DOE/RL-2005-96
DRAFT A

Strontium-90 Treatability Test Plan for 100-NR-2 Groundwater Operable Unit

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

United States Department of Energy
P.O. Box 550
Richland, Washington 99352

Approved for Public Release;
Further Dissemination Unlimited

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J. D. Aardal 12/20/2005
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Acronyms and Abbreviations

bgs	below ground surface
BHI	Bechtel Hanford, Inc.
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
Ci	curies
CMS	corrective measures study
DOE	U.S. Department of Energy
DQO	data quality objective
EBF	electromagnetic borehole flowmeter
Ecology	Washington State Department of Ecology
EDS	Energy dispersive
EPA	U.S. Environmental Protection Agency
ERA	ecological risk assessment
ERDF	Environmental Restoration Disposal Facility
FS	feasibility study
ft/d	feet per day
FT/IR	Fourier transform-infrared
gpm	gallons per minute
GWRTAC	Ground-Water Remediation Technologies Analysis Center
HRTEM	High resolution transmission electron microscopy
ITRD	Innovative Treatment and Remediation Demonstration [Program]
LFI	limited field investigation
LSC	liquid scintillation
LWDF	liquid waste disposal facility
m/d	meters per day
MCL	maximum contaminant level
MNA	monitored natural attenuation

NPL	National Priorities List
OU	operable unit
pCi/L	picocuries per liter
PNNL	Pacific Northwest National Laboratory
PPE	personal protective equipment
ppm	parts per million
PRB	permeable reactive barrier
QRA	qualitative risk assessment
RAO	remedial action objective
RL	Richland
ROD	Record of Decision
SNL	Sandia National Laboratory
^{90}Sr	strontium-90
TAG	Technical Advisory Group
TDS	total dissolved solids
TPH	total petroleum hydrocarbons
TTP	Treatability Test Plan
XRD	X-ray power diffraction

SECTION 1

Introduction

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

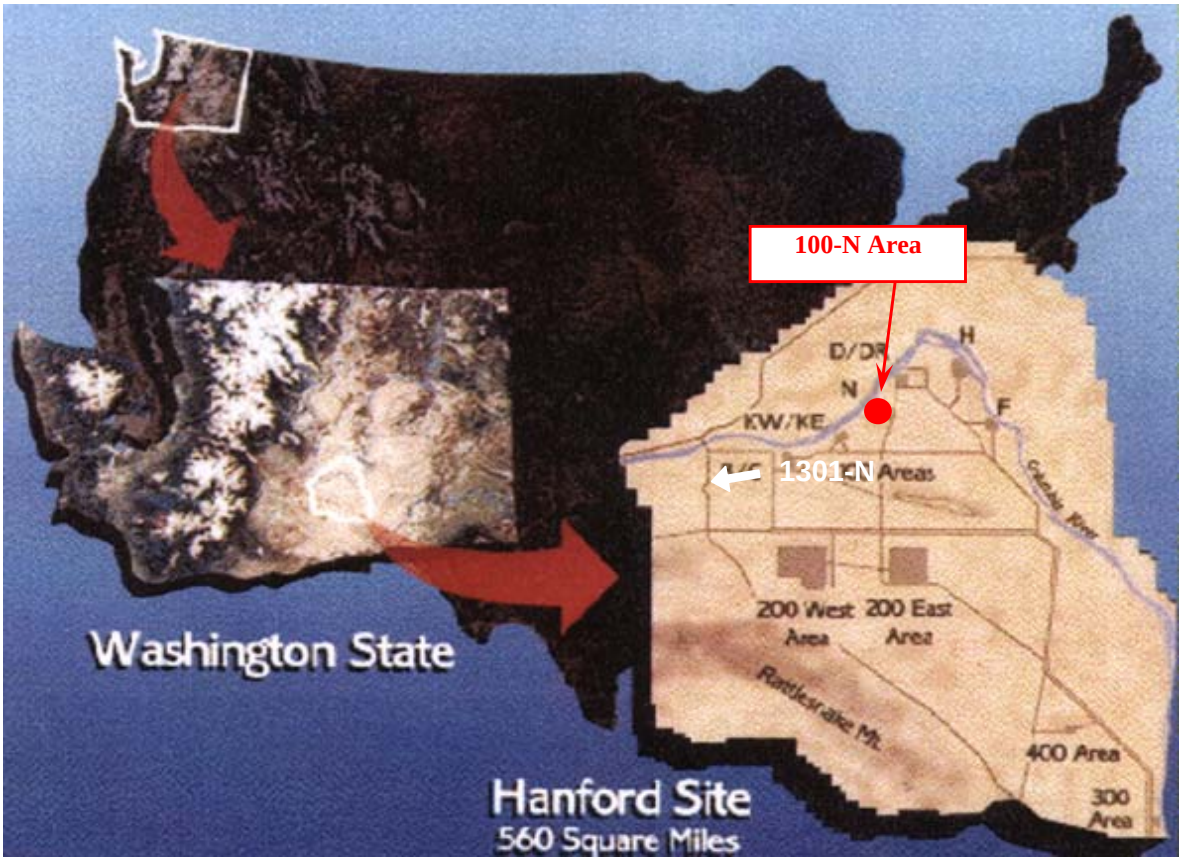
The remedy specified by the framers of the 100-NR-1/2 Interim Action Record of Decision (Ecology, 1999) included operation of a pump-and-treat system as well as a requirement to evaluate alternative ^{90}Sr treatment technologies. It was recognized from the onset that pump-and-treat was unlikely to be an effective treatment method because of the geochemical characteristics of ^{90}Sr, the primary contaminant of concern. Subsequent performance monitoring has substantiated this expectation. Accordingly, the first Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) 5-year review re-emphasized the need to aggressively pursue alternative methods to reduce impacts on the Columbia River.

With the presentation of the *Evaluation of ^{90}Sr Treatment Technologies for the 100 NR-2 Groundwater Operable Unit* (Letter Report) at the December 8, 2004, public meeting, U.S. Department of Energy (DOE), Fluor, Pacific Northwest National Laboratory (PNNL), and the Washington Department of Ecology (Ecology) agreed that the long term strategy for groundwater remediation at 100-N will include apatite sequestration as the primary treatment, followed by a secondary treatment, or polishing step, if necessary (most likely phytoremediation). Since that time, the agencies have worked together to agree on which apatite sequestration technology has the greatest chance of reducing ^{90}Sr flux to the river, for a reasonable cost. In July 2005, aqueous injection, (i.e., the introduction of apatite-forming chemicals into the subsurface) was endorsed as the interim remedy and selected for field testing. Plans are underway to assess the capability of aqueous injection to address both the vadose zone and the shallow aquifer along the 300 feet of shoreline where ^{90}Sr concentrations are highest.

This Treatability Test Plan (TTP) provides the background for this decision, a description of the technology, and a general description of the treatability testing that will be conducted. Prior to field deployment of each phase of the treatability test, a set of detailed field test instructions will be developed. These instructions will incorporate results from ongoing laboratory experiments and design analysis simulations and provide a complete description of field test operational parameters and procedures.

Based on the risk assessment (2009 through 2011), a final remedy will address the 100-N source operable unit (NR-1) as well as the groundwater contamination (NR-2). Information from this treatability test will support the selection of a final remedy, as well as provide more effective near-term treatment than the current interim remedy.

FIGURE 1-1
100-N Area, Hanford Site, Washington



This document is organized as follows:

Section 1: Introduction provides background, site description, nature and extent of ^{90}Sr contamination, regulatory history, summary of technology selection, and path forward

Section 2: Treatment Technology Description

Section 3: Bench-Scale Testing of Aqueous Injection

Section 4: Field Test Plan for Aqueous Injection

Section 5: Schedule

Section 6: References

1.1 Background

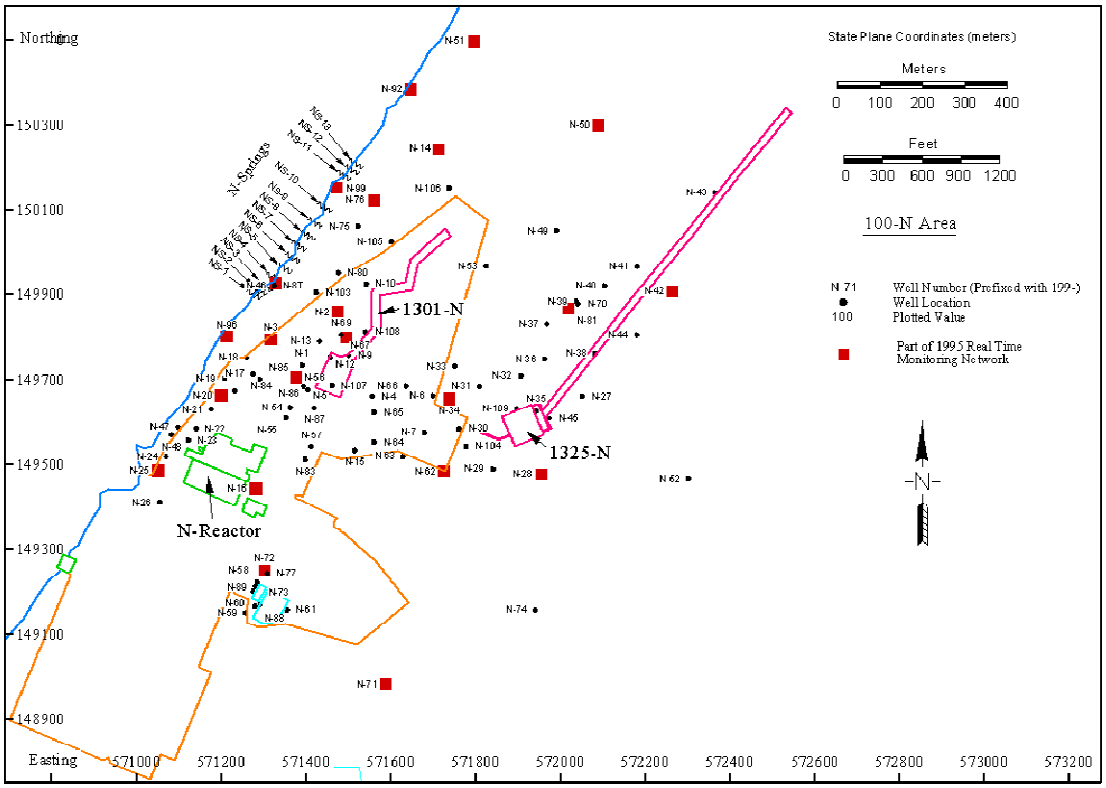
The Hanford Site is a UDOE site located in southeastern Washington State near Richland, Washington. The 100-N Area is located along the Columbia River and includes nine DOE nuclear reactors previously used for plutonium production, one of which is the 100-N Reactor.

The operation of the 100-N Area nuclear reactor required the disposal of pass-through 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. The first LWDF (1301-N) was constructed in 1963, about 244 meters (800 feet) from the river (Figures 1-2A and 1-2B). Liquid discharges to this facility contained radioactive fission and activation products, including cobalt-60, cesium-137, strontium-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 ^{90}Sr was detected at the shoreline, disposal at the first LWDF was terminated and a second crib and trench (1325-N LWDF) was constructed farther inland in 1983. Discharges to 1325-N ceased in 1993.

A more complete history of the groundwater contamination at 100-N can be found in the *Hanford 100-N Area Remediation Options Evaluation Summary Report* (TAG, 2001). In summary, as a result of wastewater disposal practices, soils beneath the LWDFs were contaminated from the surface sediments to the lower boundary of the unconfined aquifer. A portion of the contaminants migrated to the Columbia River via groundwater. To address contamination in the 100-N Area, it was divided into two operable units (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 shallow subsurface soil associated with the LWDFs. Remedial activities that address the contamination in this unit are ongoing. 100-NR-2 contains the contaminated groundwater, aquifer, and the contaminated vadose zone overlying the present-day aquifer in the 100-N Area.

FIGURE 1-2A
Test Site Location Aerial Photo
100-NR-2 Operable Unit

FIGURE 1-2B
Plot Plan Showing Site Features
100-NR-2 Operable Unit



1.2 Site Description

1.2.1 Geology

Stratigraphic units of significance in the 100-N Area include the following:

- Elephant Mountain Member of the Columbia River Basalt Group
- Ringold formation
- Hanford formation

The Elephant Mountain Member is an extensive basalt unit that underlies the fluvial-lacustrine deposits of the Ringold formation and glaciofluvial deposits of the Hanford formation. The Ringold formation is composed of several lithologic facies. Of most interest at 100-N is the Ringold Unit E, which forms the unconfined aquifer beneath the Hanford formation, and the Ringold Upper Mud Unit, which forms the base of the unconfined aquifer and is believed to be an aquitard for Unit E.

1.2.2 Hydrogeology

The uppermost stratigraphic unit in the 100-N area 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 the 100-N Area, the Hanford formation extends from ground surface to just above the water table, 5.8 to 24.5 meters (19 to 77 feet) in thickness. However, channels of Hanford gravels extending below the water table occur.

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 forms the unconfined aquifer in the 100-N Area and is approximately 12 to 15 meters thick. The base of the aquifer is situated at the contact between Ringold Unit E and the underlying, much less transmissive, silty strata referred to locally as the Ringold Upper Mud, approximately 60 meters (197 feet) thick.

The Hanford formation is much more transmissive 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 m/d have been used for modeling purposes for the Ringold and Hanford units, respectively (Hydrogeologic, Inc., 2001).

Figure 1-3 depicts a cross-section of the Hanford and upper Ringold units in the near-river environment. As illustrated in Figure 1-3, the aquifer outcrops into the Columbia River channel and the high river stage rises into the Hanford formation.

Groundwater flows primarily in a north-northwesterly direction most of the year and discharges to the Columbia River. The groundwater gradient varies from 0.0005 to 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 the Columbia River's seasonal high and low water levels, as shown in regional water table maps (Figures 1-4A and 1-4B). In June 1995, the water table was relatively flat and the hydraulic gradient was inland, away from the Columbia River in the near-river environment. By October, the water level of the Columbia River dropped, resulting in steeper hydraulic gradients and groundwater flow toward the Columbia River.

1.2.3 Groundwater-River Interaction

Fluctuations in river stage resulting from seasonal variations and daily dam operations 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, 1999). 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.

FIGURE 1-3
Site Conceptual Model in Cross-Section
100-NR-2 Operable Unit

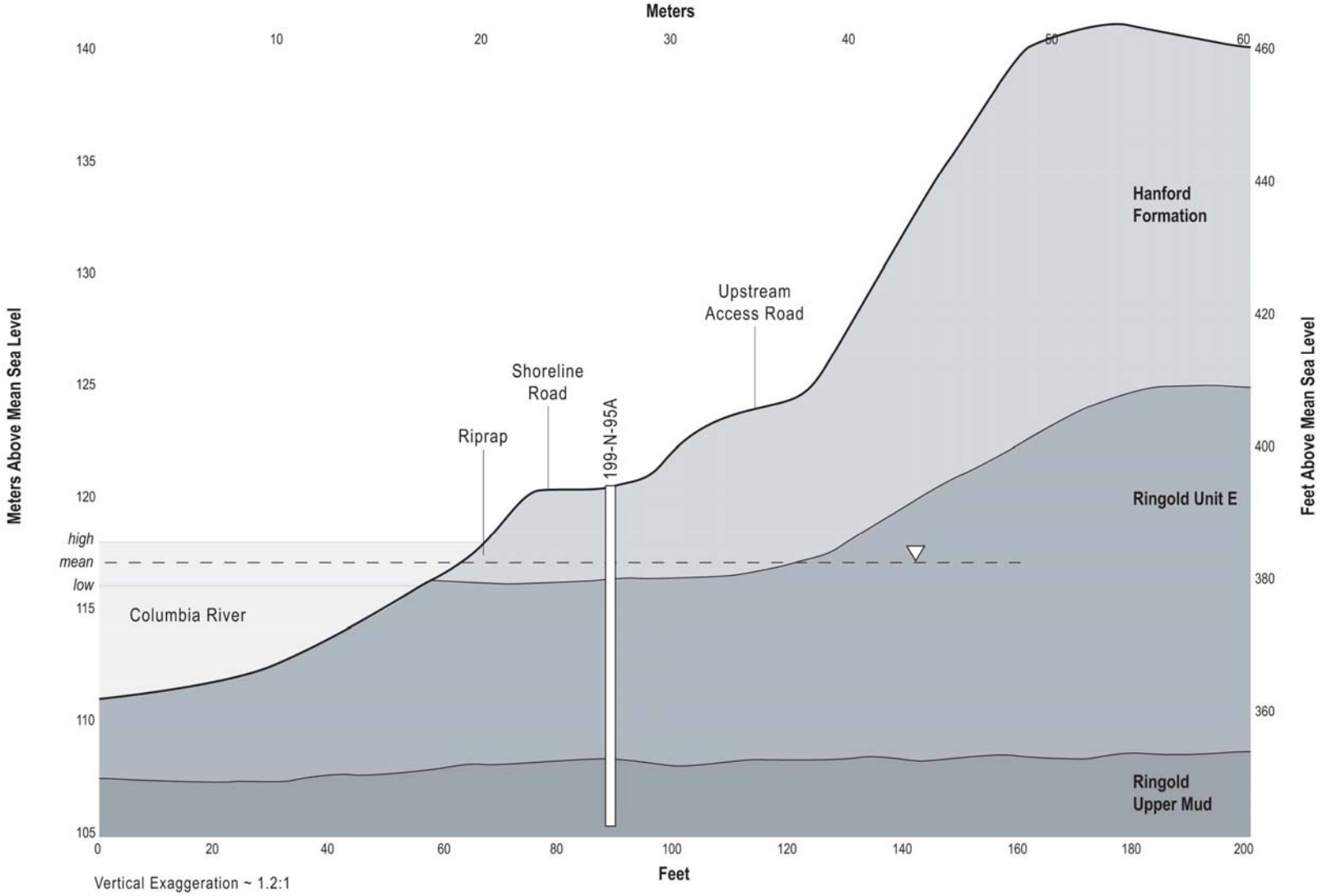


FIGURE 1-4A
Water Table Elevations: High River Stage
100-NR-2 Operable Unit

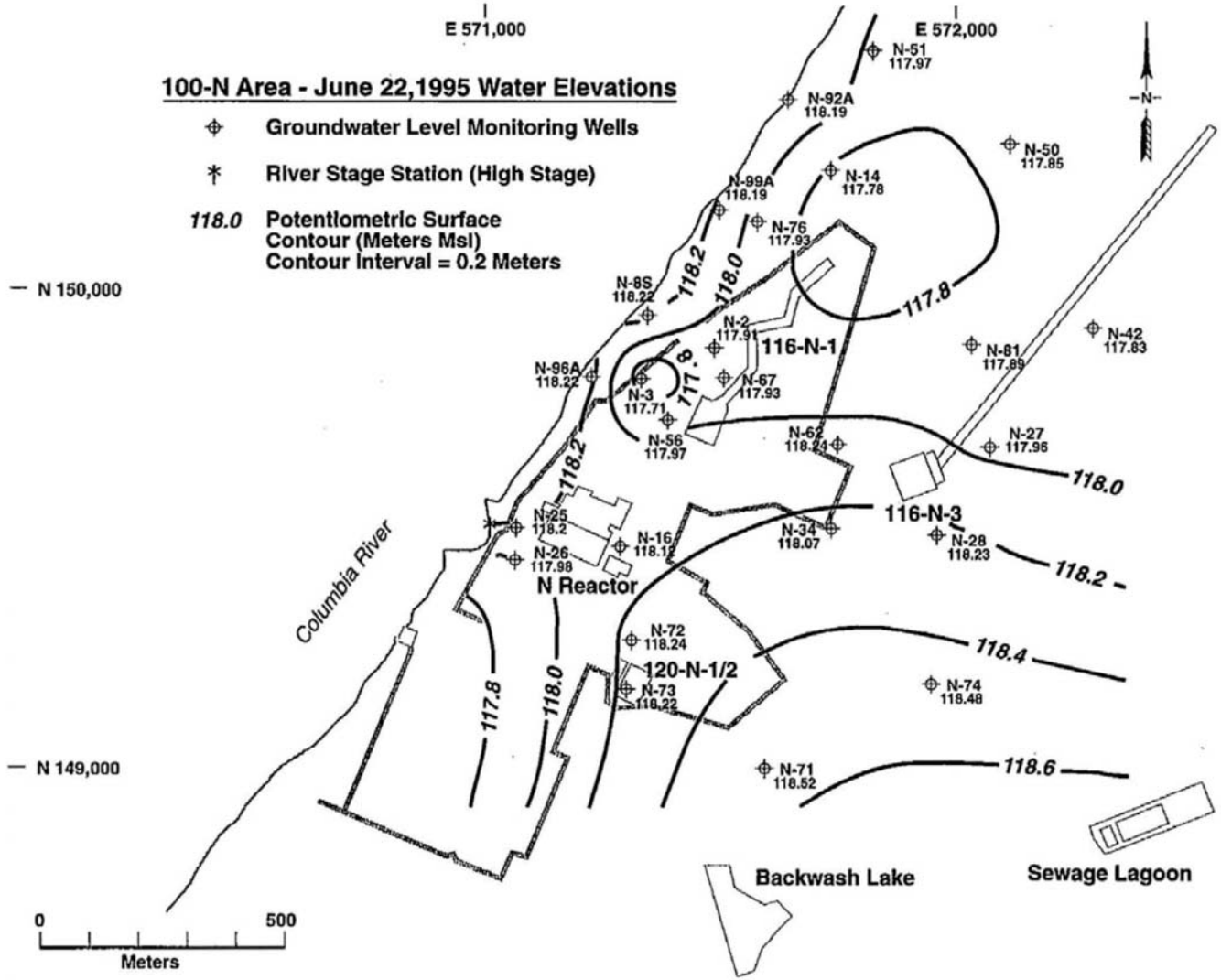
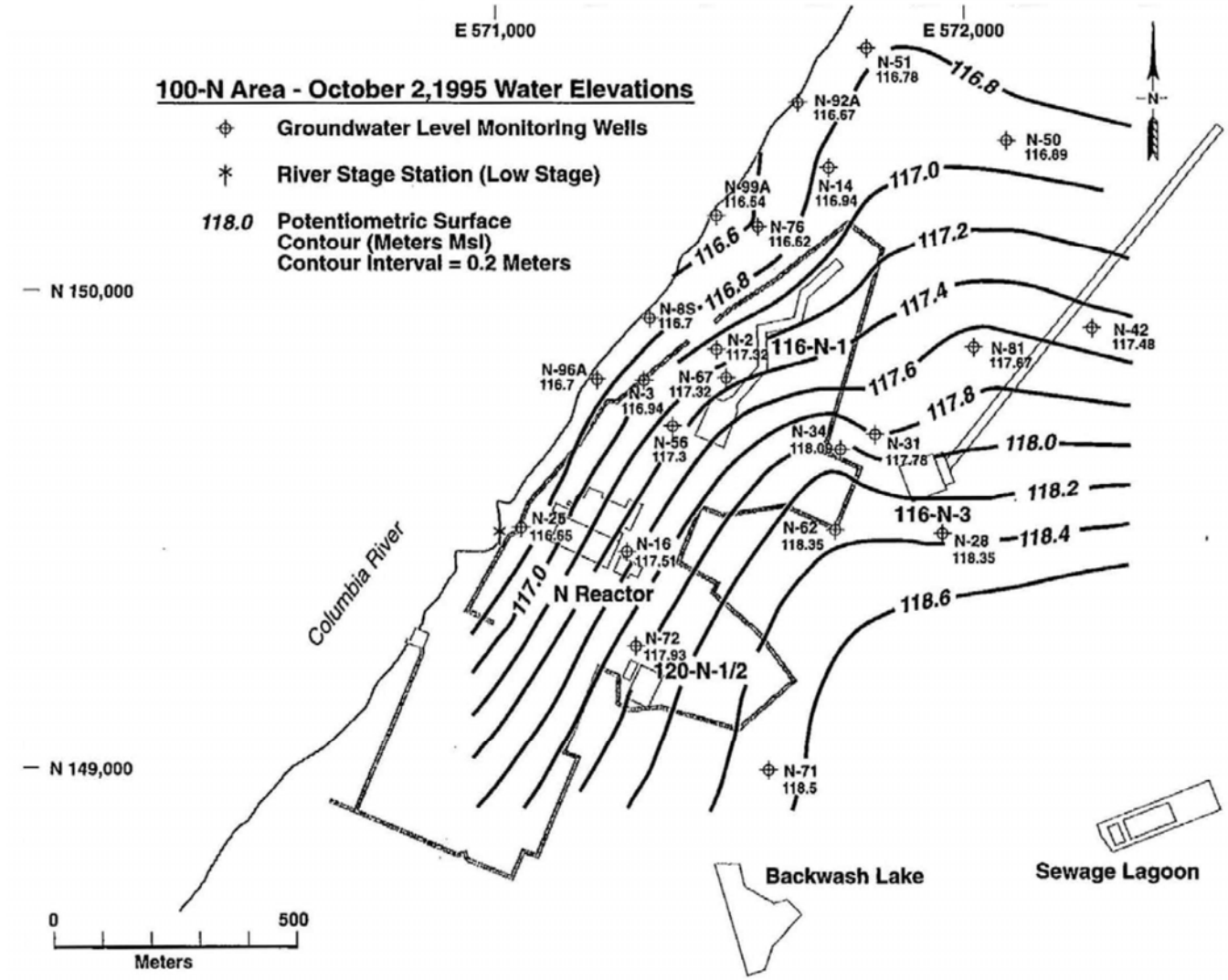


FIGURE 1-4B
Water Table Elevations: Low River Stage
100-NR-2 Operable Unit



1.3 Nature and Extent of ^{90}Sr Contamination

Groundwater at 100-N has been contaminated with various radionuclides and non-ionic and ionic constituents. Of primary concern is the presence of ^{90}Sr in the groundwater and the discharge of ^{90}Sr to the Columbia River via groundwater. ^{90}Sr is more mobile than other radiological contaminants found at the site (with the exception of tritium), and because of its chemical similarity to calcium, it bioaccumulates in plants and animals. With a half-life of 28.6 years, it will take approximately 300 years for the ^{90}Sr concentrations present in the subsurface at 100-N to decay to below current drinking water standards.

The zone of ^{90}Sr-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 1-5). During operations, a groundwater mound approximately 6 meters (20 feet) high was created. Not only was the water table raised into more transmissive Hanford and Ringold sediments, but steeper hydraulic gradients were created, increasing the groundwater flow rate toward the river. While the 100-N Reactor was operating, riverbank seepage was pronounced. 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 majority of the 1,500 curies (Ci) of ^{90}Sr remaining in the unsaturated and saturated zones in the 100-N Area as of 2003 (DOE/RL, 2004), is present in the vadose zone above the aquifer. An estimated 72 Ci of ^{90}Sr are contained in the saturated zone, and approximately 0.8 Ci are in the groundwater. Data from soil borings collected along the riverbank indicate that ^{90}Sr concentrations in soil reach a maximum near the mean water table elevation and then decrease with depth (BHI, 1995)(see Figure 1-6).Groundwater concentrations reflect the soil concentrations. Because ^{90}Sr 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 ^{90}Sr to groundwater is approximately 1:100. Under current conditions, approximately 0.14 to 0.19 Ci are released to the Columbia River from the 100-N Area annually (TAG, 2001).

In 1995, the ^{90}Sr groundwater plume extended approximately 400 meters (1,300 feet) along the river's length between the 1,000 picocuries per liter (pCi/L) contours, and approximately 800 m (1,600 feet) between the 8 pCi/L (the drinking water standard) contours (Figure 1-7) (Hydrogeologic, 1999). The highest concentrations along the shoreline were observed between wells N-94 and N-46. An area of "preferential flow" was identified in the *Technical Reevaluation of the N-Springs Barrier Wall* (BHI, 1995), that encompasses N-94, N-95, and N-46. 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 (Figure 1-8). 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 (see Figure 1-4B).

