

Remedial Investigation/Feasibility Study for the 100-FR-1, 100-FR-2, 100-FR-3, 100-IU-2, and 100-IU-6 Operable Units

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Appendix I

Technology Screening—Not Retained Technologies

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Terms

bgs	below ground surface
CERCLA	<i>Comprehensive Environmental Response, Compensation, and Liability Act of 1980</i>
CNF	Central Neutralization Facility
COC	contaminant of concern
COPC	contaminant of potential concern
CPS	calcium polysulfide
CY	cubic yard
DO	dissolved oxygen
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
Ecology	State of Washington, Department of Ecology
EPA	U.S. Environmental Protection Agency
ERDF	Environmental Restoration Disposal Facility
ESS	ex situ solidification/stabilization
FS	feasibility study
GCW	groundwater circulating well
HRC™	hydrogen release compound
INEEL	Idaho National Engineering and Environmental Laboratory
ISGR	in situ gaseous reduction
ISRB	in situ reactive barrier
ISRM	in situ redox manipulation
ISV	in situ vitrification
mM	millimoles
MTBE	methyl tert butyl ether
NPDES	National Pollutant Discharge Elimination System
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
OU	operable unit

PCB	polychlorinated biphenyl
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
RO	reverse osmosis
ROI	radius of influence
RPO	Remedial Process Optimization
RUM	Ringold Formation upper mud
SGBR	static granular bed reactor
VSEP	vibratory shear-enhanced processing
WSRC	Westinghouse Savannah River Company
WTP	Waste Treatment and Immobilization Plant
ZVI	zero-valent iron

11 Additional Information on Technologies Not Retained for Waste Site Vadose Zone Soil

This appendix presents additional information regarding technologies that were excluded from further evaluation for treatment of waste sites and contaminated groundwater.

In addition to the technologies described below, disposal through backfilling of treated soil was not retained because this technology is not applicable for the 100-F/IU waste site contaminants of concern (COCs).

11.1 Containment

Containment technologies are used to immobilize or isolate contaminants to prevent direct contact exposure. For 100-F/IU, containment would apply to mobile COCs such as Cr(VI). Containment technologies are also applicable where COC concentrations pose a relatively low long-term threat that can be addressed by isolating this material to prevent exposure until radioactive decay reduces concentrations to protective levels. Containment technologies that were not retained for treatment of soil contaminated with Cr(VI) and radionuclides are discussed in the following subsections.

11.1.1 Subsurface Solidification/Stabilization (Jet Grouting, Soil Freezing) and Barriers (Wire Saw Barriers)

Subsurface barriers were not retained for treatment of soil contaminated with mobile chemical and radionuclide COCs.

11.1.1.1 Description

Solidification/stabilization technologies immobilize contaminants by injecting an agent that transforms the contaminated soil into a dense, low-permeability monolith that resists leaching. Subsurface barriers also limit contaminant mobility by placing or creating a horizontal, low-permeability zone beneath a waste site. These bottom barriers have features similar to those of vertical barriers in that they minimize movement of contaminants, restrict infiltration of groundwater below the barrier, and are constructed primarily of native materials that are altered to lessen the permeability of the host matrix. Subsurface barrier technologies can include (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]):

- **Jet grouting:** Involves injection of Portland cement, organic polymers, or other organic or inorganic self-hardening material or treatment reagents into the soil column.
- **Soil freezing:** Involves placement of cooling media distribution systems into the subsurface to cool and ultimately freeze the soil into a solid mass. Soil freezing relies on soil moisture to form ice that is the primary structural feature of the frozen soil. In arid environments, supplemental soil moisture may be required to form adequate ice.
- **Wire saw barriers:** Uses a diamond wire saw working horizontally in grout slurry-filled border trenches surrounding a waste site. The process uses a grout slurry more dense than the target soil. The excised soil block ultimately floats free from surrounding soil and is surrounded by the grout on the sides and bottom.

11.1.1.2 Relevant Demonstration Projects

Jet grouting is a mature delivery technology that has seen wide-scale application in the construction industry to stabilize the walls of deep excavations. A jet grouting technology pilot test was completed in

2009 at the 100-NR-2 (*Treatability Test Report for Field-Scale Apatite Jet Injection Demonstration for the 100-NR-2 Operable Unit* [SGW-47062]) Operable Unit (OU) to create a permeable reactive barrier (apatite) between the water table (approximate depth of 7.5 m [25 ft]) and ground surface. This test showed that soil amendments could be readily emplaced within Hanford formation materials.

The soil freezing and wire saw barrier technologies are not as mature (RPP-ENV-34028). Several demonstrations for these two technologies have been performed at near-surface depths, but application at depths up to 15 m (50 ft), which corresponds to the maximum depth of Cr(VI) at the 116-F-16 waste site, has not been reported.

11.1.1.3 Evaluation and Screening Rationale

Because of the limited radius of influence (ROI) expected in coarse-grained materials such as the Hanford formation, the distance between injection boreholes for the solidification/stabilization and barrier technologies is expected to be less than 5 m (15 ft), which would result in a large number of boreholes and high implementation cost. In addition, barrier integrity and long-term stability are key uncertainties. Given these uncertainties, field scale pilot testing would be required to assess the effectiveness and implementability of these technologies at the Hanford Site before they could be selected for remedial application. Absent this information, solidification/stabilization and barriers were not retained for further consideration in the feasibility study.

11.1.2 Dynamic Compaction

Dynamic compaction was not retained for treatment of waste sites contaminated with mobile chemical and radionuclide COCs.

11.1.2.1 Description

Dynamic compaction is used to consolidate (increase the density of) soil and buried wastes by closing void spaces through rearrangement of the soil grains, which in turn lessens contaminant mobility by decreasing the permeability of the host matrix. The process involves dropping a weight from a predetermined height onto the area to be compacted.

11.1.2.2 Relevant Demonstration Projects

This technology has seen broad application for civil engineering-type projects (bridge and building foundations), but has not been widely used for remediation.

11.1.2.3 Evaluation and Screening Rationale

The technology is considered to have moderate-to-high effectiveness for fine-grained soil, but its effectiveness for coarse-grained gravel and cobble sized material is expected to be low because this material is not compressible. It is implementable because the equipment and vendors who provide the service are readily available, and it is expected to have a low to moderate cost. Given that there is no site-specific experience with this technology at the Hanford Site and very limited information available on its use for remedial applications, this process option was not retained.

11.2 Ex Situ Treatment and Processing

Following excavation, soil can be treated with ex situ methods to reduce contaminant concentrations or toxicity, remove contaminants (transfer to different media), or reduce volume, which allows for less costly disposal. Ex situ treatment technologies not retained for further consideration are discussed in this section.

For this effort, ex situ treatment does not include treatment performed for ultimate disposal (such as that required by the Environmental Restoration Disposal Facility [ERDF]). Treatment performed as required to meet disposal restrictions is included in the disposal to the onsite landfill process option. This option covers only technologies that could be used to treat the soil so that part or all of the soil volume could be backfilled at the locations from which it was removed.

11.2.1 Solidification/Stabilization

Ex situ solidification/stabilization (ESS) was not retained for treatment of soil contaminated with Cr(VI) or radionuclides.

11.2.1.1 Description

ESS is a treatment process that uses a binding agent to reduce the mobility of contaminants by physically binding or enclosing contaminated soil particles within a stabilized mass (solidification), or via chemical reactions between stabilizing agents and contaminants. ESS can be performed ex situ to meet disposal requirements. Varieties of solidification/stabilization agents are available, including Portland cement, or other pozzolans, silicates, bitumen, and acrylic polymers. Portland cement typically consists of calcium silicates, aluminosilicates, aluminoferrites, and sulfates. Metals are immobilized in cement-type binders as hydroxides or other stable solids. Phosphate or other chemical reagents can also be added to chemically bind metals. Polymeric compounds can be used to bind metals and radionuclides by micro-encapsulation (RPP-ENV-34028).

ESS is targeted at reducing the mobility of contaminants; it does not necessarily treat or detoxify contaminants. Consequently, it is not applicable to contaminants that are a risk to human health or the environment because of the potential for direct exposure in the top 4.5 m (15 ft) of soil. It is applicable only to contaminants that are a risk because of migration to groundwater.

11.2.1.2 Relevant Demonstration Projects

Cement solidification has been a widely used technology for treatment and ultimate disposal of hazardous, low-level, and mixed wastes. A cement solidification/stabilization treatability study was completed at the Fernald Environmental Management Project (*100 Area Source Operable Unit Focused Feasibility Study* [DOE/RL-94-61]). The test was completed at six waste pits, all of which contained radionuclide-impacted waste (primarily uranium). Portland cement (Type I/II) and blast furnace slag were used as binders. Additives included Type F fly ash, site fly ash, absorbents, and sodium silicate. The study indicated that the toxicity characteristic leaching procedure performance criteria was achieved, and leachability of uranium was controlled, except when present at high concentrations. The study also indicated a significant increase in waste volume from the cement stabilization process (DOE/RL-94-61).

The U.S. Department of Energy (DOE) has demonstrated that polyethylene encapsulation can be used to treat a number of radionuclides (e.g., cesium and strontium) and toxic metals (including chromium, lead, and cadmium). DOE's technology information profile (*Technology Catalogue* [DOE/EM-0235]) detailed polyethylene encapsulation to be applicable for stabilization of low-level radioactive and heavy metal waste components that may be in media such as aqueous salt concentrates, salt cake, sludge, fly ash, and ion-exchange resins. Scale-up from bench-scale tests demonstrated the feasibility of this process to treat wastes at approximately 907 kg (2,000 lb) per hour (DOE/EM-0235).

11.2.1.3 Evaluation and Screening Rationale

ESS is considered to have low to moderate effectiveness at immobilizing contaminants in soil that could leach to groundwater. The stabilized mass must be protected from weathering and seismic activity for long-term durability. Although ESS is a well-established technology, site-specific studies would need to

be completed to evaluate equipment requirements and appropriate cement agents. ESS was screened out in favor of disposal at the ERDF, a centralized facility engineered to protect against the effects of weathering and seismic activity.

11.2.2 Soil Washing

Soil washing was not retained for treatment of soil contaminated with Cr(VI) or radionuclides.

11.2.2.1 Description

Under this process option, soil is excavated and physically processed to remove contaminants by dissolving or suspending the contaminants in solution, or by concentrating them through particle size separation, gravity separation, and attrition scrubbing. Additives can be introduced to the water to enhance contaminant removal. The washing agent and soil fines are residuals that require further treatment or disposal. This process is applicable to coarse-grained soil contaminated with a wide variety of metals and radionuclides, particularly those that tend to bind to the fine soil fraction. The cleaned soil can then be used as fill onsite, or disposed of at an onsite or offsite landfill.

A variety of physical processes can be used for soil washing. These range from simple screening to complex grinding or scrubbing, combined with chemical dissolution. Contaminants are generally bound to the fine grained soil particles; therefore, it is sometimes possible to separate the coarse fraction, and it will be clean. However, if the contaminants are strongly sorbed to the surfaces of the coarse particles, simple separation may be ineffective, and more aggressive—and thus expensive—processes are required.

11.2.2.2 Relevant Demonstration Projects

A bench-scale treatability study was completed by Pacific Northwest National Laboratory (PNNL) in 1996 on a plutonium crib soil sample from the 100 Area of the Hanford Site (*100 Area Soil Washing: Bench-Scale Tests on 116-F-4 Pluto Crib Soil* [WHC-SD-EN-TI-268]). The study evaluated physical separation (wet sieving), physical treatment processes (attrition scrubbing and autogenous surface grinding), and chemical extraction methods to separate radioactively- contaminated soil fractions from uncontaminated soil fractions. Particle size distribution data indicated that the evaluated soil was primarily comprised of poorly graded gravel with approximately 17 percent sand and minor amounts of cobbles and silt-clay sized fractions. The effectiveness of soil-washing tests was evaluated on the basis of removal of cesium-137 from the gravel- and sand-size fractions. The study concluded that by using water-based autogenous surface grinding on the gravel media only, approximately 55 percent of media contained residual cesium-137, and could be recovered for reuse as backfill. By treating gravel (using autogenous surface grinding) and sand (using two-stage attrition scrubbing with an electrolyte followed by chemical extraction), 55 percent of the treated gravel fraction and about 11 percent of the treated sand fraction could be recovered for backfill reuse (WHC-SD-EN-TI-268).

A bench-scale treatability study was completed by PNNL in 1994 on two contaminated soil samples from the 100 Area (*100 Area Soil Washing Bench-Scale Tests* [DOE/RL-93-107]). Soil-washing tests were focused on samples from trench 116-C-1 (Batch II) and trench 116-D-1B (Batch III), and effectiveness was gauged on the potential for activity attenuation of cobalt-60, europium-152, and cesium-137. Physical (attrition scrubbing and autogenous grinding) and chemical extraction treatment methods were evaluated. Batch II was composed (97.2 percent) of materials greater than 2 mm (0.8 in.) in size (coarse fraction), and was treated using physical and chemical extraction methods. Results indicated soil washing could adequately reduce levels of cobalt-60 and europium-152; however, cesium-137 concentrations could not be significantly reduced. Batch III was comprised of 46.9 percent coarse-sized material, and results indicated soil-washing tests were effective in reducing radionuclide concentrations in bulk soil to below target performance levels. Results from tests on Batch II showed that the soil from trench 116-D-1B could

be successfully soil-washed by combining wet sieving with either two-stage attrition scrubbing in electrolyte or a single chemical extraction step. The study indicated an anticipated mass reduction of contaminated material for Batch II of approximately 84 to 87 percent.

