effect on Sr-90 and other metals released from the soil to the groundwater.

The specific steps of the high-concentration calcium-citrate-phosphate injection are as follows:

- Injection of calcium-citrate-phosphate solution
- In situ biodegradation of citrate resulting in apatite precipitation
- Adsorption of Sr-90 by the apatite surface (new Sr-90 migrating into the treated zone from upgradient sources)
- Apatite recrystallization with Sr-90 substitution for calcium (permanent)
- Radioactive decay of Sr-90 to Y-90 to Zr-90

Emplacement of apatite precipitate in groundwater by solution injection has significant advantages over other apatite emplacement technologies for application at the Hanford 100-N area. The major advantage of aqueous injection is minimal disturbance of the subsurface (especially important in the saturated zone) because this technology only requires injection wells (for groundwater remediation, in contrast with excavation of the riverbank for trench-and-fill emplacement of solid-phase apatite) or jet injection. Although each emplacement methodology has advantages and disadvantages, the aqueous apatite-forming solution injection technology was chosen for this test because it is believed to provide the most economic emplacement methodology to treat Sr-90 in the near-shore saturated sediments. A weakness of all these apatite technologies is that Sr-90 is not removed from the sediment. Rather, the Sr-90 is incorporated into the apatite crystalline structure, where it undergoes radioactive decay.

2.3 Mass of Apatite Needed for Hanford 100-N Area

Two factors control the amount of apatite needed to sequester Sr-90 in the Hanford 100-N area. First, from a mass balance standpoint, a specific amount of apatite is needed that will remove sufficient strontium and Sr-90 from groundwater over the next 300 years (i.e., assuming an initial maximum Sr-90 concentration of 8,000 pCi/L, 10 half-lives of Sr-90 decay, and a half-life 29.1 years) to protect the river. Figure 19 shows the Sr-90 decay from this initial concentration of 8,000 pCi/L. The apatite mass calculation depends on the crystal substitution of strontium for calcium in apatite. If 10 percent substitution is assumed, then 1.7 mg of apatite is sufficient to sequester strontium and Sr-90 from the estimated 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 (PNNL-18303). The 1.7 mg apatite/g sediment would occupy 13.6 percent of the pore space, so some degree of permeability decrease would be expected.

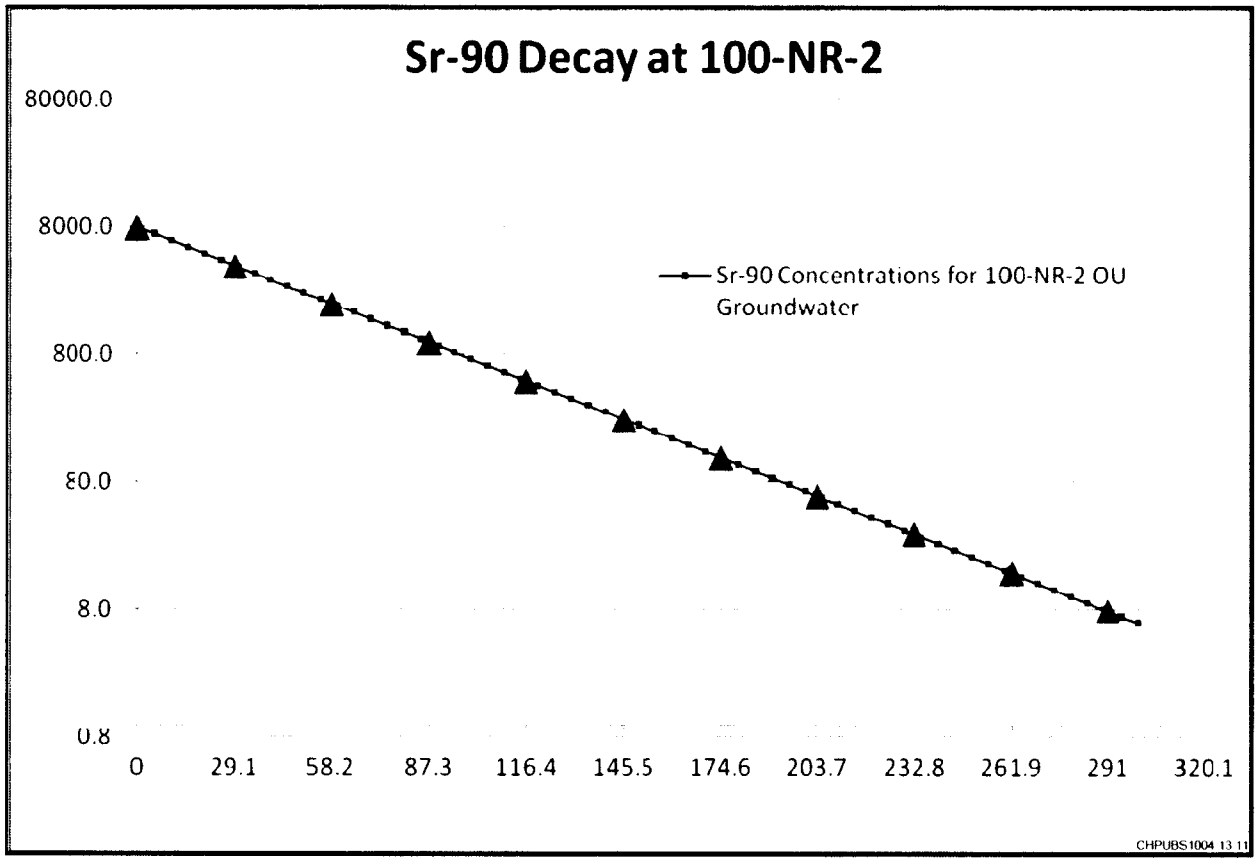


Figure 19. Sr-90 Decay at 100-NR-2

The second factor that controls the amount of apatite needed to sequester Sr-90 is the rate of incorporation. This PRB concept, which relies on emplacement of apatite in the aquifer, is viable only if the natural groundwater flux rate of strontium and Sr-90 (1.36×10^{-6} mM strontium/day/cm^2) is slower than the removal rate of strontium and Sr-90 by apatite. If the groundwater flow rate is too high, even highly sorbing strontium and Sr-90 could advect through the apatite-laden zone more quickly than it is removed. This issue can be circumvented by adding additional apatite in the groundwater system (i.e., greater than the amount needed based on the mass balance calculation [Figure 18]) to essentially remove Sr-90 at an increased rate. Experiments indicate that at an apatite content of 1.7 mg apatite/g of sediment, Sr-90 would be incorporated into apatite more rapidly than the average groundwater flow rate and most high-flow events.

The target apatite content (1.7 mg apatite/g of sediment) corresponds to a pore volume formulation concentration, on a molar basis, of 90 mM of phosphate precipitated in sediment with no retardation. The high-concentration solution was specified at 40 mM phosphate as a result of phosphate solubility limits and other technical considerations, The target apatite concentration for the saturated zone will be 1.7 mg/g, or less, depending on observed permeability changes.

2.4 Formulation Development

The dynamics of injecting an aqueous solution of high ionic strength into a Sr-90-contaminated aquifer near the Columbia River involved consideration of multiple objectives. First, sufficient mass of phosphate needed to be emplaced in the aquifer to sequester Sr-90 for 300 years, as defined by both mass balance (incorporation of Sr-90 into apatite) and Sr-90 flux rate considerations, as discussed in Section 2.1.2.

Second, any solution injected into the aquifer that is of higher ionic strength than groundwater will cause some desorption of Sr-90 (and Sr^{2+}, Ca^{2+}, Mg^{2+}) from the sediment, as 99 percent of the Sr-90 mass is adsorbed by ion exchange on sediment minerals (PNNL-17429). The ion exchange process is further complicated by not only the ionic strength of the injecting solution, but by the concentration of the monovalent and divalent ions in the solution, as well as the total volume injected. The aqueous injection formulation has developed since the initial TTP, through laboratory testing and field testing during the low and high-concentration injections and jet injections. This section summarizes the different injection formulations that have been tested and the development of the high-concentration calcium-citrate-phosphate formulation.