FIGURE 1-5
Conceptualization of Contamination from Liquid Waste
100-NR-2 Operable Unit

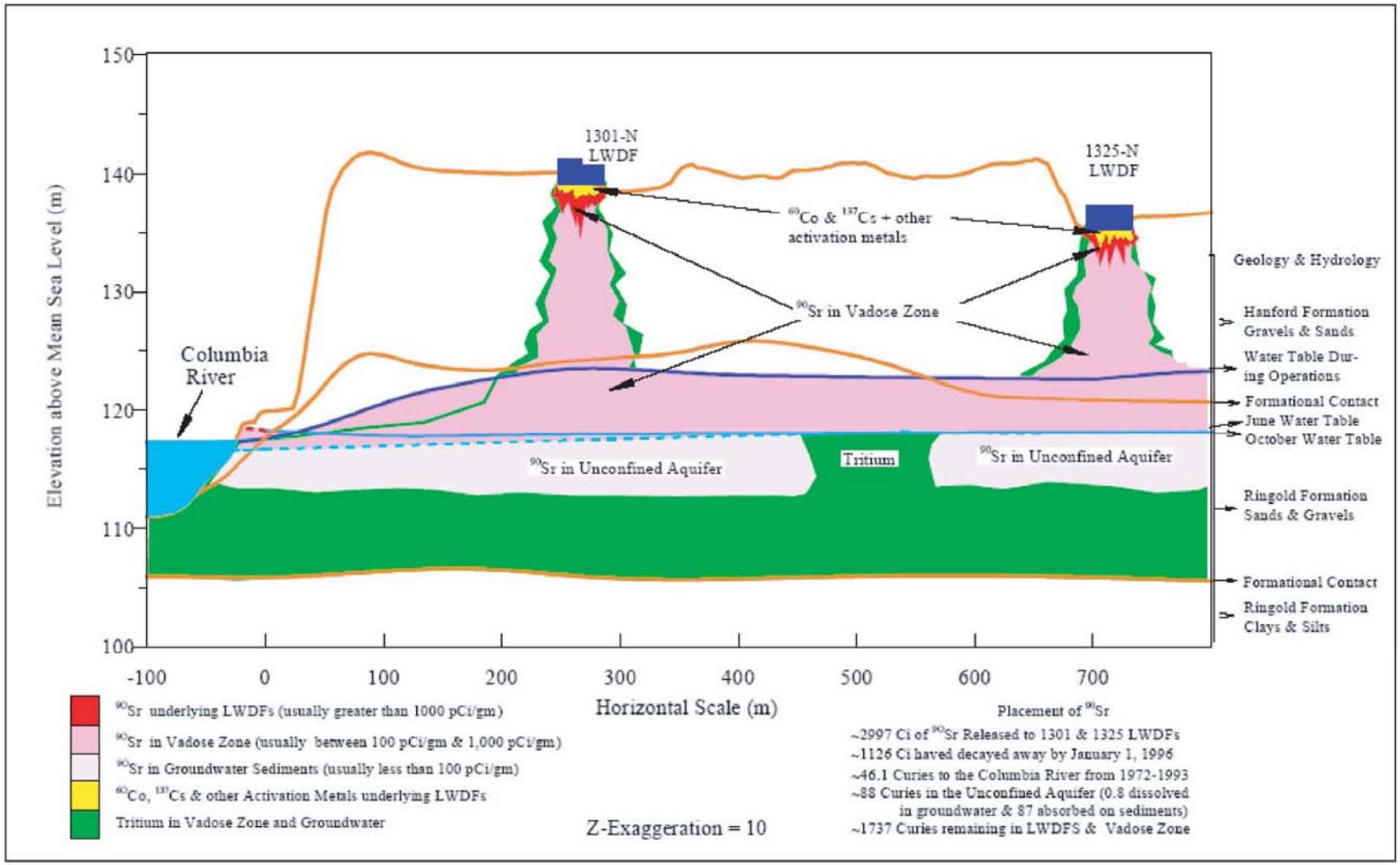


FIGURE 1-6
100-N Apatite Project, PNNL, Borehole C4473, Well 199-N-121, Geochemical Profile Results
100-NR-2 Operable Unit

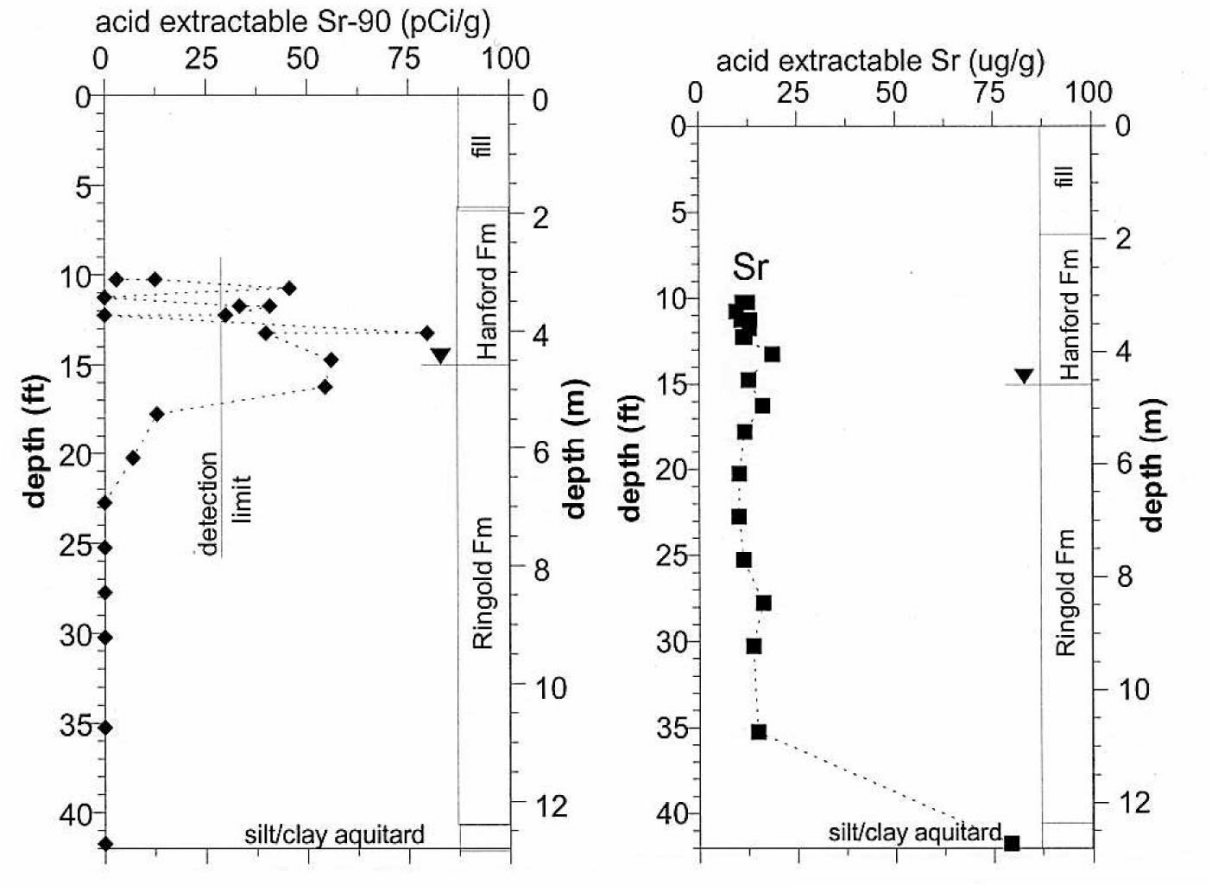


FIGURE 1-7
100-N Area ^{90}Sr Concentrations in the Unconfined Aquifer for 1999
100-NR-2 Operable Unit

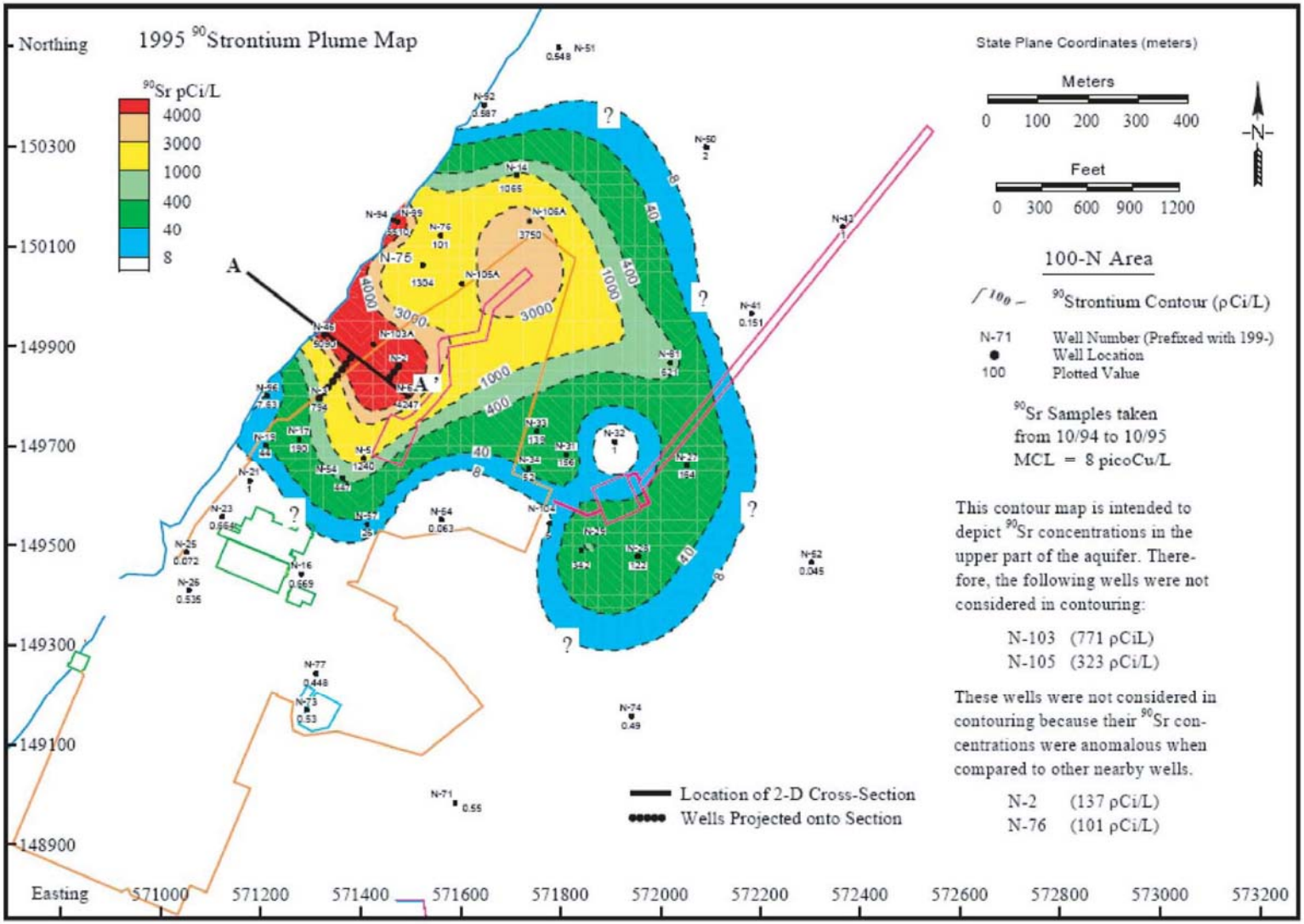
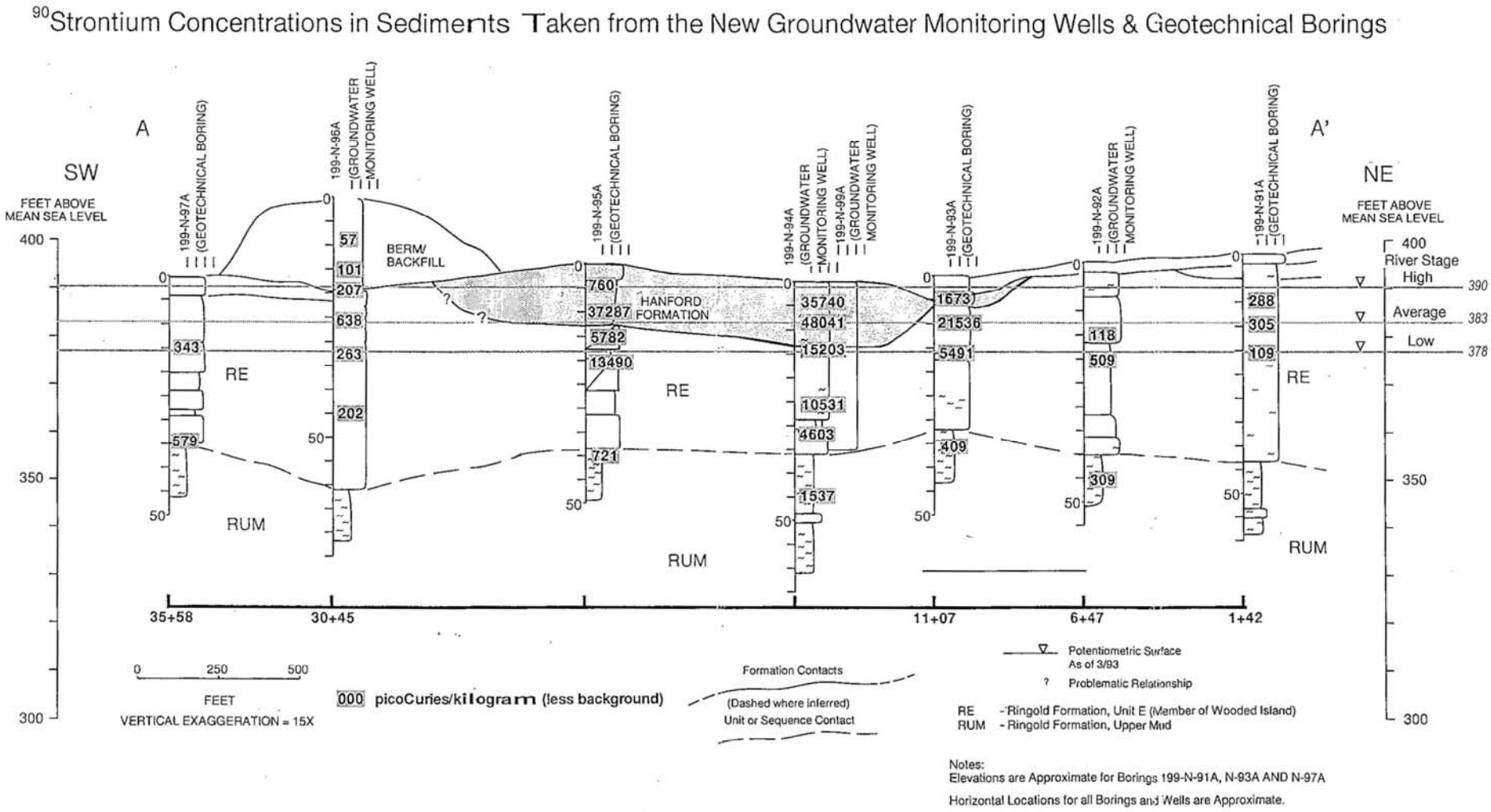


FIGURE 1-8
^{90}Sr Concentrations in Cuttings Taken from the Groundwater Monitoring Wells and Geotechnical Borings
100-NR-2 Operable Unit



N-Springs data from 1985 to 1991 showed significantly higher concentrations of ^{90}Sr in seep wells NS-2, NS-3, and NS-4 compared to the adjacent springs upstream and downstream (Figure 1-9) (BHI, 1995). Well NS-3 and the neighboring monitoring wells N-46 and N-8T have currently and historically shown the highest ^{90}Sr concentrations along the shoreline, with concentrations as high as 15,000 pCi/L ^{90}Sr observed at N-46 (TAG, 2001; DOE-RL, 2004). Recent clam data collected for the ecological risk assessment (ERA) show that the highest concentrations of ^{90}Sr in clams were observed along approximately 90 meters (300 feet of riverbank that encompasses NS-1, NS-2, NS-3and NS-4 (Figure 1-10). The previous N-Springs data, recent aquifer tube data, groundwater data, and clam data (DOE-RL, 2005) all indicate that treating the 300 feet of shoreline near N-46 will address the highest concentration portion, if not the majority, of the near-shore ^{90}Sr contamination. The targeted length of shoreline is approximately between NS-1 and NS-4 (Figure 1-11).

1.4 Remediation History

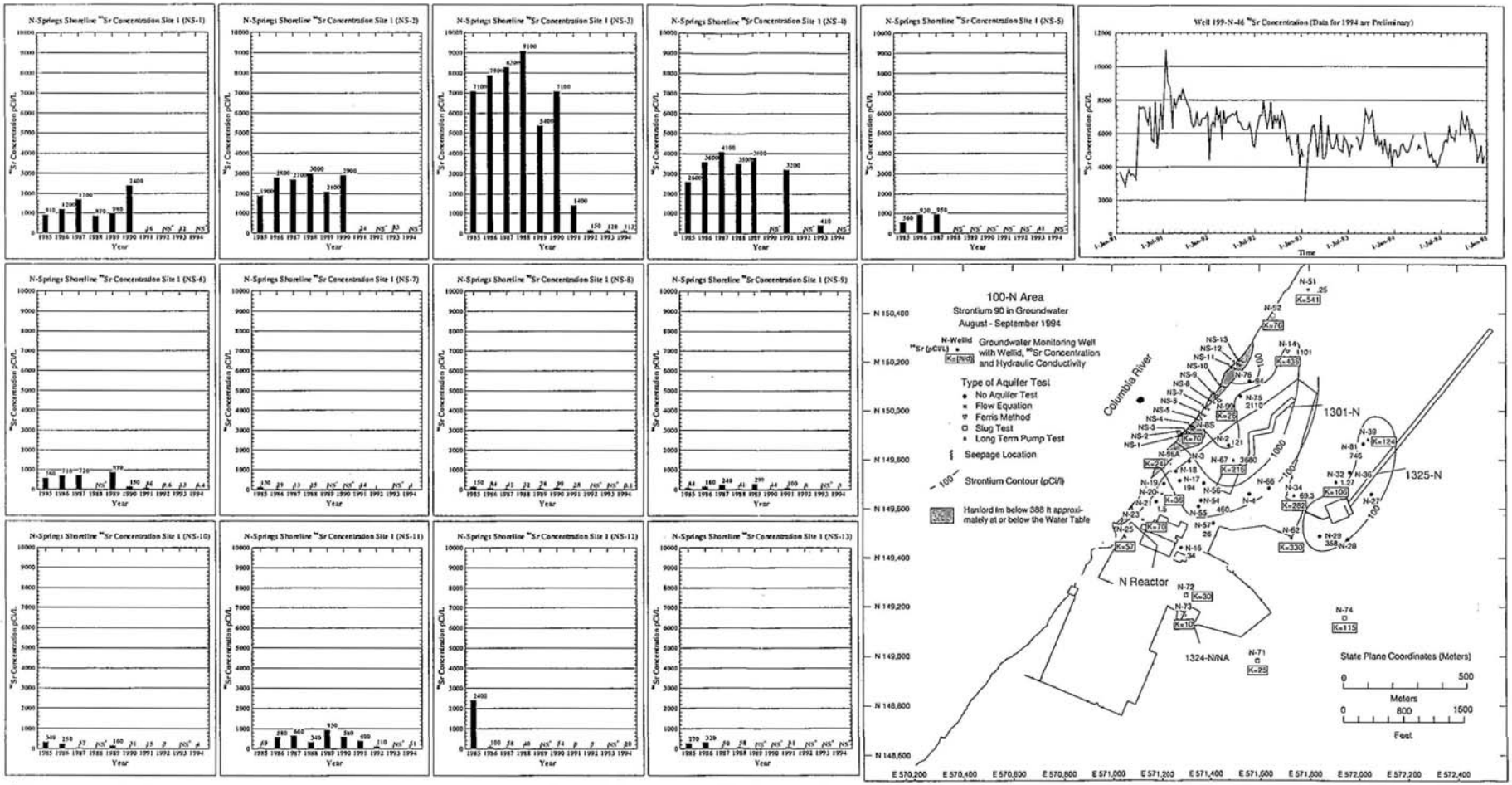
1.4.1 National Priorities List/Corrective Measures Study

The 100-N Area of the Hanford Site was placed on the National Priorities List (NPL) in 1989, the same year the Tri-Party Agreement signed by the DOE, EPA, and Ecology established the procedural framework and schedule for the remedial response actions at Hanford. In 1994, the *Limited Field Investigation Report for the 100-NR-2 Operable Unit* (LFI) (DOE-RL, 1994) 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 ^{90}Sr in groundwater. In 1995, a pump-and-treat system was installed as an interim measure to control the movement of ^{90}Sr to the Columbia River.

A corrective measures study (CMS) (DOE-RL, 1997), 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), and pump-and-treat was retained as the selected interim remedy because it provides a hydraulic barrier while removing approximately 90 percent of ^{90}Sr from extracted groundwater, and does not preclude any potential final remedies.

The results from the CMS and the Tri-Parties' preference for interim remedial action were summarized in a *Proposed Plan* (DOE-RL, 1998) that was made available to the public in March 1998. In September 1999, the Interim Action Record of Decision (ROD) (Ecology, 1999) was signed by DOE, Ecology, and EPA.

FIGURE 1-9
Time History of Contaminants Entering the River at N-Spring
100-NR-2 Operable Unit



*NS = Not Sampled. For all years except 1993, the seep well was not sample because it went dry. For 1993, the Columbia River Stage was to high and the seep well was not sampled because it was under water. (Personal Communication from Craig Perkins (WHC) to M. P. Connelly on 24-Feb-1994)

FIGURE 1-10
^{90}Sr Concentrations in Clams and Shallow Groundwater (from DOE-RL, 2005)
100-NR-2 Operable Unit

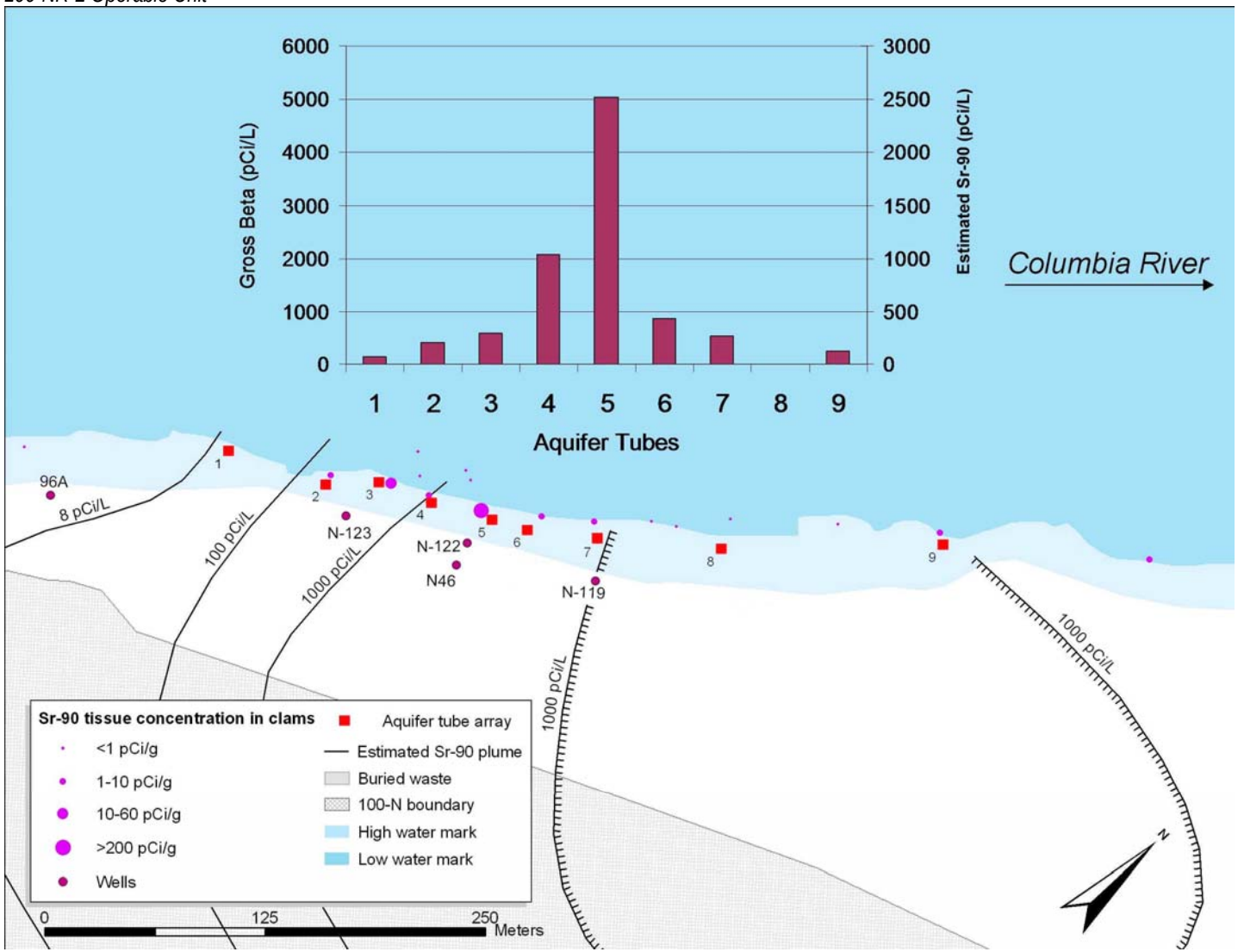
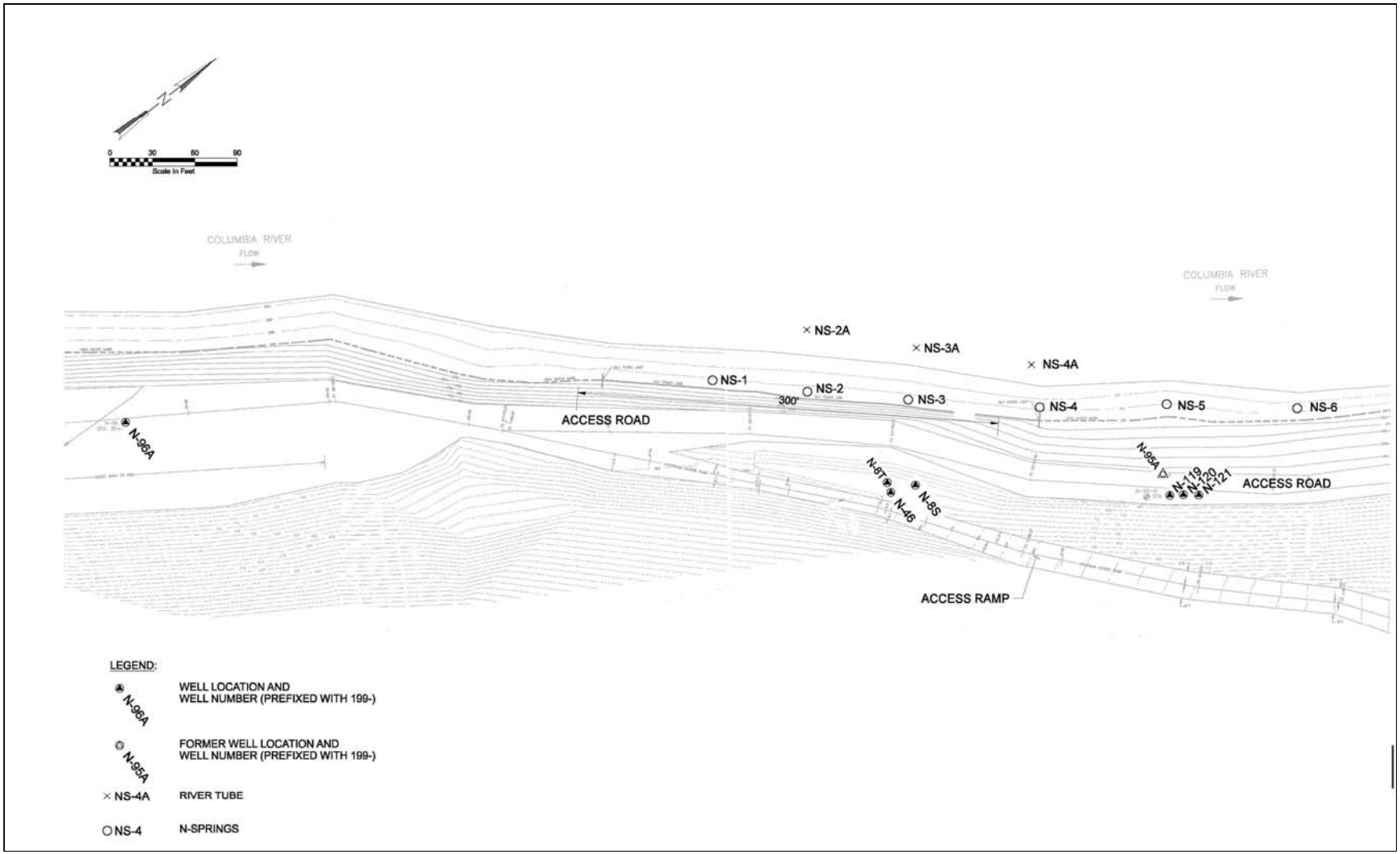


FIGURE 1-11
100-N Area Treatability Test Plan Site Map
100-NR-2 Operable Unit



1.4.2 Interim Action Record of Decision

The remedial action objectives (RAOs) for the 100-NR-2 OU were specified on page 35 of the Interim Action ROD:

- Protect the Columbia River from adverse impacts from the 100-NR-2 groundwater so that 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 non-radioactive contaminants present in the unconfined aquifer.
- Obtain information to evaluate technologies for ^{90}Sr removal and evaluate ecological receptor impacts from contaminated groundwater (by October 2005, as amended).
- 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 major components of the selected remedy for the 100-NR-2 groundwater OU as stated in the Interim Action ROD (page 52) include:

- Remove ^{90}Sr-contaminated groundwater through extraction and treatment with ion exchange and discharge treated groundwater upgradient into the aquifer.
- Maintain Ecology-approved groundwater monitoring well networks to monitor pump-and-treat operations and impacts to groundwater.
- Evaluate technologies for ^{90}Sr removal and submit information to Ecology by October 2004.
- Evaluate aquatic and riparian receptor impacts from contaminated groundwater and submit information to Ecology by October 2005 (an amendment changed the original October 2004 date to allow closer coordination with the river corridor risk assessment).

The Interim Action ROD requires that "DOE will investigate groundwater remediation and river protection technologies for ^{90}Sr contamination and submit information to Ecology within 5 years of this ROD." "…Pump-and-treat may be considered as an integral part of other alternatives; however, groundwater remediation technologies to be evaluated will focus on innovative technologies to remove ^{90}Sr from contaminated sediments and groundwater." (Page 53.)

To fulfill the requirements of the Interim Action ROD:

- The pump-and-treat system has operated continuously since 1995. Groundwater monitoring has been conducted as approved by Ecology, and annual reports

summarizing the monitoring data and pump-and-treat system have been submitted each year since the beginning of operations in 1995.

- Under the Innovative Treatment and Remediation Demonstration (ITRD) Program, the Technical Advisory Group (TAG) for the 100-N Area completed the *Hanford 100-N Area Remediation Options Evaluation Summary Report* in November 2001 (TAG, 2001).
- *Strontium-90 at the Hanford Site and its Ecological Implications* (PNNL) was submitted to DOE in May 2000.
- An ERA is underway in accordance with an approved sampling and analysis plan (DOE-RL, 2005). A comment draft report was submitted to Ecology on October 31, 2005.
- 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 (Fluor/CH2M HILL, 2004). This letter report and related public workshop comments (December 2004), together with the ITRD Report, completes the technology evaluation requirement specified in the Interim Action ROD. This TTP initiates implementation of the previous evaluation efforts.

