Appendix I

Technology Screening

This page intentionally left blank.

Contents

I1 Additional Information on Technologies Not Retained for Waste Site Treatment..... I-1

I1.1 Ex Situ Treatment and Processing.....I-1
I1.1.1 Solidification/Stabilization.....I-1
I1.1.2 Soil Washing.....I-2
I1.1.3 Ex Situ Vitrification.....I-4
I1.1.4 Ex Situ Thermal Desorption.....I-5
I1.2 In Situ Treatment—Reagent Approach.....I-6
I1.2.1 In Situ Chemical Reduction.....I-6
I1.2.2 In Situ Chemical Oxidation.....I-7
I1.2.3 Reductive Dechlorination Using Zero-Valent Metals and Bioremediation.....I-8
I1.2.4 In Situ Gaseous Reduction with Chemical Reductant or Biological Substrate.....I-10
I1.3 In Situ Treatment—Delivery Method.....I-11
I1.3.1 Mixing with Conventional Excavation Equipment.....I-11
I1.3.2 Deep Soil Mixing.....I-12
I1.3.3 Foam Delivery of Reagents.....I-13
I1.3.4 Gaseous Delivery of Reagents (In Situ Gaseous Reduction).....I-14
I1.3.5 Horizontal Injection Wells.....I-14
I1.4 In Situ Treatment—Other.....I-14
I1.4.1 Desiccation.....I-14
I1.4.2 In Situ Thermal Desorption.....I-15
I1.4.3 In Situ Vitrification.....I-17
I1.4.4 Phytoremediation.....I-19
I1.5 Containment.....I-20
I1.5.1 Horizontal Subsurface Barriers—Jet Grouting, Soil Freezing, or Wire Saw BarriersI-.....I-20
I1.5.2 Dynamic Compaction.....I-21

I2 Additional Information on Technologies Not Retained for Groundwater Treatment..... I-22

I2.1 Ex Situ Treatment.....I-22
I2.1.1 Ex Situ Chemical Precipitation.....I-22
I2.1.2 Electrocoagulation.....I-23
I2.1.3 Wetlands.....I-24
I2.1.4 Subgrade Bioreactors.....I-25
I2.1.5 Bioreactors.....I-26
I2.1.6 Phytoremediation.....I-27
I2.1.7 Membrane Separation (Reverse Osmosis).....I-28
I2.2 In Situ Treatment.....I-30

I2.2.1 In Situ Chemical Reduction I-30
I2.2.2 Hydrogen or Other Organic Gas Sparging I-30
I2.2.3 Groundwater Circulation Wells I-31
I2.2.4 Horizontal Wells I-32
I2.3 Containment I-33
I2.3.1 Containment Wall I-33
I2.3.2 Reactive Biological Barrier I-34
I2.3.3 Hydraulic Containment via Injection I-36
I3 Potential Remedial Action Technologies for Strontium-90 in the Vadose Zone of the Hanford 100 Area I-37
I3.1 In Situ Solidification I-37
I3.1.1 In Situ Grouting I-37
I3.2 In Situ Stabilization/Sequestration I-39
I3.2.1 Relevant Demonstration Projects I-39
I3.2.2 Evaluation and Screening I-40
I3.3 In Situ Jet Grouting—Delivery Method I-40
I3.3.1 Relevant Demonstration Projects I-40
I3.3.2 Evaluation and Screening I-41
I4 Bioremediation as a Potential Remedial Action for Cr(VI) in the Groundwater and Vadose Zone of the Hanford 100 Area I-41
I4.1 Introduction I-41
I4.2 Scientific Basis of Bioremediation I-41
I5 Overview of Cr(VI) Bioremediation Processes I-42
I5.1 Longevity of Treatment and the Potential for Reoxidation of Chromium(III) Phases I-42
I5.1.1 Dissolved Oxygen I-43
I5.1.2 Manganese(IV) Oxides I-43
I5.2 Fate and Transport of Some Potential Chemical Byproducts of Bioremediation I-44
I5.2.1 Iron and Manganese, and Arsenic I-44
I6 Evaluation of Potential Substrates for In Situ Bioremediation in the 100 Area I-46
I6.1 Substrate Selection for In Situ Bioremediation of the 100 Area Unconfined Aquifer I-49
I6.1.1 Initial Screening I-49
I6.1.2 Secondary Screening I-49
I6.1.3 Final Screening I-50
I7 In Situ Groundwater Remediation by Bioinjection I-53
I7.1 Conceptual Design I-53
I7.1.1 Implementation Factors I-54
I7.2 Previous Studies and Applications of Bioinjection and Similar Technologies to Cr(VI) Remediation in Groundwater I-55

I7.3 Hanford 100-D Pacific Northwest National Laboratory Biostimulation Treatability Study I-55
I7.3.1 Site Conditions I-55
I7.3.2 Technical Approach I-55
I7.3.3 Results I-56
I7.3.4 Lessons Learned I-57
I7.4 Hanford 100-H Lawrence Berkeley National Laboratory Hydrogen Release Compound Treatability Study I-57
I7.4.1 Site Conditions I-57
I7.4.2 Technical Approach I-58
I7.4.3 Results I-58
I7.4.4 Lessons Learned I-59
I7.5 Other Relevant Hanford Site Studies I-59
I7.5.1 Fortifying the 100-D Area In Situ Redox Manipulation Barrier with Iron I-59
I7.5.2 100-K Area Calcium Polysulfide Injection Treatability Test I-60
I7.6 Pacific Gas and Electric Company Hinkley Compressor Station, San Bernardino County, California I-62
I7.6.1 Site Conditions I-62
I7.6.2 Technical Approach I-62
I7.6.3 Results I-63
I7.6.4 Lessons Learned I-63
I7.7 PG&E Topock Compressor Station, San Bernardino County, California I-65
I7.7.1 Case Study References I-65
I7.7.2 Site Conditions I-66
I7.7.3 Technical Approach I-66
I7.7.4 Results I-69
I7.7.5 Lessons Learned I-70
I7.8 Abandoned Manufacturing Facility, Emeryville, California I-70
I7.8.1 Case Study References I-71
I7.8.2 Site Conditions I-71
I7.8.3 Technical Approach I-71
I7.8.4 Results I-71
I7.9 Avco Lycoming Site, Williamsport, Pennsylvania I-71
I7.9.1 Case Study References I-72
I7.9.2 Site Conditions I-72
I7.9.3 Technical Approach I-72
I7.9.4 Results I-72
I7.10 Odessa Chromium I Superfund Site, Odessa, Ector County, Texas I-73
I7.10.1 Case Study References I-73

I7.10.2 Site Conditions I-73
I7.10.3 Technical Approach I-74
I7.10.4 Results I-74
I7.10.5 Lessons Learned I-74
I7.11 Selma Pressure Treating Superfund Site, Selma, California I-74
I7.11.1 Case Study References I-75
I7.11.2 Site Conditions I-75
I7.11.3 Technical Approach I-75
I7.11.4 Results I-76
I7.11.5 Lessons Learned I-76
I7.12 Schwerin Concaves, Inc., Walla Walla, Washington I-76
I7.12.1 Case Study References I-76
I7.12.2 Site Conditions I-76
I7.12.3 Technical Approach I-77
I7.12.4 Results I-77
I7.12.5 Lessons Learned I-78
I8 Vadose Zone Treatment by Bioinfiltration I-78
I8.1 Conceptual Design I-78
I8.2 Bioinfiltration Remediation Processes and Approach I-79
I9 References I-80

Figures

Figure I-1. Cross-Section of a Recirculating In Situ Bioremediation System I-53
Figure I-2. Molasses Injected at 100-D Area Biostimulation Treatability Test Site to Nourish Bacteria I-56
Figure I-3. 100-KR-4 Plume Showing Treatability Test Site I-61
Figure I-4. PG&E Hinkley IRZ Areas I-64
Figure I-5. PG&E Topock Upland ISPT Layout I-67
Figure I-6. PG&E Topock Floodplain ISPT Layout I-68
Figure I-7. Configuration of the Schwerin Concaves Remedial Pilot Test I-77
Figure I-8. Functional Design of the Planned 100-KW Bioinfiltration System I-79

Tables

Table I-1. Substrates Used for Enhanced Anaerobic Bioremediation I-48
Table I-2. Screening Level Evaluation of Several Commonly Used In Situ Bioremediation Substrates I-51

Terms

ac	acre
ATP	anaerobic thermal processor
BFS	blast furnace slag
bgs	below ground surface
bph pathway	biphenyl pathway
CBA	chlorobenzoic acid
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
CNF	Central Neutralization Facility
COPC	contaminant of potential concern
CPS	calcium polysulfide
CSTR	continuous stirred-tank bioreactor
CVOC	chlorinated volatile organic compound
CY	calendar year
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
DTSC	Department of Toxic Substances Control (California)
ECI	Electrocoatings, Inc.
Ecology	Washington State Department of Ecology
EOS®	Emulsified Oil Substrate
EPA	U.S. Environmental Protection Agency
ERDF	Environmental Restoration Disposal Facility
ESD	Explanation of Significant Differences
ESS	ex situ solidification/stabilization
FS	feasibility study
ft	feet/foot
ft^2	square feet/foot

gal	gallon(s)
GCW	groundwater circulation well
g/kg	Grams per kilogram
gpd	gallons per day
ha	hectare
HRC	hydrogen release compound
HTTD	high-temperature thermal desorption
INEEL	Idaho National Engineering and Environmental Laboratory
IRZ	in situ reactive zone
ISB	in situ bioremediation
ISCO	in situ oxidation
ISGR	in situ gaseous reduction
ISPT	in situ pilot test
ISRM	in situ redox manipulation
ISTD	in situ thermal desorption
ISV	in situ vitrification
kg/m^3	kilograms per cubic meter
kWh	kilowatt hour
lb	pound
µg/kg	micrograms per kilogram
m	meter
m^2	square meter(s)
MCL	maximum contaminant level
mg/kg	milligrams per kilogram
mM	millimole
MRC™	Metals Remediation Compound
MTBE	methyl tert butyl ether
mT/ha	?/hectare
MWh	megawatt hour
NAPL	non-aqueous phase liquid

nm	nanometer
NOM	natural organic material
NPDES	National Pollutant Discharge Elimination System
NZVI	nano-scale zero-valent iron
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
OU	operable unit
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCE	tetrachloroethylene
PCP	pentachlorophenol
PG&E	Pacific Gas and Electric Company
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
psi	pounds per square inch
RO	reverse osmosis
ROD	Record of Decision
ROI	radius of influence
RPO	Remediation Process Optimization
RUM	Ringold Formation upper mud
scfm	Standard cubic feet per minute
SGBR	subgrade bioreactor
SPSH	six-phase soil heating
SPT	Selma Pressure Treating
SRB	sulfate-reducing bioreactors
SRS	Savannah River Site
SVE	soil vapor extraction
SVOC	semivolatile organic compounds
TCE	trichloroethylene
TOC	total organic carbon

VFA	volatile fatty acid
VOC	volatile organic compounds
VSEP®	vibratory shear-enhanced processing
WTP	Waste Treatment and Immobilization Plant
ZVI	zero-valent iron

I1 Additional Information on Technologies Not Retained for Waste Site Treatment

Information regarding technologies that were not retained for further evaluation for treatment of waste sites contaminated with radionuclides, chromium(VI), other metals, and organic compounds (polychlorinated biphenyls [PCB], polynuclear aromatic hydrocarbons [PAH], and petroleum compounds) are presented in this section.

In addition to the technologies described below, disposal through backfill of treated soil or to an offsite landfill and soil blending were not retained for treatment of impacted waste sites at 100-D/H. Because no ex situ treatment options were retained, backfill of treated soil is not applicable. Because disposal to the Environmental Restoration Disposal Facility (ERDF) is considered adequate and reliable for impacted media at 100-D/H, disposal to offsite landfills was not retained. Soil blending was not retained because it relies on contaminant dilution and is considered ineffective.

I1.1 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 at the 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.

I1.1.1 Solidification/Stabilization

Ex situ solidification/stabilization (ESS) was not retained for treatment of soil contaminated with radionuclides, chromium(IV), or other metals.

I1.1.1.1 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. A wide variety of solidification/stabilization agents is available, including Portland cement or other pozzolans, silicates, bitumen, and acrylic polymers. Portland cements typically consist 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 bind metals chemically. Polymeric compounds can be used to bind metal and radionuclides by micro-encapsulation (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [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 to them 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.

I1.1.1.2 Relevant Demonstration Projects

Cement solidification has been a widely used technique 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 Report* [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 (BFS) were used as binders. Additives included Type F fly ash, site fly ash, absorbents, and sodium silicate. The study indicated the toxicity characteristic leaching procedure was met, and leachability of uranium was controlled, except when present at high concentrations. The study also indicated a significant increase in waste volume resulted from the cement stabilization process (*100 Area Source Operable Unit Focused Feasibility Study Report* [DOE/RL-94-61]).