2.4.1 Low-Concentration Formulation

The original calcium-citrate-phosphate formulation used in the low-concentration bench-scale studies was based on the stoichiometric ratio of calcium:phosphate in apatite (5:3), and a calcium:citrate ratio of 1:2.5 to form the aqueous calcium-citrate complex (Moore et al., 2004, "Formation of Hydroxyapatite in Soils Using Calcium Citrate and Sodium Phosphate for Control of Strontium Migration"). Therefore, the initial calcium-citrate-phosphate formulation contained the ratios of 4 mM calcium, 10 mM citrate, and 2.4 mM phosphate (4:10:2.4). Early laboratory experiments with this formulation (and higher concentrations) did successfully precipitate apatite, but left considerable excess calcium in solution because there is a significant quantity of adsorbed calcium on sediment minerals (by ion exchange) that exchanges off the surface during solution injection.

The composition of the injection solution evolved over time to reflect (1) increasing use of available calcium from groundwater (and on ion exchange sites) rather than injecting all the calcium needed, and (2) minimizing strontium and Sr-90 ion-exchange release from sediments upon injection. Initially, the solution composition did not reflect use of calcium from groundwater or ion-exchange sites, so the solution injected for field injection No. 1 used a higher concentration of calcium chloride [$CaCl_2 \times 2H_2O$] and trisodium citrate [$HOC(COONa)(CH_2COONa)_2 \times 2H_2O$] compared to later injections.

The Sr-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 values measured earlier in the year. Based on these results and additional laboratory measurements, the calcium-citrate-phosphate injection concentrations were revised with lower calcium and citrate concentrations (2:5:2.4) for the second pilot test conducted in fall 2006. Average peak Sr-90 concentrations following the second pilot test injection were significantly lower than the first pilot test (3.8 times the average baseline Sr-90 concentrations) while still targeting the same level of apatite formation. The injection formulation was revised again following the second pilot test with further decreases in calcium and citrate concentrations, and approximately four times increase in the phosphate concentration (1:2.5:10) to maximize the apatite precipitate mass and minimize the initial Sr-90 increase. This final low-concentration formulation was used for the barrier well injections conducted in 2007. Monitoring of Sr-90 concentrations at the two pilot test sites in 2007 using the final low-concentration formulation showed average peak concentration of 1,996 pCi/L or a peak increase of 2.75 times the baseline average of 726 pCi/L Sr-90 at the first pilot test site and 2,863 pCi/L or 2.3 times the baseline average of 1,230 pCi/L. The observed increases in Sr-90 concentration are caused by the higher ionic strength of the solution and increases in calcium concentration resulting from this process.

2.4.2 High-Concentration Injection

Three different low-concentration formulations were tested at 100-N pilot test sites and barrier injections, with the objective of maximizing the formation of apatite, while minimizing the temporary increase in Sr-90 concentration. Preliminary performance monitoring data, of the low-concentration formulation of 1 mM $CaCl_2$, 2.5 mM citrate, and 10 mM phosphate, were used to develop the high-concentration

formulation. Based on the bench- and field-scale treatability tests, the most favorable formulation identified for the high-concentration injection consists of 3.6 mM calcium, 9 mM citrate, and 40 mM phosphate, approximately four times the low-concentration injection formulation. This same high-concentration formulation will be used for injections associated with this design optimization study. This amendment solution was identified as the best formulation for meeting the following objectives: (1) minimize the number of injection operations required, (2) minimize short-term increases in Sr-90 concentrations associated with injection of high-ionic-strength solutions, and (3) keep amendment formulations well below solubility limits to reduce the potential for operational challenges associated with solution stability.

Short-term increases in the Sr-90 concentration associated with the injection of high-ionic-strength solutions during the high-concentration treatments were generally comparable to those observed during the initial low-concentration treatments. The highest increase in Sr-90 was observed in Ringold only injection well 199-N-162 and aquifer tube NVP2 at 25,000 pCi/L and 75,000 pCi/L, respectively. After six months, the concentration in injection well 199-N-162 had dropped to 48 pCi/L and concentrations at aquifer tube NVP2 had returned to below baseline concentrations (highest and lowest Sr-90 concentration measured pre-injection). The impacts of injecting the high-concentration formula continue to be monitored through compliance monitoring wells and aquifer tube monitoring. Some reasons for variability may include but are not limited to flow rate variability, concentration of sorbed Sr-90 to sediments, volume of apatite formulation injected, and localized lithology.

The high-concentration calcium-citrate-phosphate solution will also use the existing calcium within the treatment zone to form reactive apatite and begin sequestering Sr-90. The development of in situ precipitation, for field injection and infiltration, has been optimized by using the abundant calcium adsorbed to the arid Hanford sediments (and in groundwater). The stoichiometric ratio of calcium to phosphate used in solution (5:3) reflects the ratio of these chemicals in the apatite structure. Considerable calcium is available from the sediment (50 percent to 75 percent of the 2 milliequivalent [meq]/100 g), which is equivalent to using 25 to 35 mM phosphate to form apatite.

2.4.3 Phosphate Only Injection Formula

A solution containing only phosphate has been investigated in some laboratory experiments and in a field pilot study (jet injection). The injection of phosphate only is effective to a concentration of 25 to 35 mM, with the use of adsorbed calcium on sediment. Higher phosphate concentrations would require additional calcium to precipitate. This can occur as the aqueous phosphate plume drifts downgradient into additional aquifer sediment. The phosphate solution injected during the jet injections consisted of a combination of phosphoric acid and sodium hydroxide in specific proportions for a final pH of 7.5. The phosphate solution was prepared such that a resulting mixture of 85 percent disodium hydrogenphosphate (Na_2HPO_4) and 15 percent sodium dihydrogenphosphate (NaH_2PO_4) was produced. The total aqueous concentration of phosphate did not exceed 100 mM.

The use of phosphate only (at 40 mM concentration) compared to use of the calcium-citrate-phosphate formulation (also at 40 mM phosphate) has a slightly lower (22 percent) ionic strength, so may result in slightly less Sr-90 initial mobilization. However, citrate serves two purposes: first, to complex with the calcium and slow the initial precipitation reaction. This enables the injected solution to precipitate more uniformly throughout the formation. Secondly, it initiates crystallization of the apatite through microbial activity.

3 Test Objectives

This design optimization study is being proposed to fulfill the interim RAO of evaluating treatment technologies and to evaluate the PRB technology further. Building on work completed under the original TTP (DOE/RL-2005-96), this design optimization will demonstrate the effectiveness of this technology prior to incorporation in an amended Interim ROD or Final ROD. Should this design optimization study be approved and implemented successfully, it may result in the lateral extension of the existing apatite PRB from the current 91 m (300-ft) length to a minimum 274 m (900-ft) length. The PRB is designed to prevent subsurface Sr-90 migration into the Columbia River. This design optimization study describes the test methods developed to evaluate potentially improved methods for the delivery and emplacement of apatite-forming minerals. This design optimization plan focuses on the aquifer and the capillary fringe of the near-shore area in the 100-NR 2 OU. Field testing will be accomplished through injection into multipurpose wells that were installed under DOE/RL-2009-32, *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan.*

Following are the objectives of this design optimization study:

1. Refine application of the high-concentration calcium-citrate-phosphate solution over a larger scale.

   Refine the application of the high-concentration calcium-citrate-phosphate solution through testing the well design, injection equipment, monitoring well sampling, and aquifer tube sampling for decreases in strontium concentrations and tracking transient effects of increased metals and anions.

2. Test the effectiveness of high-concentration calcium-citrate-phosphate injection in previously untested sediment to compare with areas that received sequential injections of low- then high-concentration calcium-citrate-phosphate injections.

   The effectiveness will be demonstrated through long-term monitoring of wells and aquifer tubes as explained in Section 6 of the design optimization study through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and tracking of transient effects of increased metals and anions.

3. Test the new well design installed under DOE/RL-2009-32 to evaluate the adequacy of injection solution delivery to the target zone.

   The new well design will be evaluated through monitoring of groundwater and aquifer tubes as described in Section 6 of this design optimization study through collection of field conductivity measurements in conjunction with groundwater sampling for phosphate.