1.4.3 Pump-and-treat Performance

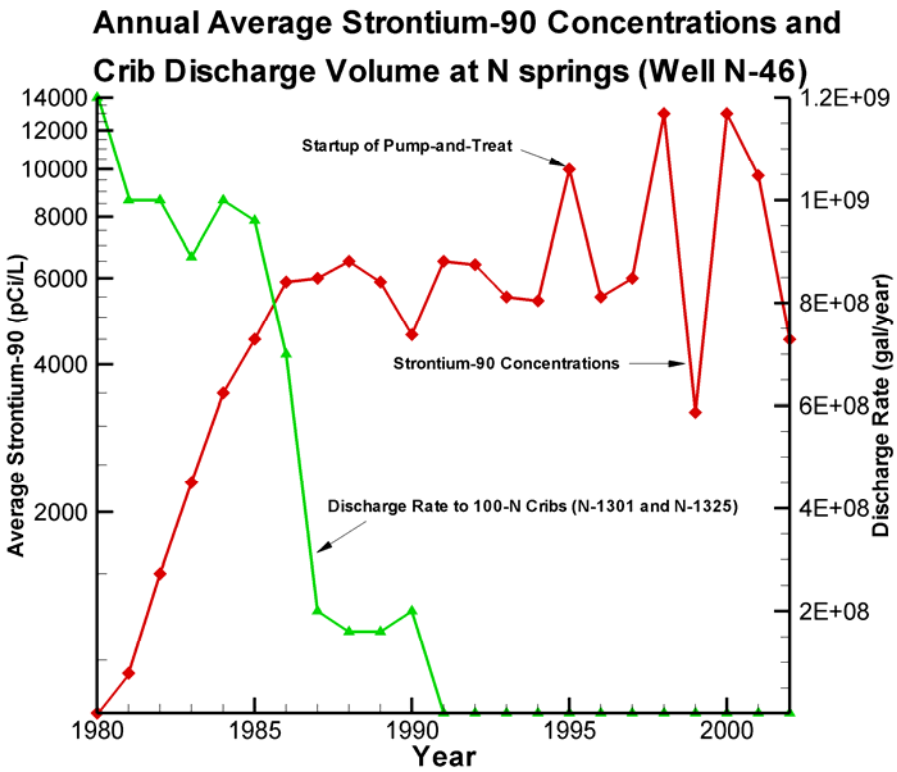
Installed in 1995, the pump-and-treat system at the 100-N Area uses four extraction wells, a treatment skid, and two injection wells. It is currently operating to retard the movement of contaminated groundwater toward the Columbia River, and in the process is removing small amounts of ^{90}Sr from the aquifer.

As described in the Interim Action ROD, insufficient information existed to recommend a final remedy for ^{90}Sr in the 100-NR-2 groundwater. Therefore, Ecology, EPA, and DOE proposed to control movement of ^{90}Sr to the Columbia River as an interim remedial action for river protection. This control was to be provided by the existing pump-and-treat system.

At a pumping rate of 60 gallons per minute (gpm), the pump-and-treat system extracts approximately 0.2-Ci/year, which is about 10 times less than the amount removed by radioactive decay of the ^{90}Sr stored in the aquifer (DOE-RL-2004)). As of June 2004, 1.6 Ci of ^{90}Sr were removed since beginning operations in 1995. Given that there is approximately 80 Ci of ^{90}Sr in the saturated sediments in the 100-N Area, at this removal rate the time needed to meet the drinking water standard (8 pCi/L) is approximately 270 years.

Despite the hydraulic containment provided by the pump-and-treat system, elevated ^{90}Sr concentrations near the shoreline have persisted since the beginning of pump-and-treat operations. Figure 1-12 illustrates the impact of the pump-and-treat system on ^{90}Sr concentrations in the groundwater at the riverbank. The green line shows that discharge to the cribs discontinued in 1991. The red line shows annual average concentrations of ^{90}Sr in porewater at well N-46, which is located at the road along the riverbank within the ^{90}Sr plume. Concentrations steadily increased from 1980 until about 1989. Since that time, concentrations have fluctuated widely, presumably in response to river stage and sampling date relative to water level. Nevertheless, near-shore pore fluid ^{90}Sr concentrations have remained elevated. This observation confirms modeling results indicating that ^{90}Sr in the near-shore aquifer or stream bank storage zone will decline primarily by radioactive decay.

FIGURE 1-12
^{90}Sr Concentrations in Groundwater at 100-N



History of annual wastewater discharge to the soil column and strontium-90 concentrations in groundwater near the shoreline at N-Springs (Well N-46.) The wide fluctuations that occur in the 1995 to 2000 period are attributed to unusually high (and low) annual average river stages during that time period. The unusually high water mobilized ^{90}Sr stored above the mean water table, causing higher average concentrations in groundwater. The correlation between water level and concentration has been observed in other nearby monitoring wells (for example, N-67).

Although the pump-and-treat system may have met the objective of reducing the flow of groundwater to the river, it has not met the objective of reducing ^{90}Sr concentrations in aquifer pore fluid at the shoreline or in the stream bank storage zone. Minimizing exposure to eco-receptors in the near-shore aquatic and riparian zone requires a different approach.

1.4.4 ITRD Report

In the ITRD Report, the TAG considered various technologies that would meet the RAOs identified in the Interim Action ROD for protecting the river and the unconfined aquifer, and retained five technologies for further evaluation. TAG's conclusions and recommendations for each technology are presented in Table 1-1.

TABLE 1-1
ITRD Technology Evaluation
100-NR-2 Operable Unit

Technology	Conclusion	Recommendation
Monitored Natural Attenuation (MNA)	May be appropriate for portion of plume far from the river, but will not limit current discharges of ^{90}Sr from N-Springs.	Should be examined in more detail when establishing Long-Term Stewardship protocols.
Soil Flushing	Likely to be effective in removing ^{90}Sr in the shortest time frame.	Should be examined in more detail with regulators.
Phytoremediation	May be the best option for controlling current releases at the river; leaf litter control may be an issue.	Needs more analysis.
^{90}Sr stabilization by phosphate injection	Design studies were insufficient to support recommendation of the option.	Re-examine this option after the Tanks Focus Area work is completed.
Barrier technologies (clinoptilolite and sheet pile/cryogenic)	Installation is considered feasible. Bank is stable and erosion potential associated with construction is considered negligible.	Precautions during construction should minimize potential damage.

Based on this evaluation, the ITRD concluded that the DOE should evaluate the following remediation scenarios in more detail:

- Monitored Natural Attenuation
- Clinoptilolite Barrier with MNA
- Clinoptilolite Barrier with Phytoremediation on the river side of the barrier
- Sheet Pile/Cryogenic Impermeable Barrier with MNA
- Sheet Pile/Cryogenic Impermeable Barrier with Phytoremediation on the river side of the barrier and Soil Flushing on the inland side

Several important developments occurred prior to and since the completion of the ITRD Report:

- Installation of a sheet pile wall was attempted and found not feasible at this particular site.
- The TAG determined that soil flushing was infeasible, primarily because of the massive volumes of lixiviant required for injection and removal, and the problems inherent in treating and disposing large volumes of radioactive wastewater.
- Renewed interest in ^{90}Sr stabilization by phosphate injection (aqueous injection) is based on reports of successful bench testing at Sandia National Laboratory (SNL).

The merits of apatite sequestration and phytoremediation were presented at a workshop in August 2003 by PNNL and SNL scientists. Because of the potential for these technologies to

remove or sequester ^{90}Sr from the near-river sediments, DOE funded two laboratory studies at PNNL in FY04 to determine their appropriateness for the 100-NR-2 OU:

- Phytoremediation of ^{90}Sr
- ^{90}Sr Sequestration by Apatite

1.5 Evaluation of ^{90}Sr Treatment Technologies

1.5.1 Letter Report

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 (Fluor/CH2M HILL 2004). Alternatives evaluated included permeable reactive barriers (PRBs), impermeable barriers, MNA, and phytoremediation. At that time, the final length of the barrier walls was assumed to be about 2,000 feet (600 meters).

Four PRB technologies were considered: vertical hydro-fracture, 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 ^{90}Sr. In aqueous injection, apatite precursors are introduced as dissolved chemicals into the aquifer via injection wells, and apatite precipitates in a treatment zone surrounding (and downgradient of) the point of injection.

Impermeable barriers reduce ^{90}Sr entering the river by increasing the groundwater flow path to allow time for the ^{90}Sr to decay. Alternatives included a slurry wall via trenching, and a bentonite grout curtain installed via hydro-fracture. MNA allows for the natural decrease of ^{90}Sr concentrations over time, and phytoremediation uses plants to extract ^{90}Sr 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 (2001) that MNA may be appropriate for portions of the plume far from the river, but will not limit current discharges of ^{90}Sr to the river. Phytoremediation was retained for consideration in conjunction with a barrier, but is not regarded as a stand-alone 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 the evaluation did not point clearly to a single approach. 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.

1.5.2 Post-Letter Report

Presentation of the Letter Report to the public in December 2004 prompted considerable debate about which technology to field test in 2006. Laboratory testing of the feasibility of ^{90}Sr sequestration by aqueous injection continued throughout 2004 and into 2005 at PNNL. In addition, column studies were conducted in 2005 at the Applied Sciences Laboratory (CH2M HILL) to determine which type of commercially available apatite would be the best choice for ^{90}Sr removal by air injection or hydrofracture PRBs, assuming that one or both of these technologies may be implemented in the future.

Based on results from recent investigations presented in Section 1.3, a decision was made to focus on the section of shoreline with the highest ^{90}Sr concentrations for a treatability test. Additionally, it was understood that even if contaminated groundwater from upgradient sources is intercepted, ^{90}Sr impacts on the near-shore aquatic and riparian zone of the Columbia River will continue until contaminants in the riverbank sediments, as well as in the vadose zone, at the near shore have been removed or stabilized. With this change in focus, the apatite sequestration technologies were reevaluated primarily on the basis of which media they target:

- Vertical hydrofracture PRB and vertical hydrofracture impermeable barrier will treat groundwater upgradient of the barrier only
- Air injection PRB will treat upgradient groundwater, and has potential to treat some of the near-shore aquifer
- Aqueous injection PRB will treat upgradient groundwater, the near-shore aquifer, and may also be used to treat the vadose zone

None of these technologies has been tested in the field at Hanford, and there is considerable uncertainty regarding the long-term success of each. However, because it is the only technology that has the potential to reach all of the target areas, the first field trials will assess aqueous injection. While the focus of this TTP will be on aqueous injection, the other technologies are potential alternatives for future testing if aqueous injection is unsuccessful. Vertical hydrofracture and air injection PRBs are addressed briefly in Section 2, and results from the apatite bench-scale testing will be presented in a separate addendum.

1.6 Path Forward

As stated in Section 1.4, the pump-and-treat system has not met the objective of reducing ^{90}Sr concentrations in aquifer pore fluid at the shoreline or riverbank storage zone. Evaluation of existing and new near-shore groundwater, aquifer tube data, and biological data collected during 2004 and 2005 indicates persistent and elevated ^{90}Sr contamination in certain sections of the near-shore zone, particularly 300 feet of shoreline near well N-46. These findings have created a sense of urgency to replace the pump-and-treat system with a more effective treatment technology.

The immediate goal, consistent with the interim ROD, has shifted from evaluating various technologies to conducting a treatability test at the near shore using the technology that has the greatest potential to reduce ^{90}Sr concentrations where elevated ^{90}Sr concentrations occur

in aquatic biota (i.e., ^{90}Sr sequestration by the injection and dispersal of apatite-forming chemical solutions).

If, as a result of this remedy, the ^{90}Sr concentrations reaching the river are reduced cost-effectively, this technology would serve as the primary component of the NR-2 treatment train. As a secondary or polishing step, phytoremediation to enhance treatment of the zone from the river to the apatite sequestration zone, may be revisited at a later time depending on the outcome of the aqueous injection test and evaluation of relative risk to aquatic biota in this zone. If aqueous injection performs poorly in the field, or if this method cannot emplace enough apatite to sequester the estimated amount of ^{90}Sr carried toward the river over the next few hundred years, then either air injection or vertical hydrofracture could be attempted as a backup to build up the mass of apatite.

1.7 Final Remedy Considerations

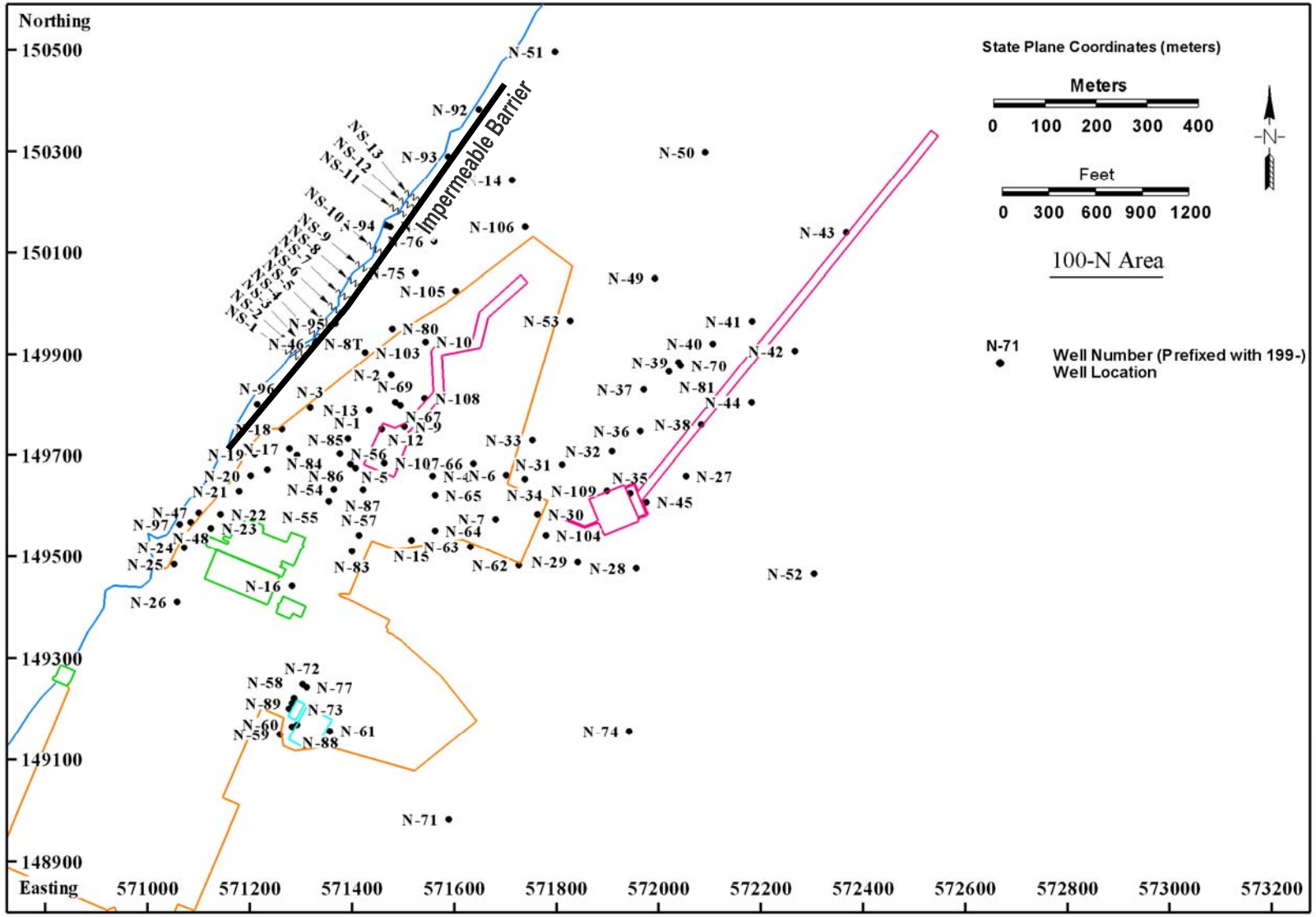
In addition to near-term treatment of the highest near-shore ^{90}Sr concentrations, results of the treatability testing can be used in designing the final remedy after completion of the 100-NR-1/NR-2 risk assessment.

If testing shows that aqueous injection can be used to treat the near-shore aquifer, then that will become part of the final remedy. If successful, and depending on the ecorisk assessment findings, this approach could be extended to greater distances along the shoreline.

If aqueous injection tests poorly in the field, then installation of an apatite PRB vertical wall via hydrofracture could be attempted, as previously indicated. Phytoremediation and dredging or excavation are potential alternatives that could be used in concert with the hydrofracture wall to address the shoreline. Dredging has not been evaluated but would require some type of coffer dam to contain the slurry of contaminated sediment produced during the dredging operation. Phytoremediation would require a long-term commitment to harvesting the willows and potential containment to prevent offsite transport of contaminated plant tissue.

If neither the aqueous injection nor the hydrofracture apatite PRBs provide adequate results, then an impermeable barrier could be considered to address contaminated groundwater beneath the 100-N Area. A trenchless impermeable wall could be installed parallel to the shoreline (2,000 to 3,000 feet [600 to 900 meters], see Figure 1-13) that would divert any ^{90}Sr upgradient of the wall that enters the groundwater along the wall in either the upstream or downstream direction. The ^{90}Sr would decay during the extended migration path prior to entering the river. This concept was demonstrated previously (BHI, 1995). If a continuous impermeable wall were chosen for the final remedy, it would be necessary to sacrifice the 300-foot PRB section. However, installation of a 300-foot PRB in FY06 would not preclude potential application of a continuous impermeable wall as part of an NR-1/NR-2 final remedy.

FIGURE 1-13
Conceptual Illustration of Final Remedy as a 3,000-foot Impermeable Barrier



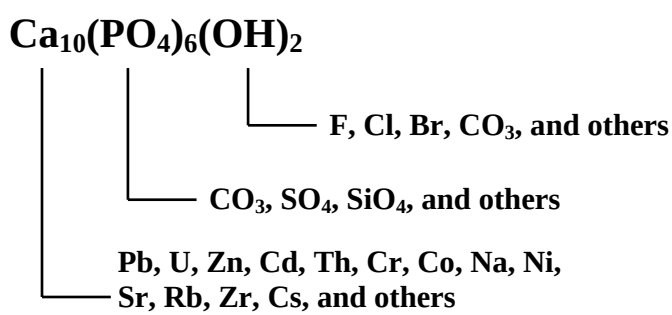
SECTION 2

Treatment Technology Description

All of the technologies considered for ^{90}Sr removal from groundwater at 100-NR-2 utilize apatite as the sequestering agent, differing only by emplacement method. This section describes apatite in general and the properties that make it an excellent sequestering agent, includes a brief description of the different forms of apatite that are commercially available and have been used in bench testing, and provides a detailed description of the aqueous injection technology.

2.1 General Characteristics of Apatite

Apatite is a natural calcium phosphate mineral occurring in the earth's crust as phosphate rock, and is 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. Because of the numerous substitution possibilities, more than 300 apatite minerals are known to exist (Nriagu and Moore, 1984). The form of apatite without any substitution is known as hydroxyapatite (or hydroxylapatite), the chemical formula of which is shown below along with some of the more common substitution possibilities.



Apatite minerals are very stable and practically insoluble in water (Wright, 1990; Wright et al., 2004). The solubility product of hydroxyapatite is about 10^{-44}, while quartz crystal, which is considered the most stable mineral in the weathering environment, has a solubility product (K_{sp}) of 10^{-4} (Geochem Software, 1994). Strontiapatite, formed when all the Ca is replaced by Sr (or ^{90}Sr), is 10^7 times less soluble than hydroxyapatite (Verbeeck et al., 1977).

Apatite can remove soluble Sr and ^{90}Sr from groundwater both during and after its formation:

- Via precipitation of Sr in solution with PO_4 anion. Precipitation directly from solution, or homogeneous nucleation, generally occurs only at very high metal concentrations, i.e., 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., 1995). The

apatite itself serves as a small, but sufficient source of phosphate to solution, and with low concentrations of cations such as Sr or Ca, heterogeneous nucleation occurs on the surface of the apatite seed crystal (Lower et al., 1998). Over time, the precipitated metals are sequestered into the apatite crystal matrix.

- Via substitution of Sr into the structure of mineral apatite. Sr and Ca are both alkaline earth metals with a 2^+ charge, and both compete for the same lattice sites in the apatite structure. Because Ca is more prevalent in the earth's crust, it is more common in apatite. However, the substitution of Sr for Ca in the crystal structure is thermodynamically favorable, and in the presence of high enough concentrations, Sr will replace Ca.

While the rate of metal incorporation into the apatite crystal lattice can be relatively slow, on the order of days to years, the precipitation reaction is nearly instantaneous on the molecular scale. Initially, the precipitate formed is amorphous apatite, however, within several days it will transform into a more stable apatite crystal.

2.2 Mineral Apatite

Vertical hydrofracture and air injection emplace existing mineral apatite particles into the subsurface, while in aqueous injection, apatite is precipitated in situ from chemical precursors in aqueous form. The advantage of aqueous injection is that it has the potential to create a larger treatment zone surrounding the point of injection than the other technologies. Because of the potential to extend the treatment zone to the shoreline where aquatic biota are exposed, aqueous injection is the focus of this initial TTP. However, the other technologies may be field tested in the future if aqueous injection does not perform as expected, or if additional sequestration capacity is needed.

Various forms of mineral apatite are commercially available, with potentially significant differences in properties that may affect the success of a site-specific field application. To determine which form of apatite would be the best choice for ^{90}Sr removal at 100-NR-2 (considering capacity, stability, cost, etc.), bench testing was conducted on several forms of apatite, including fish bone, cow bone and mineral apatite. A brief description of each follows:

- Fish bone apatite is available in large quantities under the trade name of Apatite II from PIMS NW, Inc., Carlsbad, New Mexico. The physical structure of fish bone is largely amorphous, since fish skeletons are not required to bear significant weight. The crystalline apatite exists as random nanocrystals, within the amorphous or glassy matrix of the bone, and has many pores and capillaries that greatly increase the available surface area.

- Bone char and bone ash are two different cow bone-derived materials that have potential application at 100-NR-2, available from the Ebonex Corporation in Michigan. Bone char is heated at approximately 1,000 °C in an inert atmosphere that carbonizes organic material and results in black charcoal that makes up approximately 10 percent by weight of the finished material[1]. Bone ash is produced in a similar manner except

[1] Ebonex Corporation. http://www.ebonex.com/ (address verified on November 8, 2005).

that the material is fired in the presence of oxygen at 1,100 °C, resulting in oxidation of organic matter to carbon dioxide and removal of carbon from the final material.

- Mineral apatite can be found in many phosphate rock sources mined in the U.S. for use in commercial fertilizer production. Mined from deposits that are millions of years old, they are stable minerals, but vary widely in chemistry, and may contain significant levels of Sr. Phosfill® material from North Carolina is typically much lower in trace metals than phosphate rock from the western U.S. (Crannell, 2005).

Characterization studies and column tests were initiated on the most promising forms of apatite to verify vendor performance data and statements. Results will be presented in a separate addendum.

2.3 Aqueous Injection of Apatite Precursors

Aqueous injection results in a dispersed zone of apatite precipitated in a treatment zone surrounding (and downgradient of) the injection points. Rather than physical placement of a solid apatite mineral in the subsurface, this technology involves the injection of the chemical components of apatite—principally calcium and phosphate—and then precipitation of the mineral in the formation. It is based on an approach recently published by Moore et al. (2004).

Apatite minerals are sparingly soluble, and calcium phosphate solids precipitate rapidly when any appreciable amounts of free calcium and dissolved phosphate are mixed. By using citrate to stabilize the solution of calcium and phosphate, the chemicals are able to migrate some distance from the point of injection before they precipitate, following microbial degradation of the citrate-complexing agent. The citrate acts as a chelating agent and forms stable complexes with dissolved calcium, reducing the free (uncomplexed) Ca^{2+} concentration in solution, and increasing the apparent solubility of the calcium/phosphate mixture. For example, the solution described in Table 2-1 was used by Moore et al. (2004) and was reported to be stable (without precipitates) for over 36 hours.

TABLE 2-1
Solution Used for Apatite Formation in Soils (Moore et al., 2004)

Chemical	Concentration	Remarks
Sodium Citrate ($Na_3C_6H_5O_7$)	100 mM	
Calcium Chloride ($CaCl_2$)	50 mM	
Sodium Hydrogen Phosphate (Na_2HPO_4)	40 mM	
Ammonium Nitrate (NH_4NO_3)	10 mM	Nitrogen source used to stimulate microbial activity
Potassium Hydroxide or Perchloric Acid (KOH and $HClO_4$)	Negligible.	Used as needed to adjust solution to pH 7.5

For the remedy, a solution such as the one presented in Table 2-1 is prepared and then injected into the formation. As indigenous microorganisms degrade the citrate (this is an easily metabolized carbon source), the resulting increase in free calcium will result in precipitation of calcium phosphate solids in the aquifer (see Figures 2-1A and 2-1B). The specific steps of this remediation technology are:

1) Injection of Ca-PO_4-citrate solution (with a Ca-citrate solution complex),
2) In situ biodegradation of citrate resulting in apatite [$Ca_6(PO_4)_{10}(OH)_2$] precipitation and coprecipitation of ^{90}Sr in porefluid and solids in the treatment zone,
3) Adsorption of ^{90}Sr by the apatite surface (i.e., new ^{90}Sr migrating into the treated zone from upgradient sources),
4) Apatite recrystallization with ^{90}Sr substitution for Ca (permanent), and
5) Radioactive decay of ^{90}Sr to ^{90}Y to ^{90}Zr.

In studies over the past 5 years, Robert Moore (SNL) demonstrated that citrate biodegradation/apatite precipitation occurs in several sediments, resulting in the sequestration of U, Tc, Sr, and Pb. Laboratory bench studies at PNNL and SNL during 2004 and 2005 were focused on determining if this technology could precipitate sufficient apatite at 100-NR-2 to immobilize ^{90}Sr in both the near-term as well as for 300 years, and if the ^{90}Sr removal rate would be rapid enough.

The solids are initially amorphous; however, laboratory tests show that they age to form crystalline apatite on a time scale of weeks. The apatite will reflect the chemistry at the time of precipitation and contain varying proportions of cations (calcium, magnesium, sodium, and strontium) and anions (phosphate, carbonate, and hydroxide) depending on their solution concentrations. In this respect, the physical and chemical properties of the synthetic mineral are not as well characterized as commercially available apatite, however the material is expected to remain effective at sequestering ^{90}Sr. Mechanisms of sequestration include strong sorption onto the mineral surface and isomorphic substitution within the structure of the mineral.

As previously noted, the advantage of the aqueous injection remedy is the prospect of delivering apatite over a broad area of the near-shore aquifer, possibly reaching to the river. As currently envisioned, the aqueous injection remedy involves creating a zone of apatite in the aquifer via a series of groundwater injection wells. Figure 2-2 illustrates an array of injection wells and the initial distribution of injected chemicals. The zone will extend from the initial point of injection in response to the groundwater flow regime and the microbial degradation rate. The resulting treatment zone will decrease the ^{90}Sr pore fluid concentrations and flux by sequestering ^{90}Sr currently in this area, and by intercepting ^{90}Sr as it migrates into the zone from upgradient sources. The broad treatment zone will also provide a longer residence time for adsorption and sequestration of upgradient sources.

If successful, the net effect of the treatment would be to decrease contaminant flux to the river by sequestering ^{90}Sr until radioactive decay lowers ^{90}Sr activity to acceptable levels.