A treatability study for physical separation methods was conducted at the 300-FF-1 OU in 1994 (*300-FF-1 Operable Unit Remedial Investigation Phase II Report: Physical Separation of Soils Treatability Study* [DOE/RL-93-96]). The objective of the study was to evaluate the use of physical separation systems to concentrate chemical and radiochemical contaminants (uranium-238 and uranium-235) into fine soil fractions to minimize waste volumes (with a target of 90 percent reduction by weight of contaminated soil). Physical separation methods were limited to a water-based technology to separate soil particles by size fraction without the use of chemical processes so that the coarse fraction of soil would meet cleanup levels. Physical separation methods were found to be adequate in reducing the amount of contaminated soil; however, the cost effectiveness of using this approach for soil with concentrations near background levels was questioned. The study also indicated that physical separation processes are not recommended for treating concentrated soil fines.

11.2.2.3 Evaluation and Screening Rationale

The effectiveness of soil washing and the complexity of the required processes are driven by the binding processes that exist between the contaminants and the soil particles (adsorbed or precipitated), and are expected to exhibit a wide range of variability based on the nature and solubility of the COCs.

As discussed in the *Focused Feasibility Study for the BC Cribs and Trenches Area Waste Sites* (DOE/RL-2004-66), the effectiveness of soil washing is limited for many radionuclides. The majority of contaminants appear to be strongly bound to the surfaces of all particle sizes. As a consequence, more aggressive and costly approaches would be required, which may prove ineffective. Given that pilot tests at the Hanford Site have not been highly successful, soil washing was not retained for further consideration.

11.2.3 Ex Situ Vitrification

Ex situ vitrification was not retained for treatment of soil contaminated with Cr(VI) or radionuclides.

11.2.3.1 Description

Vitrification processes are solidification methods that use heat (temperatures of 1,100 to 2,000°C [2,012 to 3,632°F]) to melt and convert waste materials into a glass or a glass and crystalline form. This technology is considered highly effective in the treatment of many COCs (specifically radionuclides), and in permanently reducing contaminant mobility, toxicity, and volume. The high temperatures destroy all organic constituents with very few byproducts. Materials such as heavy metals and radionuclides are incorporated into the glass structure, which is strong, durable, and resistant to leaching. In addition to solids, waste materials can be liquids, wet or dry sludges, or combustible materials. Borosilicate and soda lime are the principal glass formers and provide the basic matrix of the vitrified product. When the molten mass cools, it solidifies into a vitreous and crystalline rock-like monolith that is substantially reduced in volume (20 to 50 percent) (RPP-ENV-34028).

Ex situ, joule heating vitrification uses furnaces that have evolved from the melter units used in the glass industry. The electric furnace uses a ceramic-lined, steel-shelled melter to contain the molten glass and waste material (DOE/RL-94-61).

11.2.3.2 Relevant Demonstration Projects

In the early 1990s, DOE developed a transportable vitrification system to vitrify mixed -waste sludges and solids across the various DOE complex sites (*Transportable Vitrification System: Mixed Waste Focus*

Area [DOE, 1998]). Multiple studies were completed in collaboration with Westinghouse Savannah River Company (WSRC), Oak Ridge National Laboratory (ORNL), and Clemson University. A mixed-waste demonstration project was completed in 1997 using Savannah River B&C pond sludge, a mix of B&C pond sludge, and Central Neutralization Facility (CNF) sludge. The study indicated the system vitrified 84 cubic meters (m³) (276 cubic feet [ft³]) of mixed waste into 34 m³ (112 ft³) of glass waste, resulting in a 60 percent volume reduction. Results of the study indicated the need for high capital costs and extensive upfront development. However, it demonstrated the technology is capable of producing highly durable glass waste forms with long-term integrity and a significant reduction in waste volume compared to other stabilization techniques.

A vitrification plant is currently being constructed to treat tank wastes at the Hanford Site. The Waste Treatment and Immobilization Plant (WTP) will span 65 acres and consist of four nuclear facilities: pretreatment, low-activity waste vitrification, high-level waste vitrification, and an analytical laboratory. Construction activities began in 2002; it is anticipated the plant will be operational in 2019. A number of tests have been performed to support the process and design associated with this facility. Information regarding the WTP Research and Technology Program is presented in *Project Execution Plan for the River Protection Project Waste Treatment and Immobilization Plant* (DOE/ORP-2003-01). However, treatability tests on contaminated soil have not been performed.

11.2.3.3 Evaluation and Screening Rationale

Mobile (skid mounted) ex situ vitrification is considered to have high effectiveness but low implementability given the high complexity of equipment required and safety concerns with implementation, which include maintaining the integrity of the tanks. Similarly, given the relative high cost and potential application of other technologies with high effectiveness and implementability, ex situ vitrification was not considered to be implementable for treatment of contaminated soil at the 100 Area.

As evidenced by the design of the WTP, complex system requirements are inherent to this technology, such as pretreatment to segregate high-level and low-level waste and multiple vitrification systems to support both the treatment requirements of each type of waste and to allow for an accelerated cleanup strategy. After treatment, the resulting glass structures would need to be tested to ensure the glass produced by the facility meets regulatory requirements and standards. Ultimately, the glass produced would still require final disposal at a permanent facility.

As presented in *Central Plateau Vadose Zone Remediation Technology Screening Evaluation* (RPP-ENV-34028), estimated costs for implementation of this technology are high, ranging from \$500 to \$1,000 per cubic yard (CY). These costs include soil excavation, screening to remove debris, installation of the vitrification system and off-gas treatment system, operation and maintenance (O&M), utilities, site management, sampling support, and onsite disposal of vitrified material and off-gas treatment material. As reported in *Project Execution Plan for the River Protection Project Waste Treatment and Immobilization Plant* (DOE/ORP-2003-01), the total project cost for the WTP is estimated at \$5.8 billion.

Because of the complexity of the equipment, safety concerns, and associated high cost, this remedial technology was not retained for further evaluation.

11.3 In Situ Treatment—Reagent Approach

This section discusses reagents and technologies that could be used for in situ treatment of 100-F/IU COCs. Delivery of these reagents is discussed in the following section. These reagents and delivery technologies were not retained for further consideration in the feasibility study (FS).

11.3.1 In Situ Solidification

In situ solidification was not retained for treatment of soils contaminated with Cr(VI) and radionuclides.

11.3.1.1 Description

Solidification alters the physical and/or chemical characteristics of a soil through the addition of binders, including cements and chemical grouts, to immobilize contaminants. The immobilization process works by coating and isolation, processes that make the contaminants less prone to leaching. Multiple types of grouting/binding materials and emplacement techniques have been developed and demonstrated. Jet grouting and permeation grouting are the two delivery approaches potentially applicable for subsurface solidification in Hanford Site vadose zone sediments. Jet grouting uses high-energy emplacement of cement or chemical grout materials whereby the sediment is fluidized and mixed with the grouting material. Permeation grouting is injection of a liquid grout that fills the pore space of the formation and then gels to form a solid material. While permeation grouting is a relatively mature technology for many geotechnical applications, there are uncertainties with using grout materials for in situ solidification of contaminants where site-specific pilot testing has not been performed (*Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99* [WMP-27397]). The uncertainties include the following: (1) the effectiveness of delivery depends upon subsurface heterogeneity, and (2) the presence of fines adversely affects grout placement. Generally, grout is emplaced via an array of closely spaced vertical boreholes into the subsurface volume to be stabilized.

Two types of grout materials may be used: particulate (cement) grouts and chemical grouts. Cement grouts use Portland cement as the primary component. Portland cement is a mixture of preprocessed mineral solids pulverized, fired, and ground into a fine solid dust. This product is combined with up to 5 percent gypsum, and mixed with water and small quantities of additives to form a flowable mixture of solids and water that is a suspended solids grout. A chemical grout is a solution comprised of a binder (other than Portland cement) that reacts in place to form a gel or solid after injection into a porous subsurface soil, sediment, or rock volume. Chemical grouts do not contain mineral solids in suspension, and therefore their delivery in the subsurface is not limited by particle filtration. Instead, delivery is a function of grout viscosity and gelling time.

11.3.1.2 Relevant Demonstration Projects

Several DOE sites, including the Hanford Site, ORNL, Brookhaven National Laboratory, Idaho National Laboratory (INL), Savannah River Site, and Sandia National Laboratories have evaluated, tested, and/or implemented in situ grouting for shallow waste stabilization applications as summarized below.

In situ grouting has been evaluated at the Hanford Site for application to waste site isolation (e.g., near-surface formation of in situ waste barriers) through a number of efforts in the 1990s [e.g., “*Injectable Barriers for Waste Isolation*” (Persoff et al., 1995)]; *Feasibility of Permeation Grouting for Constructing Subsurface Barriers* (SAND94-0786); *Durability of Polymers for Containment Barriers* (Heiser et al., 1994); *Summary Report on Close-Coupled Subsurface Barrier Technology Initial Field Trials to Full-Scale Demonstration* (BNL-52531); and *In Situ Remediation Integrated Program FY 1994 Program Summary* (DOE/RL-95-32)]. These documents provide laboratory and field data for jet grouting techniques applied to shallow waste occurrences at the Hanford Site and Brookhaven National Laboratory.

In situ permeation grouting, using colloidal silica to develop a hydraulic barrier, was evaluated and tested for application at Brookhaven National Laboratory (*Evaluation of Alternative Designs for an Injectable Subsurface Barrier at the Brookhaven National Laboratory Site, Long Island, New York* [Moridis et al., 1999]), that included a significant program effort led by Lawrence Berkeley National Laboratory (LBNL)

(Physical Barriers Formed from Gelling Liquids: 1. Numerical Design of Laboratory and Field Experiments [LBL-35113]); Injectable Barriers for Waste Isolation (LBL-36739); Effect of Dilution and Contaminants on Sand Grouted with Colloidal Silica Gel (Persoff et al., 1999); A Field Test of Permeation Grouting in Heterogeneous Soils Using a New Generation of Barrier Liquids (LBL-37554); A Design Study for a Medium-Scale Field Demonstration of the Viscous Barrier Technology (LBNL-38916); and A Field Test of a Waste Containment Technology Using a New Generation of Injectable Barrier Liquids (LBNL-38817).

Shallow permeation grouting was conducted at ORNL to evaluate hydraulic conductivity reductions in the host-waste matrix (*Field Grouting Summary Report on the WAG 4 Seeps 4 and 6 Removal Action Project [ORNL/ER-401/V1]*). Jet injection of standard and microfine cement grout into waste trench material at ORNL improved soil stability, but did not create low hydraulic conductivity conditions (*In Situ Grouting of Low-Level Burial Trenches with a Cement-Based Grout at Oak Ridge National Laboratory [ORNL/TM-11838]*). Other efforts at ORNL included injection of a polyacrylamide grout into a waste trench that enhanced soil stability and had a moderate (two orders of magnitude) effect on the hydraulic conductivity (*Field Demonstration of In Situ Grouting of Radioactive Solid Waste Burial Trenches with Polyacrylamide [Spalding and Fontaine, 1992]*).

Detailed evaluation and treatability testing for in situ grouting of waste sites was completed at INL, demonstrating the potential viability of grouting to stabilize waste (in situ solidification) in near-surface sites (*Final Results Report, In Situ Grouting Technology for Application in Buried Transuranic Waste Sites Volume 1, Technology Description and Treatability Study Results for Operable Unit 7-13/14 [INEEL/EXT-02-00233]*). The *Feasibility Study for Operable Unit 7-13/14 (DOE/ID-11268)* provided a thorough review of in situ grouting for shallow waste sites at INL. This technology was retained as a potential alternative in an FS for OU 7-13/14 based on the ability of the technology to stabilize the waste and reduce hydraulic conductivity in localized hot spots.

The Savannah River Site has implemented in situ grouting for shallow waste sites such as the F Area seepage basins (*Corrective Measures Implementation/Remedial Design Report/Remedial Action Work Plan (CMI/RDR/RAWP) for the F-Area Seepage Basin (904-49G) (U) [WSRC-RP-97-854]*).

11.3.1.3 Evaluation and Screening Rationale

In situ solidification using commercially available grouting equipment with cement grouts is considered to have low to moderate effectiveness and moderate implementability when applied over smaller areas. Such limited areas may extend over a total area of up to 0.2 ha (0.5 ac) and to depths of 4 to 5 m (13 to 16 ft). However, there is little experience with this process option at large-scale DOE sites. The effectiveness of in situ solidification is a function of the distribution of the grout into the formation, the degree of encapsulation of contaminated sediment particles, and the long-term durability of shallow soil encapsulation when exposed to weathering elements. The effectiveness of grout emplacement depends on the application method. Typical applications would involve 0.6 m (2 ft) diameter grout columns with 0.5 m (2 ft) spacing. Using estimated installation costs for in situ solidification using jet grouting at INEEL (DOE/ID-11268), unit costs in excess of \$1,500 per CY are estimated. Consequently, the relative capital cost is high. Stabilization is typically only used for organics when free phase product is present to reduce mobility. Because of the high capital cost, the potential for incomplete contact of grout in the targeted treatment zone, and uncertainty regarding the durability of shallow soil encapsulation when exposed to weathering elements, in situ solidification was not retained for further evaluation.

11.3.2 In Situ Stabilization/Sequestration

In situ stabilization/sequestration was not retained for treatment of soils containing Cr(VI) and radionuclides.

11.3.2.1 Description

The focus of strontium-90 sequestration studies at the Hanford Site has been on apatite sequestration. 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 (*Structural Variations in Natural F, OH, and Cl Apatites* [Hughes et al., 1989]; *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes* [Spence and Shi, 2005]). Apatite minerals are very stable and have very low water solubility. The substitution of strontium for calcium in the crystal structure is thermodynamically favorable and proceeds, provided the two elements coexist. The mixed strontium - calcium-apatite solid phase has a lower aqueous solubility than calcium-apatite or strontiapatite.