4. Test and optimize operation of the new injection system to verify that the system can deliver the designed injection solution flow volume at multiple well locations. Determine whether the new well design and injection system can complete chemical injections at various river stages, thereby eliminating the need for injections during specific river levels.

   This will be evaluated by performing injections independent of river stage and collecting field conductivity measurements in conjunction with groundwater sampling for phosphate to determine the treatment area achieved.

5. Evaluate that PRB can achieve up to 90 percent reduction in Sr-90 flux to the river.

   This will be demonstrated through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and by tracking transient effects of increased metals and anions as described in Sections 6.3 and 6.4.

6. Further test the impact the high-concentration calcium-citrate-phosphate solution has on the release of Sr-90 and other metals from previously untreated sediments to groundwater.

   This will be demonstrated through monitoring well sampling and aquifer tube sampling for decreases in strontium concentrations and tracking transient effects of increased metals and anions as described in Sections 6.3 and 6.4.

4 Experimental Design

This section provides a general description of the field test design and methods to be used in extending the apatite PRB.

4.1 Injection Design

Based on design analysis and chemical arrival responses observed during low-concentration field testing and PRB treatment operations (PNNL-17429) and field tests with the high-concentration solution (PNNL-SA-70033), an injection volume of 94,625 to 454,200 L (25,000 to 120,000 gal) of calcium-citrate-phosphate solution is expected to be injected into each well. This volume was demonstrated to provide sufficient radial extent of treatment at the targeted radial extent of 6 m (20 ft), resulting in effective overlap coverage between adjacent injection wells.

An injection rate in the range of 37 to 189 L/min (10 to 50 gpm) per well is sufficient for effective delivery of the calcium-citrate-phosphate formulation. Based on previous injections, temporary groundwater mounding has been observed, which indicates the injections have overcome the localized variability in hydraulic conductivity.

4.2 Well Installation

The wells needed for the barrier extension will comprise monitoring wells and multipurpose characterization/potential remediation wells. Monitoring wells have been drilled at approximately even intervals over the length of the barrier expansion, immediately downgradient of the multipurpose wells. In addition, monitoring wells are located within the footprint of the current apatite barrier. Of the 25 wells recently installed, 3 were continuously cored to total depth (TD) to provide data about the effectiveness of the existing barrier. The multipurpose wells were drilled along the shoreline road northeast and southwest of the current apatite barrier at 6 m (15-ft) intervals. Figure 20 shows the location of the existing barrier area and its relation to the two areas of barrier expansion. Figure 21 shows the location of the new multipurpose and monitoring wells located upstream of the existing barrier area, while Figure 22 shows the location of the new multipurpose and monitoring wells located downstream of the existing barrier. Based on Sr-90 vertical profile sampling conducted during installation of the pilot test wells, well screen intervals ranging from 3.1 to 7.3 m (10 to 24 ft) below ground surface (bgs) were selected for the balance of the injection wells installed as part of the overall barrier installation (PNNL-17429). Approximately one-half are completed in the Hanford formation and are hereafter referred to as 'shallow multipurpose' well, these wells alternate with 'deep multipurpose' wells completed in the Ringold Formation.

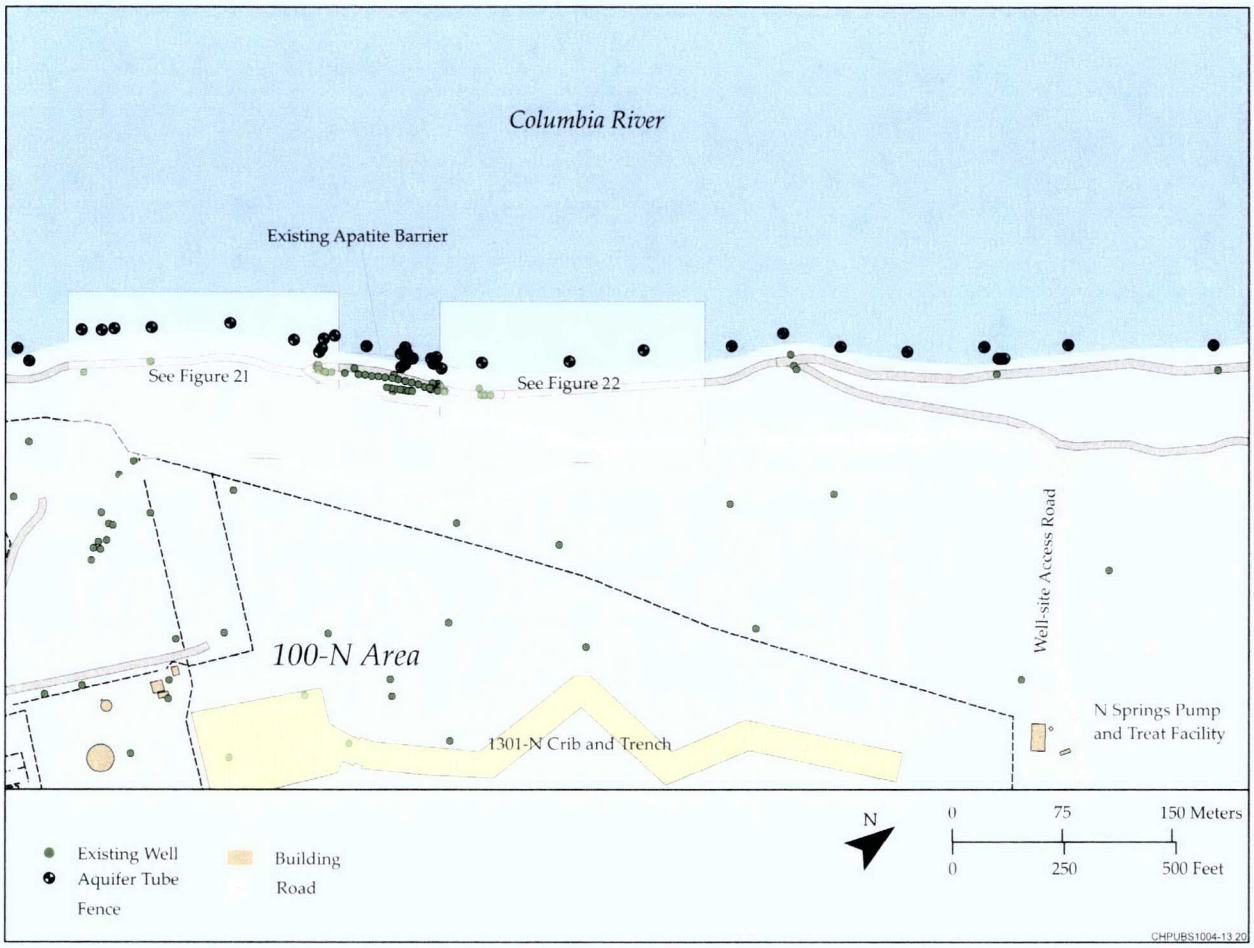


Figure 20. Injection Well Location Area

All wells have been drilled with a minimum 25 cm (10-in.) diameter temporary casing to allow construction of a 15 cm (6-in.) diameter resource protection well (i.e., the boreholes were drilled to maintain a minimum 5 cm [2 in.], annular space around the permanent well, per WAC-173-160, "Minimum Standards for Construction and Maintenance of Wells"). The monitoring wells were drilled to a TD of 7.5 m (25 ft) bgs. Shallow multipurpose wells were drilled to a TD of approximately 4.6 m (15 ft) bgs. Deep multipurpose wells were drilled to a TD of approximately 7.5 m (25 ft) bgs.

Drilling activities for the new wells were evaluated as medium radiological and chemical risk, based on the drilling and sampling data from nearby wells. Drilling activities determined to be "low risk" under the radiological hazard assessment required by Washington State Department of Health (WDOH) (2008, *The Department of Energy Hanford Site Radioactive Air Emissions License #FF-01*, Enclosure 3, "ALARACT Agreements," ALARACT 18, "Environmental Restoration Program ALARACT Demonstration for Drilling") were not restricted to any particular drilling method. The level of radiological and industrial hygiene protection support during drilling consisted of continuous surveillance. Table 1 presents the general construction details for the new 100-NR-2 OU wells.