FIGURE 2-1A

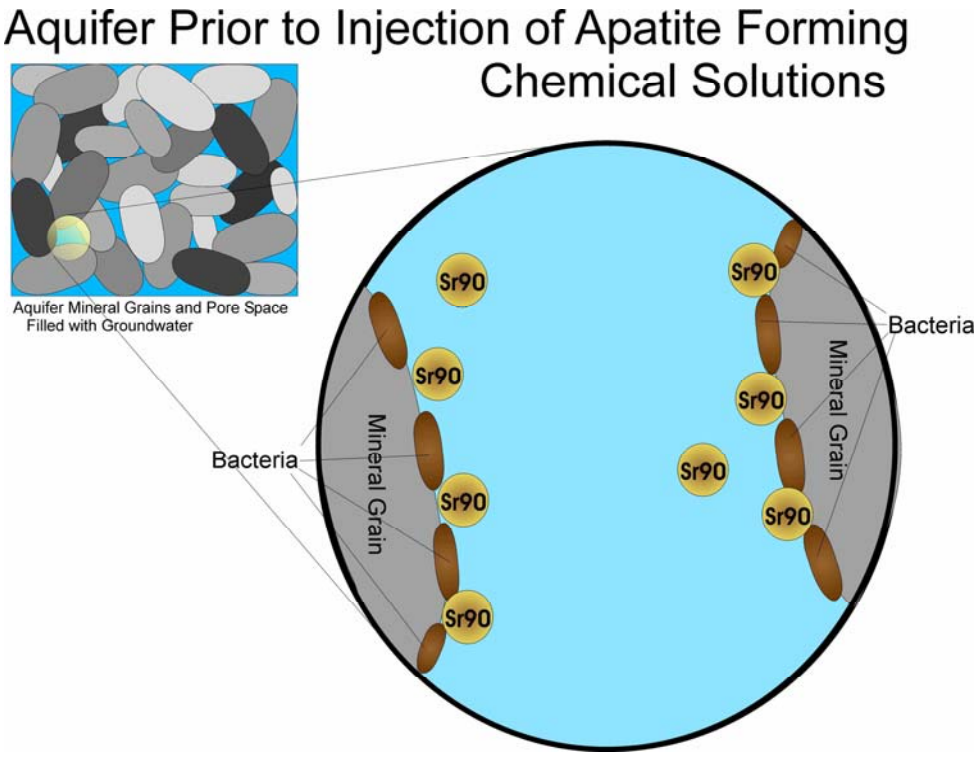


FIGURE 2-1B

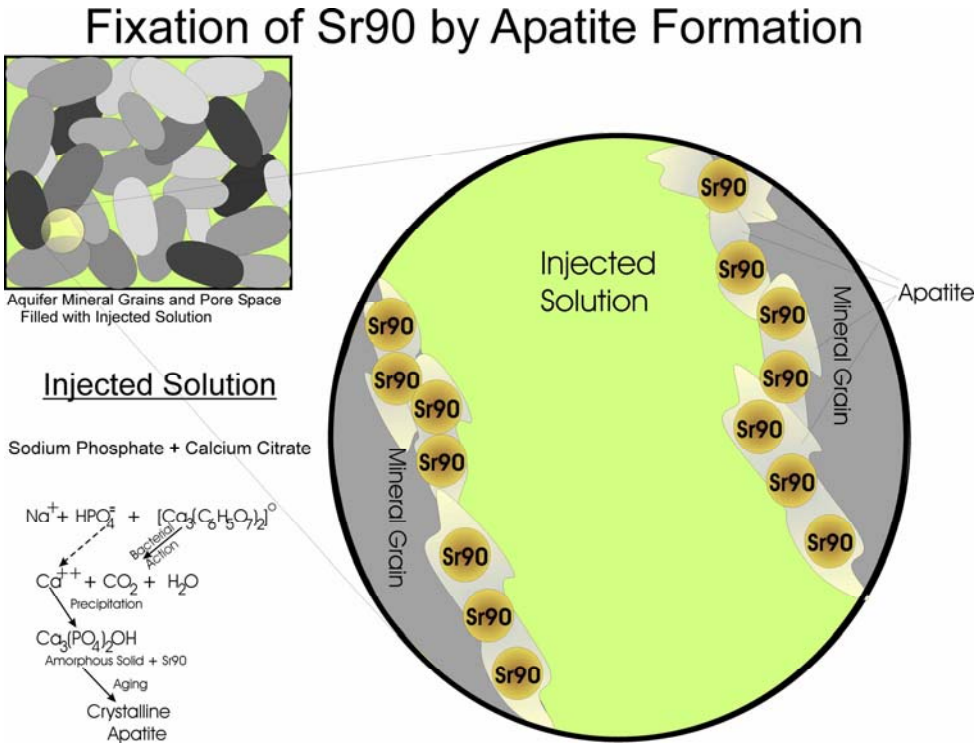
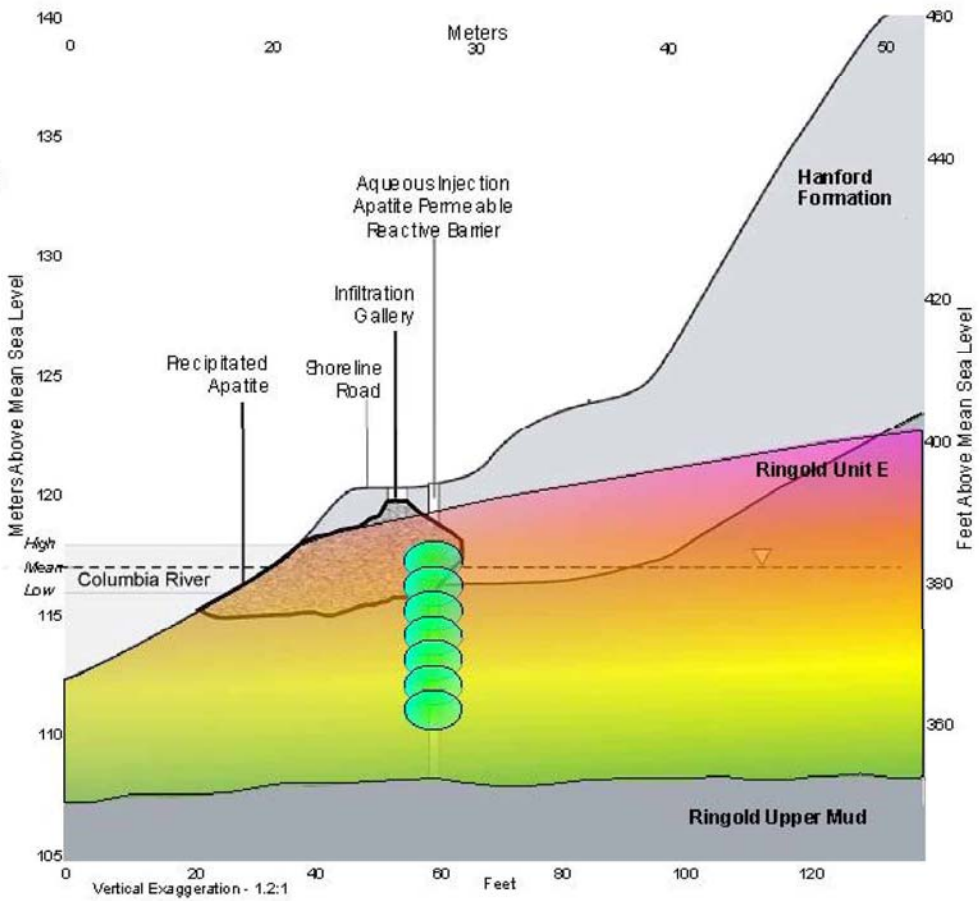


FIGURE 2-2

Alternative Interim Remedy: Apatite Sequestration

- Well injection treatability test to address upper aquifer (FY 2006)
- Apatite chemical infiltration pilot test in FY2007 to treat vadose zone.
- Target highest clam/porefluid Sr-90



2.4 Potential Chemical Effects Issues

Bench tests in 2004 and 2005, described in Section 3, were conducted to evaluate in situ apatite formation and its effectiveness, identify any unintended consequences, and address concerns raised during public briefings and workshops.

Salt Leaching Effect. One potential consequence may be increased mobility of ^{90}Sr along the margins of a treatment area. Identified as the "salt effect," the concern is that the injection solution would have higher salts than the groundwater in the treatment area. Some of the dissolved salts such as sodium and chloride do not participate in the precipitation reactions and remain in solution after calcium and phosphate precipitate. As the relatively high total dissolved solids (TDS) water migrates away from the treatment zone into an area where ^{90}Sr has not been sequestered by apatite, cations exchange with ^{90}Sr (or other cationic contaminants) adsorbed on aquifer sediments. Thus, the salt effect would result in increased pore water concentrations of ^{90}Sr downgradient of the treatment area.

To mitigate this potential problem, the apatite precursors will be introduced in steps, as discussed further in Section 3. The first step involves injection of a dilute apatite solution that results in a minimal salt effect, but emplaces sufficient apatite to sequester the ^{90}Sr mobilized by subsequent injections. In the second step, a concentrated solution is introduced. This step may be divided into two or more injections, however the goal will be to emplace enough apatite to treat the ^{90}Sr carried into this area via groundwater over the next 300 years.

Diesel-Related Chemical Effects. A large diesel spill occurred just upstream from the ^{90}Sr plume area during the 1960s. As much as 1 foot of floating product was observed in nearby monitoring wells in the past (e.g., N-18). Today there is no evidence of free product remaining; however, elevated dissolved iron (up to 24,000 ug/L) and depleted oxygen occurs in well N-18, indicating reducing conditions in the aquifer impacted by the diesel spill. Also, depleted oxygen and elevated iron in shallow aquifer tubes near the shoreline in front of the past spill area were found during summer 2005. A question was raised during the October 2005 public workshop on possible effects of the diesel and related degradation byproducts on the proposed apatite treatment remedy.

One possible impact considered was competition of the dissolved iron for the sequestration sites in the emplaced apatite. While this is theoretically possible, the specific impact of dissolved iron on apatite performance has not been evaluated. However, a monitoring well (N-96A) located near the river bank at the center of the past diesel spill site, indicates a maximum dissolved iron concentration of ~100 ug/L occurred in the past with less than 50 ug/L in 2005. Thus, it is unlikely that dissolved iron concentrations in the proposed treatment zone will be higher than in well N-96A. Two new monitoring wells drilled for the planned treatability test will be used to verify the expectation that dissolved iron concentrations are not elevated in the proposed apatite treatment zone. Laboratory studies will be needed to evaluate the long-term implications of diesel and potentially elevated dissolved iron.

Water Quality Impacts. The chemical byproducts from the apatite precipitation process include simple salts (sodium and calcium chloride) and small amounts of agricultural type

chemicals (sodium phosphate and ammonium nitrate) and any remaining unreacted calcium citrate. The initial tests will be conducted using more dilute solutions (nominally 0.01 molar) than used for initial lab studies (~0.1 molar). Thus, a conservative approach will be used during the initial field treatability testing. The array of existing aquifer tubes at the shoreline covering the planned 300-foot (91-meter) treatment zone will be used to monitor the concentrations of reaction products. Dilution by river water is expected to greatly reduce the salt concentrations at the river-riverbed interface. The non-hazardous nature of these food (e.g., citrate) and agricultural-type chemicals are highly unlikely to have a negative impact on the near-shore biota. The residual chemical plume from the treatment zone will occur as a temporary pulse that will dissipate and mix with river water in the streambank storage zone and as it discharges through the riverbed gravels. Evaluation of the monitoring data from the aquifer tubes will be used to guide future treatment regimes and injection protocol.

Creation of a New Buried Waste Site. Long-term accumulation of ^{90}Sr by the apatite emplaced along the shoreline could be considered creation of a new buried waste site along the river. The objective of the sequestration barrier is to fix the migrating ^{90}Sr in place and thereby reduce the flux to the near-shore zone. Accumulation of ^{90}Sr in the treated zone represents trading continued exposure of near shore biota for fixation of the contaminant where it is not in contact with biota. One important mitigating factor is that the shoreline along the central portion of the ^{90}Sr plume is protected with rip-rap and is thus protected from major erosional events. Thus it is highly unlikely that the buried apatite could be eroded under even extreme hydrologic event scenarios. In addition, the area in question is already contaminated with ^{90}Sr so it is not really a question of creating a new buried waste site. The change would be increasing the inventory of ^{90}Sr at that location.

2.5 Testing

PNNL conducted bench studies in 2004 and 2005 to determine if this technology could precipitate sufficient apatite in 100-N area sediments and the ^{90}Sr removal rate would be rapid enough to immobilize ^{90}Sr for 300 years. Results are presented in Section 3. Given the favorable laboratory results, a pilot test involving a single injection well and multiple monitoring points will be conducted to confirm apatite formation in the field and to determine optimum injection volumes and rates to achieve a 300-foot treatment zone. (Additional details and a schedule of planned activities for 2006 are presented in Section 4.) If the treatability test shows that this technology will precipitate apatite in 100-NR-2 sediments in situ, and that ^{90}Sr concentration in groundwater is reduced as a result, a second (and possibly third) round of injections to emplace the remaining balance of apatite treatment capacity may be required. If results from the initial treatability test are not favorable, then other options will be tested (e.g., PRB emplacement of apatite particles using vertical hydraulic fracturing or air injection).

SECTION 3

Aqueous Injection Bench Studies

Bench tests were conducted at SNL and at PNNL to demonstrate the feasibility of aqueous injection, and to quantify various processes involved in the technology. Studies at PNNL and SNL using 100-N area sediment addressed:

a. Aerobic and anaerobic citrate biodegradation pathways and rates

b. Amorphous and crystalline apatite precipitation in 100-N sediments

c. ^{90}Sr uptake in apatite-laden 100-N sediment

d. Depth profiles of ^{90}Sr and microbial population densities in the N-121, N-122, and N-123 borehole core sections

e. Adsorption properties of ^{90}Sr in treated and untreated sediments

Biodegradation rates and reagent distribution become critical injection design considerations when combined with the hydrodynamics of the near-shore zone that is subject to flow direction reversals and water table fluctuations in response to river stage. Adsorption studies are needed to define the expected capacity of the treated aquifer to sequester ^{90}Sr. This section describes these studies and discusses the significance of the results with relation to apatite formation, Sr sorption/desorption and other issues.

3.1 Apatite Formation

As described in Section 2, this technology involves the injection of a Ca-PO_4-citrate solution (with a Ca-citrate solution complex), into the aquifer. As the Ca-citrate complex biodegrades, free calcium is released, and immediately precipitates with dissolved phosphate. The rate of citrate degradation and phosphate distribution are very critical to the success of this technology.

3.1.1 Citrate Biodegradation

Moore et al. (2004) at SNL conducted batch tests using 250 grams of soil from Los Alamos, New Mexico, amended with 150 ml of the solution described in Table 2-1. Citrate degradation was documented in the Ca/citrate/phosphate-treated soils within 80 hours (a sterilized batch of treated soils showed no citrate decay, confirming a microbial degradation pathway for this complexing agent).

Degradation Rates at Different Temperature and Concentration

Recent studies at SNL focused on the biodegradation rate of citrate at different citrate concentrations and at different temperatures in 100-N Hanford formation sediments (Table 3-1). Because the injection strategy will involve an initial low-concentration (~10 mM citrate) injection followed by higher concentration (~100 mM citrate), data is needed to

describe the citrate biodegradation rate at different concentrations. The 100-N aquifer temperature varies seasonally from 14°C to 17°C, so citrate biodegradation rates are needed at this aquifer temperature. Previous laboratory data for aerobic and anerobic citrate biodegradation rates were for 15°C. Recent laboratory batch studies were conducted at 10°C, 15°C, and 21°C in order to develop the relationship between the citrate biodegradation rate and temperature.

Rates determined from experiments show that the citrate biodegradation rate increases with temperature (2.7x from 10°C to 25°C) and decreases with increasing citrate concentration (3.0x from 10 mM to 100 mM; Figure 3-1). The initial injections at 10 mM citrate and 15°C have an estimated half life of 50 h.

FIGURE 3-1
Citrate Biodegradation By Hanford 100-N Sediment at Different Temperature for Citrate Concentrations of: a) 10 mM b) 50 mM c) 100 mM

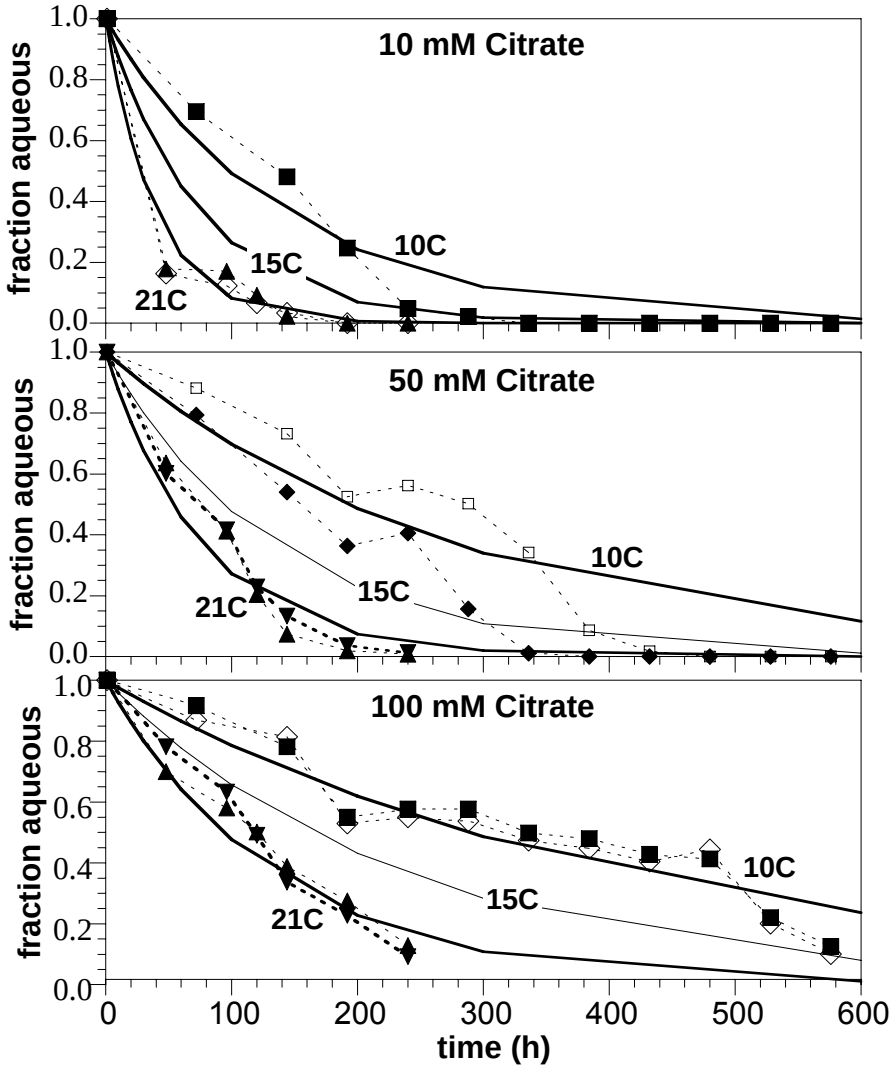


TABLE 3-1
Citrate Biodegradation Rates as a Function of Temperature and Initial Citrate Concentration

Concentration, mM	Rate Constant, 10ºC	Rate Constant, 15ºC	Rate Constant, 21ºC
10	0.0071	0.013	0.025
50	0.0074	0.0036	0.013
100	0.0024	0.0042	0.0075

Influence of Temperature and Concentration on Citrate Biodegradation Rate

Citric acid is utilized by many organic systems as part of the TCA (Krebs) photosynthetic process, where the citrate (a C6 organic acid) is converted to C6, C5, and C4 organic acids producing CO_2 and H^+, then cycled from oxaloacetic acid (C4) to citric acid (Bailey and Ollis, 1986). Citrate can also be further degraded to acetic acid (C2), formaldehyde, formic acid (C1), and CO_2. For the purpose of this study, citrate is used to complex Ca, so only the decrease in citrate concentration (by biodegradation) is of significance, as the lower molecular weight organic acids only form weak complexes with Ca.

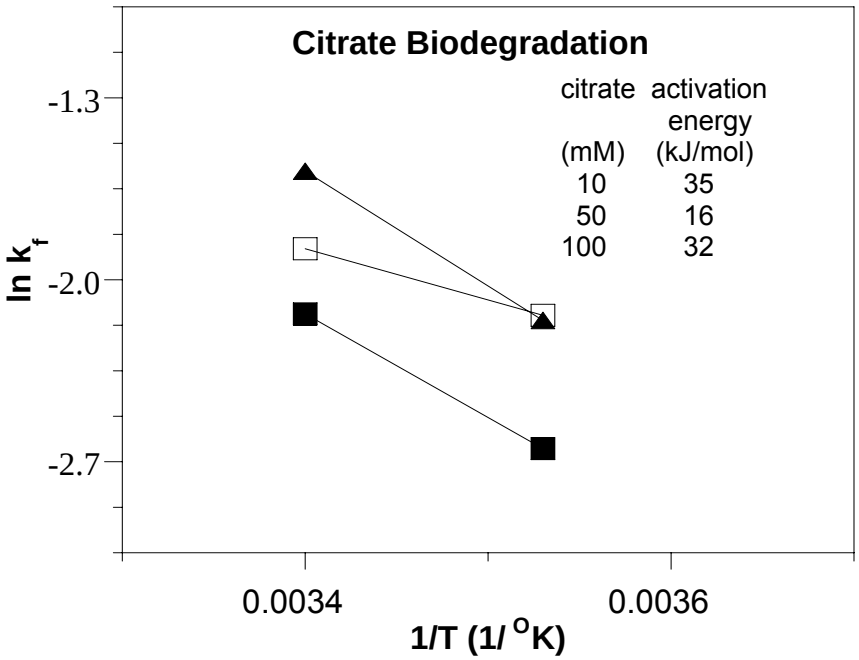
Two different modeling approaches at PNNL were considered to quantify citrate biodegradation, a first-order model and Monod model. A first-order model is an empirical approach that describes citrate removal with a single reaction rate coefficient. A Monod model is also an empirical approach that describes citrate removal externally to microbial organisms with a similar mathematical form of enzyme degradation (Michaelis-Menton kinetics). Monod kinetics is utilized when the observed data clearly shows a considerable slowing of reaction rate at low concentration that cannot be accounted for using the simpler first-order kinetic model.

Citrate biodegradation experiments show a slower rate at colder temperature and at higher citrate concentration (Figure 3-1, Table 3-1). At 10 mM citrate concentration, citrate was not detectable by 200 h (21°C) to 300 h (10°C, Figure 3-1a). At 50 mM citrate concentration, citrate was nondetect by 250 h (21°C) to 450 h (10°C, Figure 3-1b). At 100 mM citrate concentration, a small amount of citrate remained at 300 h (21°C) to 600 h (10°C, Figure 3-1c). At each concentration, duplicate experiments showed similar results.

A first-order model (lines, Figure 3-1) showed good fits, and indicated that in some cases, citrate biodegradation may be somewhat more rapid at lower concentration than a first-order approximation. For example, the 100 mM citrate data at 10°C (Figure 3-1c) showed a good first order fit to 500 h, but then citrate more rapidly degraded. This effect is observed for all citrate concentrations at 10°C, but not at 21°C. A Monod kinetic model would describe the data equally as well with small half-saturation constants, but would describe the data more poorly with higher concentration half-saturation constants, which would slow citrate biodegradation at low concentration, the opposite effect of that observed. Therefore, a pseudo first-order model was used to quantify the rate data (Table 3-1).

The citrate biodegradation rate was 3.0 x slower (10°C data) to 3.3x slower (21°C data) as the citrate concentration increased from 10 mM to 100 mM. The citrate biodegradation rate averaged 3.3x slower as the temperature decreased from 21°C to 10°C. The activation energy estimated from the reaction rate change with temperature is 35 kJ/mol (10 mM citrate), 16 kJ/mol (50 mM citrate), and 32 kJ/mol (100 mM citrate). These activation energies indicate the rate is controlled by the biochemical reaction and not diffusion, which is expected (Figure 3-2).

FIGURE 3-2
Arrhenius Plot of Citrate Biodegradation Rates versus Absolute Temperature, with Calculated Activation Energy

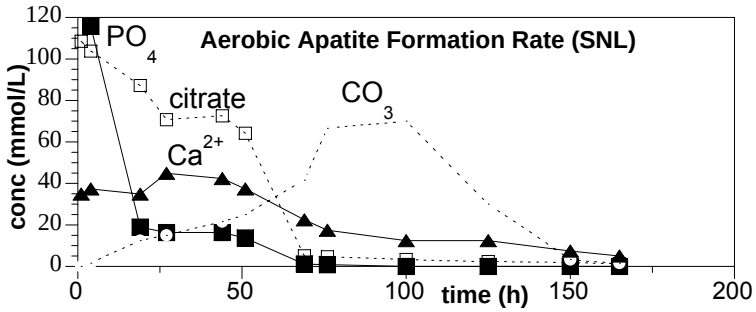


Aerobic vs. Anaerobic Degradation

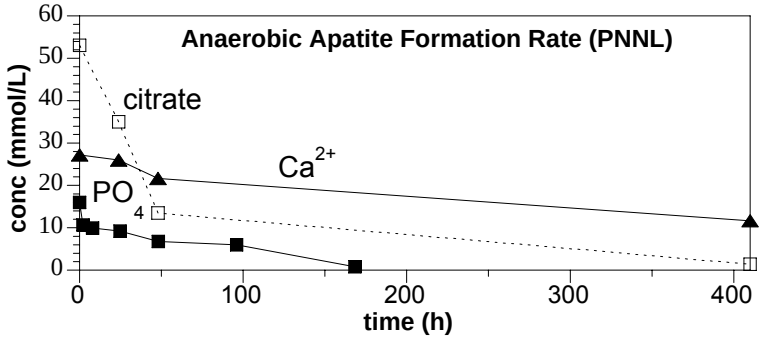
In batch and 1-D column systems, SNL and PNNL showed that citrate biodegradation to CO_2 occurred within 75-100 h in aerobic systems (Figure 3-3a), and to formate and acetate within 100-200 h in anaerobic systems (Figures 3-3b and 3-3c). In the 100-N Ringold portion of the aquifer, most of the citrate biodegradation will occur anaerobically, given the relative concentrations of citrate to oxygen. In the Hanford formation, the uppermost portion of the aquifer, degradation will most likely be aerobic.

FIGURE 3-3

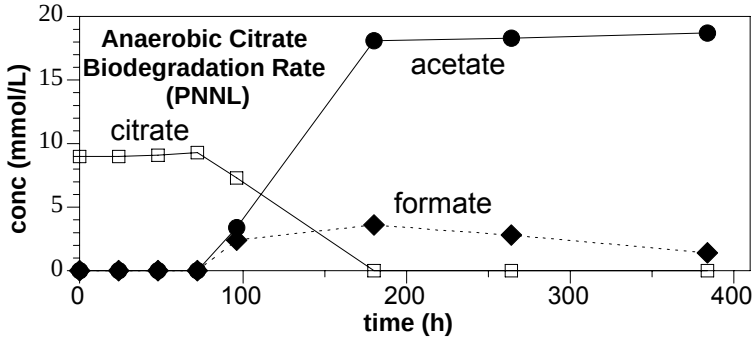
a) Apatite Precipitation Rate in Aerobic System (SNL Exp.) (CO_2 reported as CO_3)



b) Apatite Precipitation Rate in Anaerobic System (PNNL Exp.)



c) Citrate Biodegradation Rate in Anaerobic System (PNNL Exp.)

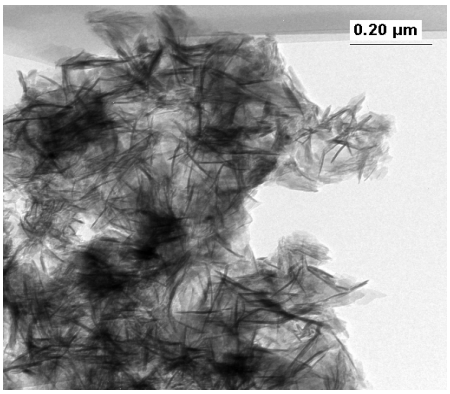


3.1.2 Apatite Precipitation

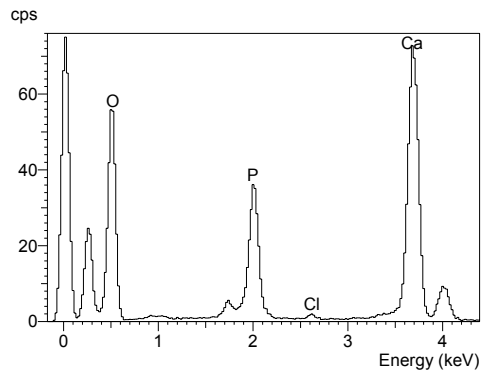
SNL observed the formation of apatite precipitate in 100-N columns. Using x-ray diffraction and other solid phase microprobe techniques, investigators at SNL observed that the initial precipitate within 100 h is amorphous, but then crystallizes within 2 to 4 weeks to hydroxyapatite (Figure 3-4). Batch experiments varying mixing, trace nutrient addition, and nitrate addition showed similar results. Figure 3-4a shows nanosize apatite crystals formed in sediment through precipitation from aqueous solution from citrate biodegradation in a batch system with 100-N sediment and excess oxygen (simulating vadose zone conditions).

FIGURE 3-4
Nanocrystalline Apatite Formed in Hanford Sediment by Microbially Mediated Ca-Citrate Degradation in the Presence of Aqueous Phosphorous

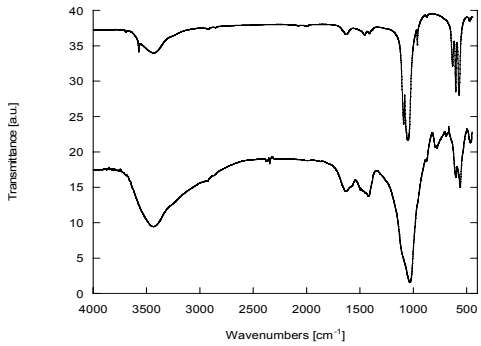
a) HRTEM



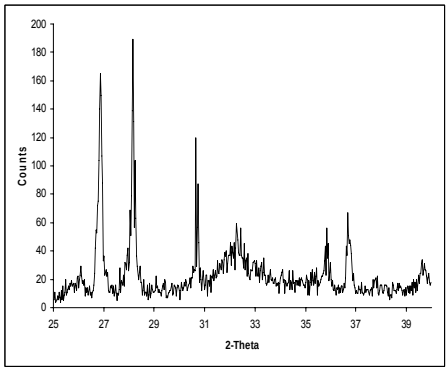
b) XRD



c) FT-IR



d) EDS



Apatite Precipitate Characterization (SNL). The mineral apatite, $Ca_5(PO_4)_3(F, Cl, OH)$, is the most abundant, ubiquitous phosphorous-bearing mineral on earth and is used broadly by earth scientists in the study of igneous, metamorphic, and sedimentary petrogenetic processes (Hughes and J. Rakovan, 2002). In addition to it geologic utility, apatite is also used in industry for such diverse applications as a source for fertilizer, a component of fluorescent lamps and lasers, as nuclear waste forms, and in biomedical applications (G. Waychunas,1989; R.C. Ewing, 2001; J.C. Elliot et al., 1973). In fact, hydroxyapatite is the primary mineral component in bone and teeth (J.C. Elliot et al., 1973). The apatite structure and its chemical facility provide the basis for its broad and varied application.

Apatite can refer to three specific end-member minerals: fluorapatite, chlorapatite, and hydroxyapatite. All can be viewed as slight modifications of the $P6_3/m$, Z=2 structure. For a complete description and structural details see Hughes et al., (1989). Several features of the structure are noteworthy. PO_4-tetrahedra are found in a hexagonal arrangement within the (00*l*) planes defining columns parallel to the *z*-axis. The PO_4 oxygens are coordinated with Ca in two different sites. The Ca1 site is intercalated between the (00*l*) planes and coordinated to nine oxygens. The Ca2 site is coordinated to six oxygens and the column anions (typically F, Cl, or OH). The Ca2 site shows the greatest degree of structural distortion upon chemical substitution. The apatite structure exhibits extensive solid solution with respect to both cations and anions. Metal cations (e.g., actinides, K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Fe) substitute for Ca and oxyanions (e.g., AsO_4^{3-}, SO_4^{2-}, CO_3^{2-}, SiO_4^{4-}, CrO_4^{2-}) replace PO_4^{3-} through a series of coupled substitutions to preserve electro neutrality (Hughes and J. Rakovan, 2002).