Methods of emplacing apatite in vadose zone soil include injection and infiltration of an aqueous solution containing a calcium-citrate complex and sodium phosphate. Phosphate adsorption is slow (hours) so rapid infiltration can result in greater phosphate mass formation at depth. Citrate is needed to keep calcium in solution long enough (days) to inject into the subsurface. A solution containing divalent calcium and phosphate only will rapidly form mono- and di-calcium phosphate, but not apatite (*Hydroxyapatite Synthesis* [Andronesco et al., 2002]; *Monoclinic Hydroxyapatite* [Elliot et al., 1973]; *Synthetic Routs for Hydroxyapatite Powder Production* [Papargyris et al., 2002]). As calcium citrate is degraded, the free calcium and phosphate combine to form amorphous apatite. The formation of amorphous apatite occurs within a week, and crystalline apatite forms within a few weeks.

11.3.2.2 Relevant Demonstration Projects

A laboratory scale study investigating apatite sequestration of strontium-90 was conducted by PNNL (*Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of a Ca-Citrate-Phosphate Solution* [PNNL-18303]). The results of the study indicate that a calcium citrate-phosphate solution can be infiltrated into vadose zone sediments to form an apatite precipitate for treatment of strontium-90 contaminated material. After 1.3 years of contact, 9 to 16 percent of the strontium-90 had substituted for calcium in the apatite. Strontium-90 substitution in apatite did not decrease with depth because the 20 to 30 nanometer (nm) sized apatite crystals conglomerated, forming a porous 10 to 50 micron precipitate. Microbial redistribution during solution infiltration and a high rate of citrate biodegradation for river water microbes (water used for solution infiltration) resulted in a relatively even spatial distribution of the citrate biodegradation rate and ultimately apatite precipitate.

Overall, the laboratory results indicate that the most effective infiltration strategy to precipitate apatite at depth may be to infiltrate a high-concentration solution (6 millimoles [mM] calcium, 15 mM citrate, 60 mM phosphate) at a rapid rate (near ponded conditions), followed by rapid, then slow water infiltration (PNNL-18303). Repeated infiltration events, with sufficient time between events to allow water drainage in the sediment profile, may also be used to build up the mass of apatite precipitate at greater depth. Low-potassium zones were effectively treated, as the higher residual water content maintained in these zones resulted in higher apatite precipitate concentration. High-potassium zones did not receive sufficient treatment by infiltration, although an alternative strategy of air/surfactant (foam) was demonstrated effective for targeting high-potassium zones.

11.3.2.3 Evaluation and Screening Rationale

Laboratory scale studies have demonstrated that in situ stabilization of strontium-90 in the vadose zone can be achieved through the infiltration of calcium citrate-phosphate solutions to induce the formation of apatite, which in turn sequesters the strontium-90. However, stabilization/sequestration for Cr(VI) and other radionuclides in soil requires treatability studies to determine potential agents and effectiveness. Therefore, in situ stabilization/sequestration was not retained for the 100-F/IU waste sites.

11.3.3 In Situ Chemical Reduction

In situ chemical reduction was not retained for treatment of soils contaminated with Cr(VI). This technology is not applicable for radionuclides.

11.3.3.1 Description

Considerable technical development and study to manipulate subsurface geochemical conditions to sequester or immobilize inorganic contaminants have been pursued over the past 25 years. Chemical reducing agents, such as dilute hydrogen sulfide gas, may be used to transform Cr(VI) to less mobile and less toxic trivalent chromium using vadose zone injection technology (*In Situ Gaseous Reduction Pilot Demonstration—Final Report* [PNNL-12121]). Alternative chemical reducing agents include calcium polysulfide (CPS), dithionite, ferrous sulfate, and zero-valent iron (ZVI). The alternate chemical agents delivered as solids or liquids are inherently limited because direct contact between the chemical agent and targeted sediment contamination is required. Chemical reductants are instantly reactive, which requires higher chemical volumes to maintain reactive strength at depth.

11.3.3.2 Relevant Demonstration Projects

The U.S. Department of Defense (DOD) conducted a field test site to evaluate the effectiveness of in situ gaseous reduction (ISGR) at a chromate-contaminated waste site located at the White Sands Missile Range (PNNL-12121). The field demonstration involved the injection of a mixture of 200 parts per million (ppm) hydrogen sulfide diluted in air. The gas mixture was drawn through the soil by a vacuum applied to extraction boreholes located at the site boundary, and residual hydrogen sulfide was removed before discharge of the extracted air to the atmosphere. The injection test lasted 76 days with no detectable release of hydrogen sulfide to the atmosphere. Comparison of Cr(VI) concentrations in soil samples taken before and after the test indicated that 70 percent of the Cr(VI) originally present at the site were reduced to trivalent chromium and thereby immobilized by ISGR. Treatment was generally better in zones of higher permeability sand containing less silt and clay, indicating that geologic heterogeneity limits treatment effectiveness.

11.3.3.3 Evaluation and Screening Rationale

The application of toxic hydrogen sulfide gas to the near-surface vadose zone sediment contamination carries significant risk. Transportation and handling of reducing agents also pose a greater health and safety concern during application when compared to biological reduction substrates. Although this technology has low to moderate effectiveness (depending on contaminant and soil type), the application of liquid, chemical-based reducing agents to uniformly contact contaminated vadose zone soil is judged to pose greater implementation challenges (moderate implementability) than biological-based substrates. Therefore, relative to these implementability and potential effectiveness issues, and expected moderate to high costs, in situ chemical reduction was not retained.

11.3.4 Biological Reduction

In situ biological reduction was not retained for further consideration for the treatment of waste sites contaminated with Cr(VI). This technology is not applicable for radionuclides.

11.3.4.1 Description

Biological reduction involves the subsurface delivery of a biological carbon source (e.g., molasses, sodium lactate, emulsified oil, butane, etc.) to the vadose zone. Biological reduction is a microbially mediated process that breaks down certain types of contaminants into less toxic/mobile forms. In the case of Cr(VI), biological activity creates reducing conditions allowing for Cr(VI) to be reduced to the less

mobile and less toxic trivalent chromium (III). The chromium is not removed from the vadose zone, but the toxicity and mobility of the chromium present are reduced.

11.3.4.2 Relevant Demonstration Projects

A treatability test is planned for evaluating the practicality of in situ bioremediation in the vadose zone at the 100 K West (100 KW) Area of the Hanford Site. Specifically, the test is designed to determine if chemically reducing conditions suitable for remediating Cr(VI) contamination can be established by stimulating anaerobic microbes via infiltration of an organic substrate.

11.3.4.3 Evaluation and Screening Rationale

The effectiveness of biological Cr(VI) reduction is considered moderate to high. Biological reduction relies on microbial activity to induce proper reducing conditions in the waste sites. Implementability is dependent on the selected delivery method. At shallow depths less than 1.5 m (5 ft), pressurized injections are not practical. Use of liquid substrates in the vadose zone may result in uneven reagent distribution in the contaminated zone. For waste sites near the Columbia River, migration of biological substrates through the vadose zone to the water table, with transport to the river, could occur. This technology was not retained because of uncertainty associated with its delivery and the potential for excess substrate to be transported to the river where it may pose an indeterminate risk to aquatic receptors.

11.3.5 Combined Chemical/ Biological Reduction

Combined chemical and biological reduction was not retained for treatment of soil contaminated with Cr(VI). This technology is not applicable for radionuclides.

11.3.5.1 Description

Both biological and abiotic methods are potentially applicable for reduction of Cr(VI). Chemical reductant (e.g., CPS, hydrogen sulfide gas, ferrous sulfate, and zero valent iron) and biological carbon source (e.g., molasses, sodium lactate, and emulsified oil) are applied in combination to the subsurface to treat contaminants present in vadose zone soil.

11.3.5.2 Relevant Demonstration Projects

Relevant demonstration projects for individual (separate) chemical and biological treatment were described in the previous sections of this appendix.

11.3.5.3 Evaluation and Screening Rationale

The combined application of chemical and biological reduction to the waste sites is expected to have moderate effectiveness and pose moderate implementation risk, at moderate costs. However, for the reasons described for chemical reduction (Section 11.3.3.3) and biological reduction (Section 11.3.4.3), the combined chemical/biological reduction process option was not retained.

11.3.6 Gaseous Ammonia Injection

Gaseous ammonia injection was not retained for treatment of waste sites contaminated with Cr(VI). This technology is not applicable for radionuclides.

11.3.6.1 Description

Gaseous ammonia injection is a conceptual process postulated to increase the pH in a soil or sediment matrix to a level that dissolves silica and over time reacts to form aluminosilicate minerals, which in turn may immobilize inorganic contaminants on sediment grains. This prospective technology is being investigated by PNNL with respect to possible application to the Hanford Central Plateau (*Remediation of*

Uranium in the Hanford Vadose Zone Using Gas-Transported Reactants: Laboratory-Scale Experiments [PNNL-18879]).

11.3.6.2 Relevant Demonstration Projects

This is a proposed technology and has not been tested in the field. PNNL is presently conducting a laboratory study as part of an ongoing gas-transported reactant study for remediation of uranium in the deep vadose zone sediments at the Hanford Site. It is not presently viewed as a treatment for the shallow vadose zone.

11.3.6.3 Evaluation and Screening Rationale

Gaseous ammonia injection is an unproven conceptual technology. The effectiveness of a mildly alkaline ammonia gas in the relatively dry vadose zone in promoting mineral phase dissolution of silica-aluminum and other metals is unknown. The geochemical reaction is reversible and remobilization of any immobilized contaminant is possible with exposure to oxygen saturated water. The implementability of the process is unknown at full scale. Furthermore, considerable health, safety, and environmental concerns exist with the injection of ammonia gas near the surface and along the Columbia River. Because the laboratory technology evaluation results remain to be determined, the implementation costs for the technology are undetermined. Given the uncertainty of effectiveness, implementability, and cost, gaseous ammonia injection was not retained for further consideration.

11.4 In Situ Treatment—Delivery Method

This section presents technologies for the delivery of reagents for the in situ treatment of vadose zone soil. The previous section discussed possible reagents.

These technologies would be considered only if an amendment-based technology is retained. No chemical or biological treatment has been retained for soil contaminated with Cr(VI) or radionuclides. For this reason, in addition to others discussed in the following sections, these technologies have not been retained for further consideration.

11.4.1 Mixing with Conventional Excavation Equipment

Mixing or delivery of amendments using conventional excavation equipment was not retained for treatment of soil contaminated with radionuclides or Cr(VI).

11.4.1.1 Description

This delivery method involves using conventional excavation equipment (such as backhoes, excavators, and front-end loaders) to mix amendments into the soil. The equipment repeatedly picks up and moves the soil around after the amendment slurry has been added. A relatively thick slurry is required to keep the amendments from flowing out of the soil, or the mixing needs to be performed in a lined basin. The depth at which it can be implemented is limited to the reach of the equipment.

11.4.1.2 Evaluation and Screening Rationale

Several other mixing methods are also highly effective, and some are more implementable than this technology given the large area that may be required for the heavy equipment operation to achieve successful contaminant - reagent contact. The costs for this type of mixing are likely to be comparable or lower than other mixing methods discussed; however, they are likely to be higher than surface infiltration methods given that surface infiltration is less intrusive. This is considered a highly effective and moderately implementable technology with low to moderate costs. However, because of depth limitations associated with this mixing method, as well as the availability of infiltration methods, mixing or delivery of amendments using conventional excavation equipment was not retained.

11.4.2 Deep Soil Mixing

Deep soil mixing was not retained for treatment of soil contaminated with Cr(VI) or radionuclides.

11.4.2.1 Description

Deep soil mixing uses large diameter augers or horizontally rotating heads to blend in reagents and homogenize the reagent – soil mix. The diameter of the augers can vary from 0.3 to 4 m (0.98 to 13 ft) (*Containment, Stabilization and Treatment of Contaminated Soil Using In-situ Soil Mixing* [Day and Ryan, 1995]). Reports indicate depths ranging from 35 to 50 m (114 to 164 ft) can be achieved with this technology (Day and Ryan, 1995; *In-Situ Stabilization and Fixation of Contaminated Soil by Soil Mixing* [Jasperse and Ryan, 1992]).

The technology provides the opportunity for uniform mixing in the soil column, with good contact and reaction between contaminants and amendments and is applicable to radionuclides and metals, including Cr(VI). The reactants could be chemical reductants or biological substrates (to treat reducible radionuclides and metals) or solidification/stabilization agents (to treat any radionuclides and metals). Soil mixing by means of auger emplacement and incorporation of agents may be effective for shallow, near-surface contamination. Overlapping auger borings effectively ensures continuity of reagent emplacement. Effective depth varies depending upon site-specific conditions. Generally, this method increases soil volume (swell); and, if necessary, excess soil will require removal and disposal. Auger penetration would be substantially reduced, or even refused, in large gravels or well-cemented materials. A backhoe may be required to move the large cobbles.

11.4.2.2 Relevant Demonstration Projects

Deep soil mixing was used to remediate an abandoned transformer repair facility in Miami, Florida (Jasperse and Ryan, 1992). Polychlorinated biphenyl concentrations within the treatment area ranged from 200 to 600 ppm, with a maximum concentration of 1,000 ppm. Contaminated media was present at depths up to 15 m (49 ft) below ground surface (bgs). Laboratory bench scale tests were completed to evaluate potential reagents, and a proprietary pozzolanic additive containing clay absorbents was selected. Full-scale implementation involved use of a four-shaft, deep soil mixing rig and a reagent mixing plant complete with a four-line pump and control system. Reagents were mixed at a rate of 275 kg/m³ of soil mixed. Results from the study showed a decrease in polychlorinated biphenyl (PCB) concentrations after treatment, as well as an increase in unconfined strength and decrease in permeability of the mixed samples over time (Jasperse and Ryan, 1992).