When possible, well development was conducted following the well installation. Well development is performed to settle the filter pack and remove fines from the damaged formation. Baseline samples (pre-injection) will be collected as needed following well development.

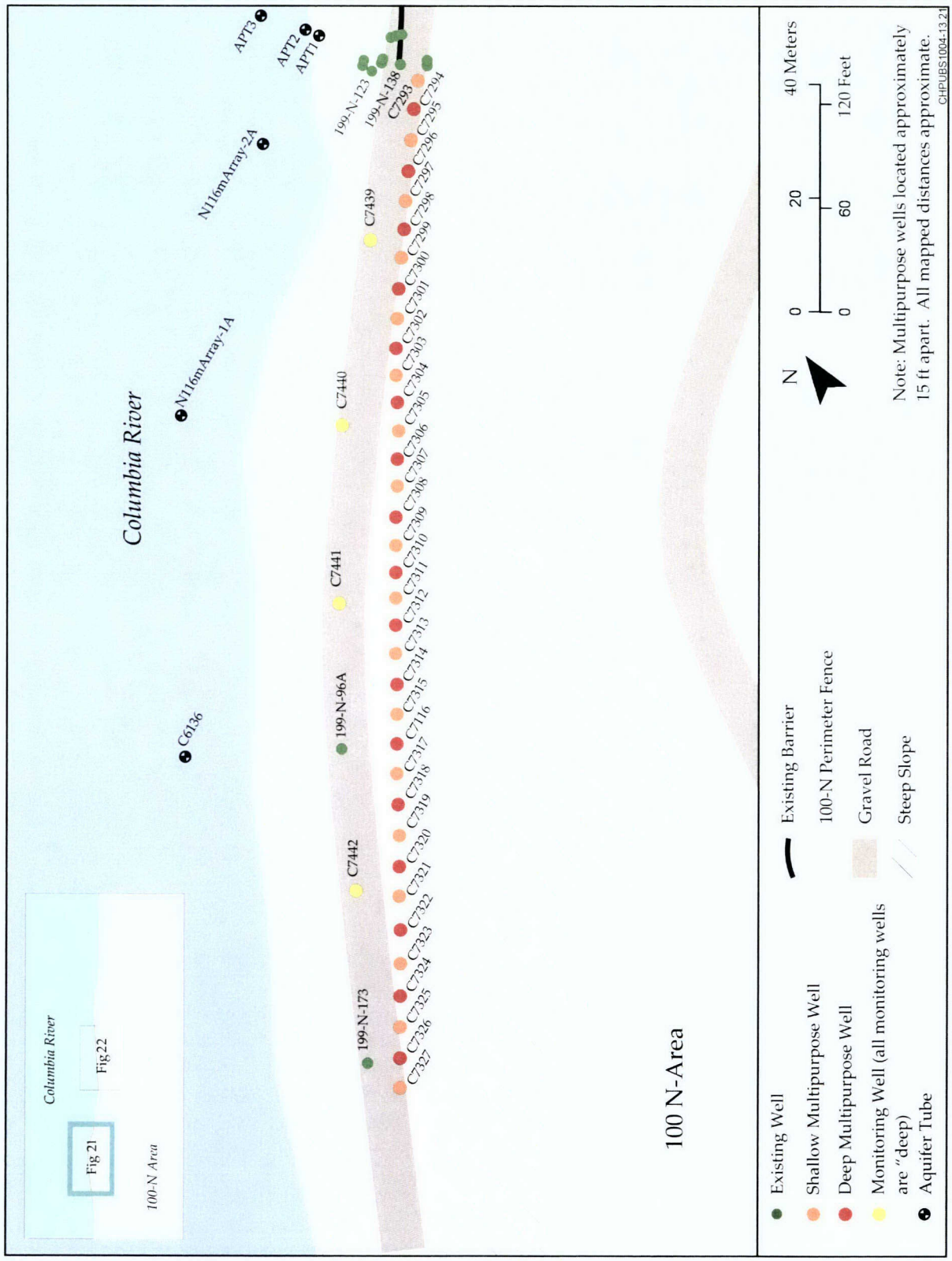


Figure 21. Well Locations—Upstream of Existing Permeable Reactive Barrier

Figure 22. Well Locations—Downstream of Existing Permeable Reactive Barrier

Table 1. Well Construction Details

Well Type	Planned Drill Depth (ft bgs)[b]	Estimated Depth to Water (ft bgs)[a]	Screen Length (ft) (anticipated)	Screen Placement (ft bgs) (anticipated)	Filter Pack Interval[b] (ft bgs)	Bentonite Pellet Interval (ft bgs)	Bentonite Crumbles Interval (ft bgs)	Cement Seal Interval (ft bgs)
Shallow Multipurpose (Hanford)	16	Dependent on river stage (expected between 8 and 17)	5	10 to 15	9 to 15	7 to 9	5 to 7	0 to 5
Shallow Multipurpose (Ringold)	25	Dependent on river stage (expected between 8 and 17)	7	17 to 24	16 to 25	13 to 16	10 to 13	0 to10

Notes:

All Wells—15 cm (6-in.) diameter polyvinyl chloride casing and screen. Screened interval and bentonite seal intervals subject to change.

a. Estimated planned drill depth and depth to water from DOE/RL-2009-32, *100-NR-2 Groundwater Operable Unit Sr-90 Plume Rivershore Sampling and Analysis Plan*.

b. Filter pack interval to consist of 6 to 9 mesh Colorado silica sand (subject to change).

5 Equipment and Materials

This section describes the site utilities, monitoring equipment, analytical equipment, injection equipment, and the integration of these components into the operational systems required to conduct the barrier extension at the 100-NR-2 OU located along the Columbia River. Access to the emplacement construction zone will be provided along the existing ramp and gravel access road near the Columbia River. Construction activities will be limited by the width of the bench, which in some areas is only 5 m (15 ft). It is assumed that no modification will be needed to permit truck and equipment access to the construction area. Injection equipment will be built to support the injections for aqueous emplacement of the additional lengths of the apatite barrier upstream and downstream of the existing barrier.

5.1 Site Utilities

Site utility requirements for this apatite injection include a generator and water supply. A substantial amount of water is needed to make up the injection solutions. Columbia River water will be used to dilute the high-concentration calcium-citrate-phosphate solution. A diesel generator will be used to operate the site facilities, the injection/monitoring equipment, and ancillary equipment.

5.2 Injection Equipment

Previous calcium-citrate-phosphate injections have been performed using injection skids to mix a dilute solution of river water and concentrated chemicals for injection. The previous injection skids had a limited capacity (injection limited to two wells at a time), which is considered insufficient to implement the larger-scale treatability study proposed in this design optimization study. Two new injection skids have been designed and are being constructed to inject aqueous solution of chemical and river water through injection wells to expand the existing 100-NR-2 apatite barrier. CH2M HILL Plateau Remediation Company (CHPRC) Soil and Groundwater Remediation Project (S&GRP) engineering (licensed professional engineers) designed the new injection systems in accordance their design procedures and standard design criteria. The new injection skids have been designed to increase the coverage area and decrease the time required for each injection. The new injection system will include skids that are each capable of injecting chemicals into six wells simultaneously. Figure 23 provides a generalized schematic of the injection system and Figure 24 shows a photograph of a completed injection skid. Upon completion of the injection system fabrication, the systems will undergo acceptance testing including but not limited to leak testing, flow testing and calibration, and National Electric Code inspection.

Each treatment skid is capable of pumping chemicals from tanker trucks or tanks and river water to form an injection solution for distribution to well heads. Flow meters and sample ports are provided on each injection skid to monitor and collect samples of pre-mixed chemical solution. Submersible pumps in the Columbia River will extract and transfer river water to the injection skid where it will be filtered prior to mixing with the chemical in a static in-line mixing chamber. Following mixing, a 2-in. transfer hose will distribute the dilute chemical solution to a manifold for distribution at up to six individual wells. A sample port is provided for sample collection of the dilute chemical prior to the manifold.