Multiple characterization techniques were employed to assess the crystal chemistry of the apatite formed by the microbial digestion of Ca-citrate in sediment from the Hanford Site. High resolution transmission electron microscopy (HRTEM) and X-ray powder diffraction (XRD) were used to assess apatite crystallinity and to document the transformation from an amorphous calcium phosphate to nanocrystalline apatite. Energy dispersive (EDS) and Fourier transform-infrared (FT-IR) spectroscopy were used to analyze the chemical constituents. The apatite was formed in sediment collected from 100-N by treatment with a solution of 50 mM sodium citrate, 25 mM calcium chloride, 20 mM sodium phosphate and nutrients for microbial activity at pH 7.4. Blade-like crystals in an amorphous matrix are approximately 0.1μm in size (Figure 3-4a). This was consistent with the observed broad overlapping peaks in the XRD pattern at 2 microns of approximately 32°C, a typical characteristic of poorly crystallized apatite (Figure 3-4b). The remaining peaks in the XRD correspond to components of the sediment. FT-IR spectra are given for pure hydroxyapatite (top spectrum) produced by precipitation and heat treatment at 700°C and calcium phosphate precipitates in the 100-N sediment after 1 month (bottom spectrum). The lower resolution of the PO_4^- bands confirms the lower crystallinity of the sample, as observed by both HRTEM and XRD. The bands at 1,455 cm^{-1} and 879 cm^{-1} indicate the presence of carbonate in the apatite structure. The TEM-EDS spectrum identifies calcium and phosphate as the major components with a stoichiometric apatite ratio of approximately 5:3.

Apatite Formation Reaction Rates and Design Considerations

Apatite formation reaction rates, and their relation to the complex groundwater flow dynamics associated with the near-river environment at 100-N, must be considered in the injection design analysis (see Section 4) for field deployment of the apatite PRB technology. Laboratory column experiments showed that amorphous apatite formed within 75 to 200 hours, with subsequent formation of crystalline apatite occurring within 2 to 4 weeks post injection. These apatite formation rates, and their relation to groundwater flow conditions, illustrate one of the important design constraints that must be considered during development of the treatment zone emplacement approach. The selected injection design must allow for the apatite-forming reagents to be in contact with the targeted treatment zone for a sufficient time period to form the desired apatite distribution. This and other design constraints will be evaluated based on laboratory testing results and simulation

results from a flow and reactive transport model. The resulting injection design will be documented in the field test instructions issued prior to commencement of field activities.

3.2 ^{90}Sr Sorption/Desorption

A second critical process in this technology is the uptake of ^{90}Sr by apatite. A number of experiments have been conducted at SNL and PNNL to assess the Sr sorption properties, adsorption rate, and the adsorption mechanism in apatite-treated soil. Because aqueous injection will result in higher groundwater salt concentrations, the influence of ionic strength on ^{90}Sr desorption from untreated and apatite-treated soil was also the subject of a series of experiments by PNNL.

3.2.1 Sorption Capacity

Researchers at SNL conducted batch tests to assess the Sr sorption properties of the apatite-treated soil versus untreated controls and a phosphate-only treatment (Figure 3-5). The sorption studies were conducted in a background of 0.1 M KNO_3. As shown, the apatite treatment enhanced strontium sorption, when compared to the other treatments and controls. Nearly 99 percent of the Sr was sorbed to the apatite-treated soil in the concentration range that will likely to be encountered in the field (2×10^{-6} mol/L or 0.2 mg/L). The partitioning between solid and liquid phases was rapid, reaching equilibrium within 1 day of contact.

FIGURE 3-5
Sr Sorption in Apatite-Treated Soil

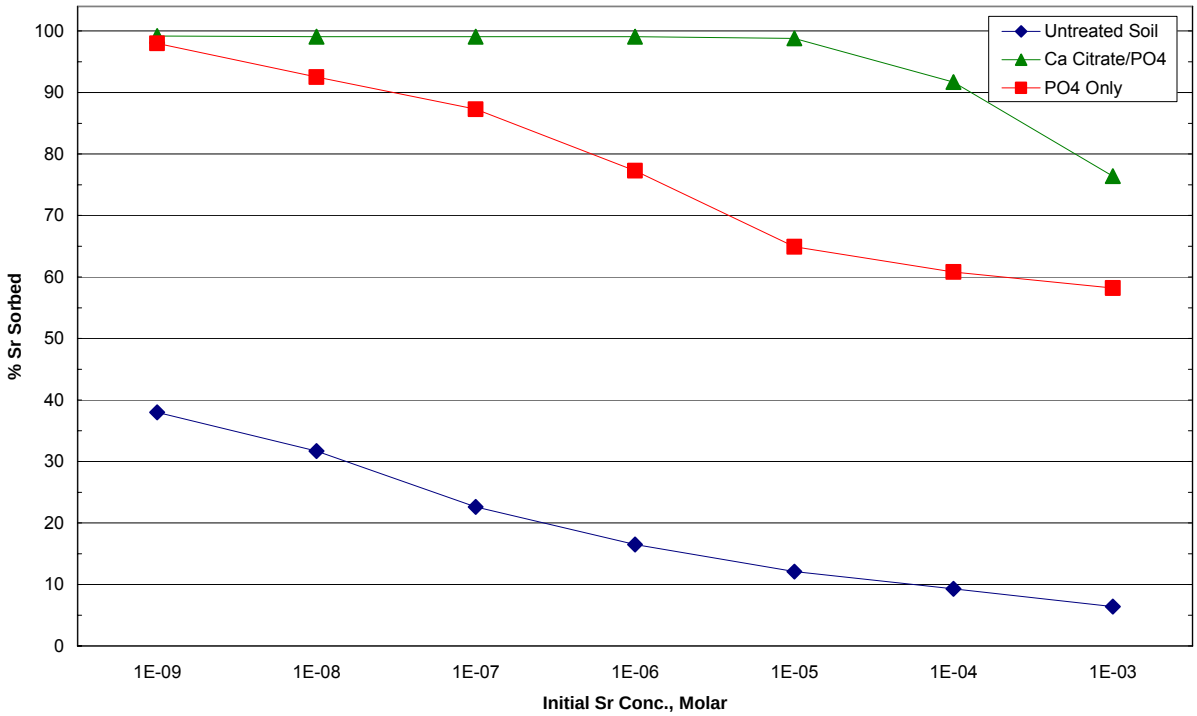


Table 3-2 presents the sorption/desorption data reported by Moore et al. (2004). As shown, significantly less Sr is removed from the apatite-treated soils when compared to the other soils, and the rate of desorption changes very little over time.

TABLE 3-2
Results of Strontium Sorption/Desorption Experiments from Moore et. al. (2004)

[Sr] Initial (molar)	Percent Sr Sorbed	Percent Desorbed After		
		1 week	1 month	6 months
Untreated Soil				
1×10^{-9}	38.0	20.4	26.8	26.6
1×10^{-8}	31.7	22.3	23.9	24.0
1×10^{-7}	22.6	25.8	28.0	28.7
1×10^{-6}	16.5	26.9	31.4	34.0
1×10^{-5}	12.1	27.5	29.1	32.5
1×10^{-4}	9.3	38.9	44.7	46.3
1×10^{-3}	6.4	41.1	56.2	57.3
Phosphate-Only				
1×10^{-9}	98.0	15.6	29.0	24.8
1×10^{-8}	92.5	18.0	20.0	29.0
1×10^{-7}	87.3	22.3	28.9	31.0
1×10^{-6}	77.3	24.0	27.8	27.0
1×10^{-5}	64.9	23.0	22.0	26.9
1×10^{-4}	60.8	21.0	26.3	29.5
1×10^{-3}	58.2	22.5	32.1	33.6
Calcium Citrate/Phosphate				
1×10^{-9}	99.2	0.1	0.1	0.2
1×10^{-8}	99.1	1.1	1.0	1.2
1×10^{-7}	99.1	1.7	3.2	3.6
1×10^{-6}	99.1	3.1	3.4	3.6
1×10^{-5}	98.8	5.6	5.9	5.9
1×10^{-4}	91.7	6.9	7.0	7.9
1×10^{-3}	76.4	11.2	10.2	11.1

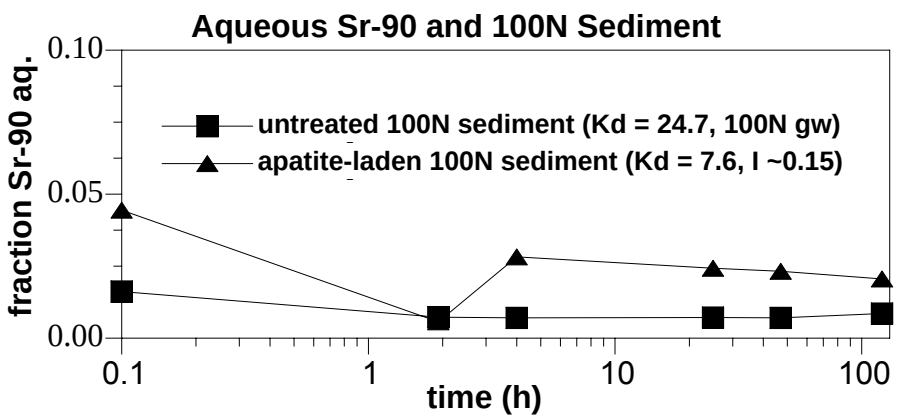
3.2.2 ^{90}Sr Adsorption Rate as a Function of Ionic Strength

Laboratory experiments were conducted to measure the ^{90}Sr adsorption rate in untreated 100-N sediments and the ^{90}Sr uptake rate by apatite-laden sediments. Sequential experiments were used to remove the ^{90}Sr on the sediment surface to determine if the ^{90}Sr was held on the surface by ion exchange or was incorporated into the apatite structure.

Methods. Using the 100-N composite sediment (from 10 to 42-foot depth at well N-121) and 100-N groundwater (Ca/Sr ratio of 220/1) with the addition of 1 mCi of ^{90}Sr, two experiments were conducted. The first experiment used no additional amendments. In the second experiment approximately 0.5 g of apatite was added, and the ionic strength was approximately 0.1 M (diluted from the original Ca, PO_4, citrate mixture).

Results. The adsorption equilibrium for the untreated sediment was reached within 2 h, resulting in a Sr Kd value of 24.7 cm^3/g (Figure 3-6). Sediment extractions show that ^{90}Sr was retained by ion exchange, so it is not surprising that equilibrium was achieved relatively quickly. In the treated sediments, the solution ^{90}Sr continued to decrease even after 120 h. The apparent Kd at 120 h was 7.6 cm^3/g, which was lower than the untreated sediment and resulted from the higher solution ionic strength.

FIGURE 3-6
Aqueous ^{90}Sr Sorption to 100-N Sediments



These results, showing the influence of major ions on Sr retention by Hanford sediments, are supported by previous work. Routson et al. (1981) reported a Sr Kd of 49 cm^3/g in the presence of 0.001M $NaNO_3$, and a Kd of 16 cm^3/g in the presence of 0.1M $NaNO_3$, or a 4x decrease in the Kd value with a 100x increase in molarity. In general, Sr^{2+} retention by ion exchange is controlled to a large extent by Ca^{2+} concentration in solution. A similar change in Ca^{2+} ionic strength (0.001 to 0.1) resulted in a 38x decrease in the Sr Kd value.

3.2.3 ^{90}Sr Sorption via Ion-Exchange versus "Sequestration"

It was hypothesized that untreated sediment sorbs Sr predominantly by ion exchange, while in apatite-laden sediments, Sr becomes more permanently sequestered over time. To test this hypothesis, untreated and apatite-laden 100-N sediments were treated by a sequence of solid phase extractions:

1. Extraction by 0.5M KNO_3 (released ions were bound by ion exchange)
2. Extraction by 6 percent 0.05M EDTA (released ions dissolved from carbonate)
3. Extraction by 4M HNO_3 at 80°C for 24 hours (ions dissolved from minerals)

Methods. Solid phase extractions were conducted on three different sediments:

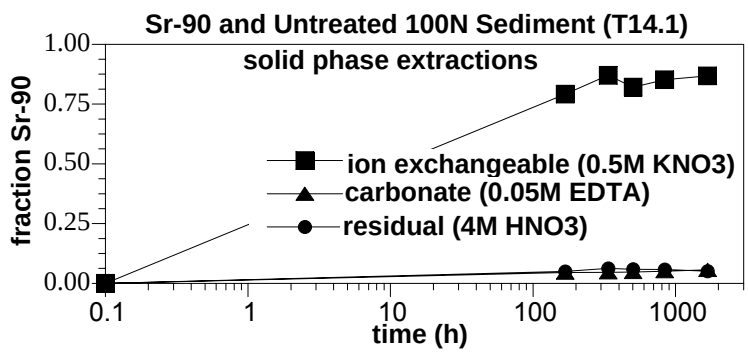
a. 100-N sediment from the 13-foot depth (which contains 80 pCi/g ^{90}Sr), ^{90}Sr solution added

b. Apatite-laden 100-N composite sediment, with ^{90}Sr solution added

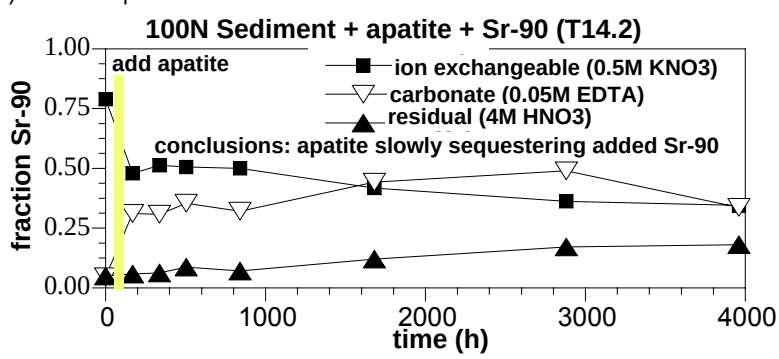
c. 100-N sediment from the 13-foot depth (which contains 80 pCi/g ^{90}Sr), apatite precipitate added

Results are presented in Figure 3-7.

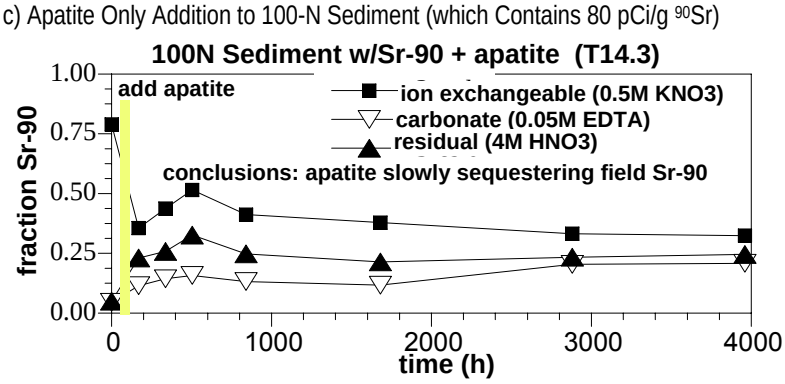
FIGURE 3-7
Solid Phase ^{90}Sr Extractions for:
a) Untreated 100-N Sediment with ^{90}Sr added



b) ^{90}Sr and Apatite Addition to Sediment



c) Apatite Only Addition to 100-N Sediment (which Contains 80 pCi/g ^{90}Sr)



Results—Untreated 100-N sediments. Solid phase extractions showed that ~86 percent of the ^{90}Sr on untreated sediments was released by ion exchange, about 6 percent was released by carbonate extraction, and about 6 percent by mineral dissolution extraction (see Figure 3-7a). The remaining 5 percent ^{90}Sr was aqueous. Therefore, ^{90}Sr was retained on untreated 100-N area sediments predominantly by ion exchange, as expected. Samples taken at weekly intervals to 10 weeks showed no difference, indicating equilibrium was reached within a week. Previous ^{90}Sr aqueous phase measurements indicated that equilibrium was likely reached within hours.

Results—Apatite-laden sediments. In contrast, the ^{90}Sr was more difficult to remove from the apatite-laden sediments. In the sediment in which ^{90}Sr was added to apatite-laden sediment, by 1 week, only 50 percent of the ^{90}Sr was released by ion exchange, 31 percent by the carbonate extraction, and 6 percent by the residual extraction (Figure 3-7b). By 10 weeks, 42 percent of the ^{90}Sr could be extracted by ion exchange, 44 percent by carbonate extraction, and 12 percent by the residual extraction. Therefore, the mass of ^{90}Sr bound by ion-exchange is about one-half after 1 week, and continues to slowly decrease between 5 and 10 weeks, while the proportion of ^{90}Sr incorporated into carbonate and minerals increased. Additional experiments will be conducted in FY06 with Sr-laden apatite (no sediment) to determine the Sr extraction efficiency by EDTA and HNO_3.

Results—100-N sediments with apatite added. For the 100-N sediment from the 13-foot depth (containing 80 pCi/g ^{90}Sr, no additional ^{90}Sr was added), addition of apatite also decreased ^{90}Sr mobility. At time zero (no apatite), 87 percent of the ^{90}Sr was extracted by ion exchange, 6.5 percent by the carbonate extraction, and 6.8 percent by the residual extraction (Figure 3-7a). These values were very similar to the sediment in which aqueous ^{90}Sr was added to untreated sediment (Figure 3-7a), indicating that the influence of approximately 40 years of aging was small. After 1 week of apatite addition, only 36 percent of the ^{90}Sr could be extracted by ion exchange, but 12 percent by carbonate extraction, and 23 percent by residual extraction. There were small changes over the next 10 weeks, indicating slow incorporation of ^{90}Sr into the apatite (Table 3-3). Therefore, the addition of the apatite decreased the ^{90}Sr mass on ion exchange sites by 59 percent in 1 week.

TABLE 3-3
Summary of ^{90}Sr Sequential Extraction Experiments

	Untreated Sediment		Apatite-Treated Sediment		
				5 weeks	24 weeks
	extraction	Sr-90 (%)	extraction	Sr-90 (%)	Sr-90 (%)
mobile >	aqueous	7.3	aqueous	9.5↑	<0.2↓
slow mobile >	exchangeable	80.1	exchangeable	44.5↓	34.6↓
immobile >	0.05M EDTA	6.5	0.05M EDTA	48.5↑	49.7↑
immobile >	4M HNO3, 80C	6.8	4M HNO3, 80C	7.0	17.2↑

Conclusion—The majority of ^{90}Sr in untreated 100-N soil is bound by ion exchange. However, in apatite-laden soil, only half of the ^{90}Sr was bound by ion-exchange, and that slowly decreases over time. The addition of apatite decreases the ^{90}Sr mass on ion-exchange sites by 59 percent in 1 week, with little change after 10 weeks.

3.2.4 Salt Effect: ^{90}Sr Desorption Associated with High Ionic Strength Reagents

As shown by the results presented previously, Sr is bound to sediment surfaces in the 100-N area primarily by ion exchange. In the presence of a higher ionic strength solution, some desorption of ^{90}Sr will occur. Apatite-forming chemicals, once injected into the aquifer, will contain higher salt concentrations than the groundwater in the treatment area. Some of these salts will not participate in the precipitation reactions, resulting in the migration of relatively high TDS water into areas where ^{90}Sr has not been sequestered by apatite, causing increases in pore water concentrations of ^{90}Sr.

To mitigate this problem, the apatite precursors will be introduced in steps. The first step involves injection of a dilute apatite solution that results in a minimal salt effect, but emplaces sufficient apatite to sequester the ^{90}Sr mobilized by the next injection. In the second step, a concentrated solution is introduced. Formation of apatite has been demonstrated at both high and low concentrations of apatite-forming chemicals.

PNNL conducted a series of experiments in FY05 to determine the influence of ionic strength on Sr adsorption. The purpose of these experiments was to measure the adsorption of Sr in natural Hanford groundwater and be able to predict how this adsorption may change with the injection of the apatite solution (Ca, Na, PO_4, citrate).

Methods. Batch experiments were conducted with the 100-N composite sediment (less than 4 mm fraction) from well N-121 (depths 10 to 42 feet) with various Sr concentrations. Sr-85 was used as the isotopic tracer. The natural Sr adsorption was measured at two different Sr concentrations. The influence of ionic strength was tested with three different solutions:

a. Na2SO4 solutions

b. Fresh apatite solution (apatite forming chemicals)

c. “Spent” apatite solution (5-week old apatite solution)

In each case, Sr adsorption and electrical conductivity were measured to understand the correlation between Kd and the ionic strength of the apatite solution.

Results—Sr adsorption in natural groundwater. Three batch vials at two differing Sr concentrations (no apatite solution) showed that the Sr Kd value in natural groundwater is 25.96 ± 0.89 (Table 3-4).

TABLE 3-4
Sr Adsorption in 100-N Groundwater (less than 4 mm fraction)

Sr (mol/L	Sr (mg/L)	Kd (cm^3/g)	n	EC (µS/cm)
2.82E-07	0.0032	25.41±1.00	3	402
2.11E-06	0.024	26.51±0.26	3	365

Results—Sr adsorption in sodium sulfate solutions. Five different concentrations of sodium sulfate were mixed in 100-N groundwater to compare with the apatite solutions to determine if sodium concentration by itself was a good predictor of Sr adsorption. The Sr Kd decreased with increasing ionic strength (Table 3-5), as predicted, and were comparable to previously published results.

TABLE 3-5
Sr Adsorption in Groundwater + Na_2SO_4

Na (mol/L)	EC (uS/cm)	Kd (cm3/g)
0.001	508	20.89
0.005	952	21.2
0.01	1515	19.67
0.02	2560	18.46
0.03	3651	14.83

*all 2.11E-6 mol/L Sr

A Hanford 200 Area sediment in $NaNO_3$ solutions (Routson et al., 1981) had a Sr Kd value of 49 cm^3/g (0.001 M $NaNO_3$), 42 cm^3/g (0.015 M $NaNO_3$), and 16 cm^3/g (0.1 M $NaNO_3$), so most of the Kd decrease occurred at ionic strength greater than 0.01 mol/L.

Results—Sr adsorption in fresh apatite solutions. Sr adsorption was measured in mixtures of fresh apatite solution and groundwater (2 percent to 100 percent). These results show a much more dramatic decrease in Sr Kd compared with the sodium sulfate, possibly due to aqueous Sr complexation with citrate (Table 3-6). These Kd values would be representative of Sr adsorption that would be expected in the first few weeks after an apatite injection. The Kd value decreased from 26 to 2.0 cm^3/g as the ionic strength increased from 0.005 mol/L to 0.1 mol/L. In comparison, the same increase in $NaNO_3$ ionic strength (Routson et al., 1981) showed a four-fold decrease in Sr adsorption.

TABLE 3-6
Sr Adsorption in Groundwater + Fresh Ca/PO_4/Citrate

Na (mol/L)	% apatite solution	EC (uS/cm)	Kd (cm3/g)
0.35	100	24992	2.66
0.0875	25	8921	1.98
0.035	10	4123	6.47
0.0175	5	2220	13.1
0.007	2	1224	15.3

*all 2.11E-6 mol/L Sr

Results—Sr adsorption in spent apatite solutions. Sr adsorption in mixtures of a 5-week-old apatite solution and groundwater showed less influence on the Sr adsorption than the fresh apatite solution (Table 3-7). The Kd value decreased from 26 to 5.1 cm^3/g (5.1x) as the ionic strength increased from 0.005 mol/L to 0.1 mol/L, which was similar to the change noted with $NaNO_3$ solutions (Routson et al., 1981). These experiments are representative of the solution that will be encountered downgradient of an apatite injection.

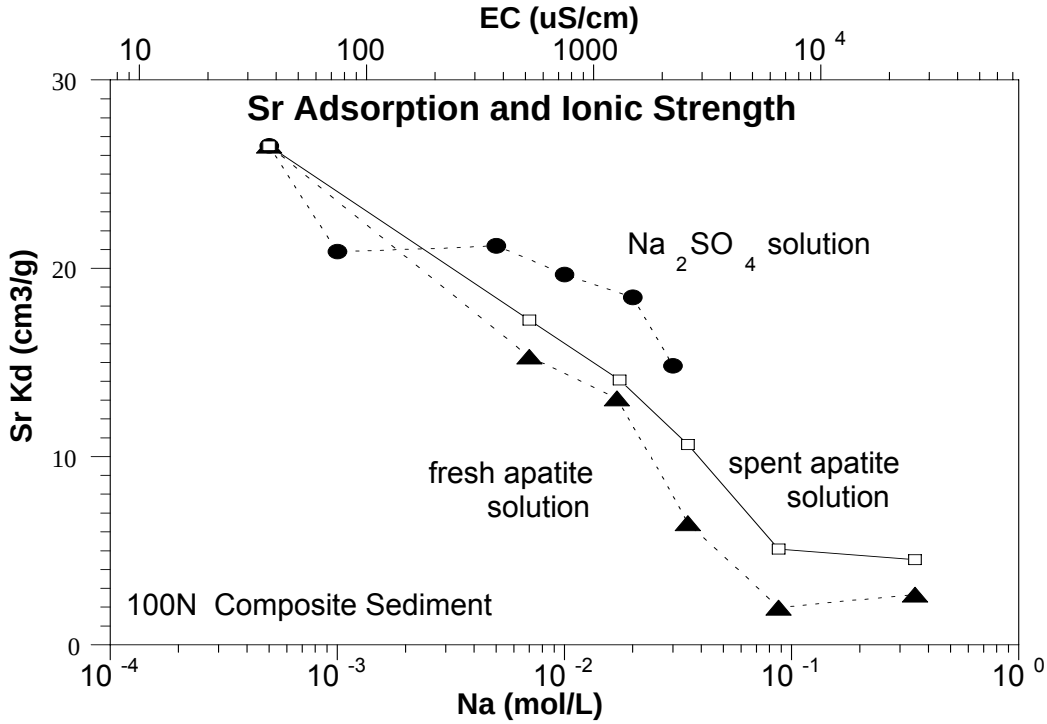
TABLE 3-7
Sr Adsorption in Groundwater + Spent Ca/PO_4/Citrate

Na (mol/L)	% apatite solution	EC (uS/cm)	Kd (cm3/g)
0.35	100	26337	4.53
0.0875	25	8596	5.1
0.035	10	3804	10.64
0.0175	5	2056	14.06
0.007	2	1089	17.26

*all 2.11E-6 mol/L Sr

Conclusion—The injection of an apatite solution will decrease adsorption of freshly adsorbed Sr from 26 cm^3/g (in groundwater) to 4.5 cm^3/g (spent apatite solution) or 2.7 cm^3/g (fresh apatite solution) for 100 percent solutions. As groundwater dilutes the plume, there is less influence on the Sr adsorption, which shows a predictable trend of Na concentration (or electrical conductivity) in the apatite solution to the Sr Kd value. The sodium sulfate solutions generally follow the same trend, but do not accurately represent the trend observed with the apatite solution. Note that the two highest ionic strength points for the apatite solutions represent actual desorption Kd values (after 5 days of adsorption of ^{85}Sr), and as such represents a worst-case scenario. The influence of ^{90}Sr Kd is graphically shown in Figure 3-8.

FIGURE 3-8
Influence of Ionic Strength on ^{90}Sr Desorption (Ion Exchange)



3.3 Solution Concentrations and Injection Strategy

To lessen the ^{90}Sr release into solution caused by high ionic strength addition (i.e., the salt effect), injections will be staged, with an initial injection of lower apatite solution concentrations, which would also provide for more rapid citrate biodegradation (and ultimately better control of the apatite placement). With a 40 mM citrate injection, the Sr Kd = 13 cm^3/g , which results in a two-fold increase in ^{90}Sr groundwater concentration. It is hypothesized that there would be less Sr desorption than predicted from these studies for actual ^{90}Sr-laden sediments that have been in contact with ^{90}Sr for decades (as opposed to the 5-day adsorption in this study). After several weeks of ^{90}Sr sequestration by the small amount of apatite, a high-concentration apatite solution can be injected.

Based on the above ionic strength ("salt effect") information, in order to keep most of the ^{90}Sr sorbed to the sediment surface (i.e., the ^{90}Sr groundwater increase kept to 2 to 3 times the ambient concentration), a low Ca/citrate/phosphate concentration needs to be injected initially to immobilize the ^{90}Sr in the immediate area. Because most of the final apatite barrier capacity is intended to sequester ^{90}Sr being advected into the precipitate zone, once the ^{90}Sr in the treatment zone (i.e., within 30 to 50 feet [9 to 15 meters] of the injection wells) is sequestered, new ^{90}Sr migrating into the treated zone will be adsorbed and then bound within the apatite structure. Subsequently, higher concentrations of Ca/citrate/phosphate can be injected and any initially desorbed ^{90}Sr will be trapped by the apatite formed by the low-concentration injections.

3.3.1 Injection Strategy

Based on the above considerations, an injection strategy is outlined as follows:

- Begin with a low Ca/citrate/phosphate injection (5 to 15 mM citrate).
- Allow a groundwater drift/apatite precipitation phase. This residence period is 3 to 7 weeks. Modeling of the citrate biodegradation experiments will determine the lag phase.
- Inject high Ca/citrate/phosphate solutions (100 mM to 160 mM citrate) to build up mass of apatite to meet 300-year or alternate long-term objective.

Batch Tests

A series of batch experiments were conducted to test this injection strategy under idealized (laboratory) conditions. Results are reported as Kd values for Sr (^{90}Sr labeled Sr used), based on aqueous ^{90}Sr concentrations.

With no treatment, the 100-N sediment (< 4 mm size fraction) has a Kd (Sr) = 25 cm^3/g. Several different "low concentration" solutions were used in separate vials:

- The 2 mM apatite solution resulted in the Kd (Sr) = 15.3 cm^3/g (60 percent increase in ^{90}Sr groundwater concentration).
- The 5 mM apatite solution resulted in the Kd (Sr) = 13.1 cm^3/g (1.9x increase in ^{90}Sr groundwater concentration).
- The 10 mM apatite solution resulted in the Kd (Sr) = 6.5 cm^3/g (3.8x increase in ^{90}Sr groundwater concentration).
- The 25 mM apatite solution resulted in the Kd (Sr) = 2 cm^3/g (12.5x increase in ^{90}Sr groundwater concentration).