11.4.2.3 Evaluation and Screening Rationale

Deep soil mixing is considered to have high effectiveness for delivering reagents to contaminated soil. Chemical agents are uniformly mixed with the soil column, providing good contact and reaction between the COC and the reagent. Cement or bentonite clay can also be mixed with the chemical slurry to reduce the hydraulic conductivity and leachability of the soil. Implementability of deep soil mixing is considered low to moderate at the Hanford Site because of the presence of cobbles and boulders in the subsurface, which also results in higher costs. Because of uncertainty on the performance of deep soil mixing equipment under Hanford Site conditions, deep soil mixing was not retained for further evaluation.

11.4.3 Foam Delivery of Reagents

Foam delivery of reagents was not retained for treatment of soil contaminated with Cr(VI). This technology is not applicable to radionuclides.

11.4.3.1 Description

Foam delivery is a relatively new method of delivering chemical reactants to the vadose zone. The foam is created by a surfactant solution and mixed with a chemical such as CPS. This mixture is then injected into the vadose zone via vertical wells. The foam helps to move the reactants out horizontally from the injection well, rather than just moving downward. Depending on the reactant used, it could be used to treat Cr(VI).

11.4.3.2 Relevant Demonstration Projects

Foam delivery of amendments is currently in developmental stage; full-scale applications have not been completed. A research plan for foam delivery of amendments to the deep vadose zone was presented by PNNL in 2009 (*Research Plan: Foam Delivery of Amendments to the Deep Vadose Zone for Metals and Radionuclides Remediation* [PNNL-18143]). The objective of this study was to develop a foam delivery technology for the distribution of amendments to deep vadose zone sediments for in situ immobilization of Cr(VI).

Laboratory batch and column tests have been conducted for foam delivery of CPS to immobilize Cr(VI) (*Foam Delivery of Calcium Polysulfide to Vadose Zone for Chromium(VI) Immobilization: A Laboratory Evaluation* [Zhong et al., 2009]). Batch tests were conducted to study foam properties, and column experiments were performed to study the foam delivery of CPS under conditions similar to field vadose zone and to determine the extent of Cr(VI) immobilization. Results from the study indicated that CPS could be delivered efficiently to unsaturated sediments to immobilize Cr(VI) in situ and to minimize Cr(VI) mobilization at the reaction front as observed when CPS is delivered in a water-based single-phase solution. However, no information is currently available on how far the foam will move out from an injection well under field conditions.

11.4.3.3 Evaluation and Screening Rationale

The technology evaluation has been limited to laboratory column tests; thus, effectiveness, implementability, and costs at the field scale are unknown. The spacing between injection points is also unknown because of limited available information on the stability and dispersing distance of the foam. Evaluation of results from the ongoing treatability study is needed before making a decision regarding its full-scale use at the Hanford Site. For this reason, foam delivery of reagents was not retained for further consideration.

11.4.4 Gaseous Delivery of Reagents (In Situ Gaseous Reduction)

In situ gaseous reduction (ISGR) is a vadose zone remediation technology that uses a gaseous reagent (such as hydrogen sulfide/ nitrogen gas mixture) to reduce or treat contaminants. This technology was discussed in Section 11.3.3. Because additional information resulting from the treatability studies is required before making decisions about the full-scale application of in situ gas reduction at the Hanford Site, ISGR was not retained for further consideration.

11.4.5 Horizontal Injection Wells

Delivery of substrates using horizontal injection wells was not retained for treatment of soil contaminated with Cr(VI) or radionuclides.

11.4.5.1 Description

Horizontal injection wells involve the delivery of amendments through wells installed using horizontal drilling techniques. Horizontal injection may have benefits over vertical injection in shallow treatment areas and where contaminants of potential concern (COPC) are characterized within a certain discrete depth interval.

11.4.5.2 Relevant Demonstration Projects

An unsuccessful horizontal well technology demonstration was conducted at the Hanford 100-D Area from November 2009 through January 2010. The scope of work consisted of two phases. First, a surface casing was installed at a 16-degree angle from horizontal through the Hanford formation to an estimated depth of 15 m (50 ft) bgs. The second phase was to drill through the Ringold Formation using horizontal directional drilling techniques and drilling mud. Once this drilling was complete, the drill bit would have been knocked off and the well screen installed inside the drill pipe. Installation of surface casing was required to facilitate circulation of drilling mud in the very porous Hanford formation. The casing was advanced with much difficulty to approximately 6 m (20 ft) bgs (85 horizontal linear feet) when downward progress ceased because of inadequate force on the down hole hammer and difficulty removing cuttings from the inclined casing. Rotary mud directional drilling through the casing and into the Hanford formation was attempted, but progress was slow and circulation was never established.

11.4.5.3 Evaluation and Screening Rationale

As with vertical injection wells, the effectiveness of horizontal injection wells can be hindered by soil heterogeneity, which causes preferential flow paths and limits the treatment effectiveness of lower permeability soil. With anisotropies in vertical hydraulically conductivity more pronounced than horizontal hydraulically conductivity, amendment distribution over a larger vertical (depth) interval would be more challenging than would be encountered with vertical wells. Furthermore, maintaining target borehole depth and alignment with horizontal drilling in gravelly/cobbly lithologies is difficult. This issue was encountered during the technology demonstration at the Hanford Site. Given the increased difficulty in installation (low implementability) and low to moderate effectiveness in amendment delivery relative to vertical injection wells, as well as the unsuccessful tests to date at the Hanford Site, delivery of substrates by horizontal injection wells was not retained.

11.4.6 Vertical Injection wells

Delivery of substrates using vertical injection wells was not retained for treatment of vadose zone soils contaminated with Cr(VI) or radionuclides.

11.4.6.1 Description

This technology involves delivery of amendments using conventional vertical wells. Wells can be temporary or permanent, depending on the application (single or multiple injections) and remedial objective.

11.4.6.2 Evaluation and Screening Rationale

No in situ biological or chemical technologies were retained for soil contaminated with Cr(VI) and radionuclides. For this reason, delivery of substrates by vertical injection wells was not retained.

11.4.7 Surface Infiltration

Surface infiltration was not retained as a delivery method for reagents for treatment of soil contaminated with Cr(VI) or radionuclides.

11.4.7.1 Description

This process option applies reagent to the ground surface to treat contaminants within the vadose zone. Surface infiltration can be accomplished through drip irrigation or shallow open bottom (barefoot) basin systems. These systems are generally designed to be 30 cm (12 in.) bgs and covered for protection.

11.4.7.2 Relevant Demonstration Projects

A study conducted at the 100-N shoreline to evaluate surface infiltration of apatite forming solutions for sequestration of strontium-90 was conducted in 2011 (*Treatability Test Plan Addendum for 100-NR-2 Groundwater Operable Unit* [DOE/RL-2005-96-ADD2]). Infiltration gallery wells were drilled approximately 5 m (16 ft) past the downriver end of the existing apatite permeable reactive barrier, along the 100-N shoreline access road, and apatite forming chemicals were delivered into the vadose zone using passive infiltration techniques. Additional information on the infiltration test and the data for test implementation are provided in *Investigation of the Strontium-90 Contaminant Plume along the Shoreline of the Columbia River at the 100-N Area of the Hanford Site* (PNNL-16894).

11.4.7.3 Evaluation and Screening Rationale

Surface infiltration is considered to be moderately to highly effective for reagent delivery, although uniform distribution of reagents is not likely. Infiltration in disturbed areas or highly compacted areas will reduce effectiveness. Surface infiltration was not retained as a potential delivery method because no in situ chemical or biological technologies were retained.

11.4.8 Void Filling/Grouting

Void filling/grouting was not retained as a delivery method for treatment of pipelines contaminated with Cr(VI) or radionuclides because no such waste sites are present in 100-F/IU.

11.4.8.1 Description

Void fill/grouting is used for immobilizing residual contaminants and solidification of buried wastes. Void fill/grouting is considered applicable for pipelines that are to be left in place. Grout can be cement based (e.g., Portland cement) or chemical based (e.g., silicates, acrylics, lignosulfonates, phenoplasts, and aminoplasts). Grouts can be mixed in batches or with mobile mixers depending on the size of the grouting project.

11.4.8.2 Relevant Demonstration Projects

In 2008, approximately 8,229.6 m (27,000 ft) of pipeline were grouted at the DOE Melton Valley Site.

11.4.8.3 Evaluation and Screening Rationale

Grouting is considered to be highly effective for filling of voids in place and solidifying material present in the pipes, especially pipelines present at depths below 4.6 m (15 ft). Implementability is also considered to be moderate to high depending on the accessibility, and length and diameter of pipeline to be grouted. Relative cost is deemed low. Because there are no deep buried pipeline waste sites in 100-F/IU to be addressed in the FS, void fill/grouting was not retained.

11.5 In Situ Treatment—Other

The following sections describe additional in situ technologies that were not retained for further consideration in the FS.

11.5.1 Jet Grouting

Jet grouting was not retained as a treatment technology for soil contaminated with Cr(VI) or radionuclides.

11.5.1.1 Description

Jet grouting involves the high pressure injection of a reactive slurry into the vadose zone. Achieving a uniform distribution of slurry is difficult in heterogeneous soil such as the Hanford formation and Ringold unit E.

11.5.1.2 Relevant Demonstration Projects

A jet grouting pilot test for apatite injection was performed in the 100-N Area for treatment of strontium-90 contaminated soil. Three test plots were injected using a phosphate solution, preformed apatite (solid), and a combination of phosphate and preformed apatite. A containment trench (approximately $9 \times 3 \times 0.6$ m [$30 \times 10 \times 2$ ft]) was constructed before jet injection. Excavated soil was used to create a berm around each trench to contain drilling spoils and/or injection fluids that potentially rise to the surface. Injection borings were drilled from the bottom of the trench (approximately 0.6 m [2 ft] bgs) to 5.2 to 7.6 m (17 to 25 ft) bgs. Jet injections were performed using a proprietary system capable of injecting the solutions at approximately 400 bars (5,800 psi). The high-pressure injection fluidized the sediment and apatite (solutions or solid) to the expected minimum radial distance of 1 m (3 ft) from the injection nozzle. Following injection, sediment cores were collected from each trench to determine the concentration of apatite formed and the resulting strontium-90 concentration. Core sampling showed that apatite was successfully emplaced in all trenches. Phosphate concentrations were higher in fine-grained soil at shallow depths compared to coarser material (SGW-47062). An expanded pilot test is currently planned for a 91 m (300 ft) section of the shoreline in the 100-N Area.

11.5.1.3 Evaluation and Screening Rationale

Jet grouting is considered to have low to high effectiveness (depending on site characteristics) in depths up to 300 feet. Implementability also ranges from low to high depending on soil characteristics, depth, and borehole spacing. Close-in injection spacing diameters (approximately 2 m [5 ft]) are often required to provide adequate coverage resulting in high cost where large areas require treatment. Because of its potential limited effectiveness in gravelly soil, jet grouting was not retained.

11.5.2 Soil Blending

Soil blending was not retained for treatment of soil contaminated with radionuclides.

Description. Contaminated soils are mechanically blended using conventional or deep excavation equipment, with clean soil or fill to reduce contaminant concentrations. Contamination is not removed from the vadose zone, but risk is reduced by diluting concentrations.

Evaluation and Screening Rationale. Soil blending is considered to have high effectiveness and can be readily implemented at low to moderate cost depending on the volume of contamination that needs to be addressed and the volume of clean or less contaminated soil that needs to be blended to reduce concentrations to the target preliminary remediation goal(s). However, because this technology is often viewed as dilution rather than treatment, it was rejected in favor of disposal of excavated soil at the ERDF.

11.5.3 In Situ Vitrification

In situ vitrification (ISV) was not retained for treatment of soil contaminated with Cr(VI) or radionuclides.

11.5.3.1 Description

Vitrification processes are solidification methods that use temperatures between 1,200 and 2,000°C (2,200 to 3,600°F), depending on the composition of the mixture being melted, to melt and convert waste materials into glass or other glass and crystalline products. In addition to solids, waste materials can be

liquids, wet or dry sludges, or combustible materials. Borosilicate and soda lime are the principal glass forming components and provide the basic matrix of the vitrified product. Off-gases generated by the process are contained under a hood covering the treatment area and are drawn to an off-gas treatment system. Organic contaminants are destroyed by pyrolysis, which occurs as the temperature increases before the actual melting, and by catalytic dechlorination reactions, which occur as contaminated soils approach melt temperatures under reducing conditions. Heavy metals and radionuclides are distributed throughout the melt because of the relatively low viscosity of the molten glass and the convective flow that occurs within the melt. When electrical current is removed, the molten mass cools and solidifies into a vitreous rock (a monolithic glass with excellent physical, chemical, and weathering properties). The resulting product typically is 10 times stronger than concrete and 10 to 100 times more resistant to leaching than glasses typically resulting from high-level radioactive waste vitrification performed in an above ground facility. The radionuclides and heavy metals are immobilized within the melt.

ISV involves passing current through the soil using an array of electrodes. If the soil is too dry, enhancements must be placed to provide an initial flow path for the electrical current. Large areas are treated by fusing together multiple vitrification treatment zones (“Remediation of Metals Contaminated Soil and Groundwater” [Evanko and Dzombak, 1997]). To accommodate soil densification, clean overburden is placed over the melt zone before the melt is initiated, thereby avoiding subsidence issues while increasing thermal efficiency and radionuclide retention. Excessive water vapor passing through the melt might disrupt or displace the melt; therefore, soil with high moisture content must be treated to remove water before in situ vitrification. The process requires 700 to 900 kWh (2,520,000 to 3,240,000 kilojoule) per ton of soil and waste treated, including soil water. The overall oxide composition of the soil determines the fusion, melt temperature, and viscosity. In addition, it is essential that the media contain sufficient monovalent alkali earth oxides to provide the electrical conductivity required (RPP-ENV-34028).