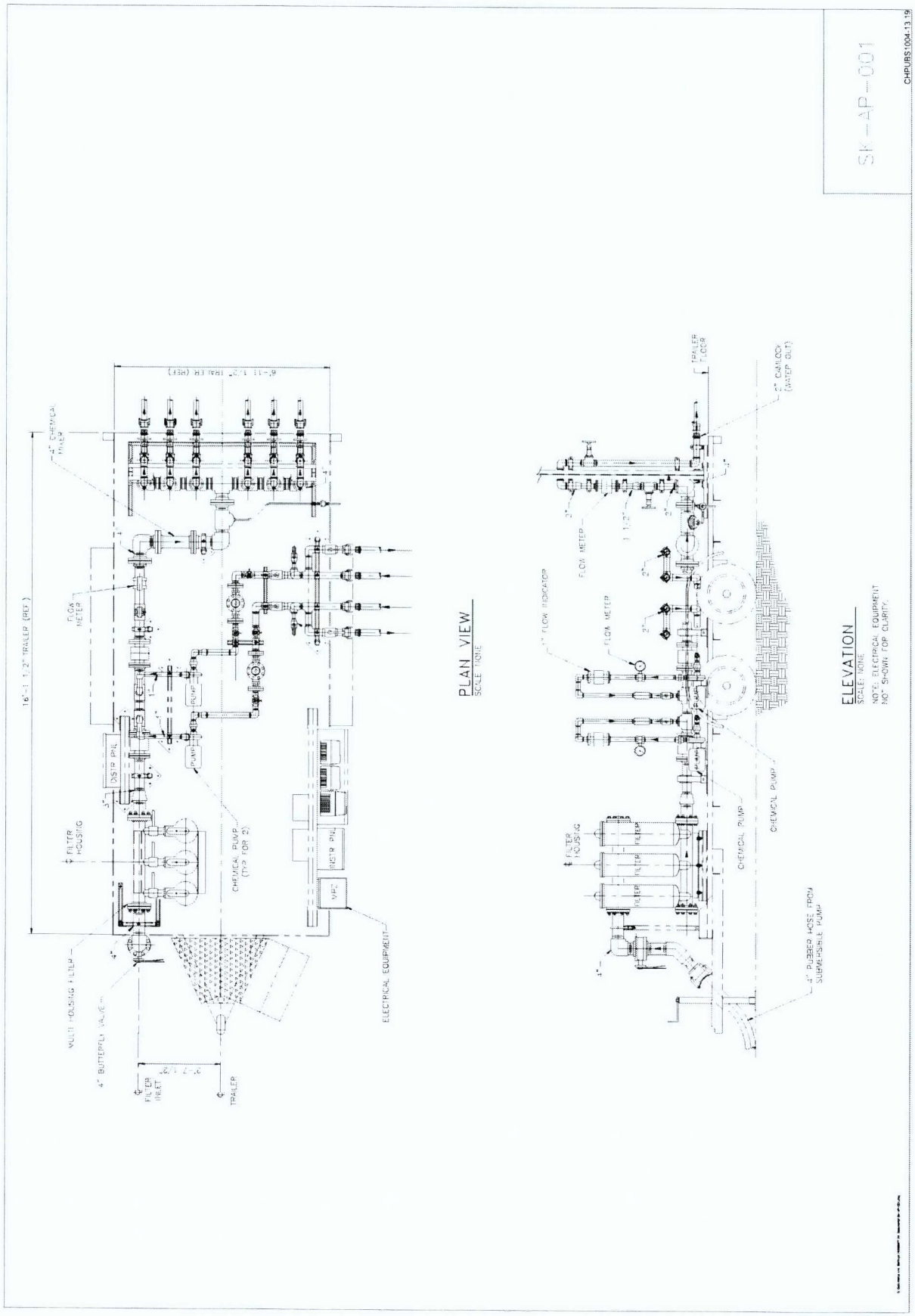


Figure 23. Generalized Schematic of Injection System

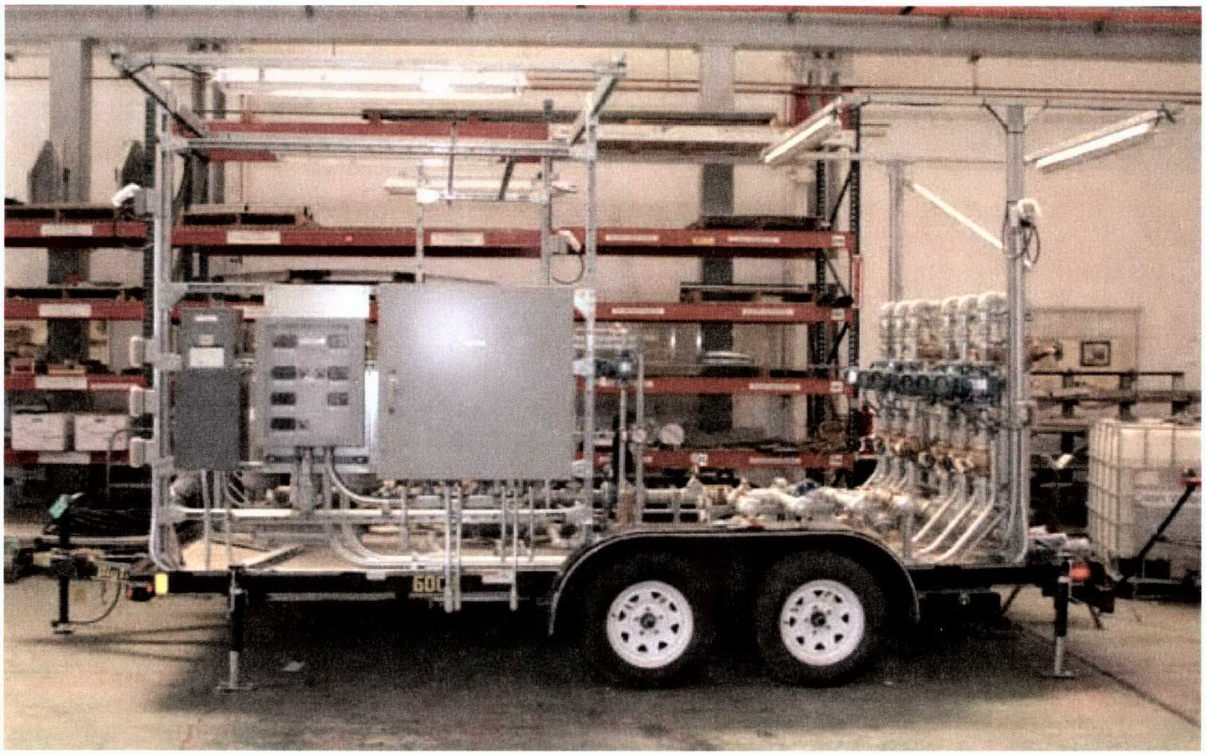


Figure 24. Injection Skid

The volume of dilute chemical for injection will likely range from 944,607 to 4,540,000 L (25,000 to 120,000 gal) per well. The injection system is capable of injecting chemical solution at a flow rate from 37 to 189 L/min (10 to 50 gpm) per well with a total capacity for each injection skid of up to 1,135 L/min (300 gpm). Actual injection volumes will be determined and presented in the test instructions.

Following completion of an injection cycle, the injection systems will be flushed with river water and the systems will be prepared for storage. The injection systems will be stored in a protected area, under cover, between injection cycles.

6 Sampling and Analysis

Sampling and analysis requirements for the high-concentration calcium-citrate-phosphate solution injections include chemical make-up sampling, injection flow rate and volume monitoring, groundwater and aquifer tube sampling, and some potential soil sampling after injections are complete. Field test instructions will be prepared prior to the injections, which will include sampling requirements, along with a detailed set of operational parameters and procedures. Sampling will occur in a number of monitoring wells and aquifer tubes located within the potential area of injection influence, along the 100-N shoreline before, during, and after treatment.

The objectives of this Design Optimization Sampling and Analyses effort are to determine the following information:

- A pre-injection baseline for groundwater, aquifer tube, and river water contaminants of concern (COCs) within the expanded PRB area.
- The COC response of the injected PRB precursors (primarily by Sr-90 level reduction and conductivity).