The U.S. Department of Energy (DOE) has demonstrated polyethylene encapsulation to treat a number of radionuclides (for example, cesium and strontium), and toxic metals (including chromium, lead, and cadmium). DOE's technology information profile (*Technology Catalogue, Second Edition* [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 (*Technology Catalogue, Second Edition* [DOE/EM-0235]).

I1.1.1.3 Evaluation and Screening Rationale

ESS is considered low to moderately effective at immobilizing mobile 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 required and appropriate cement agents. ESS was screened out in favor of the safer alternative of disposal in ERDF, a centralized facility engineered to protect against weathering and seismic activity.

I1.1.2 Soil Washing

Soil washing was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.1.2.1 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 the onsite landfill.

A wide range 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 more strongly associated with the finer-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 course particles, simple separation may not be effective, and more aggressive—and thus expensive-processes will be required.

I1.1.2.2 Relevant Demonstration Projects

A bench-scale treatability study was completed by Pacific Northwest National Laboratory (PNNL) in 1996 on a pluto 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 fractions. The effectiveness of soil washing tests was evaluated based on 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 backfill. By treating both 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 (*100 Area Soil Washing: Bench-Scale Tests on 116-F-4 Pluto Crib Soil* [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 primarily (97.2 percent) comprised of coarse fraction (greater than 2 mm [0.08 in.]), and was treated using physical and chemical extraction methods. Results indicated soil washing could adequately reduce levels of cobalt-60 and europium-152; however, the activity of cesium-137 could not be significantly reduced. Batch III was comprised of approximately 46.9 percent coarse fraction, and results indicated soil-washing tests were effective in reducing the radionuclide activities 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 Operable Unit (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 in order 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 limits. 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 such as the intact green layer or fly ash. Excavation and direct disposal may be the preferred alternative for this material.

I1.1.2.3 Evaluation and Screening Rationale

The effectiveness of soil washing and the complexity of the processes that are required are driven by the binding processes that exist between the contaminants and the soil particles (adsorbed or precipitated), and is variable based on the nature and solubility of the contaminant of potential concern (COPC).

As discussed in the draft BC Cribs Focused Feasibility Study (*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. Consequently, more aggressive and costly approaches would be required, which also may not be effective. Given that pilot tests at the Hanford Site have not been extremely effective, soil washing was not retained for further consideration.

I1.1.3 Ex Situ Vitrification

Ex situ vitrification was not retained for treatment of soil contaminated with radionuclides, Cr(VI), and other metals.

I1.1.3.1 Description

Vitrification processes are solidification methods that use heat (1,100 to 2,000°C [2,012 to 3,632°F]) to melt and convert waste materials into glass or other glass and crystalline products. This technology is considered highly effective in the treatment of COPCs, and in permanently reducing the mobility, toxicity, and volume of contaminants. The high temperatures destroy any 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) (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

Ex situ joule, heating vitrification uses furnaces that have evolved from the glass 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 (*100 Area Source Operable Unit Focused Feasibility Study Report* [DOE/RL-94-61]).

I1.1.3.2 Relevant Demonstration Projects

In the early 1990s, DOE developed a Transportable Vitrification System to vitrify applicable mixed-waste sludges and solids effectively 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, Oak Ridge National Laboratory (ORNL), and Clemson University. A mixed-waste demonstration was completed in 1997 using Savannah River B&C pond sludge, and a mix of B&C pond sludge and Central Neutralization Facility (CNF) sludge. The study indicated the system vitrified 84 m^3 (2,966 ft^3) of mixed waste into 34 m^3 (1,200 ft^3) of glass waste, resulting in a 60 percent waste volume reduction. Results of the study indicated the need for high capital costs and extensive upfront development. However, it indicated 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 cover 26 hectares (ha) (65 acres [ac]) and will 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 the WTP Project Execution Plan (*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.

I1.1.3.3 Evaluation and Screening Rationale

Ex situ vitrification is considered to have low implementability given the high complexity of equipment required and the 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 is not considered favorable for implementation 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 be sure the glass produced by the facility meets regulatory requirements and standards. Ultimately, the glass produced would still require final disposal in an alternate facility.

As presented in *Central Plateau Vadose Zone Remediation Technology Screening Evaluation* (RPP-ENV-34028), estimated costs for implementation of this technology can range from $500 to $1,000 per calendar year (CY). These costs include soil excavation, screening to remove debris, installation of the vitrification system and offgas treatment system, operation and maintenance (O&M), utilities, site management and sampling support, and onsite disposal of vitrified material and offgas treatment. For the WTP facility, *Project Execution Plan for the River Protection Project Waste Treatment and Immobilization Plant* (DOE/ORP-2003-01) indicated that the total project cost for the WTP is estimated to be $5.781 billion.

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

I1.1.4 Ex Situ Thermal Desorption

Ex situ thermal desorption was not retained for treatment of soil contaminated with organic compounds.

I1.1.4.1 Description

Ex situ thermal desorption involves the direct application of heat to increase the temperature of soil and destroy or volatilize organic compounds in the soil. A carrier gas or vacuum system is used to transport the organic-rich vapors for further treatment. All thermal desorption systems require treatment of offgas in order to remove particulates and contaminants. The process does not involve incineration or pyrolysis. Typically, ex situ thermal desorption involves use of rotary drums or similar mechanical heating devices, vapor capture, and a vacuum system to extract volatilized water and organics to the gas treatment system.

Treatment to low levels of organic contaminants can be achieved with this technology. Based on the operating temperatures, thermal desorption processes can be categorized as either high-temperature thermal desorption (HTTD, 320 to 560ºC [608 to 1,040ºF]) or low-temperature thermal desorption (90 to 320ºC [194 to 608ºF]). HTTD targets semivolatile organic compounds (SVOC), PAHs, PCBs, and pesticides. Volatile organic compounds (VOC) can also be treated with HTTD, although the process is not as cost-effective. Low-temperature thermal desorption targets nonhalogenated VOCs and fuel, and can treat SVOCs but at a reduced effectiveness.

I1.1.4.2 Relevant Demonstration Projects

A full-scale demonstration project was completed in 1992 at the Outboard Marine Corporation site in Waukegan, Illinois, for the treatment of PCBs from soil, sediments, and sludges using thermal desorption. The demonstration involved treatment using an anaerobic thermal processor (ATP) licensed by SoilTech ATP Systems, Inc. The study indicates that a total of 224 tons of PCB-contaminated soil was treated, and

treatment efficiencies for removal of PCB of approximately 99.9 percent were achieved (SoilTech *Anaerobic Thermal Processor: Outboard Marine Corporation Site SoilTech ATP Systems, Inc*. [EPA/540/MR-92/078]).

I1.1.4.3 Evaluation and Screening Rationale

Ex situ thermal desorption can be a highly effective technology. Although equipment for implementation of this technology is readily available, it is mechanically complex, posing technical implementability challenges. Given the relatively low volumes of petroleum-contaminated soil that are likely to be present, and the high mobilization costs, onsite disposal of soil is likely to be much more cost-effective. Transportability of equipment becomes challenging when the amount of soil to treat is small, and the complexity of the equipment requires skilled operators. For these reasons, ex situ thermal desorption was not retained for further consideration.

I1.2 In Situ Treatment—Reagent Approach

This section discusses reagents/technologies that could be used for in situ treatment of the COPCs. Delivery of these reagents is discussed in the following section. These reagents/technologies were not retained for further consideration.

I1.2.1 In Situ Chemical Reduction

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

I1.2.1.1 Description

Considerable technical development and study of manipulating subsurface geochemical conditions to sequester or immobilize inorganic contaminants has been pursued over the past 25 years. Chemical reducing agents, such as diluted hydrogen sulfide gas, may be used to transform Cr(VI) to less-mobile and less-toxic chromium(III) by means of injection into the vadose zone (*In Situ Gaseous Reduction Pilot Demonstration—Final Report* [PNNL-12121]). Alternative chemical reducing agents include calcium polysulfide, dithionite, ferrous sulfate, and zero-valent iron (ZVI). The alternate chemical agents delivered as solids or liquids are inherently limited because they do not fully contact the targeted sediment contamination in the vadose zone.

I1.2.1.2 Relevant Demonstration Projects

The U.S. Department of Defense (DOD) conducted a field test to evaluate the effectiveness of the in situ gaseous reduction at a chromate-contaminated waste site located at the White Sands Missile Range (*In Situ Gaseous Reduction Pilot Demonstration—Final Report* [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 site soil by a vacuum applied to extraction boreholes located at the site boundary, and residual hydrogen sulfide was removed prior to release of the air back to the atmosphere. The injection test lasted 76 days with no detectable releases of hydrogen sulfide to the site atmosphere. Comparison of Cr(VI) analyses of soil samples taken before and after the test indicated that 70 percent of the Cr(VI) originally present at the site was reduced and thereby immobilized by in situ gaseous reduction. Treatment was generally better in zones of higher permeability sand containing less silt and clay, indicating that geologic heterogeneity is a limitation to treatment effectiveness.

I1.2.1.3 Evaluation and Screening Rationale

The application of toxic hydrogen sulfide gas to the near surface carries significant risk. Transportation and handling of reducing agents also poses more of a health and safety concern during application, compared to biological reduction substrates. Because of more rapid chemical reactions, the application of

liquid reducing agents to contact contaminated vadose zone soil uniformly may be more problematic than using biological substrates. Based on these implementability and potential effectiveness issues, in situ chemical reduction was not retained in favor of in situ biological reduction.

I1.2.2 In Situ Chemical Oxidation

In situ oxidation (ISCO) was not retained for treatment of soil contaminated with organic compounds. ISCO is not an applicable technology for the treatment of soil contaminated with metals and radionuclides.

I1.2.2.1 Description

ISCO involves the subsurface delivery of chemical oxidants to destroy organic COPCs. Commercially available oxidants used in field applications include hydrogen peroxide, ozone, permanganate, persulfate, and percarbonate. The technology is capable of achieving high treatment efficiencies in unsaturated aliphatic and aromatic compounds. Petroleum hydrocarbons and PAHs can be treated with a variety of oxidants (including peroxide, percarbonate, persulfate, and ozone). However, the number of case studies demonstrating the successful treatment of PCBs with ISCO is limited.

I1.2.2.2 Relevant Demonstration Projects

A pilot study was conducted in fall 2006 to evaluate the effectiveness of permanganate injection to treat chlorinated volatile organic compounds (CVOC) in shallow unsaturated heterogeneous soil ("Challenges with an ISCO Application in the Unsaturated Zone: Case of the Missing Permanganate" [Borchert and Raphael, 2008]). The treatment zone was 4.8 meters (m) (16 [ft]) wide, 5.4 m (18 ft) long, and 2.7 m (9 ft) deep. The site geology consisted of silty clay in the upper 1.6 m (5.5 ft) with traces of sand and gravel and an intermittent sandy layer from 0.3 to 0.6 m (1 to 2 ft) below ground surface (bgs), and gravelly sand with some silt and clay from 1.6 to 4.3 m (5.5 to 14 ft) bgs with a discontinuous sandy and silty clay layer from 2.4 to 2.7 m (8 to 9 ft) bgs. Groundwater was encountered from 2.4 to 3 m (8 and 10 ft) bgs. The maximum concentrations of trichloroethylene (TCE) and cis-1, 2-DCE were 66,000 and 2,400 micrograms per kilogram (µg/kg), respectively. The permanganate soil oxidant demand ranged from about 3 to 17.1 grams per kilogram (g/kg). Approximately 1,041 L (275 gallons [gal]) of 40 percent by weight permanganate (about 3,000 pounds [lb] [1.5 tons]) were injected at nine locations within the pilot study area. Where oxidant was visually observed, the radius of influence ranged from 2.5 up to 3 m (8 to 10 ft). However, several visual borings had limited evidence of permanganate. Performance monitoring indicated that TCE and cis-1,2-DCE concentrations in soil decreased between 44 and 93 percent, respectively. However, concentrations in groundwater increased up to tenfold. Results from the pilot study indicated that a majority of oxidant migrated into the shallow groundwater and was consumed by CVOCs and high oxidant demand (up to 20.7 g/kg permanganate). Conclusions state that it is challenging to acquire fine distribution of an oxidant solution in shallow silty clay, even with controlled low pressures and flows and closely spaced injection points. Difficulty was also encountered in creating temporarily saturated zones for aqueous-based ISCO reactions in the unsaturated zone, particularly in permeable portions of the formation. Based on the results of the pilot study, excavation was selected as a more cost-effective remedial alternative for shallow soil.