11.5.3.2 Relevant Demonstration Projects

Between 1980, when the ISV process was conceived by PNNL for DOE, and 1997, more than 200 tests, demonstrations, and commercial operations of the technology have been conducted (RPP-ENV-34028). *Case Study Abstract: In Situ Vitrification* (DOE, 1997) presented information on a case study conducted at the Hanford Site. Information specific to this case study is limited; however, it does specify that a *Toxic Substances Control Act of 1976* demonstration showed destruction and removal efficiency for PCBs of greater than 99.9999 percent (*In Situ Vitrification Treatment* [EPA/540/S-94/504]).

A large-scale ISV test was completed at the 116-B-6A Crib site in 1990 (*In Situ Vitrification of a Mixed-Waste Contaminated Soil Site: The 116-B-6A Crib at Hanford* [PNL-8281]). The site contained mixed waste (chromium, lead, and cesium-137) at an approximate depth of 6 m (20 ft) bgs. The treatability test consumed 550 MW of electrical energy and resulted in a 771 tonne (850 ton) block of vitrified soil. Results from data collection indicated that the vitrified block retained over 99.99 percent of chromium and lead and over 99.98 percent of cesium-137, indicating the favorable resistance of the treated material to leaching. The final depth achieved during the treatability test was 4.3 m (14 ft), which is 1.8 m (6 ft) less than the required treatment depth. The 4.3 m (14 ft) treatment depth coincided with a cobble layer detected below the crib during the post-treatment core drilling. The rate of melt progression above the cobble layer was satisfactory, indicating that the cobble layer prevented melt propagation and treatment for the 4.3 to 6.1 (14 to 20 ft) depth interval (*In Situ Vitrification of a Mixed-Waste Contaminated Soil Site: The 116-B-6A Crib at Hanford* [PNL-8281]).

Geosafe Corporation licensed the technology from PNNL and has applied it commercially. In 1995, Geosafe Corporation evaluated the application of ISV under the U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation Program at the former Parsons Chemical Works, Inc. site in Grand Ledge, Michigan (*Geosafe Corporation In Situ Vitrification, Innovative Technology*

Evaluation Report [EPA/540/R-94/520]). The technology evaluation report summarized the findings associated with a demonstration of the ISV process and its ability to treat pesticides and mercury below EPA Region V mandated limits. The technology was evaluated against the nine *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) FS guidance criteria for decision-making in a Superfund Facility. ISV was considered effective in destroying organic contamination, immobilizing inorganic material, and reducing the likelihood of contaminants leaching from the treated soil. Among some of the limitations, the report stated that ISV is not recommended for sites that contain organic content greater than 7 to 10 percent by weight, metal content greater than 25 percent by weight, and inorganic contaminants in excess of 20 percent by volume (EPA, 1995). The report also noted that ISV would not be appropriate for sites where contaminated soil lies adjacent to buildings, other structures, or the property line.

A subsurface planar method was recently applied in a demonstration project to treat a portion of a mixed low-level radioactive liquid waste adsorption bed at the Los Alamos National Laboratory's MDA-V site (*Demonstration of Non-Traditional In Situ Vitrification Technology at Los Alamos National Laboratory* [Huddlestone et al., 2003]). Nontraditional planar ISV uses the same general process as traditional ISV; however, it involves joule heated melting within the subsurface. In contrast to the horizontally oriented melt normally started at or near the surface, this process establishes two vertically oriented planar melts in the subsurface between pairs of electrodes. The planar melts can be initiated at the desired depth and separation within the subsurface, depending on the target treatment volume (RPP-ENV-34028). *Demonstration of Non-Traditional In Situ Vitrification Technology at Los Alamos National Laboratory* (Huddlestone et al., 2003) report indicated an average treatment depth of 7.9 m (26 ft) bgs at the electrode locations. Radioactive contaminants were seen to have been distributed uniformly through the melt, and concentrations were reduced by more than an order of magnitude (Huddlestone et al., 2003).

11.5.3.3 Evaluation and Screening Rationale

The effective treatment depth of this technology is approximately 7.6 m (25 ft) bgs, and the treatment area is limited by cost (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). Elevated worker safety and exposure concerns could be associated with this process because of volatilization; however, the risk is considered lower than that of excavating highly contaminated and radioactive soil. Working in proximity to high voltage and high temperatures also requires appropriate safety precautions.

The cost associated with implementation of ISV, as compared to other technologies is considered high, where electric power is generally the most significant cost component. As presented in Table 9-1 of *Central Plateau Vadose Zone Remediation Technology Screening Evaluation* (RPP-ENV-34028), ISV has the highest of all relative technology specific costs. Given the complex equipment requirements and challenging implementation, as well as the relative high cost, in situ vitrification was not retained for further evaluation.

11.5.4 Soil Flushing

In situ soil flushing was not retained for treatment of soil contaminated with Cr(VI).

11.5.4.1 Description

In situ soil flushing consists of applying clean or treated water to flush contaminants from the vadose zone soil for capture/recovery by groundwater extraction wells and subsequent aboveground treatment. The water can be applied directly to the ground surface by sprinklers or infiltration trenches for shallow contamination or through injection wells or deep infiltration trenches for deeper contamination.

This technology is applicable to media affected with contaminants with moderate to high solubility (e.g., Cr(VI)). Solubility-enhancing solutions may be added to increase contaminant mobility.

11.5.4.2 Relevant Demonstration Projects

Soil flushing was used to treat soil and groundwater contaminated with Cr(VI) at the United Chrome Products Superfund Site in Corvallis, Oregon. Delivery of solution was completed through two infiltration basins and one infiltration trench to flush Cr(VI) from the vadose zone to the water table. Extraction wells were used to recover the solution and the water treated using skid mounted Cr(VI) reduction and precipitation equipment. *Technology Status Report In Situ Flushing* (TS-98-01) indicates that 9.7 million gallons of affected groundwater containing 12,125 kg (26,732 lbs) of Cr(VI) were removed in a 3 year period. Later investigations at the United Chrome site performed in 1998 and 1999 to assess the effectiveness of the flushing technology determined that while it was effective for some forms of Cr(VI) it was ineffective for others, and therefore, was unable to fully achieve the 6,000 mg/kg total chromium cleanup level. High concentrations of Cr(VI) present in soil and groundwater at the United Chrome site formed several different solid phase minerals, some with very low aqueous solubility.

11.5.4.3 Evaluation and Screening Rationale

The depth of Cr(VI) contamination will determine whether shallow delivery methods are applicable, or whether deep infiltration trenches and injection wells are required as viable delivery methods for soil flushing. Effective capture of flushed contamination is critical for waste sites close to the Columbia River. Expectations for low to moderate effectiveness over a large area and high implementation challenges are anticipated, therefore, soil flushing was not retained for further evaluation.

12 Additional Information on Technologies Not Retained for Groundwater Treatment

Information regarding technologies that were not retained for further evaluation for treatment of groundwater contaminated with Cr(VI), strontium-90, trichloroethene, and nitrate is presented in this Appendix.

12.1 Ex Situ Treatment

Under the general response action of pump-and-treat, treatment of contaminated groundwater is performed using a wide variety of ex situ methods specific to the contaminant and level of treatment required. Groundwater treated with ex situ methods can remove contaminants from water and concentrate them in a smaller volume, alter the contaminant's characteristics to make them less mobile (e.g., conversion of Cr(VI) to trivalent chromium) or to facilitate removal from the water stream. The ex situ treatment options that were not retained are discussed in this section.

12.1.1 Chemical Reduction/Softening and Precipitation

Chemical reduction/softening and precipitation was not retained for treatment of groundwater contaminated with Cr(VI) and nitrate.

12.1.1.1 Description

Chemical reduction/softening and precipitation involve the introduction of chemicals to transform dissolved contaminants into insoluble solids, which are removed by flocculation, sedimentation, and filtration. Chemicals used to remove Cr(VI) can include ferrous chloride, ferrous sulfide, ZVI, sulfur dioxide, and various sulfites (*Remedial Process Optimization for the 100-D Area Technical Memorandum Document* [SGW-38338], Section 4.2). Ferrous iron is commonly used for industrial wastewaters, such as from metal plating. Dissolved nitrate can be converted to nitrogen gas or biomass through chemical reduction and removed through volatilization or with biological sludge. Solids removal typically includes

flocculation and/or coagulation, settling, and filtration. Sludge handling, dewatering, and disposal are also required. The volume and/or mass of the sludge generated can be large and would need final disposal at the ERDF. Site-specific jar testing would be required to develop design and operational parameters.

12.1.1.2 Relevant Demonstration Projects

A Remediation Process Optimization (RPO) evaluation was performed for 100-D with a goal of reducing the cost and improving the performance of the existing ex situ ion exchange groundwater treatment systems (*Remedial Process Optimization for the 100-D Area Technical Memorandum Document* [SGW-38338], Chapter 6). Design criteria, preconceptual designs, and rough order-of-magnitude cost estimates were developed for three technologies: ion exchange with onsite regeneration, ion exchange with offsite regeneration, and ferrous chloride reduction. The technology with the lowest estimated O&M cost was ion exchange with onsite regeneration, followed by the ferrous chloride reduction process, whose estimated O&M costs are approximately 20 percent higher. By far, the largest solid waste stream is generated by the ferrous chloride process, whose annual solid waste mass is approximately 4 times that of ion exchange with onsite regeneration, and more than 60 times that of ion exchange with offsite regeneration.

12.1.1.3 Evaluation and Screening Rationale

This technology is effective for Cr(VI) and nitrate. Site specific testing for all COCs would be required to determine operational parameters. Vendors and equipment for this technology are readily available; however, this technology is largely unproven for conditions present at the Hanford Site, and large volumes of sludge are anticipated because of the volumes of groundwater and concentration of Cr(VI) and nitrate requiring treatment.

Based on the RPO evaluation for 100-D, chemical reduction using ferrous chloride would have a higher estimated operations cost than ion exchange with onsite regeneration. Although the capital costs for chemical reduction are similar to ion exchange, a new chemical reduction system would need to be designed and constructed, whereas the ion exchange systems are already built and operating at the Hanford Site. Chemical reduction and/or precipitation would also generate a higher volume waste stream compared to ion exchange with either onsite or offsite regeneration. For these reasons, chemical reduction was not retained for further evaluation.

12.1.2 Electrocoagulation

Electrocoagulation was not retained for treatment of groundwater contaminated with Cr(VI).

12.1.2.1 Description

Electrocoagulation is a specific form of chemical reduction and precipitation. It is used to remove a variety of suspended solids and dissolved pollutants from aqueous solutions, including Cr(VI). An electric field is applied to metal plates, which release ions into the water. To remove oxidized species such as Cr(VI), iron plates typically are used. The ferrous iron ions reduce Cr(VI) to an iron-chromium hydroxide, which is subsequently precipitated and removed.

12.1.2.2 Relevant Demonstration Projects

A 2007 treatability test evaluated the potential for this technology for 100-D of the Hanford Site (*Treatability Test Report for the Removal of Chromium from Groundwater at 100-D Area Using Electrocoagulation* [DOE/RL-2008-13]). The test objectives were to: (1) determine the operability, robustness, and treatment efficiency of an electrocoagulation system; (2) characterize the volume and composition of the resulting waste; and (3) obtain design data for scaling the process from a 190 L/min (50 gal/min) to a 1,900 L/min (500 gal/min) system.

The test setup included an electrocoagulation unit and a downstream water treatment system with a clarifier, filters, and a filter press to dewater the sludge. The water passed through the electrocoagulation unit, precipitates were removed, and the water was re-oxygenated and then re-injected into the aquifer.

The performance objective of the treatability study was to determine Cr(VI) removal efficiency with the goal of decreasing Cr(VI) concentrations to 20 µg/L or less. The test consisted of a startup phase from May 3 to July 20, 2007; a continuous testing phase from July 23 to October 12, 2007; and a final testing phase conducted on October 16 and 17, 2007, using groundwater augmented with higher concentrations of Cr(VI). Over the course of the test period, the test system treated 10.3 million L (2.8 million gal) of groundwater.

The data evaluation from the test suggested that electrocoagulation could achieve the treatment goal in more than 90 percent of the samples with one or more passes through the treatment system, but that the treatment system could not operate unattended. Therefore, it was concluded that cost and operational factors do not favor the use of this technology.

12.1.2.3 Evaluation and Screening Rationale

The effectiveness of electrocoagulation for the 100 Area is anticipated to be low to moderate, particularly in light of the challenges encountered in the above-described pilot test. The technology is not widely used for Cr(VI). Implementability is also considered low to moderate because further development of the process would be required. In addition, the process may render the treated water less suitable for reinjection. Capital costs are expected to be moderate to high and O&M costs moderate. A large fraction of the O&M cost is due to the production of significant volumes of sludge that must be managed and disposed. Because of low to moderate effectiveness and implementability and moderate to high cost, this technology was not retained for further evaluation.

12.1.3 Wetlands

Wetlands were not retained for treatment of groundwater contaminated with Cr(VI) or nitrate.

12.1.3.1 Description

Constructed wetlands are artificial swamps that act as biofilters for removing contaminants. This technology is a common process in municipal wastewater treatment. A constructed wetland typically would have a larger area and longer hydraulic retention time compared to a bioreactor, but it typically would not require added nutrients and would require less operational oversight.