- The extent of the PRB precursor travel within the vadose zone and effective Sr-90 reduction or apatite barrier establishment.
- If additional PRB precursors are needed in general, or within specific locations of the expanded apatite areas.

All sampling frequencies for groundwater, aquifer tubes, and soil cores are based on these criteria.

6.1 Sampling Frequency

Prior to injection, baseline sampling will be conducted from select multipurpose wells and monitoring wells. These samples will serve as the basis to compare the performance of the barrier. Sampling frequency will be initially increased immediately following injection to monitor any increase in Sr-90 flux toward the river. Sample frequency detail is provided in Table 2.

6.2 Injection Skid Sampling, Flow Rate, and Volume

Samples will be collected from the injection skid periodically to ensure that the apatite precursors are being injected at the correct concentrations. Flow rates and pressure within the injection skid system will be monitored during injections and any flow adjustments made as necessary. Injection skid sampling frequency is provided in Table 2.

6.3 Groundwater Sampling and Analysis

Groundwater samples will be collected from wells located within the potential area of injection influence. Groundwater samples will be collected using either a peristaltic pump or 12-V electric submersible pump. Field parameters will be measured for each sample using portable field instruments. Specific conductance, oxidation reduction potential, temperature, dissolved oxygen, and pH will all be measured in the field. Aqueous samples for analyses of other parameters will be collected. Table 2 provides groundwater sample frequency. Table 3 lists the analytic sampling requirements for the parameters, container volume, and preservation methods required for offsite analyses; Table 4 lists parameters, analytic methods, and detection limits for aqueous analytes (including aquifer tube samples).

6.4 Aquifer Tube Sampling

Aquifer tube samples will be collected from aquifer tubes located within the potential area of injection influence. Table 2 provides aquifer tube sample frequency. Previous work for the low-concentration injections (PNNL-17429) have shown that if elevated Sr-90 and other metal concentrations occur, the aquifer stabilizes within a few weeks following injections. Gross beta analysis will initially be used for estimating Sr-90 concentrations to provide a quicker turnaround on analytical results. If the sampling personnel observe floating product during sampling activities, the samples will also be analyzed for TPH. Aquifer tube samples will be collected in accordance with the *Sampling and Analysis Plan for Aquifer Sampling Tubes* (DOE/RL-2000-59) and this design optimization study.

6.5 Core Sampling and Analysis

Continuous core samples will be collected if the groundwater and aquifer tube monitoring data show a 90 percent reduction in Sr-90 flux to the river. If no considerable reduction is shown, re-injection will be implemented and soil cores will not be collected. Core samples will be collected from locations to determine the vertical and radial extent of calcium-citrate-phosphate injection into the soil column and to determine the degree of apatite formation. A determination of the amount of strontium and Sr-90 incorporated in the apatite matrix, adsorbed to apatite material by ion-exchange, and sorbed to sediments

may be completed later. Continuous soil cores will be collected following the procedures outlined in the TTP Addendum 3 (DOE/RL-2005-96-ADD3, *100-NR-2 Apatite Treatability Test Plan Implementation*) and this design optimization study.

Table 2. Approximate Sampling Locations and Frequency

Sample Purpose	Sampling Locations	Approximate Sampling Frequency	Analytes
Pre-Injection Monitoring	Nearby monitoring wells/ aquifer tubes and one river water sample	One time immediately prior to injection	Cations, anions, Sr-90, gross beta, field parameters
Injection Monitoring	Injection stream	Field parameters every 4 hours, aqueous samples every 12 hours	Cations, anions, field parameters
Injection Arrival Monitoring	Nearby monitoring wells/ aquifer tubes	Field parameters every 4 hours, aqueous samples near end of injection	Cations, anions, field parameters
Performance Monitoring	Nearby monitoring wells/ aquifer tubes	Daily for 1st week, every other day for 2nd week, 1x per week for one month, Ongoing performance monitoring	Cations, anions, gross beta, Sr-90, field parameters

Table 3. Sampling Requirements

Parameter	Media/Matrix	Volume/Container	Preservation	Hold Time
Major Cations/Metals: Al, As, Ba, Ca, Co, Cr[a], Fe, K, Mg, Mn, Ni, Zn, P, Sr, Na, Sb	Water	250 mL poly bottle	Filter (0.45 µm)[b], HNO_3 to pH <2	60 days
Anions: Cl^-, SO_4^-, PO_4^-, NO_2^-, NO_3^-	Water	120 mL poly bottle	Cool 4°C	45 days
Sr-90	Water	1 L poly bottle	Filter (0.45 µm)[b], HNO_3 to pH <2	60 days
Gross Beta	Water	500 mL poly bottle	Filter (0.45 µm)[b], HNO_3 to pH <2	60 days
Apatite[c]	Sediment	1L/liner	Cool	N/A
Phosphate[c]	Sediment	1L/liner	Cool	N/A
Sr-90[c]	Sediment	1L/liner	Cool	N/A
pH	Water	Field measurement	N/A	N/A
Specific Conductance	Water	Field measurement	N/A	N/A
Dissolved Oxygen	Water	Field measurement	N/A	N/A
Oxidation-Reduction Potential	Water	Field measurement	N/A	N/A
Temperature	Water	Field measurement	N/A	N/A

a. Filtered Cr is representative of Cr+6.

b. Samples will be filtered (0.45 µm) for increased sample quality and to aid in the laboratory's ability to analyze the samples.

c. Sediment core sampling contingent on barrier performance.

N/A = Not Applicable

Table 4. Analytical Performance Requirements

Chemical Abstract Service Number	Analyte	Matrix	Analytical Method	Required Detection Limit[a]	Accuracy Requirement (% Recovery)[b]	Precision Requirement (Relative % Difference)[b]
Radiological Constituents						
Rad-Sr	Sr-90	Water	Strontium 89/90 – Total Rad-Sr	2 pCi/L	80-120%	≤20%
12587-47-2	Gross Beta	Water	Gross beta	4 pCi/L	80-120%	≤20%
Nonradiological Constituents						
7440-90-5	Aluminum	Water	ICP Metals – 6010	50 µg/L	80-120%	≤20%
7440-36-0	Antimony	Water	ICP Metals – 6010	60 µg/L	80-120%	≤20%
7440-38-2	Arsenic	Water	ICP Metals – 6010	100 µg/L	80-120%	≤20%
7440-39-3	Barium	Water	ICP Metals – 6010	20 µg/L	80-120%	≤20%
7440-43-9	Cadmium	Water	ICP Metals – 6010	5 µg/L	80-120%	≤20%
7440-70-2	Calcium	Water	ICP Metals – 6010	1,000 µg/L	80-120%	≤20%
7440-47-3	Chromium	Water	ICP Metals – 6010	10 µg/L	80-120%	≤20%
7440-48-4	Cobalt	Water	ICP Metals – 6010	20 µg/L	80-120%	≤20%
7440-50-8	Copper	Water	ICP Metals – 6010	10 µg/L	80-120%	≤20%
7439-89-6	Iron	Water	ICP Metals – 6010	50 µg/L	80-120%	≤20%
7439-92-1	Lead	Water	ICP Metals – 6010	50 µg/L	80-120%	≤20%
7439-95-4	Magnesium	Water	ICP Metals – 6010	750 µg/L	80-120%	≤20%
7439-96-5	Manganese	Water	ICP Metals – 6010	5 µg/L	80-120%	≤20%
7439-98-7	Molybdenum	Water	ICP Metals – 6010	20 µg/L	80-120%	≤20%
7440-02-0	Nickel	Water	ICP Metals – 6010	40 µg/L	80-120%	≤20%
7440-09-7	Potassium	Water	ICP Metals – 6010	4,000 µg/L	80-120%	≤20%
7440-22-4	Silver	Water	ICP Metals – 6010	10 µg/L	80-120%	≤20%