An ozone gas vadose zone sparging system for treating PAHs operated during the summer of 2001 at the Former Fuel Oil Distribution Terminal in Ilion, New York (*Permeable Reactive Barriers: Lessons Learned/New Directions* [ITRC, 2005a]). Adsorbed PAHs were delineated from approximately 0.6 to 2.4 m (2 to 8 ft) bgs, and initial total PAH concentrations exceeded 30 milligrams per kilogram (mg/kg). The subsurface contained both fill materials and native soil consisting primarily of silty sand. Groundwater was encountered at 2.1 to 2.4 m (7 to 8 ft) bgs. To achieve a target 60-day period for project completion, a nominal 50-lb/day (23 kg/day) ozone-generation system was used to inject both ozone and

oxygen. Ten initial sparge points were installed at the site by direct-push methodology. A shallow vapor extraction system was installed to control emissions. The injection system operated over a period of 8 weeks. Post-remediation soil sampling results indicated no remaining PAH (primarily benzo[a]anthracene, benzo[a]pyrene, and chrysene) concentrations above method detection limits, achieving the remedial goals of 90 percent concentration reduction in 60 days. Naphthalene was also reduced to below New York State Department of Environmental Conservation Technical and Administrative Guidance Memorandum standards. Average reduction of naphthalene was greater than 32 percent in 60 days.

An ozone gas vadose zone sparging demonstration for treating pentachlorophenol (PCP) and creosote (PAHs) was performed in 1998 at the Former Wood Treatment Site, Sonoma County, California (*Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition* [ITRC, 2005b]). The former wood treatment facility contained creosote and PCP dip tanks used for treating wood poles. Maximum pretreatment soil concentrations were 220 mg/kg PCP and 5,680 mg/kg total PAHs. High levels of dissolved contamination and nonaqueous phase liquid (NAPL) existed in the vadose zone prior to treatment. The site subsurface consisted of very heterogeneous stratified silty sands and clays, and the depth to water varied from 1.2 to 4.6 m (4 to 15 ft). The ozone treatment system design included treatment of both the saturated and unsaturated zones. Therefore, ozone gas delivery modes included ozone sparging and ozone gas injection above the water table. Field operation and monitoring of the in situ ozonation demonstration project was conducted from December 1997 through December 1998. Approximately 3,628 kg (8,000 lb) of oxidant was delivered to the subsurface, with an average oxidant dose of approximately 1.9 g (0.07 oz) ozone per kg of soil. Soil samples collected showed an average 93 percent reduction in PCP and PAHs. Concentration at the maximum pretreatment soil contamination was reduced greater than 98 percent, from an initial value of 220 mg/kg PCP and 5,680 mg/kg total PAHs, to below detection limits. Significant contaminant mass reduction was reflected not only in soil data, but also in substantial reductions in aqueous-phase concentrations of PCP and PAHs.

I1.2.2.3 Evaluation and Screening Rationale

The treatment effectiveness of ISCO can be hindered by non-uniform oxidant distribution related to high soil oxidant demand levels in shallow fine-grained soil, and rapid oxidant reaction rates. It may also be difficult to maintain saturated conditions where oxidant can be delivered, to allow the aqueous-based ISCO reactions to occur. Successful treatment of organic COPCs has been demonstrated using ozone gas injection into the vadose zone. However, given the uncertainties in oxidant delivery effectiveness, difficulties with installing a density of injection wells, and higher relative cost compared to in situ biological methods, ISCO was not retained for further consideration.

I1.2.3 Reductive Dechlorination Using Zero-Valent Metals and Bioremediation

Reductive dechlorination using zero-valent metals and bioremediation was not retained for treatment of soil contaminated with PCBs.

I1.2.3.1 Description

Both biological and abiotic methods are potentially applicable for reductive dechlorination of PCBs. During bioremediation, anaerobic bacteria replace chlorine atoms with the electron-donating hydrogen on the PCB molecule. A similar abiotic process occurs with zero-valent metals, which include iron, palladium, and other combinations (called bi-metals). Bi-metals have been found to be more reactive. Nano-particle-sized bi-metals have also been shown to be superior to micro-sized ZVI (*Emerging Technologies for the In Situ Remediation of PCB-Contaminated Soil and Sediments: Bioremediation and Nanoscale Zero-Valent Iron* [Mikszewski, 2004]). The bioremediation process involves mixing an

electron donor (such as lactate) with the contaminated soil and maintaining anaerobic conditions for a number of months. A similar process is used with the zero-valent metals.

I1.2.3.2 Relevant Demonstration Projects

A review of emerging technologies for in situ remediation of PCB-contaminated sediments and soil was presented in *Emerging Technologies for the In situ Remediation of PCB-Contaminated Soil and Sediments: Bioremediation and Nanoscale Zero-Valent Iron* (Mikszewski, 2004). The study focused on the use of nano-scale zero-valent iron (NZVI) and bioremediation for reductive dechlorination.

The technology review indicated that NZVI particles are capable of reducing a wide range of environmental pollutants, including PCBs. In particular, the properties of NZVI and other nano-scale metals (high surface area to volume ratios, high surface energies, and a large fraction of stepped surface, zero valency) make them extremely chemically reactive. Several laboratory and field-scale demonstrations have been conducted demonstrating the performance of using NZVI for PCB dechlorination. The studies show conflicting results. Where complete dechlorination could be achieved, percent reduction of PCBs ranged from 25 to 84 percent. In the field study where 84 percent reduction was achieved ("In-Situ Dechlorination of Polychlorinated Biphenyls in Sediments Using Zero-Valent Iron" [Gardner et al., 2004]), complete dechlorination was achieved in only 1 day. In another study (*Development and In Situ Application of Sorbent/Reagent-Amended "Active" Sediment Caps for Managing HOC-Contaminated Sediments* [Lowry et al., 2004]), NZVI was shown to dechlorinate PCBs with congener half-lives ranging from 40 days to 77 years, with no biphenyl production noted (indicating incomplete dechlorination).

The technology review indicates that at present, anaerobic reductive dechlorination is not a viable stand-alone PCB remediation technology. A field treatability study conducted in Mississippi by the U.S. Army Corps of Engineers highlighted the inherent limitation of anaerobic reductive dechlorination of PCBs. Significant dechlorination of PCBs can take several years under optimal environmental conditions. Aside from length of time required for dechlorination, the limited bioavailability of PCBs severely inhibits reductive dechlorination because PCBs are often tightly bound to soil and sediment particles, rendering them resistant to the enzymes of dechlorinating organisms. Furthermore, it is difficult to establish and stimulate PCB-dechlorinating organisms at remediation sites. More field studies must be conducted to test methods of bioaugmentation and biostimulation for PCB dechlorinators.

The potential for aerobic bioremediation of PCBs was also considered. PCBs are broken down aerobically by the catabolic "biphenyl pathway" (bph pathway) ("Genetically Modified Organisms to Remediate Polychlorinated Biphenyls. Where Do We Stand?" [Sylvestre, 2004]). Broad ranges of gram-negative and gram-positive aerobic bacteria are capable of co-metabolically degrading PCBs via the bph pathway. However, the complete mineralization of PCB by the bph pathway is extremely rare. Most of the time, the enzymes degrade the ring with fewer chlorines while releasing the second ring as a chlorobenzoic acid (CBA). This is problematic because CBAs can be toxic and inhibitory to PCB degraders. As a result, genetic engineering has become a necessary tactic to produce organisms with the bph pathway and a CBA degradation pathway. Even with the recent advances of genetically engineered strains, the major problem in field application would be, as it is with anaerobic dechlorination, the limited bioavailability of the PCBs.

I1.2.3.3 Evaluation and Screening Rationale

The effectiveness of these treatment technologies is considered to be poorly known, given the limited availability of published testing results and/or conflicting technology demonstration data. Implementability is considered moderate because it could be executed by soil mixing using conventional excavation equipment if the treatment depth is shallow. However, the issue common with all these technologies is the limited availability of PCBs in soil and sediments. The hydrophobic nature of PCBs

allows tight adsorption to organic matrices within soil and sediments, rendering them resistant to microbial attack and chemical reduction. Reductive dechlorination using zero-valent metals and bioremediation are not proven technologies and were therefore not retained for further consideration.

I1.2.4 In Situ Gaseous Reduction with Chemical Reductant or Biological Substrate

In situ gaseous reduction (ISGR) was not retained for treatment of soil contaminated with radionuclides, Cr(VI), and other metals.

I1.2.4.1 Description

ISGR is a vadose zone remediation technology that uses a gaseous reagent (such as a hydrogen sulfide/ nitrogen gas mixture) to reduce or treat contaminants. It is applicable to oxidation reduction- (redox) sensitive contaminants. The objective is to reduce the contaminant chemically (metal or radionuclide) to a less mobile and sometimes less toxic form, preventing further migration and reducing the risk of contaminating the groundwater. For contaminants such as Cr(VI), uranium, and technetium, the reduced species are significantly less mobile than the oxidized species. With the reduction of iron associated with sediment, the ISGR technology creates a reducing zone within the subsurface that continues to reduce contaminants or other oxidants (for example, oxygen) that migrate into the treatment zone until the reducing capacity becomes depleted (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

I1.2.4.2 Relevant Demonstration Projects

An ISGR pilot demonstration test was completed at the White Sands Missile Range in New Mexico between 1996 and 1998 (*In Situ Gaseous Reduction Pilot Demonstration—Final Report* [PNNL-12121]). A combination of gas injection and vacuum extraction wells was used to distribute hydrogen sulfide gas. In the demonstration, six extraction wells surrounded a central vacuum well in a hexagonal pattern. The study indicated that 70 percent of the Cr(VI) was reduced to its trivalent state (chromium(III)). Highest treatment efficiencies were seen at 1.2 to 3 m (4 to 10 ft) bgs, which was the zone of highest contaminant concentration. Low treatment efficiencies were seen at 3 to 4.8 m (10 to 16 ft) bgs. The study concluded that the treatment gas mixture was largely channeled through the upper zone and bypassed the less-permeable, lower-zone soil (*In Situ Gaseous Reduction Pilot Demonstration—Final Report* [PNNL-12121]).

A second demonstration test was planned at the former 183-DR facility in 100-D/DR of DOE's Hanford Site, which is associated with a significant groundwater contaminant plume (*Characterization Activities Conducted at the 183-DR Site in Support of an In Situ Gaseous Reduction Demonstration* [PNNL-13486]). Site characterization efforts were completed in 2001 in order to obtain information regarding distribution of Cr(VI) and other chemical and geological data that could support an ISGR demonstration. Site characterization data collected from two boreholes at the site failed to show signs of a Cr(VI) vadose zone source for the groundwater plume. Therefore, the project was suspended until additional site characterization could be completed.

I1.2.4.3 Evaluation and Screening Rationale

The use of a gas as the reducing agent is advantageous compared to a liquid-based delivery method because the risk of mobilizing contaminants is lower and better diffusion of reagent is expected (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). However, significant uncertainties have been identified regarding the effectiveness of ISGR. Key uncertainties, as identified in *Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99* (WMP-27397), include:

- Physical heterogeneity of the vadose zone sediments presents a challenge for an even distribution of the hydrogen sulfide gas. Fine-grained soil is likely to contain more contaminants and is more difficult to treat.
- Heterogeneity occurs in the distribution of reducible iron.
- Re-oxidation of the treated zone is likely because of flux of oxygen in soil air into the pore spaces.

Technetium-99 readily re-oxidizes under aerobic conditions, requiring periodic treatment to maintain reducing conditions. Cr(VI), and to some extent uranium, are not likely to re-oxidize when aerobic conditions are re-established. Strong reducing conditions can mobilize other constituents (for example, arsenic and manganese). However, these constituents would likely re-oxidize rapidly once they mobilize outside the treatment zone.

The equipment and processes required to implement ISGR are readily available and have been demonstrated in the field. The major challenge for ISGR is the large number of wells that must be installed to achieve overlapping radii of influence. Boreholes drilled through large vertical contaminated zones would generate substantial amounts of waste. Implementation of this technology could also lead to risk to workers with respect to exposure and safety. Hydrogen sulfide gas is extremely hazardous, and it would be necessary to install effective engineering controls to mitigate risk to worker safety (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

Better tools are needed to evaluate potential designs for vadose zone remediation using reactive gases. For example, a multiphase flow model would assist in evaluating the applicability of reactive gas technologies to the deep vadose zone. In situ gaseous reduction is now used for further study in *Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau* (DOE/RL-2007-56) because it has the potential to immobilize technetium-99 and uranium, and has been demonstrated at the field scale for similar applications.

Additional information resulting from the ongoing treatability studies is required prior to making decisions about the full-scale application of ISGR at the Hanford Site. For this reason, ISGR was not retained for further consideration.

I1.3 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. Chemical and biological treatment has been retained for soil contaminated with radionuclides, Cr(VI), and other metals. However, delivery of amendments through infiltration is considered more cost-effective than the approaches discussed below. For this reason, in addition to others discussed in each section below, these technologies have not been retained for further consideration.