Wetlands are used to treat groundwater, industrial wastewater, and municipal wastewater. Cr(VI) can be removed in wetlands primarily by microbiological and chemical reduction. Some Cr(VI) uptake by wetland plants may also occur. The plants also function as a method of regenerating the reducing sediments by dying and falling to the bottom (“Effects of Plants on the Removal of Hexavalent Chromium in Wetland Sediments” [Xu and Jaffe, 2006]).

Wetlands can also be used to treat nitrate. Several removal mechanisms for treatment of nitrate in water, such as decomposition, nitrification/denitrification, settling, volatilization, adsorption, and nutrient uptake (*Literature Survey for Groundwater Treatment Options for Nitrate, Iodine-129, and Uranium, 200-ZP-1 Operable Unit, Hanford Site* [SGW-37783]) have been identified.

12.1.3.2 Relevant Demonstration Projects

A number of demonstration projects use wetlands to remove nitrates (*Literature Survey for Groundwater Treatment Options for Nitrate, Iodine-129, and Uranium, 200-ZP-1 Operable Unit, Hanford Site* [SGW-37783]). For example, a constructed wetland is used to remove nitrate from the municipal drinking

water supply in Orange County, California. Up to 1.5 m³/s (33 million gal/day) is treated. The influent contained 3.1 to 10.9 mg/L of nitrate (as nitrogen). The average nitrate removal was 522 mg (0.018 oz) of nitrate (as nitrogen) per m²/day, and effluent nitrate concentrations were reduced to as low as 0.1 mg/L nitrate (as nitrogen), with hydraulic detention times from 0.3 to 9.6 days. Bacterial denitrification was thought to be the primary nitrate treatment mechanism. A review of 19 surface flow wetlands showed that nearly all reduced total nitrogen concentrations. A comparison of surface and subsurface flow wetlands showed that subsurface flow wetlands outperformed surface flow wetlands and yielded lower effluent nitrate concentrations (ranging from less than 1 to less than 10 mg/L).

12.1.3.3 Evaluation and Screening Rationale

The land area required for wetlands is likely to be very large for the volume of groundwater that needs to be treated for the 100-F/IU nitrate plume. Even more area would be required for effective treatment in the winter, when plants and micro-organisms in the wetland would be less active. Problems with freezing would be likely, as average minimum temperatures are below freezing more than half of the year (*Hanford Site National Environmental Policy Act (NEPA) Characterization* [PNNL-6415]). Therefore, the technology is not well suited to the climate at the Hanford Site. The effectiveness of this technology at the site is considered moderate to high for nitrate but additional testing would be required to refine operational parameters and verify the effectiveness of the technology for Cr(VI). Implementability is considered low to moderate. Construction of wetlands at the Hanford Site would require lining to prevent the infiltration of the water as well as provision of organic substrate to support wetland plants. Wetland treatment does not have significant advantages over ion exchange, which is already in place and performing well.

Although wetlands provide a potentially more sustainable (or greener) technology than ion exchange (in terms of energy use and because they are natural systems), winter conditions at the Hanford Site introduce significant performance uncertainty, and land area requirements would be extensive. For these reasons, this technology was not retained for further evaluation.

12.1.4 Subgrade Bioreactors

Subgrade bioreactors were not retained for treatment of groundwater contaminated with Cr(VI) and nitrate.

12.1.4.1 Description

Biological treatment using bioreactors is a potential treatment technology for Cr(VI) and nitrate in groundwater. If implemented on a full-scale, a static granular bed reactor (SGBR) would consist of a lined excavation backfilled with a mixture of sand/gravel, a biodegradable substrate such as wood mulch, and possibly ZVI. The contaminated groundwater would pass through the basin in which the Cr(VI) and nitrate are chemically and/or biologically reduced to trivalent chromium and nitrogen gas. A second stage, aeration/filtration basin could be provided to remove any residual organic carbon that may be present and to remove any dissolved by-products of biodegradation (ferrous iron, arsenic, and manganese), as well as suspended solids, before the discharge of the treated groundwater back to the aquifer.

12.1.4.2 Relevant Demonstration Projects

SGBRs for Cr(VI) and nitrate removal have not been demonstrated on a full scale. The biological processes involved in biological treatment of reducible metals like Cr(VI) are similar to those involved in other bioreactor concepts used in the remediation industry, such as sulfate-reducing bioreactors that are used to treat acid mine drainage. Based on case studies, the effectiveness of bioreactors has been demonstrated at temperatures between 2 and 16°C (36 and 61°F) (“Passive Treatment of Acid Mine

Drainage in Bioreactors Using Sulfate Reducing Bacteria: Critical Review and Research Needs” [Neculita et al., 2007]).

12.1.4.3 Evaluation and Screening Rationale

Although SGBRs provide a potentially more sustainable technology compared to other ex situ treatment technologies, the technology has not been demonstrated on a full scale for Cr(VI) or nitrate remediation. The logistics of constructing and operating SGBRs for Cr(VI) treatment may also be more difficult compared to ion-exchange, which has already been used on a wide scale at the Hanford Site, has an established equipment/material supply chain, has an established O&M support structure, and takes up less land area than a full-scale array of SGBRs. For these reasons, this technology was not retained for further evaluation.

12.1.5 Phytoremediation

Phytoremediation was not retained for treatment of groundwater and soil contaminated with Cr(VI) or nitrate.

12.1.5.1 Description

For groundwater, phytoremediation is limited to the depth to which the plants can extract water. Water cannot be wicked and delivered vertically more than about 6 m (20 ft); thus, the potentiometric surface must be within 3 or 6 m (10 or 20 ft) from the bottom of the root mass for this technology to be viable (*Enhanced Attenuation: Approaches to Increase the Natural Treatment Capacity of a System* [WSRC-TR-2005-00198]). Because of this limitation, unless groundwater was first extracted (by pumping) and then phytoremediated (i.e., the plants would be irrigated with the contaminated groundwater), phytoremediation would not be suitable for groundwater remediation in 100-F/IU except along the river shoreline. There are methods of encouraging plant roots to grow deeper, but not to the depths that would be required elsewhere in 100-F/IU. Phytoremediation systems (including by land application) are only operational when the soil is warm and plants are active, so treatment effectiveness would decrease or stop altogether in the winter. The land requirements for phytoremediation are also relatively large compared to physical and chemical processes.

12.1.5.2 Relevant Demonstration Projects

Uptake of Cr(VI) by a variety of plants has been documented (Shahandeh and Hossner, 2000). Cr(VI) can accumulate in the plants and may become toxic to them. A land application/irrigation system has been installed at a confidential site in California with groundwater containing Cr(VI). Subsurface application of the groundwater is conducted via a drip irrigation system and the Cr(VI) is primarily microbially reduced in the shallow soil.

Perhaps the best example of deep rooting of trees is at Argonne National Laboratory in Illinois. Hybrid poplars were deep rooted in tree wells, plastic lined holes bored to a depth of 10 m (30 ft). Boreholes were filled with topsoil and then surface capped, which isolates the tree from surface water and forces the roots to use contaminated groundwater. Root extension of 3 m (10 ft) has been observed (WSRC-TR-2005-00198).

A treatability demonstration project is being conducted at the Hanford Site for treatment of strontium-90 in soil and groundwater along the banks of the Columbia River in 100-N using Coyote willows. Additional information on this and other treatability studies is presented in Section I2.2.4.

12.1.5.3 Evaluation and Screening Rationale

Because of the large depth to groundwater in most portions of 100-F/IU, phytoremediation would be feasible in the areas adjacent to the river only. Therefore, implementability of phytoremediation is considered

low to moderate. It is usually implemented over long-time scales, such as years or decades. The sparse vegetation that naturally grows on the Hanford Site suggests that significant efforts and inputs (such as organic matter and water) would be required to establish a vigorous plant community. However, capital costs would still be relatively low. Once the plants are established, O&M costs would also be low because requirements to sustain them are low (food and water). However, Cr(VI) may accumulate in the plants to the point that they must be disposed of periodically in a secure facility, such as ERDF. Ultimately, the plants would need to be disposed of at ERDF to avoid returning Cr(VI) to the soil (as plants decompose) unless contaminants such as nitrate are reduced to innocuous forms.

Phytoremediation is effective only when the plants are active; therefore, the technology would not be effective during the winter. Because of the uncertainty of continued effectiveness throughout the year as well as the very limited ability of the plants to root deep enough to effect groundwater in most areas at the Hanford Site, effectiveness is considered low to moderate. There are also concerns about contaminants entering the food chain as animals eat the vegetation or bees pollinate flowers. In summary, the technology would only be effective for low concentrations of Cr(VI) and nitrate where groundwater is shallow for long periods of time. If Cr(VI) accumulates in the plants, it could pose potential risks to ecological receptors. For these reasons, phytoremediation was not retained for further evaluation.

12.1.6 Membrane Separation (Reverse Osmosis)

Reverse osmosis (RO) was not retained for treatment of groundwater contaminated with Cr(VI), strontium-90, trichloroethene or nitrate.

12.1.6.1 Description

RO is a pressure driven process that uses semi-permeable membranes to purify water. Contaminated water is passed through the membrane while contaminants with molecular sizes greater than the membranes are excluded. The water that passes through the membrane is called the permeate and typically contains only a small fraction (less than 5 percent) of the ions in the influent water. The water that does not pass through the membrane (containing the ions that do not pass through the membrane) is called the brine. It has a high total dissolved solids concentration and would contain the COCCs being treated. With appropriately sized membranes configured in multiple stages, very low COC concentrations can be achieved. RO is among the technologies that EPA considers effective for removing total chromium to below 100 µg/L (along with coagulation/filtration, ion exchange, and lime softening) (“Basic Information about Chromium in Drinking Water” [EPA, 2010]). In addition to chromium, RO can remove nitrate, trichloroethene, some volatile organic compounds (VOC), and some petroleum compounds (*Drinking Water Treatment: Reverse Osmosis* [Dvorak and Skipton, 2008]). In New Hampshire, the typical production efficiency of RO for nitrate removal is approximately 25 percent, i.e., for every 15 L (4 gal) of untreated water entering the device, only 3.7 L (1 gal) of treated water is produced (*Nitrate and Nitrite in Drinking Water* [WD-DWGB-3-9]). This low efficiency is a result of New Hampshire’s cold groundwater temperatures, which are likely similar to groundwater temperatures at the Hanford Site.

Brine production is a significant issue with RO. The need to manage (e.g., evaporate) the brine can lead to significant increases in water treatment costs. RO is commonly used to desalinate seawater, which typically generates much greater volumes of brine than for treating groundwater; however, in this application, the brine can simply be returned to the seawater.

Nano-filtration is very similar to RO but uses membranes with larger openings (*Membrane Filtration Guidance Manual* [EPA 815-R-06-009]). Options for managing brine and other process residuals include discharge to a suitable surface water body, discharge to a sanitary sewer, deep well injection, land application, or treatment with supernatant recycle and solids disposal. The treatment processes can

include clarification, sedimentation in lagoons, gravity thickening, centrifuging, belt filter pressing, and evaporation (EPA 815-R-06-009).

12.1.6.2 Relevant Demonstration Projects

A RO process was bench tested at the 200 West Area of the Hanford Site that combines three different membrane technologies: RO, coupled transport, and nano-filtration. These technologies were used to purify 72 L (19 gal) of groundwater while extracting and concentrating uranium, technetium, and nitrate into separate solutions (significant Cr[VI] concentrations were not present). This separation approach allows for the future use of the radionuclides, if needed, and reduces the amount of waste requiring disposal. This process was able to concentrate the contaminants into solutions with volumes in a ratio of 1 to 10,000 of the original treatment volume, compared to a volume reduction of 10 to 100 for ion exchange and stand-alone RO (*Testing of a Benchscale Reverse Osmosis/Coupled Transport System for Treating Contaminated Groundwater* [WHC-SA-2755-FP]). The experiment demonstrated the effectiveness of the process for all ions except technetium.

The Effluent Treatment Facility in the 200 East Area of the Hanford Site treats liquid effluent to remove toxic metals, radionuclides, and ammonia, and to destroy organic compounds. The treatment process constitutes pH adjustment, filtration, ultraviolet light, and hydrogen peroxide destruction of organic compounds, RO to remove dissolved solids, and ion exchange to remove trace contaminant concentrations. The facility began operating in December 1995. The maximum treatment capacity of this facility is 570 L/min (150 gal/min) (*Hanford Site Environmental Report for Calendar Year 2008* [PNNL-18427]).

A pilot test of RO with vibratory shear-enhanced processing (VSEP[®]) to minimize brine production was conducted at a Central Arizona Project water treatment plant (*Reverse Osmosis Treatment of Central Arizona Project Water—Brine Minimization Via Vibratory Shear-enhanced Processing* [Corral and Yenal, 2009]). Whereas brine production without VSEP was approximately equal to 20 to 25 percent of the volume of the water being treated, VSEP reduced brine production to 2 to 4 percent of the initial volume treated. The cost of VSEP treatment was significant but less than the costs of RO without VSEP associated with increased brine disposal and lost drinking water supply.

12.1.6.3 Evaluation and Screening Rationale

With the appropriate design, RO can be effective for almost any compound. A system design, however, would require site-specific testing, and pretreatment would likely be necessary. Capital and O&M costs are high; therefore, implementability is considered low to moderate. A major disadvantage of RO that underlies these unfavorable ratings is the large volume of brine generated. The volume varies depending primarily on groundwater characteristics. The brine would contain Cr(VI) and other COCs, which would require further treatment and then disposal. It would also have a high concentration of total dissolved solids, which could be a problem for disposal. Brine production and disposal was the primary reason that RO was not retained for this evaluation.

12.2 Discharge

Discharge process options that were not retained for further consideration in the FS included surface infiltration and offsite discharge as discussed in the following subsections.