Table 4. Analytical Performance Requirements

Chemical Abstract Service Number	Analyte	Matrix	Analytical Method	Required Detection Limit[a]	Accuracy Requirement (% Recovery)[b]	Precision Requirement (Relative % Difference)[b]
7440-23-5	Sodium	Water	ICP Metals – 6010	500 µg/L	80-120%	≤20%
7440-24-6	Strontium	Water	ICP Metals – 6010	10 µg/L	80-120%	≤20%
7440-62-2	Vanadium	Water	ICP Metals – 6010	25 µg/L	80-120%	≤20%
7440-66-6	Zinc	Water	ICP Metals – 6010	10 µg/L	80-120%	≤20%
16887-00-6	Chloride	Water	Anions by IC – 300.0	200 µg/L	80-120%	≤20%
16984-48-8	Fluoride	Water	Anions by IC – 300.0	500 µg/L	80-120%	≤20%
NO2-N	Nitrogen in nitrate	Water	Anions by IC – 300.0	75 µg/L	80-120%	≤20%
NO3-N	Nitrogen in nitrite	Water	Anions by IC – 300.0	75 µg/L	80-120%	≤20%
PO4-P	Phosphorus in phosphate	Water	Anions by IC – 300.0	500 µg/L	80-120%	≤20%
14808-79-8	Sulfate	Water	Anions by IC – 300.0	100 µg/L	80-120%	≤20%
Field Measurements						
pH – 150.1	pH	Water	150.1 – pH-Field	0.1 pH unit	[c]	[c]
Temp – 170.1	Temperature (°C)	Water	170.1 – Temperature-Field	0.1 °C	[c]	[c]
Cond – 120.1	Specific conductance (µS/cm)	Water	120.1 – Conductivity-Field	0.1 µS/cm	[c]	[c]
Oxygen – 360.1	Dissolved oxygen (mg/L)	Water	360.1 – Oxygen-Field	0.1 mg/L	[c]	[c]
REDOX_FLD	Oxidation-Reduction Potential (mV)	Water	Redox_Probe_Field	±1 mV	[c]	[c]
PNNL Apatite Formation Testing[d]						
14265-44-2	Phosphate, Apatite	Sediment	XRD	N/A	[e]	[e]
14265-44-2	Phosphate, Apatite	Sediment	SEM/EDS	N/A	[e]	[e]

Table 4. Analytical Performance Requirements

Chemical Abstract Service Number	Analyte	Matrix	Analytical Method	Required Detection Limit[a]	Accuracy Requirement (% Recovery)[b]	Precision Requirement (Relative % Difference)[b]
14265-44-2 Rad-Sr	Phosphate, Sr-90	Sediment	Acid dissolution of sediment and phosphate measurement	N/A	e	e
N/A	Apatite	Sediment	Fluorescence of substituted apatites	N/A	e	e

a. Project specific detection limits—actual laboratory detection limits are laboratory specific and may be lower.

b. Accuracy criteria for associated batch matrix spike percent recoveries. Evaluation based on statistical control of laboratory control samples is also performed. Precision criteria for batch laboratory replicate matrix spike analyses or replicate sample analyses.

c. This method has no quantitative requirements beyond adherence to the field measurement methodology.

d. Sediment core sampling contingent on barrier performance.

e. PNNL laboratory procedures and QA plan will apply to all analyses performed by PNNL.

EDS = energy dispersive X-ray spectroscopy

ICP = inductively coupled plasma

PNNL = Pacific Northwest National Laboratory

QA = quality assurance

SEM = scanning electron microscope

XRD = X-ray diffraction

7 Data Management

The Sample Management and Reporting Organization, in coordination with the project manager, is responsible for ensuring analytical data are appropriately reviewed, managed, and stored in accordance with the applicable programmatic requirements governing data management procedures. Electronic data access, when appropriate, will be via a database (e.g., Hanford Environmental Information System [HEIS] or a project-specific database). All data collected as part of this design optimization will be entered into HEIS. Where electronic data are not available, hard copies will be provided in accordance with Section 9.6 of the *Hanford Federal Facility Agreement and Consent Order Action Plan* (Ecology et al., 1989b).

7.1 Sample Collection and Analysis

Planning for sample collection and analysis will be in accordance with the programmatic requirements governing fixed laboratory sample collection activities, as discussed in the sample team's procedures. In the event specific procedures do not exist for a particular work evolution, or it is determined that additional guidance to complete certain tasks is needed, a work package will be developed to control the activities adequately. Examples of the sample team's requirements include activities associated with the following:

- COC/sample analysis requests
- Project and sample identification for sampling services
- Control of certificates of analysis
- Logbooks
- Checklists
- Sample packaging and shipping

Approved work control packages and procedures will be used to document field activities, including radiological measurements. All field activities will be recorded in the field logbook. Examples of the types of documentation for field radiological data include the following:

- Instructions regarding the minimum requirements for documenting radiological controls information as per 10 CFR 835, "Occupational Radiation Protection."
- Instructions for managing the identification, creation, review, approval, storage, transfer, and retrieval of primary contractor radiological records.
- The minimum standards and practices necessary for preparing, performing, and retaining radiological-related records.
- The indoctrination of personnel on the development and implementation of sample plans.
- The requirements associated with preparing and transporting regulated material.
- Daily reports of radiological surveys and measurements collected during conduct of field investigation activities. Data will be cross-referenced between laboratory analytical data and radiation measurements to facilitate interpretation of the investigation results.
- Daily reports of radiological surveys and measurements collected during the field investigation activities. Data will be cross-referenced between laboratory analytical data and radiation measurements to facilitate interpreting the investigation results.

7.2 Resolution of Errors

Laboratory errors are reported to the Sample Management and Reporting Organization on a routine basis. For reported laboratory errors, the sample issue resolution process will be initiated in accordance with Contractor procedures. This process is used to document analytical errors and to establish their resolution with the Project Manager.

8 Data Analysis and Interpretations

This chapter discusses the data analysis and interpretations used for determining whether the data meet the project objectives.

8.1 Data Validation and Usability

The following sections address the quality assurance (QA) activities that occur after the data collection phase of the project is completed. Implementation of these elements determines whether data conform to the specified criteria, thus satisfying project objectives.

8.1.1 Data Review, Verification, and Validation

The criteria for verification may include review for completeness (all samples were analyzed as requested), use of the correct analytical method/procedure, review for transcription errors, correct application of dilution factors, appropriate reporting of dry weight versus wet weight, and the correct application of conversion factors. Laboratory personnel may perform data verification.

Data validation will be performed to ensure that the data quality goals established during the planning phase have been achieved. Data validation will be in accordance with internal procedures. The criteria for data validation are based on a graded approach. The primary contractor has defined five levels of validation, A through E. Level A is the lowest level and is the same as verification. Level E is a 100 percent review of data (e.g., calibration data; calculations of representative samples from the dataset). Validation will be performed to contractor Level C, which is a review of the quality control (QC) data. Level C validation specifically requires verification of deliverables and requested versus reported analyses and qualification of the results based on analytical holding times, method blank results, matrix spike/matrix spike duplicate, surrogate recoveries, duplicates, and analytical method blanks. Level C validation will be performed on at least 5 percent of the data by matrix and analyte group. Analyte group refers to categories, such as radionuclides, volatile and semivolatile chemicals, metals, and anions.

Relative to analytical data in sample media, physical data and/or field screening results are of lesser importance in making inferences of risk. Data validation will not be performed for physical property data and/or field screening results.

8.1.2 Verification and Validation Methods

Validation activities will be based on EPA functional guidelines (EPA540/R-99/008, *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*). Data validation may be performed by the analytical laboratory, Sample Management and Reporting, and/or by a party independent of both the data collector and the data user.

Data qualifiers assigned during data validation will be compatible with HEIS.

When outliers or questionable results are identified, additional data validation will be performed. The additional validation will be performed for up to 5 percent of the statistical outliers and/or questionable

data. The additional validation will begin with Level C and may increase to Levels D and E as needed to ensure that data are usable. Level C validation is a review of the QC data, while Levels D and E include review of calibration data and calculations of representative samples from the dataset. Data validation will be documented in data validation reports. One example of questionable data is the positive detections are greater than the practical quantitation limit or reporting limit in soil/aquifer sediment from a site that should not have exhibited contamination. Similarly, results below background would not be expected and could trigger a validation inquiry.

Data validation will be documented in data validation reports, which will be included in the project file.