I1.3.1 Mixing with Conventional Excavation Equipment

Mixing or delivery of amendments using conventional excavation equipment was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.3.1.1 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 a slurry of the amendment has been added. A relatively thick slurry would be

required to keep the amendments from readily draining out of the soil, or the mixing would need to be performed in a lined basin. This is considered a highly effective and moderately implementable technology; however, the depth at which it can be implemented is limited to the reach of the equipment.

I1.3.1.2 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 below; however, they are likely to be higher than surface infiltration methods given that surface infiltration is likely less intrusive. Because of the depth limitation of this mixing method, as well as the availability of infiltration methods, mixing or delivery of amendments using conventional excavation equipment was not retained.

I1.3.2 Deep Soil Mixing

Deep soil mixing was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.3.2.1 Description

Deep soil mixing uses large-diameter augers or horizontally rotating heads to blend in reactants and homogenize soil. The diameter of the augers can vary from 0.3 to 4 m (0.98 to 13 ft) (*Containment, Stabilization and Treatment of Contaminated Soils 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 (*Containment, Stabilization and Treatment of Contaminated Soils Using In-Situ Soil Mixing* [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 on site-specific conditions. Generally, this method increases soil volume, and if necessary, excess soil will require 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.

I1.3.2.2 Relevant Demonstration Projects

Deep soil mixing was used to remediate an abandoned transformer repair facility in Miami, Florida (*In-Situ Stabilization and Fixation of Contaminated Soil by Soil Mixing* [Jasperse and Ryan, 1992]). PCB concentrations over the affected area ranged from 200 to 600 ppm, with a maximum concentration of 1,000 ppm. Impacted media was encountered to approximately15 m (49 ft) 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 kilograms per cubic meter (kg/m^3) of soil mixed. Results from the study show a decrease in concentrations of PCBs after treatment, as well as an increase in unconfined strength and decrease in permeability of the mixed samples over time (*In-Situ Stabilization and Fixation of Contaminated Soil by Soil Mixing* [Jasperse and Ryan, 1992]).

I1.3.2.3 Evaluation and Screening Rationale

Deep soil mixing is considered highly effective at delivering reagents to contaminated soil. Chemical agents are uniformly mixed with the soil column, providing good contact and reaction between the contaminant of concern 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 marginal at the Hanford Site because of the presence of cobbles and boulders in the subsurface. Because the equipment cannot mix to depths significantly deeper than the reach of a backhoe, and ERDF is available for soil disposal at the Hanford Site, excavating the soil and disposing of it at ERDF is a much more straightforward and proven option. In addition, because implementability will be limited by site conditions and required depth of treatment, deep soil mixing is not retained for further evaluation.

I1.3.3 Foam Delivery of Reagents

Foam delivery of reagents was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.3.3.1 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 calcium polysulfide. 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), technetium-99, and uranium.

I1.3.3.2 Relevant Demonstration Projects

Foam delivery of amendments is currently in its 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 metal and radionuclide contaminants.

Laboratory batch and column tests have been conducted for foam delivery of calcium polysulfide 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 calcium polysulfide under conditions similar to those of the field vadose zone, and to determine the extent of hexavalent immobilization. Results from the study indicated that a column test calcium polysulfide 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 calcium polysulfide is delivered in a water-based, single-phase solution. However, no information is currently available on how far the foam will migrate from an injection well in field conditions.

I1.3.3.3 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 prior to making a decision regarding its full-scale use at the Hanford Site. For this reason, foam delivery of reagents is not retained for further consideration.

I1.3.4 Gaseous Delivery of Reagents (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 previously discussed in Section I1.2.4. Because additional information resulting from the treatability studies is required prior to making decisions about the full-scale application of ISGR at the Hanford Site, ISGR was not retained for further consideration.

I1.3.5 Horizontal Injection Wells

Delivery of substrates using horizontal injection wells was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.3.5.1 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 in areas where COPCs are characterized within a certain discrete depth interval.

I1.3.5.2 Relevant Demonstration Projects

An unsuccessful horizontal well technology demonstration was conducted at the Hanford 100-D area from November 2009 through January 2010 (*Treatability Demonstration Report for Directional Drilling in the 100-D Area* [SGW-45974]). 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 (49 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 ft) when downward progress ceased because of inadequate force on the downhole 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.

I1.3.5.3 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 hydraulic conductivity more pronounced than horizontal hydraulic conductivity, amendment distribution over a larger depth interval would be more challenging compared to vertical wells. Furthermore, maintaining target borehole depth and alignment with horizontal drilling in gravelly/cobbly lithologies would be difficult. This issue was encountered during the technology demonstration at the Hanford Site. Given the increased difficulty in installation and amendment delivery compared to vertical injection wells, as well as the unsuccessful tests to date at the Hanford Site, horizontal injection wells were not retained.

I1.4 In Situ Treatment—Other

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

I1.4.1 Desiccation

Desiccation was not retained for treatment of soil contaminated with radionuclides, Cr(VI), and other metals.

I1.4.1.1 Description

Desiccation involves drying a targeted portion of the vadose zone by injecting dry air and extracting soil moisture at soil gas extraction wells (*Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau* [DOE/RL-2007-56]). Because desiccation removes water already in the vadose zone, it reduces the amount of pore fluid available to support downward transport of contaminants in the deep vadose zone, impedes water movement, and augments the impact of surface water infiltration control.

The impact of desiccation on the movement of Cr(VI), technetium-99, and uranium is based on physical removal of water from the subsurface. Removing moisture from the contaminated material reduces the driving force for continued vertical migration. Theoretically, desiccation would be effective in immobilizing contaminants to the extent that moisture content is lowered below the point for unsaturated flow to occur. The longevity of the "dry" conditions depends on the soil moisture infiltration rate, the relative humidity of atmospheric air, and the proximity to groundwater. In time, moisture levels recover to pre-extraction concentrations (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). Without surface infiltration control, moisture content would eventually return to a state of equilibrium with surface infiltration rates. Therefore, this technology is considered not to be effective in the long term without concurrent infiltration control. A more detailed evaluation of this technology, including some initial feasibility calculations, is presented in *Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99* (WMP-27397).

I1.4.1.2 Relevant Demonstration Projects

A very limited desiccation test showing that subsurface airflow can be induced in the Central Plateau vadose zone was performed in conjunction with a leak detection test (*200-BP-1 Prototype Hanford Barrier Annual Monitoring Report for Fiscal Year 2003* [CP-18187]).

I1.4.1.3 Evaluation and Screening Rationale

Equipment and technology required for implementation of desiccation is well-established and common. Soil vapor extraction (SVE) is a well-established technology, and moisture extraction has been safely demonstrated at the Hanford Site (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). However, there is uncertainty with the number of wells, well spacing, and well configuration details required for optimal field/full-scale implementation. In addition, uncertainties are associated with specific aspects of implementation and long-term effectiveness. Desiccation was included in the March 2008 *Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau Site* (DOE/RL-2007-56) and is expected to provide information in addressing these uncertainties.

Additional information resulting from the treatability studies is required prior to making decisions about the full-scale application of desiccation at the Hanford Site. Therefore, desiccation was not retained for further evaluation.

I1.4.2 In Situ Thermal Desorption

In situ thermal desorption (ISTD) was not retained for treatment of soil contaminated with organic compounds.

I1.4.2.1 Description

ISTD involves the direct application of heat (for example, using electrical current to heat soil; electrical heater elements; injection of hot air, steam, or hot water; or radio frequency) to increase the temperature of soil and destroy or volatilize organic compounds. The use of electrical heating elements installed in closely spaced soil borings (1.5 to 3 m [5 to 10 ft] intervals) is the most common approach for

implementing ISTD. Conductive heating is the primary mechanism that transmits heat to the soil. The technology can achieve rapid removal/destruction of a mix of VOCs and SVOCs, and achieve low residual concentrations. Vapors produced would require removal using extraction wells or trenches using a vacuum pump. The vapor stream would be pre-conditioned by a moisture separator or heat exchanger and treated by a vapor treatment system.

I1.4.2.2 Relevant Demonstration Projects

Field demonstrations were performed in 1993 and 1994 at the Savannah River Site (SRS) and the Hanford 300 Area to evaluate six-phase soil heating (SPSH), a form of electrical resistive heating, as a vadose remedial technology for tetrachloroethylene (PCE) and TCE (*Six-Phase Soil Heating* [DOE/EM-0272]). The demonstration site at the Hanford Site was located in the 300 Area at an uncontaminated, undisturbed site. The objective of the 300 Area demonstration was to refine the design of the six-phase electrodes and other system components, and address scale-up issues in the field. The demonstration site at the SRS was located at one of the source areas within the 2.6 km^2 (1 mi^2) VOC groundwater plume. The contaminated target zone was a 3 m (10 ft) thick clay layer at a depth of approximately 12 m (40 ft). TCE and PCE concentrations in sediments ranged from zero to 181 µg/kg and zero to 4,529 µg/kg. Six electrodes were placed in the ground in a 9 m (30 ft) diameter area in a hexagonal pattern. An extraction well was placed in the center of the hexagon. Approximately 3.8 to 7.6 L/hr (1 to 2 gal/hr) of water with 500 mg/L sodium chloride were added at each electrode to replenish evaporated water and provide an electrically conductive solution. The soil surrounding each electrode was supplied with water through a drip system. A vacuum system removed contaminant vapors from the subsurface, which were passed through a condenser to remove the steam. The extracted VOCs were treated by electrically heated catalytic oxidation. Key results of the demonstration at SRS indicate 99.7 percent removal of contaminants from within the electrode array. Outside the array, 93 percent of contaminants were removed at a distance of 2.4 m (8 ft) from the array. Clays were heated more rapidly than the adjacent sands because of their higher moisture content (and, thus, electrical conductivity). Completion of a cost-benefit analysis by Los Alamos National Laboratory showed that SPSH could be performed for a cost of $88 per yd^3, assuming that a contaminated site of 30 m (100 ft) in diameter and 6 to 36 m (20 to 120 ft) deep could be remediated in 5 years.

A full-scale thermal conductive heating treatment system was operated at a confidential chemical manufacturing facility in Portland, Indiana, from July to December 1997 (*In Situ Thermal Treatments of Chlorinated Solvents: Fundamentals and Field Applications* [EPA 542-R-04-010]). The two target treatment areas were 45 m (150 ft) long and 12 m (40 ft) wide to a depth of 5 m (16 ft), and 9 m (30 m) and 6 m (20 ft) wide to a depth of 3.4 m (11 ft). Target source areas contained TCE up to 79 mg/kg and PCE up to 3,500 mg/kg. The site geology included fill, which was a combination of sand, clayey sand and construction debris, to a depth of about 2 m (7 ft). Till consisting of moist, damp, silty clay extended to a depth ranging from 5.4 to 5.7 m (18 to 19 ft), with sand seams running through the till. Below the till was a sand and gravel layer extending to a depth of 9 m (30 ft) and consisting of poorly sorted sand. Groundwater was encountered in the sand and gravel layer at depths of 6.7 to 7.6 m (22 to 25 ft). Heater/vacuum wells were installed on a 2.2 m (7.5 ft) triangular spacing with approximately one well per 15 m^2 (161 ft^2) of surface area treated. Wells were operated at 760 to 871°C (1,400 to 1,600°F) and soil gas was extracted through the wells using a vacuum pump. The surface area between wells was covered by an impermeable silicone rubber sheet to prevent fugitive emissions, and thermally insulated mats were used to minimize surface heat loss. The maximum soil temperature in the treatment area at a depth of 13 ft (3.96 m) ranged from 100 to 260°C (212 to 500°F). Offgases were treated with an 1,800-standard cubic feet per minute (scfm) flameless thermal oxidizer with an operating temperature range of 982 to 1,037°C (1,800 to 1,900°F). Results of confirmatory sampling showed that concentrations of PCE and TCE in both areas were reduced to below the cleanup goals of 8 mg/kg for PCE and 25 mg/kg for TCE.

I1.4.2.3 Evaluation and Screening Rationale

With ISTD, contaminants are primarily removed as vapors and treated above ground. Collection of volatilized COPCs requires a means of active vapor recovery, typically an SVE network, in conjunction with a vapor barrier constructed over the entire treatment area. ISTD is mechanically complex and challenging to implement. Therefore, ISTD was not retained for further evaluation.

I1.4.3 In Situ Vitrification

In situ vitrification (ISV) was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.4.3.1 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. Offgases generated by the process are contained under a hood covering the treatment area and are drawn to an offgas 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 soil approaches 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 (like a monolith 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 used to immobilize high-level wastes. The radionuclides and heavy metals are retained 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 prior to in situ vitrification. The process requires 700 to 900 kilowatt-hours per ton (kWh/ton) of soil to be 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 (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

I1.4.3.2 Relevant Demonstration Projects

Between 1980, when the ISV process was conceived of by PNNL for DOE, and 1997, more than 200 tests, demonstrations, and commercial operations of the technology have been conducted (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). A 1997 DOE case study abstract document (*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 (*Abstracts of Remediation Case Studies, Volume 2* [EPA 542-R-97-010]).