After 29 days, the apatite precipitated and due to some incorporation of ^{90}Sr into the apatite structure , less ^{90}Sr remained in solution, so the ^{90}Sr Kd values changed to reflect this increase in solid phase ^{90}Sr. The Kd values were:

- 23 cm^3/g (2mM citrate)
- 49 cm^3/g (5 mM citrate)
- 61 cm^3/g (10 mM citrate)
- 124 cm^3/g (25 mM citrate)

The high ionic strength residual solution maintains some ^{90}Sr in solution in these batch vials, whereas in the field, the solution would be slowly diluted by downgradient advection.

To demonstrate that once ^{90}Sr is sequestered by the apatite, a high ionic strength solution can be injected with little or no increase in the ^{90}Sr groundwater concentration, a 10 mM citrate solution was removed from the sediment and replaced with a 100 mM citrate solution. The resulting Kd value for ^{90}Sr was 340 cm^3/g. Apparently, ^{90}Sr is sequestered by the apatite, and it is not desorbing into aqueous solution.

Column Studies

A series of column experiments are in progress to demonstrate the apatite injection strategy concepts, as described above in batch studies. Two column experiments were conducted to demonstrate Sr natural transport (i.e., high retention due to ion exchange). Both of these experiments (Figures 3-9a and b) consisted of 100-N sediment columns that were treated with Sr-85 (radio-labeled tracer) for 1 week, then 100-N groundwater was injected through the column for 150 to 350 pore volumes (pv) at a rate of 0.5 pv/h or 1.0 pv/h. In both cases, the resulting Kd was 12 to 13 cm^3/g, or slightly lower than in the previous batch study (Kd = 35). There was some additional tailing observed at the faster flow rate (Figure 3-9b, tailing to 100 pv compared with 85 pv).

If a solution containing 100 mM citrate were injected into Sr-laden sediment, the Sr would desorb due to the high ionic strength of the injection solution, as described earlier in Figure 3-8. Ion exchange in a 1-D flow field will cause an initial peak, as illustrated in Figure 3-9c (100 mM citrate injection), in which the Kd of 2.04 (from area integration under the breakthrough curve) was the same as the batch experiment. This high amount of ^{90}Sr adsorption can be avoided by the sequential injection system consisting of: 1) 10 mM citrate injection, 2) allow a few months to incorporate ^{90}Sr into the apatite, and then 3) high 100 mM citrate injections.

A column experiment of the 10 mM citrate injection into Sr-85 laden sediment (Figure 3-9d) shows a small initial peak, but the Sr Kd decreased from 12 to 6.9 (i.e., only a 2x groundwater increase). At the field scale, this initial peak may be less due to lateral dispersion (i.e., the column experiment represents the worst case results—similar to sampling a well at the downgradient edge of the injection plume). Additional columns are in progress to show: a) groundwater injection into ^{85}Sr /apatite-laden sediment, and b) 100 mM citrate injection into ^{85}Sr/apatite-laden sediment.

3.4 Summary of Bench Testing

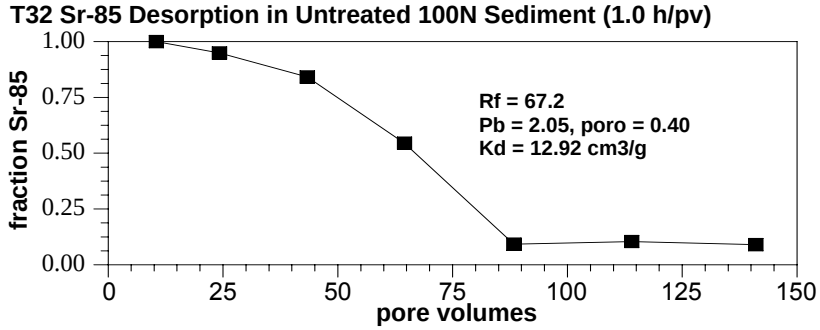
Laboratory or bench studies have quantified the sequential processes of the aqueous injection apatite technology in 100-N sediment. The principal findings and results obtained to date are:

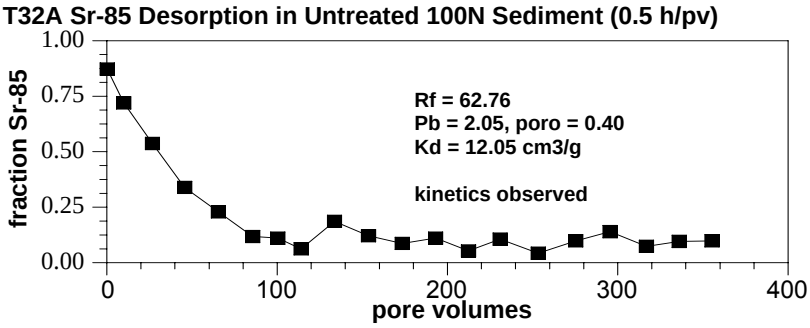
- Amorphous and crystalline apatite precipitation occurs
- Aerobic and anaerobic citrate biodegradation pathways and rates were quantified,
- ^{90}Sr uptake in apatite-laden 100-N sediment occurs
- ^{90}Sr is initially held by ion exchange, but then over 6 to 20 weeks is more permanently held (presumed incorporated into apatite)

Additional details of findings and laboratory work either underway or planned, and its relationship to field deployment, are discussed as follows.

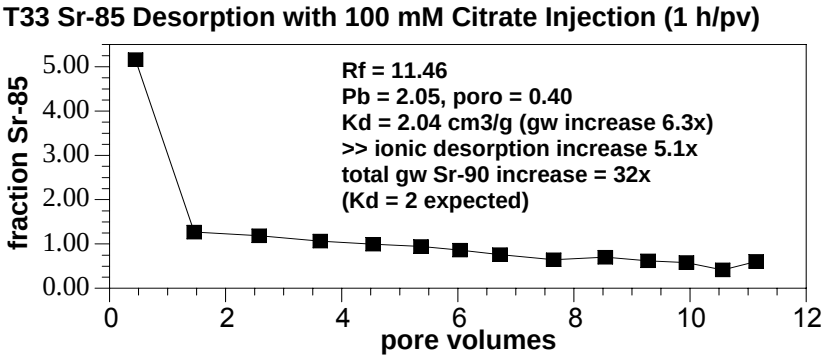
FIGURE 3-9
Column Studies of ^{85}Sr Desorption from 100-N Sediments

a) and b) With Natural Groundwater Injection

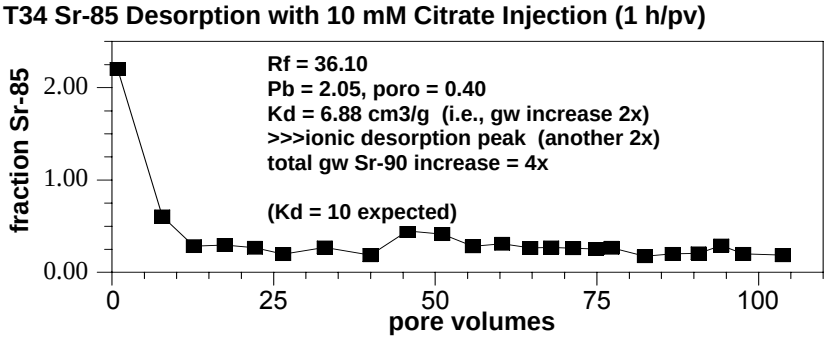




c) With 100 mM Citrate Injection



d) With 10 mM Citrate Injection



Apatite precipitation in batch and 1-D column systems occurred within 75-100 h in aerobic systems (100 mM citrate biodeg. to CO_2) and within 100-200 h in anaerobic systems (100 mM citrate biodeg. to formate and acetate). In the 100-N aquifer, most of the citrate biodegradation will occur anaerobically, given the relative concentrations of citrate to oxygen. The initial precipitate that forms within 100 h is amorphous and then crystallizes within 2 to 4 weeks to apatite. Batch experiments varying mixing, trace nutrient, and nitrate addition showed similar results. Apatite precipitate was formed in both batch tests and 100-N sediment columns. Precipitation experiments were conducted over a range of temperature and citrate concentrations to determine rates applicable to field-scale injection of 10 mM and 100 mM Ca/citrate/PO4 at 15°C.

Performance testing of the apatite precipitate to sequester ^{90}Sr was accomplished with a variety of different experiments. Without apatite, sequential chemical extractions to remove ^{90}Sr from sediment showed that 90 percent of the ^{90}Sr could be removed from the sediment by ion exchange. With the addition of apatite, long-term experiments showed that by 6 weeks, only 45 percent of the ^{90}Sr could be removed by ion exchange, and this slowly decreased to 32 percent by 24 weeks. This may be caused by the slow ^{90}Sr incorporation into apatite.

To minimize ^{90}Sr mobilization (by ion exchange) during barrier emplacement, a sequence of injections from low to high concentration Ca-citrate/phosphate is needed. ^{90}Sr mobilization is minimal with the low concentration injection, and the apatite formed in the injection zone (after 4 weeks) immobilizes most of the ^{90}Sr, as demonstrated in a sequence of batch experiments and column experiments. A high concentration injection can then be injected with minimal ^{90}Sr desorption, as demonstrated in batch experiments. This finding is currently being confirmed in column studies. Additional laboratory studies quantifying ion exchange are needed to refine the design of field injections. Results of this effort, as available, will be used to update the initial injection conceptual design for the field testing described in Section 4.

Successful field-scale deployment will require injection of a sufficient volume of the Ca/citrate/PO4 solution to achieve a relatively homogeneous precipitate over a specified lateral distance from the injection well. Laboratory scale parameters needed to refine design of field injection strategies include:

a. Citrate biodegradation rates at appropriate temperature and concentration

b. Ion exchange parameters to predict spatial variability of Ca/Na/Sr during injections

c. Reagent adsorption

Techniques to test field performance include measurement of downgradient ^{90}Sr, measurement of apatite mass in field-treated cores, and measurement of ^{90}Sr ion exchange and/or leaching in field-treated cores.

Field pilot test data and injection simulations (Section 4) will be used to develop an initial injection strategy that incorporates reaction rates and parameters determined from the bench testing.

SECTION 4

Aqueous Injection Field Testing

The purpose of this treatability test is to determine whether introducing a solution of apatite precursors into the aquifer at the 100-N Area results in formation of apatite and subsequent reduction of ^{90}Sr concentrations in groundwater. This section provides a general description of the field-test design, performance assessment parameters, and general responsibilities.

4.1 Test Objectives and Conceptual Design

Field testing will consist of two phases: an initial pilot injection well test followed by installation and treatment of a sufficient number of wells for a 300-foot (91-meter) treatability test barrier.

The objective of the pilot test phase is to address the following questions:

- Will apatite precipitate in the target zone?
- Does the apatite result in reducing ^{90}Sr in groundwater?
- Given a fixed well spacing of 30 feet, what is the optimal injection volume per well for installation of a 300-foot barrier wall?

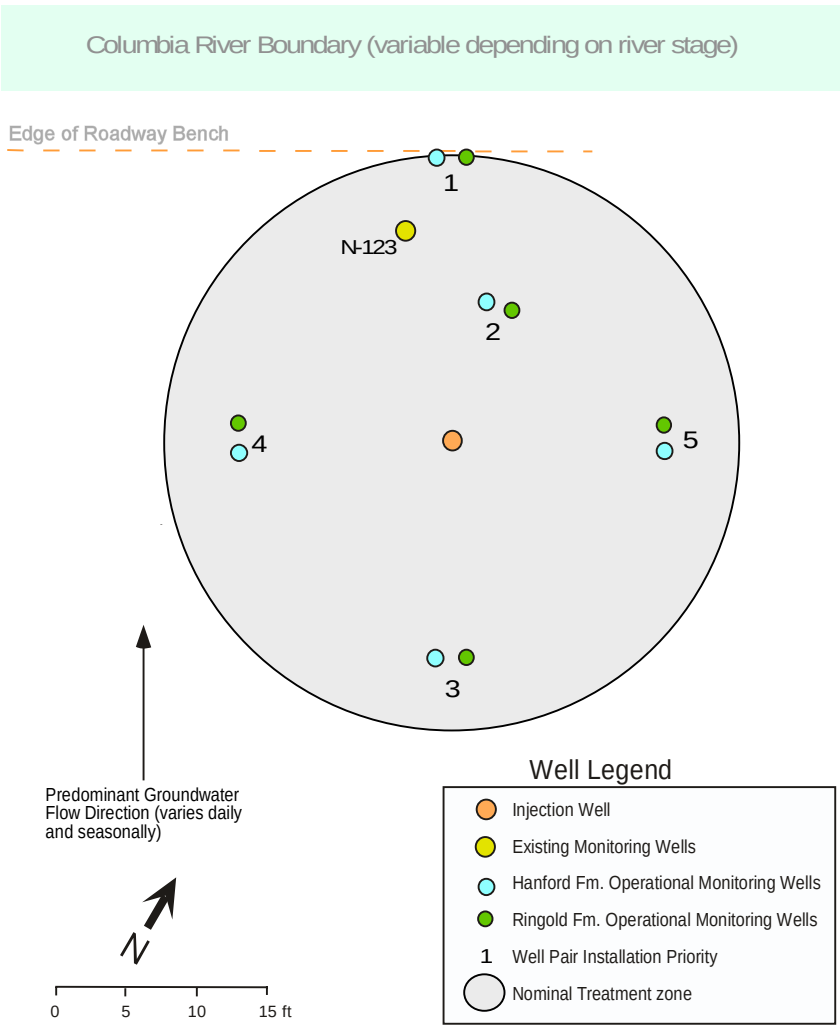
Pilot testing will consist of a single injection well and associated monitoring wells installed at various radial distances. The proposed well layout design for the pilot test site is provided in Figure 4-1 (the actual configuration as staked and drilled may deviate somewhat from the general layout shown). Each of five monitoring locations shown (numbered 1 through 5) will consist of a two well set: one completed in the Hanford formation and one in the Ringold.

A tracer test and/or low-concentration apatite injection will be conducted first to determine the radius and volume affected by injection at a single well point. If schedule constraints allow for performing a conservative tracer test prior to the low-concentration apatite injection, this information will be used in estimating the apatite-forming chemical solution volume, and concentration, to inject for a pilot test. Injection will be followed by performance assessment monitoring that may include a multi-pore volume withdrawal to force contaminated groundwater through the treatment zone.

If the pilot test phase indicates that the aqueous injection approach is effective for the installation of an apatite barrier at the 100-N Area, the second phase of the treatability test will move forward with treatment of 10 injection wells for emplacement of a 300-foot PRB. Existing aquifer tubes near well N-46 and three compliance monitoring wells will be used to test the longer-term effectiveness of the barrier. Results of the pilot test will be used to determine the volume needed to obtain continuous coverage across the 30-foot well spacing chosen for the 10 injection wells to be drilled (Section 5).

As discussed in Section 3, the concentration of calcium citrate and sodium phosphate for the initial injections will be maintained at concentrations low enough to minimize potential mobilization of ^{90}Sr due to the salt leaching effect. Temporary release of ^{90}Sr from aquifer solids during subsequent injections at higher salt concentrations will be attenuated by the apatite in the formation from the initial low-concentration injections. Injection of the higher concentrations of apatite-forming solutions will be necessary to build up a sufficient load of apatite to treat ^{90}Sr for up to a 300-year period.

FIGURE 4-1
Pilot Test Site Well Layout

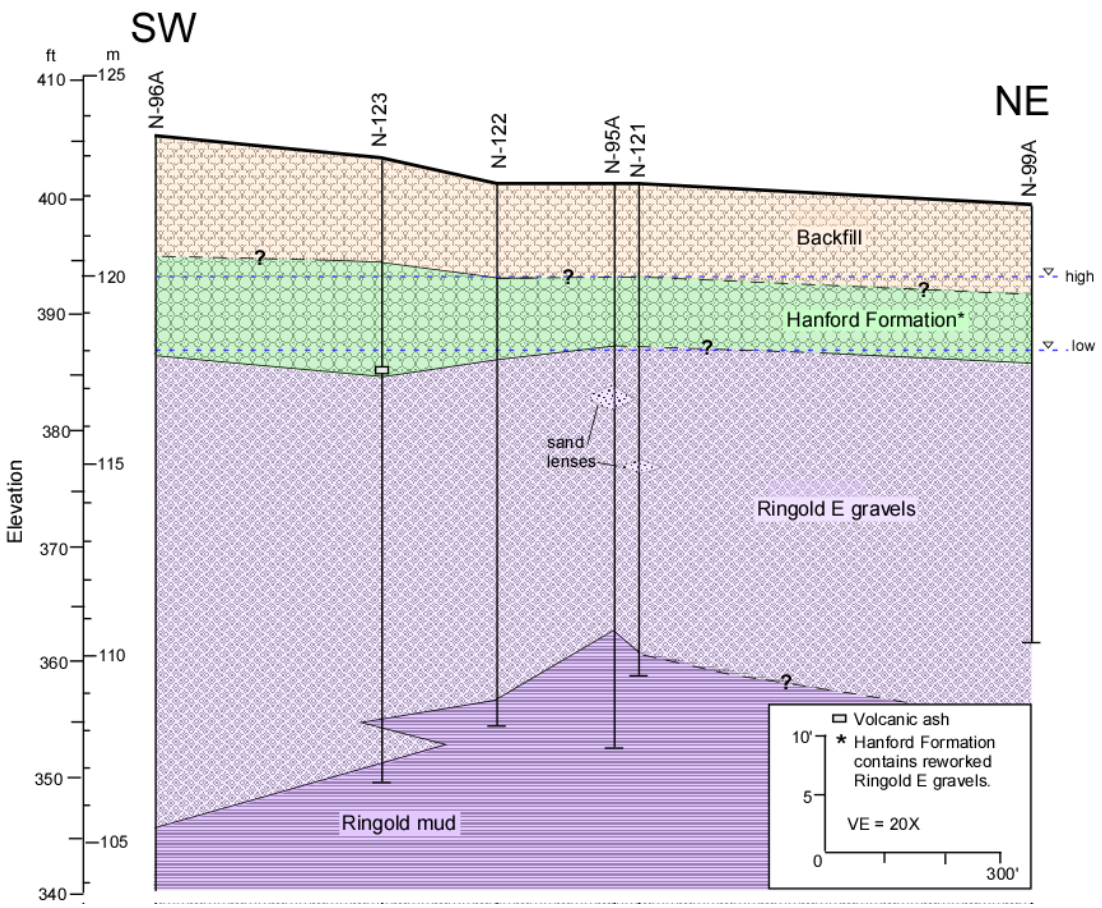


4.2 Site-specific Characterization

Two boreholes (N-122 and N-123) were drilled in FY 05 to provide hydrogeologic and geochemical characterization data needed for the pilot test and overall barrier emplacement design analysis. A geologic cross-section running along the proposed barrier alignment is provided in Figure 4-2. This cross-section was constructed based on hydrogeologic information obtained during the installation of the two new boreholes and geologic logs

from previous well installations. It should be noted that the zone designated as the Hanford formation contains a significant amount of reworked Ringold formation materials, with this effect more evident at the N-123 location. Both of the boreholes were completed as downgradient performance assessment monitoring wells. As the boreholes were advanced, continuous core samples were collected and submitted for grain-size analysis, microbial characterization, and determination of ^{90}Sr concentration with depth. These data will be used to determine the depth interval for initial treatment and will decrease uncertainty associated with the depth to the Hanford/Ringold contact and the vertical distribution of ^{90}Sr in the proposed target area where clam tissue data indicate the highest impact.

FIGURE 4-2
Geologic Cross-section



Because of the large difference in aquifer permeability between the Hanford and Ringold formations, determining the primary formation requiring treatment is essential to the injection design. In the event treatment is required in both the Hanford and Ringold formations, the two formations would need to be treated independently. Electromagnetic borehole flowmeter (EBF) testing will be conducted at the site to help quantify the permeability of each formation and determine the contact depth. The hydrogeologic and geochemical characterization data collected from this site will be the basis for a flow and

reactive transport model. This design tool will be used to develop the design for the pilot study as well as for the final barrier.

4.3 Flow and Reactive Transport Simulations

The injection design analysis will be used to develop a strategy for injecting the apatite-forming reagents. This approach will target a depth interval of the unconfined aquifer as determined from the results of ^{90}Sr vertical profiling described previously (see Section 4-2) and from prior ^{90}Sr vertical profiles.

There are two potential zones of treatment: 1) Ringold formation E Gravels (lower contaminated portion of the unconfined aquifer), and 2) Hanford formation (upper contaminated portion of the unconfined aquifer). The permeability of the Hanford formation gravels can be 10 to 1,000 times greater than the permeability of the Ringold formation gravels. The material properties of these units will impact the injection rates and volumes, extent of injection mounding, extent of reagent plume, ambient groundwater velocities (e.g., plume drift after injection period), and density effects.

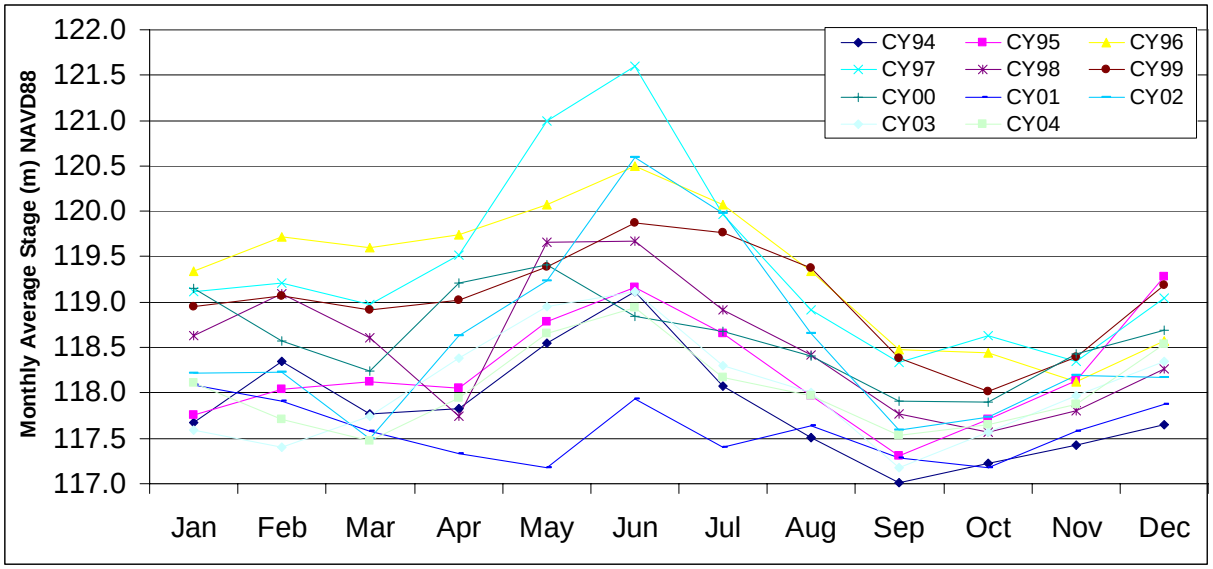
The pilot test design will provide specifications of the injection and monitoring wells, injection rate, injection volume, reaction period duration, withdrawal rate for multi-pore volume performance assessment extraction test, and the sampling/analysis plan. The timing of the injection relative to the river stage regime is also a critical factor for treating the targeted portion of the aquifer due to the strong influence of the river stage on the water table elevation and the groundwater flow directions and velocities. The river stage is very dynamic with large hourly, daily, weekly, and seasonal variations.

While the timing and extent of the large seasonal variations in the Columbia River stage changes from year to year depending on weather and dam operations, hourly measurements from the RS-1 river stage recorder at the 100-N Area for the years 1994 through 2004 show a high river stage season typically from April to June and a low river stage season typically from August to November (see Figure 4-3). During seasonal high conditions, groundwater flow is predominantly directed inland at distances approximately 40 meters (131 feet) from the river (simulation results discussed below). During seasonal low conditions, larger groundwater velocities are directed toward the river.

The timing of the injection test relative to the Columbia River stage will also control the portion of the aquifer that can be treated. This may be an important factor based on previous studies showing that the highest ^{90}Sr concentrations in the sediment are in the upper portions of the aquifer or slightly above the mean water table. Injections during periods of relatively high river stage will enable treatment of this portion of the aquifer.

Following the reagent injection, from 70 to 200 hours is required for apatite precipitation based on bench-scale laboratory studies. During this period, the injected reagent plume will drift with the ambient groundwater flow. The timing of the pilot-scale test relative to the river stage will be important in determining the direction and amount of plume drift that will occur during this phase of the test, which in turn will determine where the apatite precipitate will form.

FIGURE 4-3
Monthly Average River Stage at N-Area from RS-1 for 1994 to 2004
Averages were calculated from hourly measurements; elevations are NAVD 1988 Datum



With the immediate proximity of the pilot-scale test to the Columbia River, the potential exists for reagent and reaction products to enter the river. This is particularly true for treatment of the Hanford formation (with its high groundwater velocities) at low river stage when the velocities are directed toward the river. Heterogeneities in the formations can also create highly conductive channels toward the river. Site-specific tracer tests and simulations will be used to provide guidance on the extent and relative concentrations of reagent that could enter the river during the treatment phase.

Numerical simulations will be used initially to aid in the design of the pilot-scale test (e.g., injection volume and rate). These models will be refined as additional site-specific characterization data become available from additional boreholes and tracer tests conducted at the site. If the pilot-scale test is successful, results will be used to update the models and aide in the design of the large-scale implementation (e.g., injection volumes and rates, timing of injections relative to river conditions).

4.3.1 Previous Modeling Studies

As part of the 100-N Area ITRD Program, detailed groundwater modeling studies were conducted with a calibrated, transient, two-dimensional cross-section model using hourly measurements of water levels in wells and the river stage from 1995 (Connelly et al. 1997, Connelly 1999, and Connelly 2001). The results of these simulations and the animations developed along with them illustrate the dynamic behavior of the groundwater flow at the site that is driven by the fluctuating river stage. The modeling study found "flow velocities in excess of 20 m/day were often predicted for the Hanford formation, while the highest velocities predicted in the Ringold formation were approximately 1 – 2 m/day" (Connelly, 1999, pg 33). Animations of the simulation results showed the higher velocities within the aquifer occurring closer to the river particularly during the low river stage season.

4.3.2 Simulations for Designing the Pilot-Scale Test

Initial simulations for designing the pilot-scale test used the 100-N Area cross-section model developed for the ITRD project discussed above (Connelly et al., 1997; Connelly, 1999; and Connelly, 2001), and used the STOMP computer code, which was developed by PNNL for simulating subsurface flow and transport in the aquifer and vadose zone (White and Ostrom, 2004; 2003; Nichols et al., 1997). The STOMP code will also be used for other design analyses. Material properties for these models will use the values developed for the calibrated ITRD Model (hydraulic conductivity, porosity, dispersivity, and soil characteristics) shown in Table 3-2 of Connelly (1999). These parameters will be updated as additional characterization data becomes available.

The following list outlines the models that will be developed and used in the design analysis for the pilot-scale test:

- Two-Dimensional Cross-section Model (ITRD model or a revised cross-section model if geology for specific site does not match the ITRD cross-section). The purpose of this model will be to investigate groundwater flow velocities at different locations and the drift of instantaneous plumes at different periods of the year / river stage regimes.
- Three-Dimensional Model. This model will be used for simulating the plume formation during injection and plume drift following the injection of the pilot-scale test and will provide for a fluctuating river boundary and an inland held head boundary. These simulations will be run at different times of the year with different river stages.
- Two-Dimensional Radial Model (may not need if the resolution of the three-dimensional model is adequate). This model will be used for simulating near-well effects during injection.

To support the construction of the three-dimensional model and other two-dimensional model cross-sections, an EarthVision GIS database of the Hanford Site was refined and updated for the 100-NArea based on detailed well logs and additional wells. This process identified some facies within the Hanford and Ringold formations (see Figures 4-4 and 4-5 for a transect location map and a geologic cross-section through the ITRD model transect location, respectively). The EarthVision hydrostratigraphy will be sampled at finite difference STOMP model node locations to determine the hydrostratigraphic unit for each node. One past limitation has been that the topographic data was insufficient to resolve the road and bank near the river at N-springs. A new topographic survey was conducted by PNNL in September 2005, which provided detailed elevations around the proposed pilot-scale test site.

Simulations will be conducted to investigate the impacts on the reagent plume extent and drift by potential heterogeneities and by fluid density from the injected reagent. Simulations will be conducted using both the low-concentration and the full-concentration injection fluid densities.

Conservative tracer and reactive transport simulations will also be conducted to predict apatite precipitation within the aquifer under varying conditions. To test the models used, reaction mechanisms and rates from bench testing laboratory studies will be compared to results from simulated bench tests. The reaction rates for the field test simulations will be suitable for ambient aquifer temperatures measured at the pilot-scale site.