8.1.3 Reconciliation with User Requirements

The data quality assessment (DQA) process compares completed field sampling activities to those proposed in corresponding sampling documents and provides an evaluation of the resulting data. The purpose of the data evaluation is to determine whether quantitative data are of the correct type and of adequate quality and quantity to meet the project data quality objectives (DQOs). The project manager is responsible for determining whether a DQA is necessary and ensuring that it is performed, if required. The results of the DQA will be used in interpreting the data and determining if the objectives of this activity have been met.

The DQA (if performed) with be in accordance with EPA's DQA process, *Data Quality Assessment: A Reviewer's Guide*, QA/G-9R (EPA/240/B-06/002) and *Data Quality Assessment: Statistical Methods for Practitioners*, EPA QA/G-9S (EPA/240/B-06/003).

8.1.4 Corrective Actions

The responses to data quality defects identified through the DQA process will vary and may be data-specific or measurement-specific. Table 5 identifies some pre-identified corrective actions.

8.2 Data Interpretation

Data interpretation will be performed to assess the performance of the calcium-citrate-phosphate injection. The primary interpretation of the data will be to assess the effectiveness of the calcium-citrate-phosphate solution in reduction of Sr-90 and metals flux to the Columbia River relative to baseline concentrations. The secondary interpretation will be measuring apatite formation through collection of core samples; this will not be necessary if there is no measurable decrease in Sr-90 flux to the River.

9 Health and Safety

All field operations will be performed in accordance with CHPRC health and safety requirements, outlined in the latest revision of the S&GRP health and safety plan. Radiological contamination is expected to be encountered during performance of the well drilling and sampling activities. The sampling processes and associated activities will take into consideration exposure reduction and contamination control techniques (e.g., ALARA and Integrated Safety Management System) that will minimize chemical exposure to the sampling team. Health and safety personnel will use data collected during the activities addressed in this design optimization study as input to determine exposure levels to workers, and to conduct health and safety assessments during all field activities, in accordance with the health and safety plan.

Table 5. Data Quality Indicators

Data Quality Indicator	Definition	Example Determination Methodologies	Project-Specific Information*	Corrective Actions Examples
Precision	The measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions; calculated either as the range or as the standard deviation. May also be expressed as a percentage of the mean of the measurements, such as relative range, relative percent difference, or relative standard deviation (coefficient of variation).	Use the same analytical instrument to make repeated analyses on the same sample. Use the same method to make repeated measurements of the same sample within a single laboratory or have two or more laboratories analyze identical samples with the same method. Split a sample in the field and submit both samples for sample handling, preservation and storage, and analytical measurements. Collect, process, and analyze collocated samples for information on sample acquisition, handling, shipping, storage, preparation, and analytical processes and measurements.	Precision criteria shall apply: **Laboratory analysis:** Adherence to QAPP Table 2-2 and laboratory SOPs provides the level of precision adequate for data use. One duplicate collected for one in 20 water samples. **Field measures:** Achieved by adherence to SOPs. **Apatite Formation Testing:** Achieved by adherence to PNNL laboratory SOPs and PNNL QA plan, yielding the needed precision.	Data interpretation or data assessment may be performed.
Accuracy	A measure of the overall agreement of a measurement to a known value; includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations.	Analyze a reference material or re-analyze a sample to which a material of known concentration or amount of pollutant has been added (a spiked sample); usually expressed either as percent recovery or as percent bias.	Accuracy criteria shall apply: **Laboratory analysis:** Adherence to QAPP Table 2-2 and laboratory SOPs provides the level of accuracy for data use. Laboratory QC **Field measures:** Achieved by adherence to SOPs. **Apatite Formation Testing:** Adherence to PNNL SOPs and PNNL QA plan, yielding the needed accuracy.	Data interpretation or data assessment may be performed.

Table 5. Data Quality Indicators

Data Quality Indicator	Definition	Example Determination Methodologies	Project-Specific Information*	Corrective Actions Examples
Representativeness	A qualitative term that expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition (ANSI/ASQC E4-1994).	Evaluate whether measurements are made and physical samples collected in such a manner that the resulting data appropriately reflect the environment or condition being measured or studied.	**Laboratory Analysis:** Groundwater samples will be collected from each of the wells along the river shore. The results will represent linear variability across the study area and track trends over time. It provides a practical method for designating sample locations and ensures uniform coverage of the test site area. **Apatite Formation Testing:** Soil samples will be collected in a focused design within a representative central portion of the barrier in accordance with the design optimization study.	Data interpretation or data assessment may be performed.
Comparability	A qualitative term that expresses the measure of confidence that one data set can be compared to another and can be combined for the decision(s) to be made.	Compare sample collection and handling methods, sample preparation and analytical procedures, holding times, stability issues, and QA protocols.	**Laboratory Analysis:** The sample results need only be internally comparable. All sampling personnel will use the same sampling protocols. All samples will be submitted to the laboratory for analysis by the same methods; thus, data results will be comparable. Field splits will provide some measure of inter-laboratory comparability. **Apatite Formation Testing:** The internal data set is not expected to be comparable to any other data set. Lateral comparability will be ensured through standard methods.	If data are not comparable to other data sets: Assess potential impacts in data quality assessment if performed.

Table 5. Data Quality Indicators

Data Quality Indicator	Definition	Example Determination Methodologies	Project-Specific Information*	Corrective Actions Examples
Completeness	A measure of the amount of valid data needed to be obtained from a measurement system.	Compare the number of valid measurements completed (samples collected or samples analyzed) with those established by the project's quality criteria (DQOs or performance/acceptance criteria).	**Laboratory and Field Analyses:** The water samples from 170 wells will be collected in order to meet the completeness criteria. **Apatite Formation Testing:** The soil samples from three boreholes will be collected in order to meet the completeness criteria.	Evaluate the impact to the resulting data set and ability to define treatability test design criteria.
Sensitivity	The capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest.	Determine the minimum concentration or attribute that can be measured by a method (method detection limit), by an instrument (instrument detection limit), or by a laboratory (quantitation limit). The practical quantitation limit is the lowest level that can be routinely quantified and reported by a laboratory.	Sensitivity criteria will apply: **Laboratory Analysis:** Adherence to this QAPjP and laboratory SOPs provides the level of sensitivity for data use. **Apatite Formation Testing:** Achieved by adherence to PNNL laboratory SOPs and PNNL QA plan, yielding the needed sensitivity.	Data interpretation or data assessment may be performed.

Notes: ANSI/ASQC E4-1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs.*

* Field sampling requirements are noted. Laboratories will follow contract requirements for use and interpretation of laboratory control samples. Precision, accuracy, and sensitivity requirements are satisfied by following method procedures because analyses are being performed to support treatability test design (not for regulatory decision making).

ANSI = American National Standards Institute

ASQC = American Society for Quality Control

QAPjP = quality assurance project plan

SOP = standard operating procedure

10 Residuals Management

All regulated waste generated from this design optimization study, including sampling activities, will be managed in accordance with the *Interim Action Waste Management Plan for the 100-NR-2 Waste Operable Unit* (DOE/RL-2000-41). Disposition of purgewater and miscellaneous solid waste will be conducted in accordance with DOE/RL-2000-41.

Unused samples and associated laboratory waste for the analysis will be dispositioned in accordance with the laboratory contract and agreements for return to the project site. Pursuant to 40 CFR 300.440, "Procedures for Planning and Implementing Off-Site Response Actions," U.S. Department of Energy, Richland Operations Office project manager approval is required before returning unused samples or waste from offsite laboratories (as applicable).

11 Reports

Following completion of the design optimization study, a final design optimization report will be prepared summarizing the results of the test. Interim reports may be produced during the implementation of the test as determined by the project team. Updates will be provided at Unit Management Meetings and in the Annual Groundwater Monitoring Report as data become available.

12 Schedule

A project field schedule will be developed and provided separately, outside of this design optimization study. This working schedule may be modified as necessary. Updates to the schedule will be provided on a regular basis in the Unit Manager Meetings.

13 References

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40 CFR 300, "National Oil and Hazardous Substances Pollution Contingency Plan," Appendix B, "National Priorities List," *Code of Federal Regulations*. Available at: http://edocket.access.gpo.gov/cfr_2009/julqtr/40cfr300AppB.htm.

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