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 megawatt-hours (MWh) of electrical energy, and resulted in a 771 tonne (850 ton) block of vitrified soil. Results from data collection indicated 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. Results also indicated greater treatment depths were in homogeneous soil. The final depth achieved during the treatability test was 4.3 m (14 ft), which is 18 m (60 ft) less than the required treatment depth. The 4.3 m (14 ft) vitrified 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 the effect of the cobble layer on the achieved treatment depth (*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 EPA's Superfund Innovative Technology Evaluation Program at the former site of Parsons Chemical Works, Inc. 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) feasibility study (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. The report also noted that ISV would not be appropriate for sites where contaminated soil exists 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 ("Non-Traditional In Situ Vitrification—A Technology Demonstration at Los Alamos National Laboratory" [Huddleston et al., 2003]). Nontraditional planar ISV uses the same general process as in 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 (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). "Non-Traditional In Situ Vitrification—A Technology Demonstration at Los Alamos National Laboratory," (Huddleston et al., 2003) 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 ("Non-Traditional In Situ Vitrification—A Technology Demonstration at Los Alamos National Laboratory" [Huddleston et al., 2003]).

I1.4.3.3 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 implementing ISV, as compared to other technologies, is considered high, where electric power is generally the most significant contributor. 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.

I1.4.4 Phytoremediation

Phytoremediation was not retained for treatment of soil contaminated with radionuclides, Cr(VI), other metals, and organic compounds.

I1.4.4.1 Description

Phytoremediation is the use of plants and microorganisms associated with plant roots to extract, evapotranspire, immobilize, contain, or degrade contaminants. In the case of the radionuclides and metals considered in this analysis, degradation would not be among the phytoremediation mechanisms, although it is conceivable that microorganisms could reduce reducible metals and radionuclides to some unknown extent. Phytoremediation is typically used as a polishing step and not for high concentrations of contaminants.

I1.4.4.2 Relevant Demonstration Projects

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. The Coyote willow is considered the most suitable plant for use along the Columbia River shore. Known for its rapid and robust regrowth abilities, Coyote willow is used extensively along the Columbia and Yakima rivers for bank stabilization and revegetation purposes. As part of a treatment train of remedial technologies aimed at treating strontium-90 in 100-K, phytoremediation using Coyote willow would be the final polishing step.

A pilot study began in the late spring of 2007 with the planting of 50 Coyote willow starts in a fenced area at 100-K (*100-N Area Strontium-90 Treatability Demonstration Project: Food Chain Transfer Studies for Phytoremediation Along the 100-N Columbia River Riparian Zone* [PNNL-18294]; *Project Work Plan 100-N Area Strontium-90 Treatability Demonstration Project: Phytoremediation Along the 100-N Columbia River Riparian Zone* [PNNL-SA-49953]). This part of the study targeted plant growth rather than phytoremediation capabilities because this location is not contaminated with strontium-90. Often flooded well into June because of the annual high Columbia River stage, this site is a severe test of the Coyote willow shrubs' ability to survive realistic field conditions.

Greenhouse, laboratory (growth chamber), and field studies have shown that strontium-90 is a nutritional analog of calcium, a plant macronutrient. As such, the Coyote willows will actively accumulate strontium-90 in their leaves and stems to concentrations greater than 70 times those present in the soil pore water surrounding their roots. Given the steadily increasing growth rate of the trees at 100-K following yearly harvests of their aboveground tissue, this type of plant can remove significant amounts of contamination from the shoreline area while not disturbing the natural sediment structure. Laboratory studies have also shown that herbivorous insects such as aphids or moth larvae would not be a source of strontium-90 offsite transport from the trees. Further, controlled harvesting schedules and engineered barriers (fencing and netting) would prevent animal intrusion and plant detritus release (*100-N Area Strontium-90 Treatability Demonstration Project: Food Chain Transfer Studies for Phytoremediation Along the 100-N Columbia River Riparian Zone* [PNNL-18294]).

The phytoremediation demonstration is ongoing at 100-K. Biomass production over the first 3 years followed a typical growth curve. On an mT/ha basis, biomass production amounted to 0.2 mT/ha in 2007, 0.87 mT/ha in 2008, and 4.3 mT/ha in 2009. Growth curve extrapolation predicts 13.2 mT/ha during a fourth year and potentially 29.5 mT/ha during a fifth year. The most recent report concludes that the projected biomass yields suggest the trees could prove effective in removing the strontium-90 from the 100-NR-2 riparian zone (*100-N Area Strontium-90 Treatability Demonstration Project: Phytoextraction Along the 100-N Columbia River Riparian Zone—Field Treatability Study* [PNNL-19120]).

Phytoremediation was implemented at DOE Idaho National Engineering and Environmental Laboratory OU 21 with limited effectiveness. COPCs in surface soil to be treated using phytoremediation included metals (mercury, zinc, chromium and selenium) and cesium-137. Based on bench-scale testing, it was determined that phytoremediation would not be successful in meeting remedial action objectives in two areas of concern. Similarly, based on greenhouse experiments, it was determined that phytoremediation would take longer to achieve cleanup goals than what was estimated in the site Record of Decision (ROD).

I1.4.4.3 Evaluation and Screening Rationale

Implementability of phytoremediation is considered moderate. It is usually implemented over extended 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. Although a large quantity of plant material would likely be required, capital costs relative to other technologies are low. Once the plants are established, O&M costs would be relatively low because requirements to sustain them are low (food and water). However, metals concentrations and radionuclide activities may accumulate in the plants to the point that they must periodically be disposed of in a secure facility, such as ERDF. Ultimately the plants would require final disposal (for example, at ERDF) to avoid returning contaminants to the soil from which they were originally extracted (as plants decompose) if phytoremediation is used for contaminants that are not transformed to innocuous forms by the plants or microorganisms.

Phytoremediation is effective only when the plants are active; therefore, the technology would not be effective during the winter. In addition, phytoremediation is effective only to the approximate depth of the plant roots; thus, only shallow soil would be treated. 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 contaminants in shallow soil over long periods, and many metals and radionuclides would accumulate in the plants rather than being treated, posing risks to ecological receptors. For these reasons, phytoremediation was not retained for further evaluation.

I1.5 Containment

Containment technologies that were not retained for treatment of soil contaminated with radionuclides, Cr(VI), and other metals are presented below. Containment process options were not evaluated as potential treatment alternatives for soil contaminated with organic compounds.

I1.5.1 Horizontal Subsurface Barriers—Jet Grouting, Soil Freezing, or Wire Saw Barriers

Horizontal subsurface barriers were not retained for treatment of soil contaminated with radionuclides, Cr(VI), and other metals.

I1.5.1.1 Description

Emplaced horizontal barriers are positioned beneath existing in situ contaminants. These bottom barriers, which have features similar to those of vertical barriers in that they minimize movement of contaminants and restrict infiltration of groundwater, are constructed of similar materials using similar technologies. Horizontal 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 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 addition 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 that the target soil. The excised soil block ultimately floats free from surrounding soil and is surrounded by the grout on the sides and bottom.

I1.5.1.2 Relevant Demonstration Projects

Each of these horizontal barrier technologies is in the early development and testing stages (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]). Several demonstrations have been performed at near surface depths, but application within the deep vadose zone could prove to be costly and impractical.

I1.5.1.3 Evaluation and Screening Rationale

Because of the limited radius of influence, distance between injection boreholes would be very short and the cost of implementation prohibitive. In addition, the barrier integrity and long-term stability are key uncertainties. Given the significant uncertainty on the completeness of the barrier with all methods, the effectiveness of this process option is considered low. Similarly, implementability is considered low because all methods would be difficult or impossible to implement at the Hanford Site to the depths required (because of the gravels and cobbles). Given the low potential for successful implementation of this technology and the limited benefit provided, horizontal subsurface barriers were not retained for further consideration.

I1.5.2 Dynamic Compaction

Dynamic compaction was not retained for treatment of waste sites contaminated with radionuclides, Cr(VI), and other metals.

I1.5.2.1 Description

Dynamic compaction is used to consolidate soil and buried wastes, and can be used to minimize the potential subsidence for a subsequent barrier. The process involves dropping a weight from a predetermined height onto the area to be compacted.

I1.5.2.2 Evaluation and Screening Rationale

The technology is considered to have moderate to high effectiveness. It is effective in removing void spaces and compacting surface soil where voids exist around buried waste; however, it is not an effective containment process option for native soil or treatment of hazardous wastes. Implementability is high,

given that the technology is simple and widely used. However, because no waste sites containing solid and buried waste are present at the treatment area, this process option was not retained.

I2 Additional Information on Technologies Not Retained for Groundwater Treatment

Information is presented here regarding technologies that were not retained for further evaluation for treatment of groundwater contaminated with Cr(VI) and/or other COPCs.

I2.1 Ex Situ Treatment

Following extraction of groundwater via extraction wells, groundwater is treated with ex situ methods to reduce contaminants to a less mobile form (for example, Cr(VI)) to chromium(III) and remove it from the water stream. The ex situ treatment options that were not retained are discussed in this section.

I2.1.1 Ex Situ Chemical Precipitation

Ex situ chemical precipitation was not retained for treatment of groundwater contaminated with Cr(VI) and carbon-14.

I2.1.1.1 Description

Ex situ chemical precipitation involves the introduction of chemicals to transform dissolved contaminants into insoluble solids, which are removed by 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. Carbon-14, which is typically in chemical forms of carbonate and bicarbonate (depending on the pH) (*Management of Waste Containing Tritium and Carbon-14* [IAEA, 2004]), can be removed by raising the pH of the water. This is effective post-treatment for solids removal, but conditioning is required. 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 extremely large and would need final disposal at ERDF. Site-specific jar testing would be required to obtain design and operational parameters.

I2.1.1.2 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 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.

I2.1.1.3 Evaluation and Screening Rationale

This technology is effective for Cr(VI) and could possibly be effective for carbon-14. Additional testing would be required to determine the efficacy of this technology to carbon-14. Site-specific testing for all COPCs would be required to determine operational parameters. Vendors and equipment for this technology are readily available; however, this technology is unproven at the Hanford Site and large volumes of sludge are produced.

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 much larger waste stream compared to ion exchange with either onsite or offsite regeneration. For these reasons, chemical reduction was not retained for further evaluation.

I2.1.2 Electrocoagulation

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

I2.1.2.1 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 iron ions reduce Cr(VI) to an iron-chromium hydroxide, which subsequently is removed from the water.

I2.1.2.2 Relevant Demonstration Projects

A 2007 treatability test evaluated the potential for this technology for 100-D at 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 at the conclusion of 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.

I2.1.2.3 Evaluation and Screening Rationale

The effectiveness of electrocoagulation at the 100 Area is anticipated to be low or moderate, particularly in light of the challenges encountered in the above-described pilot test. The technology is not widely used for Cr(VI), although it may be applicable to technetium-99; however, the technetium-99 plume is small and, therefore, the benefit would not be significant, and additional challenges related to the reversible potential of technetium-99 reduction may result. Implementability is also considered low or moderate because further development of the process would be required. In addition, the process may render the

treated water less suitable for re-injection. Capital costs are moderate or high, and O&M costs are moderate. Part of the high cost is a result of the production of significant volumes of sludge that must be managed and disposed of. The costs for electrocoagulation do not appear to be any lower than for the existing ion exchange systems. Because of poor performance and implementability, as well as high cost, the technology was not retained for further evaluation.

I2.1.3 Wetlands

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

I2.1.3.1 Description

Constructed wetlands can be described as artificial swamps that act as biofilters for removing contaminants, and are common processes in wastewater treatment. A constructed wetland typically would require a much larger area and a much 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 Jaffé, 2006]).

Wetlands can also be used to treat other COPCs, such as nitrate, petroleum, and TCE. Several removal mechanisms have been identified 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]). Biodegradation is an important mechanism for removal of petroleum hydrocarbons, and uptake by plants is an important mechanism for removal of TCE. Phytoremediation (one component of wetland treatment) has been used to treat strontium-90, but it is not known to treat other radionuclides (*Alternative Remediation Technology Study for Groundwater Treatment at 200-PO-1 Operable Unit at Hanford Site* [SGW-34562]).

I2.1.3.2 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 nitrates from the municipal drinking water supply in Orange County, California. Up to 1.5 cubic meters per second (m^3/s) (33 million gal/day) were treated prior to groundwater recharge. 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 m^2/day, and exiting nitrate concentrations sometimes fell 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 concluded to be the primary nitrate loss mechanism. A review of 19 surface flow wetlands showed that nearly all reduced total nitrogen. 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).