FIGURE 4-4
Plan View Map Showing Locations of EarthVision Cross-sections

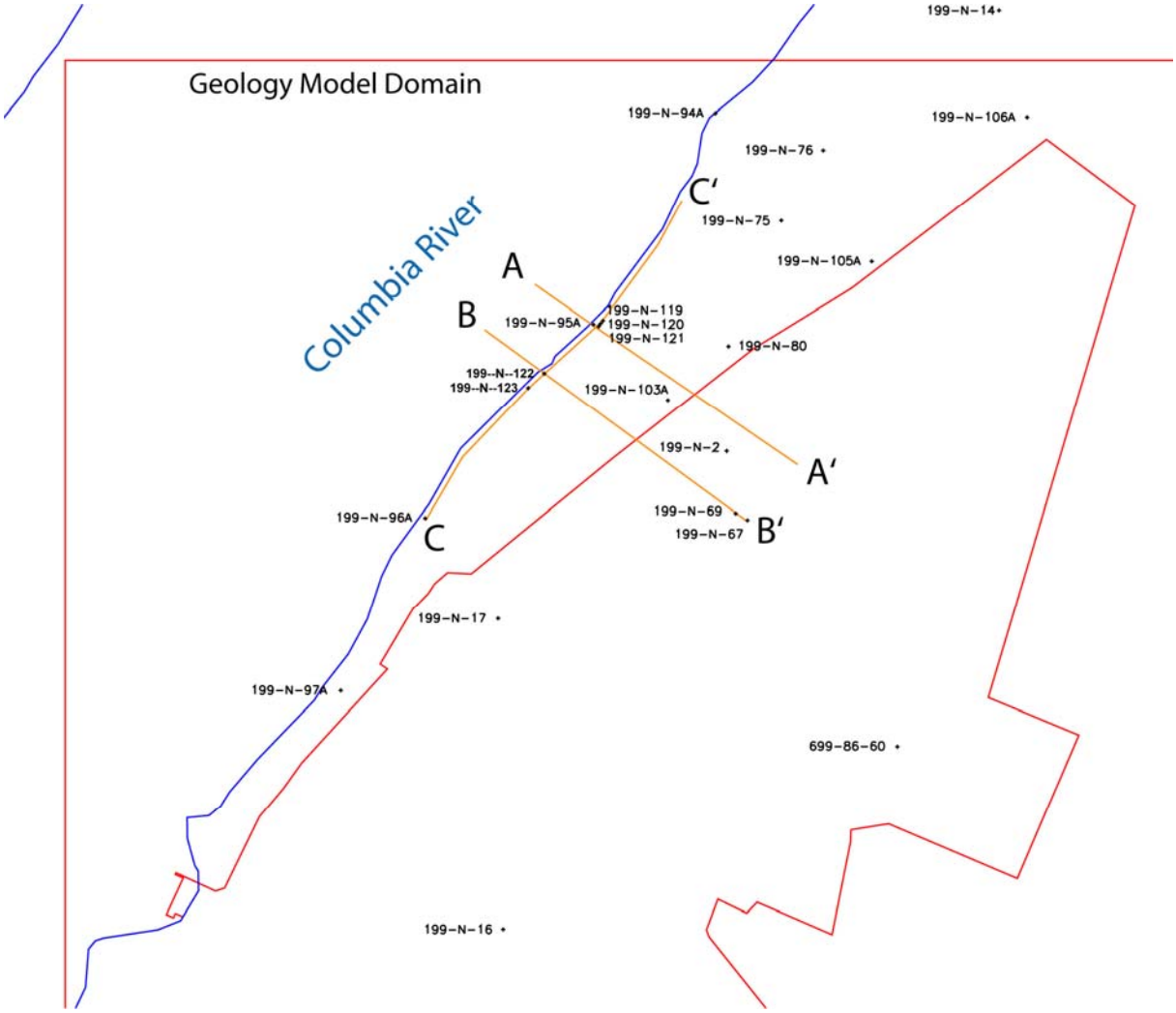
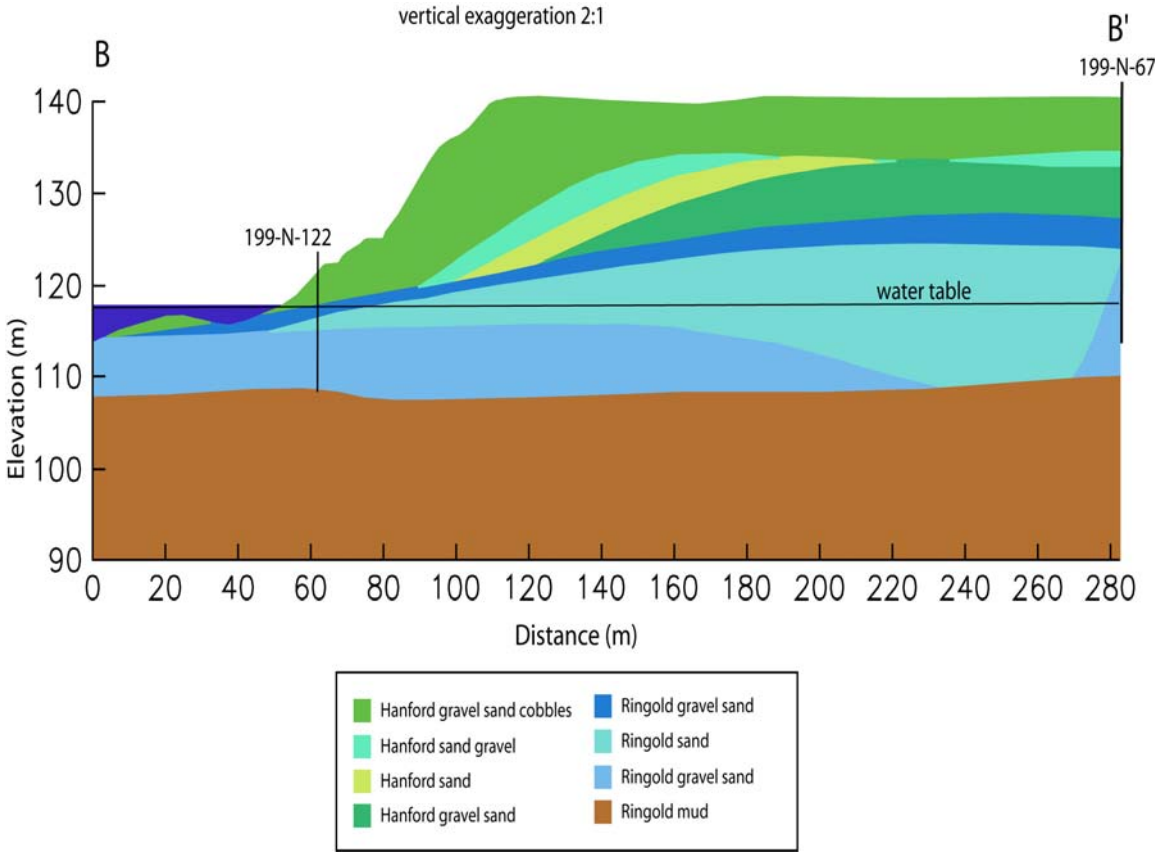


FIGURE 4-5
A-A' Cross-section
Elevation in NAVD88 Vertical Datum



Prior injection tests conducted at the Hanford site have demonstrated the impact of heterogeneities on the extent, coverage, and shape of the reagent plume formed. A limited number of simulations will be conducted with heterogeneous hydraulic conductivity distributions to investigate the potential impact on the plume formation and drift. While site-specific data on heterogeneities at the proposed pilot-scale site may not be available, data collected at the other sites at Hanford will be used to generate stochastic realizations for the Hanford and Ringold units (e.g., EBF data collected in the Ringold formation E Gravels at 100-D Area ISRM site). A conservative tracer test conducted at the site will provide the best information on the impact of heterogeneities on the plume formation and drift.

4.3.3 Tracer Simulations

Preliminary simulations were conducted using a two-dimensional cross-section model along the transect shown in Figure 4-5, to help understand the amount of plume drift that could be expected during different periods of the year near the river at 100-N Area. These simulations are similar to those developed by Connelly et al. (1997; 1999; 2001) and used the same material properties, however the geology and topography were updated based on field work conducted in FY05 (i.e., topographic survey and additional wells installed). Tracer pulses were created at midnight during high and low river stage periods in 1995. The tracer pulses were created by specifying a solute source over the Hanford and Ringold formations to create a unit concentration for an approximately 5-meter (16-foot) width. The

initial tracer plumes were created near the center of the road in the cross-section between well N-46 and the Columbia River. These tracer pulses were created almost instantaneously and were not simulating well injection (e.g., no fluid sources). Following the tracer pulse release, simulation results were output hourly and daily for 10 days to illustrate the plume drift with the ambient groundwater flow as it fluctuates with river stage.

Figure 4-3 shows the calculated monthly averages of the 100-N Area river stage for the years 1994 through 2004. Typically, the highest monthly average is during the spring, with the lowest in September. 1995 was not a typical year since the December monthly average river stage was slightly greater than the June average stage.

Figures 4-6 and 4-7 show the results of a tracer pulse in the Hanford and Ringold formations during the highest (late June) river stage period in 1995 (Figure 4-6). The resulting movement of the tracer plume over this 10-day drift is shown in Figure 4-7. Simulation results show the tracer moved a significant distance away from the river in the Hanford formation during this period with relatively little movement in the Ringold formation. Animations of the plume movement in the Hanford formation showed that the daily changes in river stage had a large impact on the drift, with plumes moving toward and then away from the river as the river stage shifted. It is important to note that the river stage was relatively low for a few days prior to this tracer pulse (see Figure 4-6), which would yield steep hydraulic gradients initially. These simulations also show some tracer in the vadose zone above the water table due to simulated fluctuations of the water table. While the tracer concentrations may remain high in the soil moisture within the vadose zone, the overall tracer mass in the zone would be low due to the low moisture content.

Figures 4-8 and 4-9 show the results of a tracer pulse in the Hanford and Ringold formations during the lowest (early September) river stage period in 1995. The timing of this tracer pulse occurred after a long period of much greater river stages at the end of August (Figure 4-8). At the beginning of this period, there was a thin layer of saturated Hanford formation, but by the end of this period the water table had dropped into the Ringold formation (Figure 4-9). As the water table lowered, there was substantial movement of the tracer toward the river in the Ringold formation due to the steeper hydraulic gradients in that formation. During the high river stage period (Figure 4-7), not much movement was seen in the Ringold formation since the water table was mostly in the much more permeable Hanford formation during that pulse.

While these simulations demonstrate the dynamic nature of plumes near the river at the 100-N Area, a number of limitations and assumptions in this model could still be under-predicting the extent of spread and variability in the plume geometry expected in the field. These factors include heterogeneities (the model assumes homogeneous Hanford and Ringold formations), density effects, and field-scale porosity (site-specific values are needed and may be lower than the values used in the model). Actual tracer tests conducted at the proposed test site would help in further understanding the plume behavior. The general river stage during the creation and reaction period of the plume is important in determining vertically where the treatment zone will be created (e.g., generally high river stage is needed to treat the zone above the average water table). Additionally, these simulations show the importance of the relative daily changes in river stage over the reaction period of a plume on the direction, extent, and distribution of reagent.

FIGURE 4-6
100-N Area River Stage for the First Half of 1995 Showing Timing of 10-day High River Stage Tracer Pulse (see Figure 4-7). Bottom Plot Shows Detailed View.

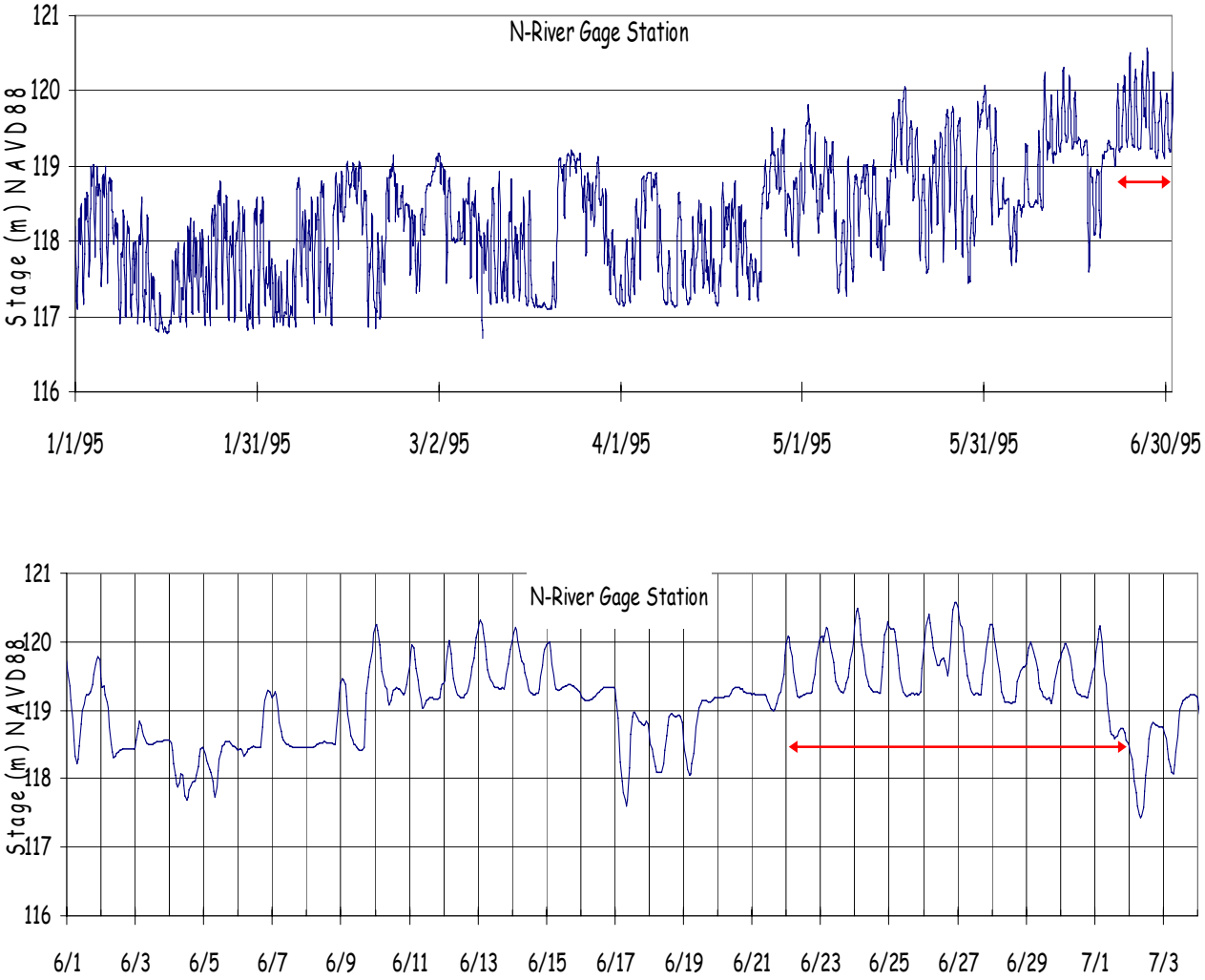


FIGURE 4-7
Simulated Tracer Concentrations in Hanford and Ringold Formations during a High River Stage Period (June 22 To July 1, 1995 – see Figure 5.6 For River Stage During This Period).
View along cross-section centered on road. Results are shown at the start of pulse, 1 day after pulse, 5 days after pulse, and 10 days after pulse. Black line shows the water table. Green line shows the Hanford/Ringold contact. Elevations are NAVD 1988 Datum.

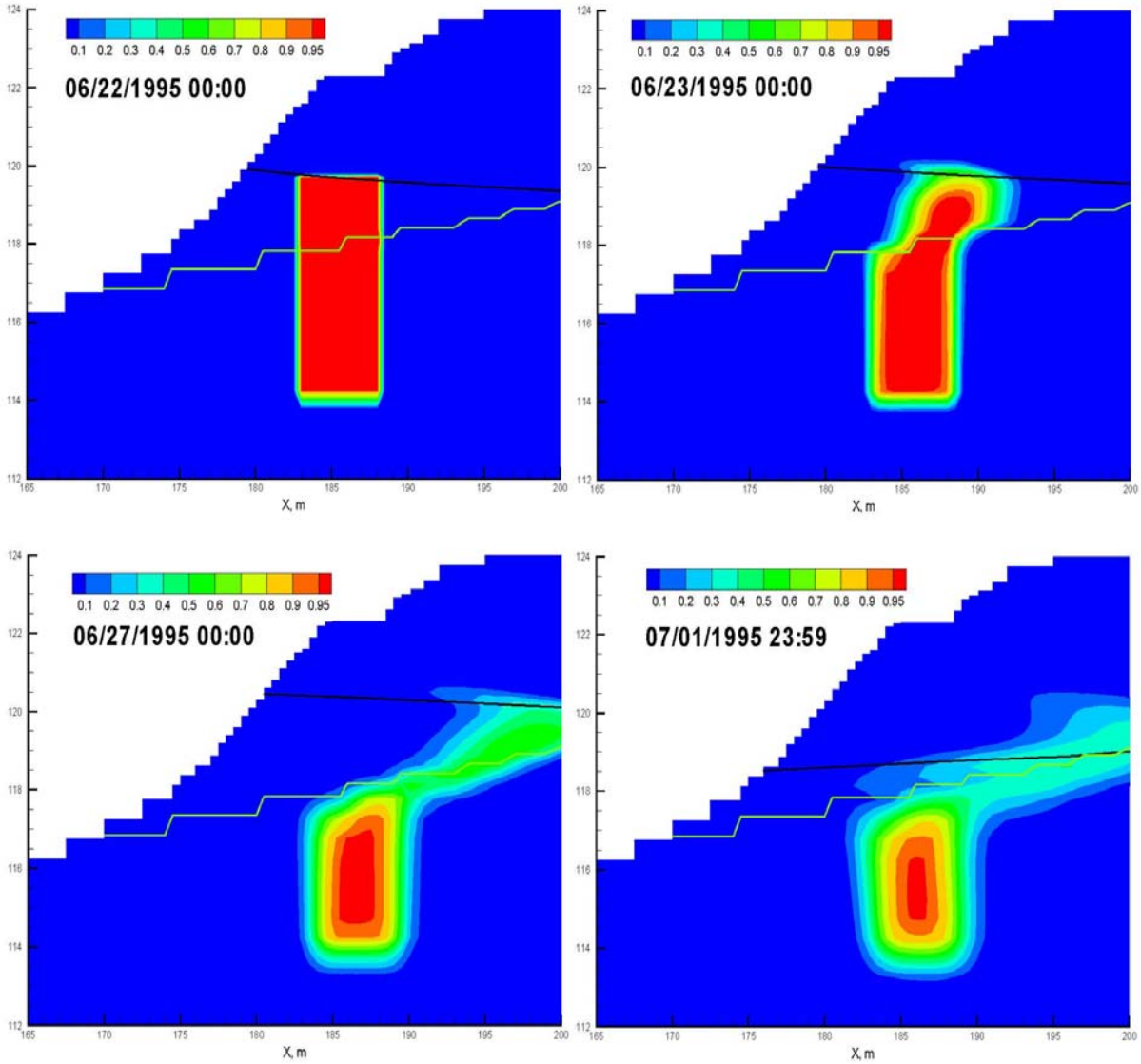
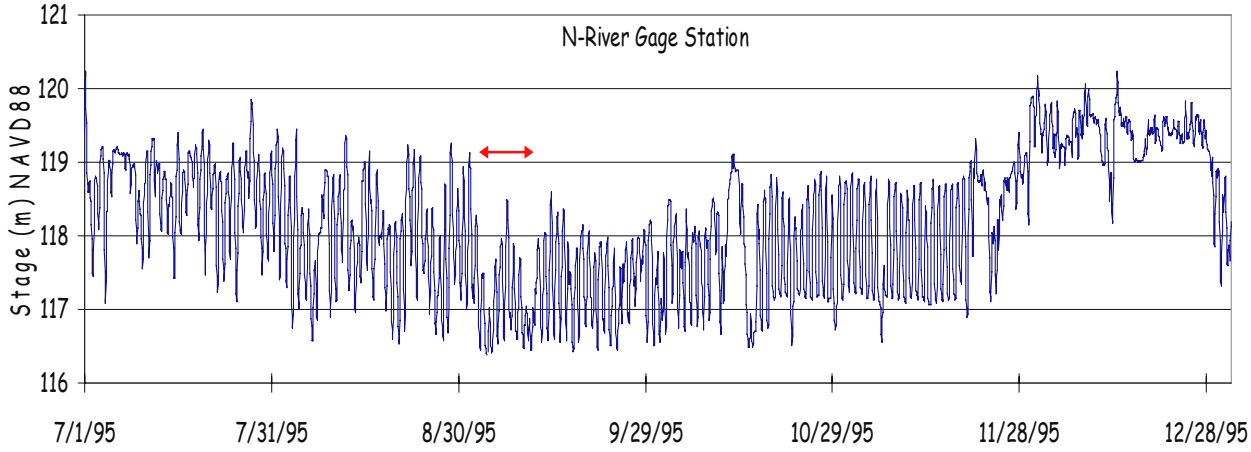


FIGURE 4-8
100-N Area River Stage for the Second Half of 1995 Showing Timing of 10-Day Low River Stage Tracer Pulse (see Figure 4.9). Bottom Plot Shows Detailed View.



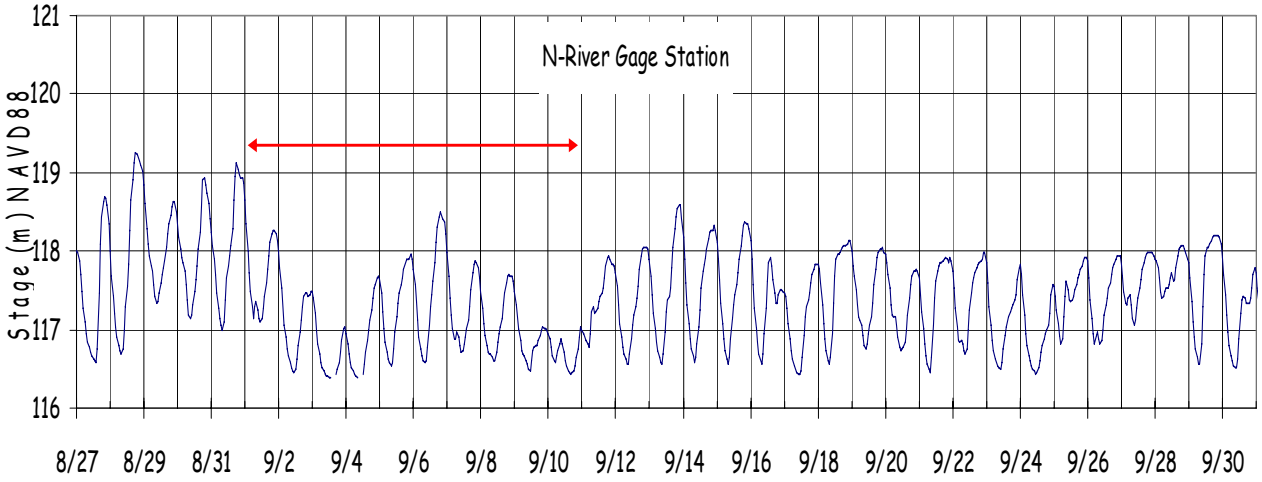
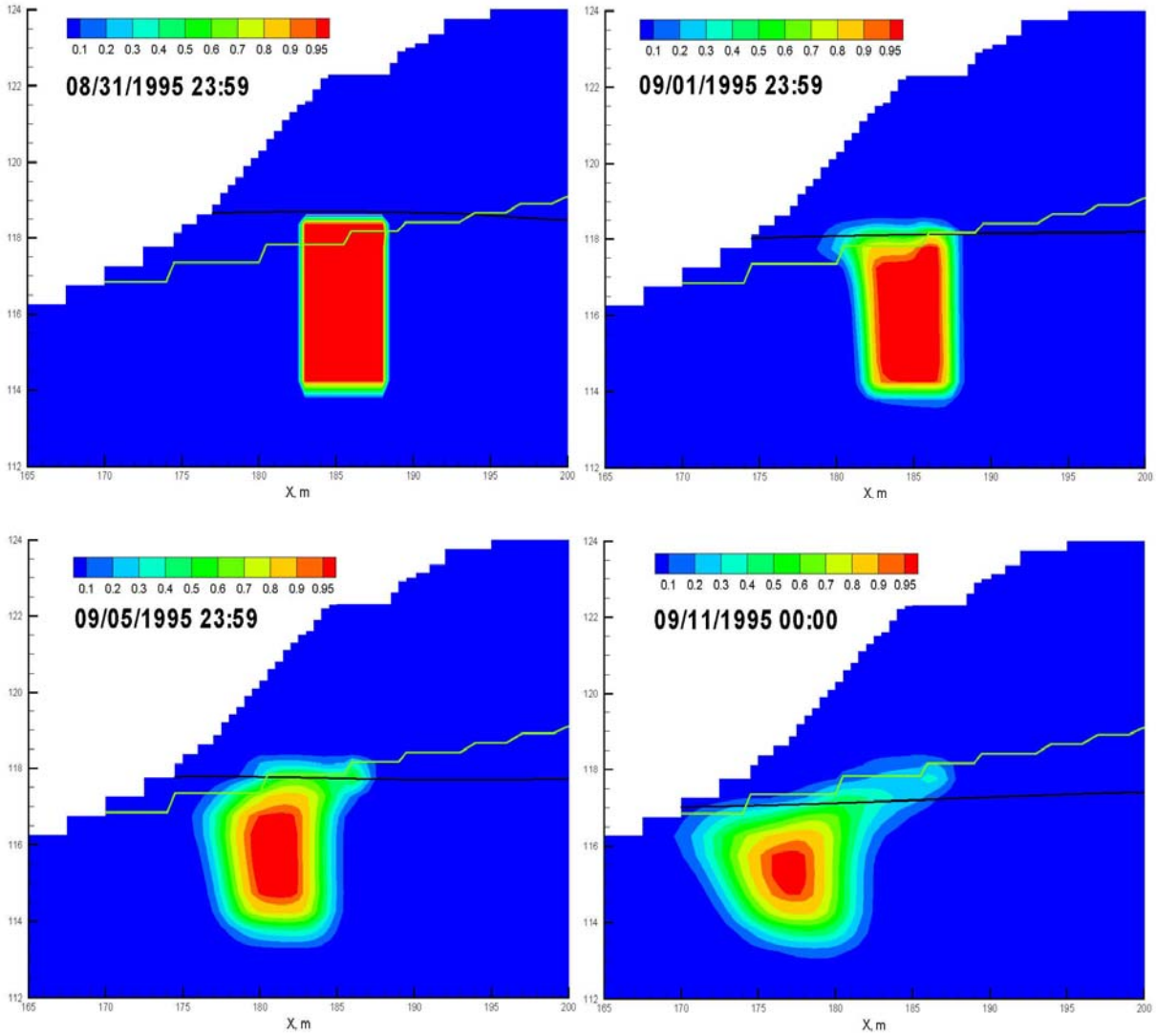


FIGURE 4-9
Simulated Tracer Concentrations During a Low River Stage Period (September 1 to September 10, 1995 – see Figure 5.8 for River Stage During This Period).
View along cross-section centered on road. Results are shown at the start of pulse, 1 day after pulse, 5 days after pulse, and 10 days after pulse. Black line shows the water table. Green line shows the Hanford/Ringold contact. Elevations are NAVD 1988 Datum.



4.4 Field Test Specifications

This section provides the basis, specifications, and responsibilities for preparation of supporting work plans and documents to implement the planned testing activities. A general schedule of major activities is included in Section 5.

4.4.1 Field Test Location

The pilot test injection well, and the injection wells for the 300-foot barrier, will be located within the section of the shoreline where the highest ^{90}Sr concentrations have been observed in clam tissue and aquifer tubes (see photo, Figure 4-10). Based on the characterization data discussed in Section 4-2, a pilot test site will be conducted within the planned barrier location. The site will be located within the reach showing elevated ^{90}Sr concentrations but may not necessarily be located at the location of maximum observed concentration.

Access to the 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 15 feet. It is assumed that no modification will be needed to permit truck and equipment access to the construction area. PNNL will perform the initial pilot test of the technology with field site logistical support (i.e., electrical service or generators, waste handling, site access, etc.) provided by Fluor/Hanford. Upon successful completion of the pilot test and subsequent development of the PRB emplacement design, PNNL will transfer the technology to Fluor/Hanford for full-scale deployment. Injection equipment and field support trailers from the 100-D Area ISRM site will be used to conduct the injections for emplacement of the 300-foot barrier.

Following are the site-selection criteria that were used to select the proposed site. These same criteria will be used to guide selection of the final pilot test site location.

- **High ^{90}Sr Contamination –** The site location was chosen because it was identified as the area of greatest ^{90}Sr contamination along the river at the 100-N Area, as discussed in Section 1.
- **Test Site Accessibility –** The site location is accessible by the heavy equipment needed to install the PRB and monitoring wells, allowing sufficient space for material delivery and staging upstream of the proposed barrier wall.
- **No Disturbance, or Minimal Disturbance, of Culturally Sensitive Areas –** The site location is in a previously disturbed area along the Columbia River shore, and natural bank and floodplain areas will be minimally disturbed. No known cultural resource sites should be affected.
- **Adjacent to Existing Monitoring Wells –** Locating the pilot test injection point in immediate proximity to existing monitoring wells, and or aquifer tubes, provides the potential to reduce cost and/or provide more testing data. It is possible that an existing well can be used to replace one of the new test wells in the scope of this test, or can be used to collect additional data to supplement that gathered from new monitoring wells. Installation will be located to minimize potential impact to existing wells or monitoring wells.

FIGURE 4-10

- **Sufficient Area for Construction –** There is sufficient area at the selected site to accommodate the following:
  - Minimize risk of exposure to workers and environment (e.g., sufficient area for the establishment of a controlled contaminated area to allow for the safe loading and transport associated with the construction),
  - Provide for development of a safe construction zone throughout the entire area required for PRB and monitoring well installation and access for construction equipment,
  - Sufficient area for staging of equipment and materials, and
  - Retain ability to use access road after injection well installations

4.4.2 Test Well Specifications

Well locations and design specifications will be developed based on site-specific characterization data and results from the design analysis discussed previously. As dictated by cost and technical requirement, injection wells will be constructed using either 4-inch- or 6-inch-diameter casing and screen and monitoring wells will be constructed using either 1-inch, 2-inch, or 4-inch-diameter casing and screen. It is anticipated that the pilot test will require one injection well and five monitoring well pairs (Hanford and Ringold completions). In addition, nine additional injection wells will be required to emplace the remainder of the 300-foot PRB. Up to four additional operational monitoring wells will be installed at intervals along the barrier to provide a measure of the consistency in emplacement operations along the full length of the barrier.