[®] VSEP is a registered trademark of New Logic Research, Inc., Emeryville, California.

I2.2.1 Surface Infiltration

Surface infiltration was not retained for treatment of Cr(VI), strontium-90, trichloroethene, or nitrate contaminated groundwater.

I2.2.1.1 Description

Treated groundwater is discharged to unlined trenches and allowed to naturally infiltrate through the vadose zone back to the groundwater.

I2.2.1.2 Evaluation and Screening Rationale

Surface infiltration of treated water is considered to be highly effective at the Hanford Site because of the high permeability of the Hanford formation. Infiltration could be used for hydraulic control or flushing if the infiltration trenches are located appropriately. Trenches would be located outside of contaminated zones to prevent recontamination of treated water. Costs for surface infiltration are considered low to moderate because little O&M is required following excavation of trenches. Surface infiltration was screened out because of the land area required and the potential disruption of culturally sensitive areas.

I2.2.2 Surface Water Discharge under a NPDES Permit

Surface water discharge under a National Pollutant Discharge Elimination System (NPDES) permit was not retained for treatment of groundwater contaminated with Cr(VI) or other COCs.

I2.2.2.1 Description

Almost any type of treated groundwater may be discharged to surface water under an NPDES permit. This is common practice for municipal and industrial wastewaters, as well as groundwater at many hazardous waste sites. The discharge standards are set based on the flows and water quality in the receiving stream so that the discharge does not have any adverse effects on the quality of the stream. Routine monitoring is required to verify compliance. This monitoring often includes bioassay testing to confirm there is no toxicity to aquatic organisms. The physical location of the discharge point can also be designed to minimize effects to the stream (e.g., mid-stream diffusers can be used to distribute the flow).

I2.2.2.2 Relevant Policy

Establishment of the Hanford Reach National Monument (Presidential Proclamation 7319) issued in June 2000 reserved 79,000 ha (195,000 acres) of land as the Hanford Reach National Monument for the purpose of protecting ecological habitat and natural and cultural resources along the 82 km (51 mi) long Hanford Reach stretch of the Columbia River (“Establishment of the Hanford Reach National Monument” [65 FR 37253]). The proclamation prohibits new development along the Hanford Reach, including the lower river corridor where an outfall would need to be constructed to discharge treated groundwater to the river under an NPDES permit.

I2.2.2.3 Evaluation and Screening Rationale

Surface water discharge to the river would require construction of a discharge outfall along the river corridor within the boundaries of the Hanford Reach National Monument, which likely will not be allowed under *Establishment of the Hanford Reach National Monument* (Presidential Proclamation 7319). Furthermore, for other groundwater remediation systems in the 100 Area, the treated water has been re-injected into the groundwater to help flush contaminants, and, as such, surface discharge is not used. For these reasons, surface water discharge was not retained for further consideration.

I2.3 In Situ Treatment

The following sections describe in situ technologies that were not retained for further consideration in the FS.

I2.3.1 In Situ Chemical Reduction

In situ chemical reduction was not retained for treatment of groundwater contaminated with Cr(VI).

I2.3.1.1 Description

Chemical reducing agents such as CPS or dithionite are injected into the contaminated groundwater plume to transform Cr(VI) to less mobile and less toxic trivalent chrome, thereby facilitating lower concentrations of Cr(VI) in groundwater. Alternative chemical reducing agents include ferrous sulfate and ZVI.

I2.3.1.2 Relevant Demonstration Projects

A field treatability test was conducted at 100-K during the summer of 2005 to evaluate the effectiveness of using CPS to reduce Cr(VI) in groundwater [*Treatability Test Report for Calcium Polysulfide in the 100-K Area* (DOE/RL-2006-17)]. The field test used a “five-spot” well configuration, which involved four injection wells drilled orthogonally around an existing central monitoring well from which groundwater was withdrawn and mixed with CPS. This solution then was injected in approximately equal amounts to set up a circulation cell within the aquifer treatment zone. The test was conducted for a period of 45 days. Cr(VI) was eliminated from the treated aquifer, as demonstrated by the absence of Cr(VI) concentrations in groundwater in the injection wells and extraction well. Measurements of dissolved oxygen (DO) and oxidation-reduction potential showed that the treatment zone was strongly reduced resulting in elevated concentrations of manganese, iron, and arsenic, although concentrations remained below drinking water standards. Elevated levels of sulfate were also produced from the disassociation of the CPS.

Implementability problems encountered during the field study included precipitation of chemicals inside pipes, flow meters, and pumps caused by the chemical changes induced by addition of CPS. Sulfur accumulated on the screen of the extraction pump, which caused reduced flow and required the pump to be changed or cleaned every few days near the end of the test. The injection pump needed to be manually adjusted frequently because calcium carbonate precipitated on its impeller, causing extra internal friction.

I2.3.1.3 Evaluation and Screening Rationale

Transportation and handling of reducing agents also poses health and safety concerns for workers and the environment during application relative to biological reduction substrates. Because of more rapid chemical reactions, the application of liquid reducing agents to treat large areas of a plume may be more challenging than using biological substrates. Based on these implementability and potential effectiveness issues, in situ chemical reduction was not retained.

I2.3.2 Hydrogen or Other Organic Gas Sparging

Hydrogen or other organic gas sparging was not retained for treatment of groundwater contaminated with Cr(VI).

I2.3.2.1 Description

Gas sparging involves the injection of biodegradable organic gases (i.e., methane, propane, or butane) or hydrogen gases into the subsurface via sparge wells that are screened below the water table. Distribution of gases is affected by lithologic heterogeneity, and gas flow may channelize through preferential flow

paths. The gases serve as electron donors to promote anaerobic reduction of certain compounds, such as Cr(VI), trichloroethene, and nitrate. This approach is an alternative to supplying electron donor using a liquid organic substrate, such as lactate.

12.3.2.2 Relevant Demonstration Projects

A propane biosparging field demonstration was conducted at the National Environmental Technology Test Site in Port Hueneme, California, from May 2001 to March 2002 (*Cost and Performance Report In-Situ Remediation of MTBE Contaminated Aquifers Using Propane Biosparging* [TR-2230-ENV]). The COPCs in groundwater included fuel constituents and methyl *tert*-butyl ether at concentrations up to 6,300 µg/L and *tert*-butyl alcohol up to 470 µg/L. Unconsolidated sediments at the site were comprised of sands, silts, clays, and small amounts of gravel and fill material. The uppermost water bearing unit was a shallow, semi perched, unconfined aquifer (upper silty sand, underlain by fine to coarse grain sand, and a basal clay layer). Depth to groundwater ranged from 1.8 to 2.4 m (6 to 8 ft) bgs, and the saturated aquifer thickness was 4.8 to 5.4 m (16 to 18 ft).

The field demonstration area (27 × 18 m [90 × 60 ft]) included a test plot consisting of seven propane injection points and a control plot consisting of eight oxygen injection points and seven bacteria injection points. The propane system operated for four 10 minute cycles per day and yielded approximately 0.226 kg/day (0.5 lb/day) of propane at the test plot. After several months of operation, the propane flow was decreased from 0.03 m³/hr to between 0.0085 and 0.0113 m³/hr (1 standard ft³/hr to between 0.3 and 0.4 standard ft³/hr). The oxygen control system was operated for four 6-minute cycles per day, yielding approximately 2.26 kg/day (5 lb/day) of oxygen in the test and control plots.

In the test plot, methyl *tert*-butyl ether concentrations decreased by 62 to 88 percent in shallow wells and by 86 to 97 percent in deep wells. In the control plot, methyl *tert*-butyl ether concentrations decreased by 86 to 97 percent in shallow wells and by 88 to 90 percent in deep wells. However, methyl *tert*-butyl ether concentrations were reduced to less than 5 µg/L in only 3 of the 30 monitoring wells in the propane test plot. In the control plot, methyl *tert*-butyl ether concentrations remained above 5 µg/L in all wells. The most active methyl *tert*-butyl ether degradation appeared to occur near the oxygen injection points, indicating that distribution of gases was not effective or uniform in the heterogeneous soil.

12.3.2.3 Evaluation and Screening Rationale

This technology is an alternate approach for delivering electron donor over the more typical liquid organic substrates such as lactate. However, a disadvantage is the safety risk associated with using potentially explosive gases, which will likely be a major implementation challenge at the Hanford Site. In addition, the ROI of sparge wells is likely to be relatively low, so that a large number of wells would be required, making implementation more challenging. For these reasons, this technology was not retained for further evaluation.

12.4 Delivery Methods

Retained in situ treatment methods require a delivery method to emplace reagents in the subsurface. The following delivery methods were not retained for further consideration for delivery of reagents for in situ technologies.

12.4.1 Groundwater Circulating Wells

Groundwater circulating wells were not retained as a delivery method for treatment of 100-F/IU COCs.

12.4.1.1 Description

Groundwater circulating wells are installed as a single well with two isolated screened zones. Groundwater is typically hydraulically pumped or air-lifted out of the formation from the lower screen, and injected back into the formation at the upper screen. A three-dimensional flow pattern (circulation cell) is created in the formation. Depending on site-specific conditions, both upward (reinjection into the upper screen) and downward (reinjection into the lower screen) circulation modes can be used.

The recirculated groundwater can be aerated and re-injected into the formation to enhance aerobic biodegradation, stripped in-well to remove trichloroethene, treated with in-well reactive media, or amended in-well with soluble biological or chemical reagents. The circulation of groundwater can also be used to enhance the distribution of amendments or reagent directly injected into the formation within the circulation cell.

The zone of influence that can be achieved with groundwater circulating wells (GCW) is highly sensitive to site lithologic conditions. A viable circulation cell may not develop if vertical anisotropy in lithology (i.e., the presence of laterally extensive silty-clay layers) impedes the circulation flow path or if there is not enough anisotropy. Typically, this technology will not be successful when the ratio of horizontal to vertical hydraulic conductivity is greater than 10 (*Groundwater Circulating Well Technology Assessment* [NRL/PU/6115-99-384]). A single thin layer of low permeability material can also prevent development of a recirculation cell. If the anisotropy is too low, the radius of the circulation cell will be very small; this could be the case at the Hanford Site. Other common problems include well clogging resulting from changing redox conditions within the GCW and down well equipment (e.g., packers) problems.

12.4.1.2 Relevant Demonstration Projects

A summary and analysis of more than 50 GCW field demonstrations were provided in *Groundwater Circulating Well Technology Assessment* (NRL/PU/6115-99-384). One case study was a GCW demonstration sponsored by DOD that was originally scheduled to be performed at the Hanford Site but was relocated to Edwards Air Force Base OU 1, Site 19. This site was selected based on its high hydraulic conductivity (KH = 10 ft/d, KV = 1 ft/d) and the presence of trichloroethene. One GCW was installed to a depth of 15 m (50 ft) bgs and operated for 191 days during the demonstration. Results of the demonstration indicate a ROI of approximately 9 m (30 ft), an asymmetrical circulation cell, and groundwater flow short-circuiting near the GCW. Post-operation data showed contaminant rebound in monitoring wells. Of the remaining GCW case studies, few sites demonstrated clear success, and at just as many sites, the technology failed to meet remedial objectives. However, most of the case studies indicated that the data collected were insufficient to demonstrate the efficacy of the GCW technology.

12.4.1.3 Evaluation and Screening Rationale

It is likely that a large number of wells would be required to implement this technology at 100-F/IU because of the large plume areas and highly permeable nature of the site lithology, which would result in a small ROI. Even if implemented with tight well spacing, variable lithology could cause asymmetrical groundwater flow or groundwater flow short-circuiting; and contaminant rebound would ultimately limit the effectiveness of GCWs. Given the high cost of installing wells and the likelihood of limited treatment effectiveness, this technology was not retained for further evaluation.

12.4.2 Horizontal Wells

Horizontal wells were not retained as a delivery method for groundwater extraction or reinjection.

12.4.2.1 Description

Horizontal wells are horizontally drilled or trenched screened borings installed along or across the plumes. Horizontal wells can be used to extract soil vapor and groundwater, or inject water, chemical reagents, or biological substrates. Horizontal well technology has been incorporated into many current environmental remediation applications (and associated contaminants), such as in situ bioremediation, air sparging, vacuum extraction, soil flushing, and free product recovery. This technology is most applicable to sites with relatively shallow soil and/or groundwater contamination, and can potentially enhance remediation efforts at sites with low hydraulic conductivities (*Technology Overview Report: Horizontal Wells* [Miller, 1996]).

Horizontal wells have an advantage over vertical wells in that their long horizontal screens can contact a larger plume area and may more effectively transmit amendments. Because of their superior alignment with natural lithologic stratigraphy, horizontal wells may also be more efficient for recovering groundwater or soil vapor. When installed with directional drilling techniques, horizontal wells can be installed in areas where surface (culturally sensitive areas) and subsurface obstructions would preclude other remediation alternatives.

Disadvantages of horizontal wells are primarily associated with the physical and operational limitation of directional drilling techniques.

12.4.2.2 Relevant Demonstration Projects

An unsuccessful horizontal well technology demonstration was conducted at the Hanford 100-D Area from November 2009 through January 2010. The scope of work consisted of two phases. First, a surface casing was installed at a 16 degree angle from horizontal through the Hanford formation to an estimated depth of 15 m (50 ft) bgs. The second phase was to drill through the Ringold Formation using horizontal directional drilling techniques and drilling mud. Once this drilling was complete, the drill bit would have been knocked off and the well screen installed inside the drill pipe.

Installation of a surface casing was required to facilitate circulation of drilling mud in the porous Hanford formation. The casing was advanced with significant difficulty to approximately 6 m (20 ft) bgs and 25 m (85 horizontal linear feet) when downward progress ceased because of inadequate force on the down hole hammer and difficulty removing cuttings from the inclined casing. Rotary mud directional drilling through the casing and into the Hanford formation was attempted, but progress was slow and circulation was never established.