I2.1.3.3 Evaluation and Screening Rationale

The land area required for wetlands is likely to be very large for the volume of groundwater that will be produced by the 100 Area pump-and-treat systems, even under favorable (warm) conditions. Even more area would be required for effective treatment in the winter, when plants and microorganisms in the wetland would be less active. Problems with freezing would be likely, because 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 because additional research and testing would be required to verify the effectiveness of this technology for COPCs other than nitrate. 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.

I2.1.4 Subgrade Bioreactors

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

I2.1.4.1 Description

Biological treatment using SGBRs is a potential treatment technology for Cr(VI) and nitrate in groundwater. If implemented on a full-scale basis, a SGBR may 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 less mobile and/or less toxic compounds (that is, chromium(III) 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 byproducts of biodegradation (ferrous iron, arsenic, and manganese), as well as suspended solids, prior to the discharge of the treated groundwater back to the aquifer.

I2.1.4.2 Relevant Demonstration Projects

SGBRs for Cr(VI) and nitrate removal have not been demonstrated on a full-scale basis.

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 16ºC ("Passive Treatment of Acid Mine Drainage in Bioreactors Using Sulfate-Reducing Bacteria: Critical Review and Research Needs" [Neculita et al., 2007]).

Ex situ bioreactors for nitrate removal have been pilot-tested at the Hanford Site in the past (*Development of a Biological Treatment System for Hanford Groundwater Remediation: FY 1989 Status Report* [PNL-7290]). A pilot-scale test was conducted in 1989 using simulated Hanford Site groundwater with a continually stirred tank bioreactor (CSTR). The CSTR system was operated continuously for 5 months with a simulated groundwater influent containing 400 mg/L nitrate. Using acetate as the primary

carbon source for microbial growth, a nitrate removal efficiency of greater than 99 percent was maintained at an influent flow rate of 6 L/hr (8-hour residence time).

I2.1.4.3 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 basis 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.

I2.1.5 Bioreactors

Ex situ bioreactors were not retained for treatment of groundwater contaminated with Cr(VI) or other COPCs.

I2.1.5.1 Description

Ex situ bioreactors can be used to biologically reduce and precipitate Cr(VI), as well as to denitrify nitrate. Groundwater is amended with an electron donor (carbon source) and passed through a matrix with microbial films where contaminants are biologically reduced. Types of matrices include fixed beds, fluidized beds, and membranes.

I2.1.5.2 Relevant Demonstration Projects

There are few reported applications of ex situ bioreactors specifically for Cr(VI) ("Preliminary Studies on Continuous Chromium(VI) Biological Removal from Wastewater by Anaerobic-Aerobic Activated Sludge Process" [Chen and Gu, 2005]). However, bioreactors for nitrate removal have been pilot-tested at the Hanford Site in the past (*Hanford Site National Environmental Policy Act (NEPA) Characterization* [PNNL-6415]; *Development of a Biological Treatment System for Hanford Groundwater Remediation: FY 1989 Status Report* [PNL-7290]). A pilot-scale test was conducted in 1989 using simulated Hanford Site groundwater with a CSTR. The CSTR system was operated continuously for 5 months with a simulated groundwater influent containing 400 mg/L nitrate. Using acetate as the primary carbon source for microbial growth, a nitrate removal efficiency of greater than 99 percent was maintained at an influent flow rate of 6 L/hr (8-hour residence time).

The biological processes involved in biological treatment of Cr(VI) are similar to those involved in other bioreactor concepts used in the remediation industry, such as sulfate-reducing bioreactors (SRB) that are used to treat acid mine drainage. Based on case studies for SRBs, the effectiveness of bioreactors has been demonstrated at temperatures between 2 and 16ºC ("Passive Treatment of Acid Mine Drainage in Bioreactors Using Sulfate-Reducing Bacteria: Critical Review and Research Needs" [Neculita et al., 2007]). Daily average low temperatures at the Hanford Site are typically below 0ºC (32ºF) during the winter months, which may necessitate heating/insulating portions of the ex situ bioreactor system to maintain the viability of the microbes.

I2.1.5.3 Evaluation and Screening Rationale

Bioreactors are commonly used for nitrate removal, and the Hanford Site pilot test described above was successful. However, bioreactors for Cr(VI) and other COPCs are less common and have not been tested at the Hanford Site. Therefore, there is uncertainty in the performance ability of this technology.

A system for the 100 Area would be very similar to the system being constructed at 200 West (although nitrate concentrations are somewhat lower in the 100 Area than in 200 West).

These systems are large and rather complex, including the anaerobic bioreactor, substrate feed system, aerobic reactors to re-aerate the water, solids removal systems, and a biomass handling system. As a result, they can be relatively expensive to construct and operate.

Because ion exchange treatment plants are already in place, it is not likely that replacing them with ex situ bioreactors will be as implementable or cost-effective as operating the existing system. Therefore, ex situ bioreactors have not been retained for further evaluation.

I2.1.6 Phytoremediation

Phytoremediation was not retained for treatment of groundwater and soil contaminated with Cr(VI) or other COPCs. Additional information on this process can be found in Section I1.4.4.

I2.1.6.1 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) of the bottom of the root mass for this system to be viable (*Enhanced Attenuation: A Reference Guide on 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 (that is, the plants would be irrigated with the contaminated groundwater), phytoremediation would not be suitable for groundwater remediation at the Hanford Site except immediately adjacent to the river. There are methods of encouraging plant roots to grow deeper, but not to the depths that would be required at most of the 100 Area of the Hanford Site. Phytoremediation systems (including by land application) are only operational when the soil is warm and plants are active, so treatment effectiveness would be reduced in the winter. The land requirements for phytoremediation are also relatively large.

I2.1.6.2 Relevant Demonstration Projects

Uptake of Cr(VI) by a variety of plants has been documented ("Enhancement of Cr(III) Phytoaccumulation" [Shahandeh, 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 (*Enhanced Attenuation: A Reference Guide on Approaches to Increase the Natural Treatment Capacity of a System* [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.

I2.1.6.3 Evaluation and Screening Rationale

Because of the large depth to groundwater at most of the Hanford Site, phytoremediation would only be feasible immediately adjacent to the river. Therefore, implementability of phytoremediation is considered

low or moderate. It is usually implemented over long periods, 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, metals concentrations and radionuclide activities 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 contaminants to the soil from which they were originally extracted (as plants decompose) if phytoremediation is used for contaminants that are not transformed to innocuous forms by the plants or microorganisms.

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 affect 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 contaminants where groundwater is shallow over long periods, and many metals and radionuclides would accumulate in the plants and not actually be treated, posing risks to ecological receptors. For these reasons, phytoremediation was not retained for further evaluation.

I2.1.7 Membrane Separation (Reverse Osmosis)

Reverse osmosis (RO) was not retained for treatment of groundwater contaminated with Cr(VI) and other COPCs.

I2.1.7.1 Description

RO is a pressure-driven process that uses semipermeable membranes to purify water. Contaminated water is passed through the membrane while the contaminants are contained within the membrane. The water that is allowed to pass through the membrane is called the permeate, and typically contains only a small fraction (less than 5 percent) of the ions in the feed solution. The water that does not pass through the membrane (containing the ions that do not pass through the membrane) is called the retentate or brine, concentrate, or reject. It has a high total dissolved solids concentration and would contain most of the COPCs being treated. With appropriately sized membranes and multiple stages of membranes, very low concentrations of ions 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, other COPCs that RO can remove include nitrate, TCE, some VOCs, and some petroleum compounds (*Drinking Water Treatment: Reverse Osmosis* [Dvorak and Skipton, 2008]).
In New Hampshire, for example, the typical production efficiency of RO for nitrate removal is approximately 25 percent. That is, for every 15 L (4 gal) of untreated water entering the device, only 3.7 L (1 gal) of treated water is produced (*Nitrate/Nitrite in Drinking Water* [WD-WSEB-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.

RO for removal of strontium-90 "shows promise" (*Environmental Engineers' Handbook* [Liu and Lipták, 1999]), and a later study (*Environmental Technology Verification Joint Verification Statement for Ecowater Systems ERO-R450E Point-of-Use Drinking Water Treatment System* [EPA and NSF, 2005]) showed 97 percent removal (from 960 to 33 µg/L) of strontium by RO. No commercial treatment option is available to remove tritium from groundwater (*Groundwater Treatment at SRS: An Innovative Approach* [WSRC-RP-97-849]).

Brine production is a significant issue with RO. The need to minimize and manage (for example, 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. Nanofiltration is very similar to RO but uses membranes with large 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 (*Membrane Filtration Guidance Manual* [EPA 815-R-06-009]).

I2.1.7.2 Relevant Demonstration Projects

A process was bench-tested at the 200 West Area of the Hanford Site that combines three different membrane technologies: RO, coupled transport, and nanofiltration. 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 allows for the future use of the radionuclides, if needed, and reduces the amount of waste that will need to be disposed of. This process has the potential to concentrate the contaminants into solutions with volumes in a ratio of 1 to 10,000 of the feed volume, compared to a volume reduction ration 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 as theorized for all ions except for technetium, suggesting that design modifications may be necessary.

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 best available technology and includes pH adjustment, filtration, ultraviolet light, and hydrogen peroxide destruction of organic compounds; RO to remove dissolved solids; and ion exchange to remove the last traces of contaminants. The facility began operating in December 1995. The maximum treatment capacity of the 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.

I2.1.7.3 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. Implementability is therefore considered low to moderate. A major disadvantage of RO that underlies these unfavorable ratings is the large volume of brine that is typically generated. The volume will vary depending primarily on groundwater characteristics. The brine would contain Cr(VI) and other COPCs, which would require further treatment and then disposal. It would also have a high concentration

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

of total dissolved solids, which could be a problem for disposal. Brine production was the primary reason that RO was not retained for this evaluation.

I2.2 In Situ Treatment

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

I2.2.1 In Situ Chemical Reduction

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

I2.2.1.1 Description

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

I2.2.1.2 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" configuration, which involved four injection wells drilled orthogonally around an existing monitoring well from which groundwater was withdrawn and mixed with CPS. This solution was then injected in approximately equal amounts to set up a circulation cell in the aquifer. The test was conducted for a period of 45 days. Cr(VI) was eliminated from the treated aquifer, as demonstrated by the lack 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 treated aquifer also was strongly reduced by the treatment. Analysis of groundwater chemistry before, during, and after the test shows that manganese, iron, and arsenic were mobilized under the strongly reducing conditions in the aquifer, but all of these remained far below drinking water standards.

Implementability problems encountered during the field study included precipitation of chemicals inside pipes, flowmeters, 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/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.

I2.2.1.3 Evaluation and Screening Rationale

Transportation and handling of reducing agents also poses more of a health and safety concern during application compared 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 in favor of in situ biological reduction.

I2.2.2 Hydrogen or Other Organic Gas Sparging

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

I2.2.2.1 Description

Gas sparging involves the injection of biodegradable organic gases (that is, methane, propane, or butane) or hydrogen gases into the subsurface via sparge wells that are screened below the water table. Distribution of gases will be affected by lithologic heterogeneity and gas flow may channelize through preferential flow paths. The gasses serve as electron donors to promote anaerobic reduction of certain compounds, such as Cr(VI) and nitrate. It is an alternative approach for supplying an electron donor compared to using a liquid organic substrate, such as lactate.

I2.2.2.2 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 (MTBE) 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, semiperched, 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 m [90 ft] long and 18 m [60 ft] wide) included a test plot consisting of seven propane injection points, 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 m^3/hr to between 0.0085 and 0.0113 m^3/hr (1 standard ft^3/hr to between 0.3 and 0.4 standard ft^3/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, MTBE concentrations decreased by 62 to 88 percent in shallow wells and by 86 to 97 percent in deep wells. In the control plot, MTBE concentrations decreased by 86 to 97 percent in shallow wells and by 88 to 90 percent in deep wells. However, MTBE 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, MTBE concentrations remained above 5 µg/L in all wells. The most active MTBE degradation appeared to occur near the oxygen injection points, indicating that distribution of gases was not effective or uniform in the heterogeneous soil.

I2.2.2.3 Evaluation and Screening Rationale

This technology is a direct competitor to supply an electron donor through the injection of liquid organic substrates such as lactate. However, a disadvantage is the safety risk associated with using explosive gases, which will likely be a major obstacle if implemented at the Hanford Site. In addition, the radius of influence (ROI) of sparge wells is likely to be relatively low, so a large number of wells would be required, making the implementation more challenging. For these implementation reasons, this technology was not retained for further evaluation.

I2.2.3 Groundwater Circulation Wells

Groundwater circulation wells were not retained as a delivery method for treatment of groundwater contaminated with Cr(VI) and other COPCs.