4.4.3 Field Test Performance Assessment

The pilot test will be considered successful if post-emplacement performance assessment testing indicates favorable results described as follows. After an approximately 3-week residence period (i.e., approximately 1 week for formation of amorphous apatite and another 2 or more weeks for conversion to the crystalline form), a volume of water three times the injected volume will be extracted. The extraction rate will be based on results from the design analysis and will be selected to remove the desired volume of groundwater in as short a time as possible without exceeding ^{90}Sr adsorption kinetics. ^{90}Sr concentrations and associated chemical parameters (e.g., major anions and cations, EC, pH, temperature) will be measured in the purged water. If ^{90}Sr concentrations in purge water are reduced by tenfold, the proof of principle will be demonstrated. After consultation and agreement between DOE and Ecology, a decision will be made to proceed with the next phase of the testing. Results from the pilot test will be used to prepare a final deployment field installation plan to complete the Treatability Test.

The 300-foot low concentration PRB test will be considered successful if the following parameters are met:

- ^{90}Sr is removed from groundwater in the treatment zone (i.e., > 90 percent reduction in ^{90}Sr concentrations in water samples withdrawn from pilot test and performance monitoring wells and/or injection wells)

- Damage control measures will include the following:
  - Protective berms and runoff controls will be field located as necessary to prevent sediment transport to the Columbia River.
  - An area will be demarcated specifically for the temporary storage of contaminated soil and groundwater.
  - A lined decontamination (decon) pad will be constructed to permit containment of contaminated material removed from equipment.
  - Impacts from injected reagents on Columbia River water quality will be evaluated and provided to DOE and Ecology for their concurrence to proceed.

High concentration injections, to establish sufficient apatite for long-term treatment, will be conducted in 2007 or 2008. Core sampling and associated laboratory testing will be conducted after the final injections to assess the mass distribution of in situ apatite and to evaluate barrier longevity (an addendum to this TTP will be issued for the high-concentration injection phase).

4.4.4 Responsibilities

PNNL will be responsible for treatment design and field implementation of the pilot test; Fluor Hanford is responsible for full-scale implementation of the 300-foot apatite PRB.

General field test tasks include:

1. Test Design—PNNL
   - Spec and locate injection well and monitoring wells
   - Tracer solution, volume and injection rate
   - Tracer test sampling plan
   - Evaluate tracer test results
   - Pilot test injection volume, concentration, timing
   - Pilot test sampling plan
   - Evaluate pilot test results
2. Mobilization and Demobilization – Fluor/Hanford
   - Confirm suitability of the access ramp and road
   - Utility check and provide electrical service/generator(s) and fueling for site operations
   - Mobilization and demobilization of equipment, vehicles, and personnel to the Hanford site test location
   - Setup and preparation before the construction of the PRB
3. Well Construction - Fluor/Hanford
   - Assume a single injection well and up to 10 monitoring wells for pilot well test and nine additional injection wells for up to a 300-foot barrier.

- Well logs, reporting

4. Implement pilot test plan - PNNL
   - tracer study
   - Pilot well test.
5. Implement barrier installation plan - F/H
   - 300-foot barrier
6. Waste Management – F/H
   - Storage and disposal of contaminated soil cuttings, purge water, and decon fluids
   - Disposal of personal protective equipment (PPE), unused apatite, trash, etc.

Detailed field instructions will be prepared for the pilot test and for the 300-foot barrier installation prior to execution of the planned work. Information from the pilot test will be needed finalize the 300-foot barrier work plan.

SECTION 5

Implementation Schedule

A general schedule for conducting the pilot test and installation of up to a 300-foot (91-meter) barrier is shown in Figure 5-1. Contingencies, schedule constraints, and associated activities are discussed as follows by major activity shown in Figure 5-1.

5.1 Treatability Test Plan

The work described in this document, the treatability test plan (TTP), will be conducted through issuance of various field instructions and related work plans. The primary document, the TTP, will be issued first as a comment draft and in final form in February 2006.

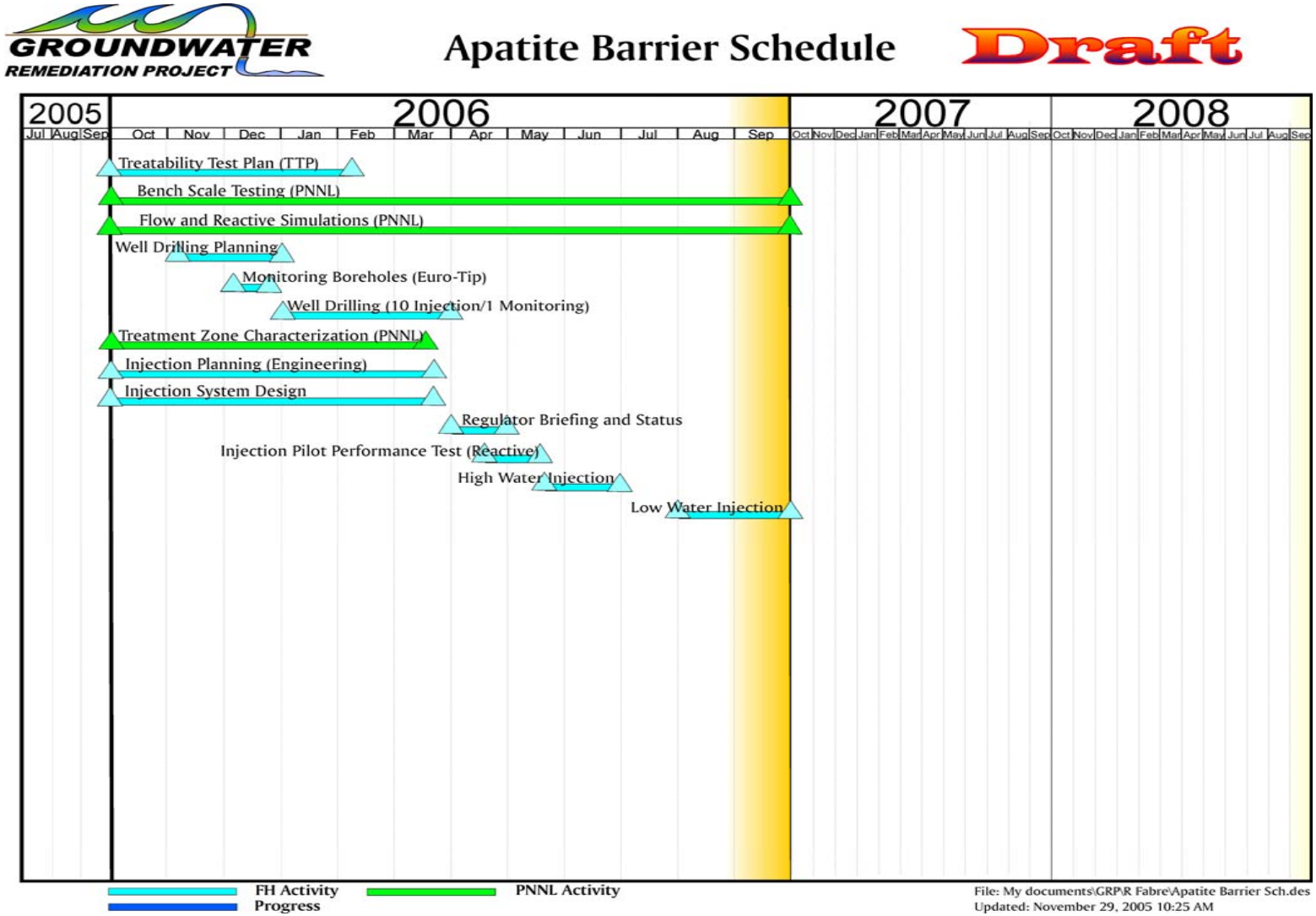
5.2 Bench Testing

This activity will continue throughout the year to support the planned work in FY2006 and to support out year planning. The primary products of this work are: 1) the final injection solution composition for both the pilot test and the barrier; and 2) chemical and microbial reaction rates and processes from which the injection design will be established. Most of the information from this activity will be provided by PNNL prior to the pilot injection test in April/May as shown in Figure 5-1.

5.3 Flow and Reactive Transport Simulations

Modeling results will be used to design the pilot and barrier injection systems. Input parameters needed include results from the treatment zone characterization activity (Figure 5-1) as described below. Results must be available in time to finalize the injection protocol for the pilot test in April/May and for initial injection system design. Pilot injection test results in turn will be used to update flow and transport simulations and to finalize the system design for the 300-foot barrier injections. There is a very narrow window between the end of the pilot test period and the high water injection phase for the 300-foot barrier. Thus, all analytical work and simulations must be completed within approximately 3 to 6 weeks following the pilot test. The amount of time available for interpreting the pilot test operational monitoring data and evaluating treatment zone performance will depend on the nature of the 2006 water year and its effect on dam operations. If it is anticipated that less than 4 weeks will be available between the pilot test and required start date for the 300-foot barrier emplacement, performance assessment of the pilot treatment zone will not be completed prior to proceeding with the installation. Tracer measurements will be conducted in the field so that information will be available on a real-time basis. ^{90}Sr results for pilot test monitoring wells are needed to determine if the treatment reduces ^{90}Sr in aquifer porewater under the conditions of the test. Following the reactive (chemical) pilot injection test, a 3 to 4 week incubation period is needed for the apatite-forming reactions to occur. Thus,

FIGURE 5-1
Apatite Barrier Schedule

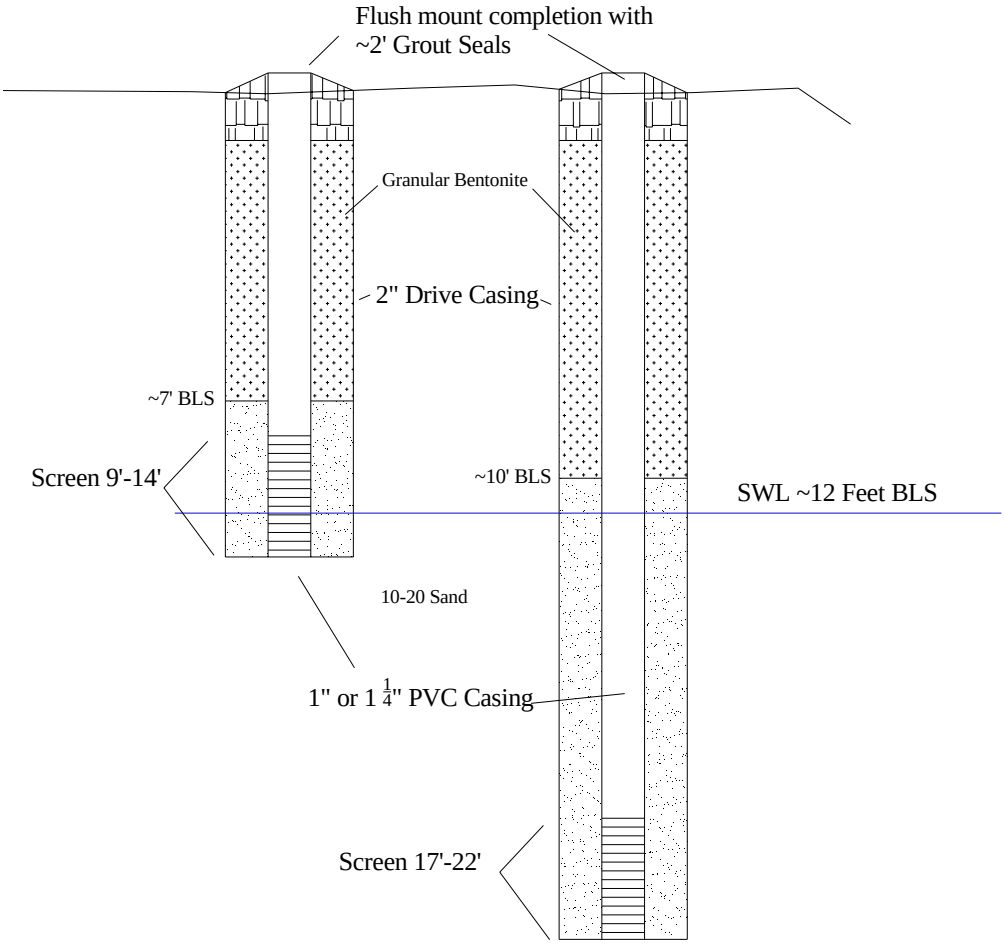


samples taken at the end of that period must be analyzed by quick turnaround methods. Liquid scintillation (LSC) counting will be used for this purpose, which will provide –1- to 2-day turnaround times.

5.4 Well Drilling

1. Up to 10 small-diameter pilot test monitoring wells will be drilled during December or January using direct-push methods. A schematic of the completion design is presented in Figure 5-2. The staked array for the injection well and surrounding monitoring wells (five locations with completion in the Hanford and Ringold at each of five monitoring positions) is shown Figure 5-3. A new, more cost-efficient method will be tested (Eurotip) to drill these wells. If the new method does not work, standard methods will be used.

FIGURE 5-2
Proposed Small-Diameter Well Completion Design for Pilot Test Wells



2. Ten 6-inch-diameter injection wells will be drilled between January and March 2006. A fixed spacing of 30 feet (9 meters) was chosen as the nominal well spacing design with injection volume acting as a design variable to ensure coverage between the fixed well spacing (the injection volume will be established from the pilot injection test). This approach was chosen so that advantage could be taken of high water conditions in 2006. Otherwise, it would be necessary to wait until the next high water period in 2007 for full deployment of a 300-foot barrier. The injection well completion may need to be designed so that the deeper portion of the contaminated aquifer (Ringold formation) can be injected separately from the more permeable Hanford formation.

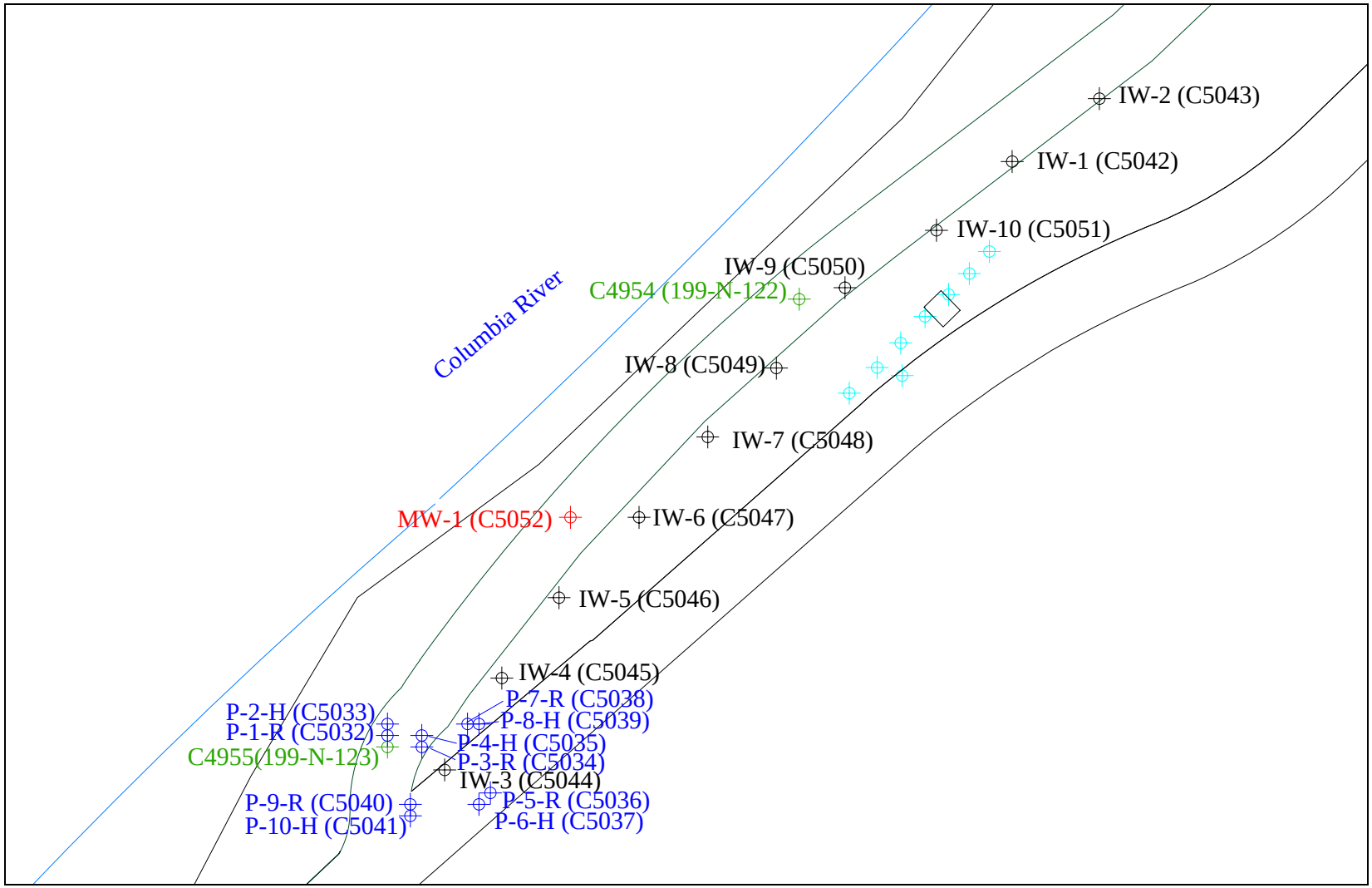
3. An additional performance monitoring well (located between the two new wells N-122 and N-123), will be drilled as part of the 11 well drilling campaign shown on the schedule. Figure 5-3 shows the staked locations for the 11 new wells (10 injection wells and one new monitoring well) to be drilled in the planned January to March time period. All well drilling should be completed prior to the pilot injection test (February through April time period, depending on river stage). However, the pilot injection well (IW-3, Figure 5-3) will be drilled first to ensure it is ready in time for the pilot test in the event high water occurs earlier than expected or if adequate high water conditions occur to conduct the test earlier. If, for some reason, drilling at the other injection well locations extends into the pilot test period, an existing alternate access route must be used to avoid interferences between the two activities.

5.5 Treatment Zone Characterization

Two new wells were drilled in September 2005 (wells N-122 and N-123) to provide information for determining the vertical interval for initial treatment. Information from these wells has reduced the uncertainty concerning the depth to the Hanford/Ringold contact and the vertical distribution of ^{90}Sr in the proposed target area where clam tissue data indicate the highest impact. The completed wells will also serve as part of the performance monitoring well network for the 300-foot barrier. Because of the large difference in aquifer permeability, the Hanford formation will likely need to be injected separately from the Ringold. To assess the magnitude of the difference in permeability, a vertical velocity profile/flow meter test will be conducted in these wells as soon as the water level is high enough to reach into the Hanford formation (December through February time frame). Both lithologic and hydraulic characterization data from these two wells are critical for determining optimum drill depths, screen placement, and injection volumes. The characterization information must be available for the pilot injection test design as well as for the final barrier design (i.e., final design requirements for drilling contract bid package).

Chemical conditions in the test zone aquifer will also be characterized during the flow testing and/or as part of the baseline monitoring well network sampling. Well water will be analyzed for redox parameters, dissolved oxygen, dissolved iron, and total petroleum hydrocarbons (TPH) to determine if diesel and its reaction products, which originate from a diesel spill that occurred upstream of the site, have impacted the proposed location of the NR-2 apatite barrier treatability test. This information is needed at the earliest date possible

FIGURE 5-3
Staked Well Locations and Temporary Identification Numbers for the Pilot Test Small-Diameter Wells (P Series) and 6-inch-Diameter Injection Wells (IW Series). The P wells have an H and R designation for completion in the Hanford Formation pr Ringold Formation, respectively. Design of the P wells is shown in Figure 5-2.



to ensure there are no delays related to hydrochemical conditions (e.g., high dissolved iron that could compete with ^{90}Sr for fixation by the apatite).

5.6 Pilot Injection Test

The pilot injection test will consist of both a non-reactive tracer test and a reactive test. The tests will be conducted as early as high water conditions are available to ensure an adequate part of the Hanford formation is saturated. This could occur as early as February or as late as April, depending on the 2006 water year and the resulting impacts on drainage basin/river conditions.

The non-reactive tracer test will involve injection of a bromide solution and monitoring the arrival at the small-diameter monitoring wells located at distances of 3, 4, and 7 meters (10, 15, and 20 feet) from the injection well (see Figures 4-1 and 5-3). This information will be used to establish the volume of reagent solution needed to cover a nominal 20-foot (6-meter) radius from the injection well. With 30-foot (9 meter) spacing between injection wells, a 20-foot nominal injection radius provides adequate overlap for continuous coverage between wells. The reactive test will be conducted using the proposed solution matrix for the full 300-foot barrier. The injection volume for the reactive test will be based on the bromide tracer test result. Chemical parameters (e.g., conductance, phosphate, and citrate) will be monitored during the injection phase and periodically during a 3-week post-injection observation period. Reduction in citrate relative to the conductivity will be an indication of microbial degradation of the citrate and indirect evidence that apatite is forming. ^{90}Sr will be analyzed in water samples collected after indication of citrate breakdown. Quick turnaround analytical methods will be used for ^{90}Sr (gross beta by LSC) as previously indicated to minimize delay between sample collection and information needed for decision making purposes.

Following the pilot test, finalization of the design parameters, and evaluation of the initial performance of the apatite; a decision to proceed with injection of the other nine injection wells must be made in time to conduct the planned chemical injections (high water) in the June through July time frame. This will require close coordination among DOE, Ecology, and contractor decision-makers. Regulator briefing and status meetings (Figure 5-1) will be held for this purpose.

5.6.1 Injection Planning and Injection System Design (Engineering)

Procurement of chemicals and associated materials for injection of the pilot test and the 10 wells for the 300-foot barrier must be completed in time to be available for the pilot test and injections to occur during the high water period (usually occurs in June). Prior arrangements will be made with a vendor for chemicals, mixing, and transport from a Tri-Cities area location. This will facilitate transport of the large volumes of dilute chemical solutions that will be needed for the full 300-foot barrier. Once the injections start, they must be done continuously so that all 10 wells are injected within a 2 to 3 week time period during relatively constant high water conditions. This constraint mandates that the wells be drilled in advance of the window of time for optimum injections. Thus, as previously indicated, the injection well spacing was chosen as 30 feet to accommodate this constraint. This means that injection volume must be adjusted to ensure overlap of injected solution

occurs between injection wells. As previously noted, the volume and rate of injection will be specified based on the modeling and pilot test results. Thus the engineering design and planning for the 300-foot barrier injections must be flexible in order to accommodate changes in injection protocol (e.g., volumes and rates of delivery).

5.6.2 Barrier Injections (High and Low Water Periods)

Injections for the 300-foot barrier must occur within the high water period in order to ensure that as much of the vadose zone is treated as possible. The ideal time period would be to inject just before high water begins to subside so that as much of the injected chemical is carried toward the shoreline as possible. Careful attention to regional weather conditions (snow pack, warming trends, etc.) and river flows will be necessary to pick the optimum time to begin the injections.

If required, a low water injection will be conducted to address the deeper contamination in the Ringold formation. Lowest water usually occurs in September. Because of the lower permeability of the Ringold formation, the injection rates will likely be slower than for the high water injections. Information from the treatment zone characterization activity, pilot test, and ISRM experience with injections in the Ringold formation will be used to design the injection protocol for both the low and high water stage treatments.

SECTION 6

References

Bechtel Hanford, Inc. (BHI). 1995. *Technical Reevaluation of the N-Springs Barrier Wall*. BHI-00185, Rev. 0, Bechtel Hanford, Inc. Richland, Washington.

Connelly, M. P. 2001. *Strontium-90 Transport in the Near River Environment at the 100-N Area*, (unpublished white paper for The Innovative Treatment and Remediation Demonstration Program), Rev. 0, HydroGeoLogic, Inc, Herndon, VA.

Connelly, M. P. 1999. *Groundwater-River Interaction in the Near River Environment at the 100-N Area*, (unpublished white paper for The Innovative Treatment and Remediation Demonstration Program), Rev. 0, HydroGeoLogic, Inc, Herndon, VA.

Connelly, M. P., C.R. Cole, and M.D. Williams. 1997. *Bank Storage Modeling at the 100-N Area*, (unpublished white paper for Pacific Northwest National Laboratory), Rev. 0, CH2Mhill Hanford Company, Richland, Washington.

Crannel, B.S. 2005. Environmental Research Group, University of New Hampshire, personal communication, April 8, 2005.

Department of Energy, Richland (DOE-RL). 1994. *Limited Field Investigation Report for the 100-NR-2 Operable Unit*, DOE/RL-93-81, US Department of Energy, Richland Operations Office, Richland, Washington.

DOE-RL. 1997. *Corrective Measures Study for the 100-NR-1 and 100-NR-2 Operable Units*, DOE/RL-95-111, US Department of Energy, Richland Operations Office, Richland, Washington. July 1997.

DOE-RL. 1998. *Proposed Plan for Interim Remedial Action at the 100-NR-1 Source Sites Operable Unit and the 100-NR-2 Groundwater Operable Unit*, DOE/RL-102, US Department of Energy, Richland Operations Office, Richland, Washington. March 1998.

DOE-RL. 2004. Calendar Year 2003 Annual Summary Report for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Unit (OU) Pump & Treat Operations. DOE/RL-2004-21, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE-RL, 2005. *Aquatic and Riparian Receptor Impact Information for the 100-NR-2 Groundwater Operable Unit*. (http://www.washingtonclosure.com/projects/endstate/risk_library.html#narea).

Ecology, 1999. Interim Remedial Action Record of Decision for the 100-NR-1 and 100-NR-2 Operable Units of the Hanford 100-N Area, Washington State Department of Ecology, Olympia. Washington.

Elliot, J.C., P.E. Mackie and R.A. Young (1973) Monoclinic hydroxyapatite, Science, vol 180, 1055-1057Ewing, R.C. (2001) The design and evaluation of nuclear waste forms: clues from mineralogy, Can Mineral, vol 39, 697-715. Fluor/CH2M HILL. 2004. Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2

Groundwater Operable Unit. Letter Report. (http://www.washingtonclosure.com/projects/endstate/risk_library.html#narea).

Geochem Software, Inc. 1994. Mac MINTEQ-A2: Aqueous Geochemistry for the Macintosh. Published by Geochem Software, Inc. Reston, VA.

Hughes, J.M. and J. Rakovan (2002) The crystal structure of apatite, Ca5(PO4)3(F,OH,Cl) in Phosphates: Geochemical, Geobiological and Materials Importance, Reviews in Mineralogy and Geochemistry, vol 48, Mineralogical Society of America, Washington, DC, p. 1-12.
Hydrogeologic, Inc. 1999. Groundwater-River Interaction in the Near River Environment at the 100-N Area, Rev. 0, Hydrogeologic, Inc. Herndon, Virginia.

Hydrogeologic, Inc. 2001. Strontium-90 Transport in the Near River Environment at the 100-N Area. Rev. 0. Hydrogeologic, Inc., Herndon, Virginia. November 2001.

Lower, S. K., P.A. Maurice, S. J. Traina, and E.H. Carlson. 1998. "Aqueous lead sorption by hydroxylapatite: Applications of atomic force microscopy to dissolution, nucleation and growth studies." American Mineralogist. 83: 147-158.

Ma, Q.Y., S.J. Traina, and T.J. Logan. 1995. "In Situ Lead Immobilization by Apatite." Env. Sci. Tech. 27: 1803-1810.

Moore, Robert C., Charles Sanchez, Kathleen Holt, Pengchu Zhang, Huifang Xu, and Gregory R. Choppin. 2004. Formation of hydroxyapatite in soils using calcium citrate and sodium phosphate for control of strontium migration. Radiochimica Acta. Vol. 92, Issue 9-11/2004, pages 719-723.

Nichols, W.E., N.J. Aimo, M. Oostrom, and M.D. White. 1997. STOMP Subsurface Transport Over Multiple Phases: Application Guide PNNL-11216 (UC-2010), Pacific Northwest National Laboratory, Richland, Washington.

Nriagu, J.O., and P. B. Moore (Eds.). 1984. Phosphate Minerals. Springer-Verlag, New York.

Pacific Northwest National Laboratory (PNNL). 2000. Strontium-90 at the Hanford Site and its Ecological Implications. May 2000.

Routson, R. C., G. Barney, R. Smith, C. Delegard, and L. Jensen, 1981, Fission product sorption parameters for Hanford 200 area sediment types, RHO-ST-35, Rockwell Hanford Operations, Richland, Washington.TAG. 2001. Hanford 100-N Area Remediation Options Evaluation Summary Report. November 2001.

Verbeek, R. M. H., M. Hauben, H.P. Thun, and F. Verbeek. 1977. "Solubility and Solution Behavior of Strontium hydroxyapatite." Z. Phys. Chem. (Wiesbaden), 108 (2). pp. 203-215.

Waychunas, G. (1989) Luminescence, X-ray emission and new spectroscopies. Rev Mineral, vol 18, 638-698.White, M.D., and M. Oostrom. 2000. STOMP Subsurface Transport Over Multiple Phase: Theory Guide PNNL-11216 (UC-2010), Pacific Northwest National Laboratory, Richland, Washington.

White, M.D., and M. Oostrom. 2003. STOMP Subsurface Transport Over Multiple Phase: User's Guide PNNL-14286 (UC-2010), Pacific Northwest National Laboratory, Richland, Washington.

Wright, J. 1990. "Conodont Apatite: Structure and Geochemistry." In Joseph Carter (Ed.), Biomineralization: Patterns, Processes and Evolutionary Trends, p. 445-459. Van Nostrand Reinhold, New York.

Wright, Judith, Ken R. Rice, Brian Murphy, and James Conca. 2004. "PIMS Using Apatite II™: How It Works To Remediate Soil and Water." In Sustainable Range Management. (Eds.) R.E. Hinchee and B. Alleman. Battelle Press, Columbus, OH. www.batelle.org/bookstore, ISBN 1-57477-144-2, B4-05.