12.4.2.3 Evaluation and Screening Rationale

Based on the unsuccessful technology demonstration at the Hanford Site, horizontal wells were not retained as a groundwater remediation delivery technology.

12.5 Containment

Containment technologies that were not retained for the treatment of contaminated groundwater are presented below.

12.5.1 Containment Wall

A containment wall was not retained as a method of containing groundwater contaminated with Cr(VI) or other COPCs.

12.5.1.1 Description

Containment walls include soil bentonite slurry walls, grout walls, and sheetpile walls. Walls have been used successfully for hydraulic containment of groundwater plumes at many hazardous waste sites. Groundwater pumping or diversion upgradient of the wall is required to prevent groundwater mounding and bypassing of the wall. Containment walls increase the potential to achieve effective hydraulic containment, and they may reduce the amount of water that requires treatment. Installation methods include conventional or continuous trenching with soil/bentonite slurry, vibrating beam cutoffs, mixed-in-place walls, tangent caisson walls, and driven sheetpiles.

12.5.1.2 Relevant Demonstration Projects

“Action Memorandum: N-Springs Expedited Response Action Cleanup Plan, DOE Hanford Site, Richland, Washington” (Ecology and EPA, 1994) was issued to DOE to initiate groundwater remedial actions at 100-N in 1994, to include the design, construction, and operation of a pump-and-treat system and the construction of a sheetpile barrier wall at N-Springs. However, 6 months later, the State of Washington, Department of Ecology (Ecology) and EPA concurred with DOE that installation of the sheetpile wall could not be achieved in the manner specified, based on results of a construction test in late 1994. The two agencies subsequently directed DOE to proceed with the pump-and-treat system only (*Annual Summary Report Calendar Year 2000 for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Units and Pump-and-Treat Operations* [DOE/RL-2001-04]). A grouted hinge sheetpile barrier in the aquifer near the river’s edge had been specified, but attempts to install a sheetpile barrier were unsuccessful (*Coordination of Groundwater Activities in the 100 N Area* [WHC-EP-0878]).

12.5.1.3 Evaluation and Screening Rationale

Containment walls are typically extended into a confining unit, such as the Ringold Formation upper mud (RUM) unit, which at most locations in the 100 Areas may be 15 to 60 m (50 to 200 ft) bgs. Installation to these depths is possible using specialized excavation equipment such as a hydraulic clamshell but is very challenging and expensive. Only at locations very near the river would the required depths be shallow enough to make installation reasonably economical; and, as noted, a previous attempt in the 100-N Area was unsuccessful.

There is also uncertainty as to how well the RUM unit would serve as a confining unit. The hydraulic conductivity in the RUM unit has not been evaluated in detail, and the RUM unit was scoured by past river channel migration and glacial flood erosional events that ultimately laid down the Hanford formation. Thus, the RUM unit has an undulating surface that could limit the effectiveness of a containment barrier unless detailed mapping of the surface was performed during design.

Most of the installation methods would be technically challenging at the Hanford Site because of the depths of the unconfined aquifer and the presence of cobbles and coarse gravel. Cobbles will prevent or deflect most insertion methods or items such as sheetpiles, vibrating beams, and drilled caissons. While conventional trenches can likely be kept open in the Hanford formation, slurry loss may be excessive in zones of coarse cobbles or gravels that lack fine-grained materials that limit fluid loss. Slurry loss can lead to trench instability.

The effectiveness of this technology is considered moderate for several reasons: (1) it depends on the ability to key into a low permeability unit; (2) it does not treat contamination; and (3) groundwater upgradient of the wall or within a closed wall system must be pumped to keep hydraulic pressure against the wall within design parameters. Implementability is low, as evidenced by failed attempts to install a sheetpile wall at N-Springs. Capital costs would be high, while O&M costs would be low to moderate depending on the magnitude of pumping required. Because of implementation challenges and high capital costs, containment walls were not retained for further evaluation.

12.5.2 Reactive Chemical Barrier

An in situ reactive barrier (ISRB), similar to the in situ redox manipulation (ISRM) barrier installed at 100-D, was not retained for containment of contaminated groundwater at 100-F/IU.

12.5.2.1 Description

ISRBs involve the subsurface delivery and/or circulation of chemical reagents along an offset, a linear array of injection wells installed perpendicular to the groundwater flow direction. Reagent chemicals pumped into the injection wells are retained in the aquifer matrix so that Cr(VI), nitrate, or trichloroethene are treated as contaminant plumes through the treatment zone under the influence of the natural hydraulic gradient. Passive groundwater pumping wells placed downgradient of the ISRB can be used to draw the plume using a “funnel” approach, thereby reducing the length of ISRB. Sodium dithionite, CPS, or zero valent iron may be used as reductants for Cr(VI), trichloroethene and nitrate treatment.

12.5.2.2 Relevant Demonstration Projects

The use of a zero valent iron barrier has been field tested in the 100-D Area for the treatment of Cr(VI). The zero valent iron injected into the ISRM barrier creates strong reducing conditions that reduce Cr(VI) to trivalent chromium. The ISRM barrier was implemented to passively treat Cr(VI) contamination in the 100-D southern plume (*U.S. Department of Energy Hanford Site – 100 Area Benton County, Washington Amended Record of Decision, Decision Summary and Responsiveness Summary (100-HR-3 Operable Unit Interim Remedial Action)* [EPA et al., 1999]). At the time the ISRM barrier was implemented, the magnitude and extent of Cr(VI) concentrations in the 100-D hot spot upgradient of the barrier were not understood. When performance monitoring data indicated that Cr(VI) was breaking through the ISRM treatment zone, scientists proposed fortifying the barrier with zero valent iron to restore its long-term effectiveness. A treatability study was conducted to evaluate whether augmentation of the ISRM barrier with nano-scale ZVI would be an effective approach to augmenting the performance and longevity of this passive treatment system.

In 2006, DOE began a test to determine whether injections of nano-scale iron particles (70 nanometers [3 millionths of an inch] in diameter) could fortify the weaker portions of the ISRM barrier. The small size of the particles allows them to flow into the aquifer, thus treating the water more effectively given the very large surface area of the iron particles (30 m²/g [150,000 ft²/lb]). Higher surface area means that more of the iron would be available to react with and remediate the Cr(VI) contaminated groundwater.

Selecting the right iron particles was critical to the success of the test; therefore, initial stages of the project focused on identifying potential ZVI products for injection. During evaluation, the RNIP-M2 ZVI formulation was selected for field testing because of its injection characteristics and ability to sustain the treatment zone.

The field injection test was conducted in August 2008 at 100-D. The first goal was to inject enough ZVI into the more permeable portions of the barrier to ensure that the ZVI could disperse at least 7 m (23 ft) from the injection well. The second goal was to determine whether the selected ZVI could effectively reduce Cr(VI) concentrations in the groundwater.

Over a period of approximately 5 days, 370,970 L (98,000 gal) of the RNIP-M2 solution was injected into the Ringold Formation aquifer at a rate of 53 L/min (14 gal/min). The ZVI penetrated at least 3 m (9.8 ft) away from the injection well. A borehole was drilled 7 m (23 ft) from the injection well in March 2009 to evaluate the ROI. Analysis of aquifer materials showed that approximately 4 weight percent ZVI was present in the targeted permeable layer near the bottom of the aquifer. This verified that the goal of emplacing ZVI at least 7 m (23 ft) into the aquifer was achieved. Groundwater monitoring has shown that

redox conditions are highly reduced transforming Cr(VI) to trivalent chromium. The test demonstrated that RNIP-M2 could be an effective, easily injected ZVI product to fortify the ISRM barrier.

12.5.2.3 Evaluation and screening rationale

The effectiveness of ISRM is considered moderate to high; however, past experience with this technology has shown Cr(VI) breakthrough where reagents are not uniformly distributed, where water levels are highly variable, and where high contaminant concentrations are present. This technology treats the leading edge of the plume as it enters and passes through the barrier, with the balance of the plume treated over longer periods of time as it passes through the ISRB under the influence of the natural or enhanced groundwater flow gradient. To ensure long-term effectiveness, the ISRB requires periodic rejuvenation. Given the large widths of the Cr(VI), trichloroethene and nitrate plumes in 100-F/IU, the ISRB technology was not retained.

12.5.3 Reactive Biological Barrier

An ISRB using a biological based treatment media was not retained as a containment technology for groundwater contaminated with Cr(VI), trichloroethene and nitrate at 100-F/IU.

12.5.3.1 Description

Reactive biological barriers are constructed similarly to ISRB except that an organic substrate is injected to promote biological treatment and containment of the contaminant plume. Substrate injections stimulate the growth of biomass so that Cr(VI), trichloroethene and nitrate are passively treated/removed as groundwater moves through the treatment zone. Biological barriers would operate much like the ISRM. Rejuvenation of the barrier by reinjection of substrate may be required periodically to maintain treatment effectiveness. Common substrates include acetate, molasses, cow manure, fruit juice, lactate, whey, polylactate, and sulfur-containing products (e.g., Metals Remediation Compound), and waste organic material (e.g., from beer manufacturing) (*Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site* [SGW-38255]).

The indigenous organisms use the substrate as a carbon source for biomass generation and as an electron donor for energy production through a number of metabolic processes. Cr(VI), trichloroethene, and nitrate are highly oxidized compounds and, therefore, act as electron acceptors in oxidation-reduction reactions. Through these reactions, Cr(VI) is transformed to trivalent chromium, trichloroethene to cis 1,2-dichloroethene, and nitrate to nitrogen gas. Biological processes may include bioreduction, bioaccumulation, biomineralization, and bioprecipitation, which use specific substrates to drive the treatment. These processes can be used within reactive biological barriers (*In Situ Treatment of Soil and Groundwater Contaminated with Chromium: Technical Resource Guide* [EPA/625/R-00/005]).

12.5.3.2 Relevant Demonstration Projects

Biological barriers can be effective, depending on the contaminant flux rate and concentration of dissolved oxygen present in the groundwater. These two factors dictate how often the barrier needs to be rejuvenated.

A field experiment was conducted at the Hanford Site using hydrogen release compound (HRC), a slow-release glycerol polylactate, to bioimmobilize Cr(VI) (*In Situ Long-Term Reductive Bioimmobilization of Cr(VI) in Groundwater Using Hydrogen Release Compound* [Faybishenko, 2009]). The results of this experiment show that a single HRC injection into groundwater stimulated an increase in biomass, a depletion of terminal electron acceptors oxygen, nitrate, and sulfate, and an increase in ferrous iron, resulting in a significant decrease in soluble Cr(VI) concentrations. The Cr(VI) concentration remained below the detection limit in the injection well for at least 3 years after the HRC injection. The

degree of sustainable Cr(VI) treatment under different redox conditions at this and other contaminated sites was currently under study as of the publication date.

Biological barriers have been used at other Cr(VI) sites (SGW-38255). One site was the Selman Pressure Treating Superfund Site in California, where an existing pump-and-treat system was projected to take more than 30 years to clean up the site. To accelerate remediation, molasses was injected by direct push methodology to a ROI of 4.6 m (15 ft) to treatment depths up to 37 m (120 ft). Cr(VI) concentrations fell to less than the performance standard of 50 µg/L and in most cases to below 10 µg/L. In a downgradient portion of the plume, a recirculation process was used to amend the groundwater with lactate to treat to greater depths. Cr(VI) reduction was initiated before nitrate reduction. Dosing was adjusted to minimize overly reducing conditions that led to the temporary mobilization of iron and manganese, as well as biofouling.

Molasses and lactate were injected at a Cr(VI)-contaminated site near Flanders, Belgium, in 2005 to 2006 (“Stimulation of In Situ Bioprecipitation for the Removal of Cr(VI) from Contaminated Groundwater” [Vanbroekhoven et al., 2007]). Frequent reinjections were needed to maintain reduced conditions. Results of this pilot test showed efficient Cr(VI) removal from the groundwater for the lactate injection zone within 200 days, while for the molasses zone efficient removal was observed only after approximately 400 days. Based on the success of this pilot test, a full-scale process was planned.

A recent study evaluated a biological barrier comprised of sand and sawdust that had been treating nitrate for 15 years (“Nitrate Removal Rates in a 15-Year-Old Permeable Reactive Barrier Treating Septic System Nitrate” [Robertson et al., 2008]). Sediment cores were retrieved, and reaction rates were measured in column tests and compared to rates measured in year 1 using the same reactive mixture. The rates after 15 years were within about 50 percent of the year-1 rates. Near the end of the year 15 column test, wood particles were removed from the reactive media, and nitrate removal subsequently declined by about 80 percent, indicating that the wood particles were principally responsible for denitrification. The authors concluded from this work that some denitrifying biological barriers can remain maintenance free and be adequately reactive for decades.

12.5.3.3 Evaluation and Screening Rationale

In addition to consuming DO, biological barriers have the potential to result in unwanted dissolved byproducts such as ferrous iron, manganese, and arsenic. As a consequence, they should not be placed too close to the river (or extraction wells) unless re-oxygenation systems (such as sparging wells) are installed downgradient of the biobarrier.

Effectiveness is deemed low to moderate. Given the concentrations present, rejuvenation would be needed to maintain effectiveness. Implementation challenges are considered to be moderate to high while capital costs are considered moderate to high. O&M costs are considered moderate. The current remedies at both the 100-KR-4 and 100-HR-3 OUs include hydraulic containment using extraction wells. Consequently, additional technologies to create barriers to contaminant migration would duplicate efforts and are not needed. In addition, barriers do not support cleanup of the entire plume. For these reasons, biobarriers were not retained for further evaluation.

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