I2.2.3.1 Description

Groundwater circulation 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 reinjected into the formation to enhance aerobic biodegradation, stripped in-well to remove VOCs, 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 circulation wells is highly sensitive to site lithologic conditions. A viable circulation cell may not develop if vertical anisotropy in lithology (that is, 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 groundwater circulating well (GCW) and down-well equipment (for example, packers) problems.

I2.2.3.2 Relevant Demonstration Projects

A summary and analysis of more than 50 GCW field demonstrations was provided in *Groundwater Circulating Well Technology Assessment* (NRL/PU/6115-99-384). One case study was a GCW demonstration sponsored by the 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 (K horizontal = 10 ft/d, K vertical = 1 ft/d) and the presence of TCE contamination. One GCW was installed to 15 m (50 ft) bgs and operated for 191 days during the demonstration. Results of the demonstration indicate an 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.

I2.2.3.3 Evaluation and Screening Rationale

It is likely that a large number of wells would be required to implement this technology at the Hanford Site because of the 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.

I2.2.4 Horizontal Wells

Horizontal wells were not retained as a delivery method of treated groundwater that was contaminated with Cr(VI) or other COPCs.

I2.2.4.1 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 (*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 at recovering groundwater or soil vapor. When installed with directional drilling techniques, horizontal wells can be installed in areas where surface and subsurface obstructions would preclude other remediation alternatives.

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

I2.2.4.2 Relevant Demonstration Projects

An unsuccessful horizontal well technology demonstration was conducted at 100-D 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 porous Hanford formation. The casing was advanced with significant difficulty to approximately 6 m (20 ft) bgs (25 m [85 horizontal linear ft]) when downward progress ceased because of inadequate force on the downhole 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.

I2.2.4.3 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.

I2.3 Containment

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

I2.3.1 Containment Wall

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

I2.3.1.1 Description

Containment walls include soil bentonite slurry walls, grout walls, and sheetpile walls. Walls have been used successfully to assist with hydraulic containment of groundwater plumes at many hazardous waste sites. Groundwater pumping or diversion upgradient of the containing 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.

I2.3.1.2 Relevant Demonstration Projects

In 1994, the Washington State Department of Ecology (Ecology) and EPA issued an action memorandum to DOE to initiate groundwater remedial actions immediately at 100-N, to include the design, construction, and operation of a pump-and-treat system and the construction of a sheetpile barrier wall at N-Springs ("Action Memorandum: N-Springs Expedited Response Action Cleanup Plan, U.S. Department of Energy Hanford Site, Richland, Washington" [Ecology and EPA, 1994]). However, 6 months later, 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]).

I2.3.1.3 Evaluation and Screening Rationale

Containing walls typically must be extended into a confining unit, such as the Ringold Formation upper mud (RUM) unit, which at most sites in the 100 Area 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, previous attempts at the Hanford Site were 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 river channel migration and erosion by the glacial floods that ultimately laid down the Hanford formation. Thus, the RUM unit has an undulating surface with periodic depressions, further complicating the ability to effectively key into this unit.

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 gravels. Cobbles will prevent or deflect most insertion methods or items such as sheetpiles, vibrating beams, and drilled caissons. Although conventional trenches likely can be kept open in this formation, slurry loss may be excessive in zones of clean coarse cobbles or gravels. Sudden loss of slurry related to penetration into such a zone could lead to trench instability.

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 must be removed 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 and O&M costs would be low or moderate. As a consequence of installation challenges and high costs, containing walls were not retained for further evaluation.

I2.3.2 Reactive Biological Barrier

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

I2.3.2.1 Description

Reactive biological barriers involve the subsurface delivery and/or recirculation of biological substrate along cross-gradient rows transecting the plume. Residual reducing byproducts and biomass are retained in the aquifer matrix so that Cr(VI), nitrate, TCE, and possibly technetium-99 are passively removed as groundwater moves through the treatment zone. Biological barriers would operate much like the in situ redox manipulation (ISRM). Rejuvenation of the barrier by reinjection of biological substrate may be required periodically to maintain reducing power. Common substrates include acetate, molasses, cow manure, fruit juice, lactate, whey, polylactate, and sulfur-containing products (for example, Metals Remediation Compound), and waste organic material (for example, 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) is a highly oxidized compound and, therefore, can act as an electron acceptor, becoming reduced to chromium(III) in the process. Biological processes may include bioreduction, bioaccumulation, biomineralization, and bioprecipitation, which use specific substrates to drive the treatment and affect the reduction, uptake, or precipitation of Cr(VI). 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]).

I2.3.2.2 Relevant Demonstration Projects

Biological barriers can be effective, depending on the natural groundwater flow rates that would pass through them, which will dictate how often they need to be rejuvenated (as a result of the consumption of the residual reducing power by the oxygen and nitrate in the groundwater).

A field experiment was conducted at the Hanford Site using hydrogen release compound (HRC)[1], 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 the terminal electron acceptors oxygen, nitrate, and sulfate, and an increase in ferrous iron, resulting in a significant decrease in soluble Cr(VI). The Cr(VI) concentration remained below the background concentration in the downgradient pumping/ monitoring well and below the detection limit in the injection well for at least 3 years after the HRC injection. The degree of sustainability of hexavalent reductive bioimmobilization 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 (*Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site* [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

[1] HRC—Hydrogen Release Compound, manufactured by Regenesis—Advanced Technologies for Contaminated Site Remediation, 1011 Calle Sombra, San Clemente, California.

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 important 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.

I2.3.2.3 Evaluation and Screening Rationale

In addition to consuming DO, bioreducing barriers have the potential to result in unwanted dissolved biodegradation 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 reoxygenation systems (such as sparging wells) are installed downgradient from the biobarrier.

Effectiveness is deemed low to moderate. Given the highly toxic groundwater flowing at relatively high rates, re-amendment would likely need to be frequent to maintain reducing conditions. Implementability is considered moderate or high, capital costs are considered moderate or high, and 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. As a consequence, 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.

I2.3.3 Hydraulic Containment via Injection

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

I2.3.3.1 Description

Hydraulic containment via injection involves injecting water into a line of closely spaced injection wells or a trench installed close to and parallel to the river. A groundwater mound would be created under the injection points, which would result in an inward gradient and stop the migration of groundwater to the river. This injection would mimic the natural conditions encountered during periods of high river stage. Some extraction of groundwater upgradient of the barrier, with discharge into wells side gradient, would be required to maintain the water balance. Source of water for injection could be from existing permitted Columbia River supply and/or groundwater.

I2.3.3.2 Relevant Demonstration Projects

Fresh water injection systems used to prevent saltwater intrusion along coastlines are conceptually similar to injection of water to contain COPCs hydraulically. Saltwater intrusion barriers consist of a line of

injection wells paralleling the coast to inject water into a fresh water aquifer to create and maintain a "fresh water ridge," which produces an outward gradient to stop the migration of saltwater into the aquifer (*The Class V Underground Injection Control Study Volume 20 Salt Water Intrusion Barrier Wells* [EPA/816-R-99-014t]). A total of 315 saltwater intrusion barrier wells have been documented in the United States. Well clogging is a common issue when operating these injection wells. Maintaining high-quality waters and chlorination of injection water are methods employed to reduce the frequency of well clogging. However, even when using high-quality water, clogging is inevitable. When clogging occurs and the injection head has increased above acceptable levels, redevelopment of the injection wells is necessary (approximately every 3 years when using high-quality injectate water). Injection wells also need to be supplied with pressure, either individually or in small groups, to prevent the complete collapse of the pressure ridge barrier in cases of system shutdowns.

I2.3.3.3 Evaluation and Screening Rationale

The primary disadvantage of hydraulic containment via injection is that the injection locations will need to be a considerable distance from the river because of logistics issues. As a consequence, the Cr(VI) that is currently downgradient from the injection points would be flushed into the river without control. This flushing should only be temporary, but is likely to be considered dilution by the regulators and, therefore, not allowed. Based on extensive experience with saltwater intrusion barriers, operational complexity associated with injection well clogging rehabilitation likely would be encountered. In addition, the current remedies at both 100-K and 100-HR-3 include hydraulic containment using extraction wells. As a result, additional technologies to create barriers to contaminant migration are not needed. For these reasons, hydraulic containment via injection was not retained for further evaluation.

I3 Potential Remedial Action Technologies for Strontium-90 in the Vadose Zone of the Hanford 100 Area

I3.1 In Situ Solidification

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 primarily works by coating and isolation, processes that make the contaminants less prone to leaching or dissolution. Multiple types of grouting/binding materials and emplacement techniques have been developed and demonstrated. Jet grouting and permeation grouting are the two general grout approaches potentially applicable for subsurface contaminant solidification in Hanford Site vadose zone sediments. Jet grouting uses high-energy emplacement of cement or chemical grout materials whereby the sediment is displaced 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. Although permeation grouting is a relatively mature technology for many geotechnical applications, there are uncertainties with grout for in situ contaminant stabilization (*Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99* [WMP-27397]). The uncertainties include: 1) the effectiveness of delivery depends on 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.

I3.1.1 In Situ Grouting

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, and composing 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.

I3.1.1.1 Relevant Demonstration Projects

Several DOE sites, including the Hanford Site and ORNL, Brookhaven National Laboratory, Idaho National Laboratory, SRS, and Sandia National Laboratories have evaluated, tested, and/or implemented in situ grouting for shallow waste isolation applications as summarized below. In situ grouting has been evaluated at the Hanford Site for application to waste site isolation (for example, near-surface formation of in situ waste barriers) through a number of efforts in the 1990s (for example, "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 isolation 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]), including a significant program effort led by Lawrence Berkeley National Laboratory (*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 reduce hydraulic conductivity (*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 (2 orders of magnitude) impact 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 Idaho National Laboratory, 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]), and *Feasibility Study for Operable Unit 7-13/14* (DOE/ID-11268) provided a thorough review of in situ grouting for shallow waste sites at Idaho National Laboratory. This technology was retained as a potential alternative in a FS for OU 7-13/14 based on the likely ability of the technology to stabilize the waste and reduce hydraulic conductivity in localized hot spots.

The SRS 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]).

I3.1.1.2 Evaluation and Screening

In situ solidification using commercially available grouting equipment with cement grouts is considered to have 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 large-scale grouting of soil volumes. 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 the elements. The effectiveness of grout emplacement depends on the application method. Typical applications would involve 0.6 m (2 ft) diameter grout column with 0.5 m (1.6 ft) spacing. Using estimated installation costs for in situ solidification using jet grouting at Idaho National Laboratory (INL) (*Feasibility Study for Operable Unit 7-13/14* [DOE/ID-11268]), unit costs in excess of $1,500 per yd^3 are estimated. Consequently, the relative capital cost is high. Negative factors associated with in situ solidification include 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 the elements.

I3.2 In Situ Stabilization/Sequestration

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 CI Apatites" [Hughes et al., 1989]; *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes* [Spence and Shi, 2005]). Apatite minerals are very stable and practically insoluble in water. The substitution of strontium for calcium in the crystal structure is thermodynamically favorable, and will proceed provided the two elements coexist. The mixed strontium calcium-apatites have lower solubility than either 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 deeper phosphate mass at depth. Citrate is needed to keep calcium in solution long enough (days) to inject into the subsurface; a solution containing Ca^{2+} and phosphate only will rapidly form mono- and di-calcium phosphate, but not apatite ("Hydroxyapatite Synthesis" [Andronescu 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.

I3.2.1 Relevant Demonstration Projects

A laboratory-scale study investigating apatite sequestration of strontium-90 was conducted by the 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 laboratory study indicate that calcium-citrate-phosphate solution can be infiltrated into unsaturated sediments to result in apatite precipitate to provide treatment of strontium-90 contamination. After 1.3 years of contact, 9 to 16 percent strontium-90 had substituted for calcium in apatite. Strontium-90 substitution in apatite did not decrease

with depth because the 20 to 30 nanometer (nm) apatite crystals conglomerated, forming a porous 10- to 50-micron conglomerate 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 millimole (mM) calcium, 15 mM citrate, 60 mM phosphate) at a rapid rate (near-ponded conditions), followed by rapid, then slow water infiltration (*Sr-90 Immobilization by Infiltration of a Ca-Citrate-PO4 Solution into the Hanford 100N Area Vadose Zone* [PNNL-SA-61818]). Repeated infiltration events, with sufficient time between events to allow water drainage in the sediment profile, also may be used to build up the mass of apatite precipitate at greater depth. Low-potassium zones were effectively treated, because 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.

I3.2.2 Evaluation and Screening

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, there is still uncertainty with regard to how uniformly phosphate solutions can be delivered on a field scale in heterogeneous soils, and how nonuniformity would affect the percentage of strontium-90 that can be sequestered in the vadose zone. Furthermore, sequestration of strontium-90 does not remove the COPC, and hence does not change the potential risk from human or ecological direct contact with shallow soil.

I3.3 In Situ Jet Grouting—Delivery Method

Grout injection addresses subsurface contaminants by high-pressure injection of a grout or binding agent into the subsurface to physically or chemically bind or encapsulate contaminants (*Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau* [DOE/RL-2007-56]). Grout injection technologies using multiple types of grouting materials have been applied and are currently undergoing testing for in situ contaminant stabilization at other sites. Similarly, more standard grouting techniques may also potentially be useful for selected applications.

I3.3.1 Relevant Demonstration Projects

In situ grouting has been approved by regulating agencies and implemented at several small-scale sites, although in situ grouting has not been applied to large-scale sites with many radiological and chemical hazards (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

This technology was briefly considered for treating technetium-99 in the vadose zone at the Hanford Site (*Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99* [WMP-27397]). Grouting had been used as a stabilizer in several demonstrations and remedial actions had involved limited and contained volumes (for example, beryllium reflector blocks, and control cylinders). However, it was not considered practicable for use in the Hanford Site vadose zone because of the number of boreholes that would be required for complete coverage of the grout, the cost of drilling to depth, and the difficulty in confirming a continuous volume (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

Grouting of buried mixed waste at DOE's SRS was rejected as a remedial technology (*100 Area Source Operable Unit Focused Feasibility Study Report* [DOE/RL-94-61]). Evaluations concluded that grouting would not fill enough voids without creating uncontrolled surface cracking and surface releases of grout contaminated with hazardous and radioactive constituents.

I3.3.2 Evaluation and Screening

Significant uncertainties are associated with the use of grouting for in situ contaminant stabilization, especially for the deep vadose zone (*Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99* [WMP-27397]). The principal challenges to implement this technology are application, transport of the grout to the deep vadose zone, and verification of proper placement. Vertical variations in stratigraphy, with some levels having relatively low potential permeability to grout flow, pose significant challenges for the technology (*Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau* [DOE/RL-2007-56]).

Because grouting technologies have the potential for use as part of a remedy for the deep vadose zone, further efforts to evaluate the performance of grouting technologies are included in the *Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau* (DOE/RL-2007-56). Additional information resulting from the treatability studies is required prior to making decisions about the full-scale application of grouting technologies at the Hanford Site.

I4 Bioremediation as a Potential Remedial Action for Cr(VI) in the Groundwater and Vadose Zone of the Hanford 100 Area

I4.1 Introduction

Bioremediation has been used successfully to treat groundwater contaminated with a range of inorganic and organic contaminants at a large number of sites throughout the country (for example, the Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program [SERDP and ESTCP website]). One of the primary advantages of this technology is that it appears that it can be cost-effectively applied to a variety of in situ settings ranging from focused remediation of specific, small-scale target areas to applications that consist of large-scale, plume-wide remediation efforts.

Because of the potential benefits of this technology and the flexibility in the scale of implementation that is possible, bioremediation is considered a strong remedial action candidate for inclusion as part of the final remedy for the Cr(VI) contamination within the 100 Area. This appendix summarizes information that has been compiled and evaluated to support the detailed analysis of in situ bioremediation as one of the remedial technologies that may be applied to the remediation of Cr(VI) as part of the final remedy for the 100 Area groundwater OUs. A representative selection of case studies and treatability studies applicable to the evaluation and implementation of in situ bioremediation of Cr(VI) are summarized in Section I7.2 of this appendix

I4.2 Scientific Basis of Bioremediation

The aqueous speciation and mobility of chromium in groundwater are governed by the chemical (for example, redox) and physical characteristics of the aquifer system and the composition and abundance of the microbial assemblage that is present. Chromium is stable in solution as the highly mobile anionic Cr(VI) species in oxygen-rich aquifers with a near-neutral pH (like the unconfined aquifer at Hanford) that contain low quantities of natural organic material (NOM). Conversely, Cr(VI) can be

reduced to the highly insoluble trivalent form (chromium(III)) if the aquifer conditions are sufficiently reducing to convert Cr(VI) to chromium(III).

The imposition of reducing conditions on an oxidizing aquifer by the addition of a carbon source (substrate) that is easily metabolized by the native microbial assemblage forms the foundation of engineered bioremediation applications for Cr(VI) and many other contaminants.

I5 Overview of Cr(VI) Bioremediation Processes

In situ bioremediation for Cr(VI) in oxygenated groundwater (or vadose zone pore water) typically employs the injection or infiltration of organic carbon compounds (substrates) to stimulate microbial activity and lower the redox state within the subsurface. Once a sufficient amount of substrate is added, the native population of microbes in the subsurface will increase rapidly until the population reaches equilibrium with the increased food supply. If sufficient substrate is supplied, the increased metabolic oxygen demand of the expanded microbial population will exceed the rate that oxygen is being supplied to the system and oxygen levels in the groundwater will approach zero. Once oxygen in the targeted aquifer zone is depleted, microbes able to use other constituents (for example, nitrate, ferric iron, and sulfate) as electron acceptors for their metabolic reactions will further lower the redox state of the aquifer. Consequently, in situ bioremediation is an effective method for imposing reducing conditions on a targeted zone of an oxidizing aquifer in order to convert soluble and mobile Cr(VI) to chromium(III). Once chromium(III) is formed, it typically precipitates as low solubility hydroxide phases (for example, $Cr(OH)_3$; "Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese Dioxide" [Eary and Rai, 1987]).

Numerous aerobic and anaerobic microbes are known to enzymatically catalyze the reduction of Cr(VI) to chromium(III) (either for detoxification or possibly for metabolic purposes (*Microbial Cr(VI) Reduction: Role of Electron Donors, Acceptors, and Mechanisms, with Special Emphasis on Clostridium spp.* [Sharma, 2002]; *In Situ Long-Term Reductive Bioimmobilization of Cr(VI) in Groundwater Using Hydrogen Release Compound* [Faybishenko, 2009]). However, the direct reduction of Cr(VI) to chromium(III) by microbial enzymatic processes is believed to be a slower process than the reduction of Cr(VI) by sulfide and ferrous iron ("Iron Promoted Reduction of Chromate by Dissimilatory Iron-Reducing Bacteria" [Wielinga et al., 2001]). These Cr(VI) reducing compounds may be produced rapidly and in great abundance by sulfate- and iron-reducing bacteria that are common in many aquifers where the organic carbon supply is high enough for the available oxygen to have been depleted. Compared to the ability of ferrous iron or sulfide to reduce Cr(VI) to chromium(III), methane is a poor reductant for Cr(VI) and high levels of methane indicate an inefficient use of substrate during bioremediation activities.

I5.1 Longevity of Treatment and the Potential for Reoxidation of Chromium(III) Phases

If iron- and sulfate-reducing conditions are sustained long enough during active bioremediation activities, substantial amounts of ferrous iron and sulfide-rich phases may be produced as secondary phases within the aquifer matrix. If produced in sufficient abundance, these strongly reducing minerals or phases will maintain reducing conditions in the treatment zone for a substantial period of time after substrate addition has ceased (for example, 1 to 2 years). This residual reducing capacity will provide an additional treatment capacity that will continue to remediate Cr(VI) from lower permeability layers that may migrate into the higher permeability treated zone after active treatment is completed. This residual treatment capacity will gradually wane as the reduced iron and sulfide phases are progressively reoxidized by the influx of upgradient oxygenated groundwater into the treatment zone. The longevity and effectiveness of

the residual treatment effect (for example, ranging from a few months up to a year or more) will, in part, be a function of the groundwater flow rate and the distribution and total mass of the reduced phases that were produced within the target area during bioremediation. After any future full-scale implementation of this technology, periodic reapplication of substrate into the treatment zone could be used to regenerate and extend the longevity of the reductive capacity stored in the aquifer matrix.

Despite the demonstrated effectiveness of Cr(VI) bioremediation, concerns are sometimes raised about the stability and permanence of chromium(III) compounds after bioremediation activities are completed and oxidizing conditions are gradually re-established in the aquifer. In general, chromium(III) is highly resistant to reoxidation under environmental conditions, and DO and manganese oxides are the only commonly occurring inorganic oxidants that could conceivably oxidize chromium(III) to Cr(VI) in most waste materials and soils ("Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese Dioxide" [Eary and Rai,1987]). The remainder of this section summarizes the information obtained concerning the potential reoxidation of chromium(III) compounds by DO or manganese(IV) oxides after bioremediation are completed in 100-D.

I5.1.1 Dissolved Oxygen

The stability of chromium(III) compounds under oxygenated groundwater conditions is fundamental to the successful long-term remediation of Cr(VI) using in situ bioremediation. Based on thermodynamic considerations alone, chromium(III) compounds are predicted to be unstable under oxygenated groundwater conditions; however, as a result of kinetic and other barriers to this reaction, the oxidation of chromium(III) compounds by DO is essentially nonexistent under environmental conditions ("Environmental Chemistry of Chromium" [Rai et al., 1989]; "Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese Dioxide" [Eary and Rai, 1987]). Consequently, chromium(III) compounds precipitated during bioremediation will not be reoxidized to Cr(VI) by DO, even after fully oxygenated conditions are re-established in the aquifer.

I5.1.2 Manganese(IV) Oxides

Reductive dissolution of natural manganese(IV) oxides and the subsequent reprecipitation of the dissolved manganese as more poorly structured and reactive manganese(IV) oxides are a common process in aquifers undergoing bioremediation. Reactive manganese(IV) oxides (for example, birnessite and pyrolusite) have been demonstrated to oxidize aqueous species of chromium(III) in laboratory tests and in some relatively unusual natural environments (for example, "Long-Term Stability of Organic Carbon-Stimulated Chromate Reduction in Contaminated Soils and Its Relation to Manganese Redox Status" [Tokunaga et al., 2007]; "Behavior of Chromium in Soils: V. Fate of Organically Complexed Cr(III) Added to Soil" [James and Bartlett, 1983]; "Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese Dioxide" [Eary and Rai, 1987]; and "Oxidation of Chromium(III) to (VI) by Manganese Oxides" [Kim et al., 2002]). At least one of these field studies indicated that oxidation of solid phase chromium(III) by manganese oxides can occur at rates high enough to exceed the groundwater standard for total chromium. These findings, however, were limited to field settings with extremely chromium- and manganese-oxide-rich sediments (for example, 60,000 mg/kg chromium(III), as the ultramafic-mineral chromite). The geochemical conditions and mineralogy of these sites are significantly different from those of the Hanford Site and the evidence of chromium(III) oxidation by manganese(IV) under such extreme conditions is not relevant to the proposed test area.

Laboratory testing has demonstrated the rate of chromium(III) oxidation by manganese(IV) compounds is much lower if the chromium(III) is present as a solid phase. Laboratory testing of mixed chromite and manganese oxide suspensions over a range of pH values ("Genesis of Hexavalent Chromium from Natural Sources in Soil and Groundwater" [Oze et al., 2007]) confirmed that chromite was subject to

oxidative dissolution in the presence of high-concentration manganese oxides. However, the rates of chromite oxidative dissolution by manganese oxides decreased steadily as the solution pH was increased from 3 to 5 to approximately 6.8. Oxidative dissolution had essentially ceased near a pH of 8 (approximately the pH of Hanford Site groundwater). Even under the extreme conditions of this laboratory study, the fastest oxidation rates observed for solid phase chromium(III) were much slower than the rates typically observed for dissolved chromium(III) species ("Genesis of Hexavalent Chromium from Natural Sources in Soil and Groundwater" [Oze et al., 2007]). Although the oxidation of chromium(III) in ultramafic minerals does occur at noteworthy rates under the very unusual geologic settings described above, there is substantial evidence that reoxidation of solid phase chromium(III) by manganese(IV) oxides is not realistic under the groundwater and aquifer matrix conditions during and after in situ bioremediation. The factors and processes gleaned from relevant publications that are expected to prevent or greatly minimize post-treatment reoxidation of chromium(III) by manganese(IV) oxides include the following:

- Manganese(IV) oxides are most effective as an oxidizer when dissolved chromium(III) is sorbed directly onto the reactive manganese oxide surface. At neutral or slightly basic pH conditions that will eventually be re-established after bioremediation, the concentrations of dissolved chromium(III) available for reoxidation will be minimized by the extremely low solubility of the chromium(III) and mixed iron(II), and chromium(III) phases that will be formed in groundwater during bioremediation ("Genesis of Hexavalent Chromium from Natural Sources in Soil and Groundwater" [Oze et al., 2007]; "Long-Term Stability of Organic Carbon-Stimulated Chromate Reduction in Contaminated Soils and Its Relation to Manganese Redox Status" [Tokunaga et al., 2007]).
- In those relatively rare cases where a chromium(III) phase may be in direct contact with a freshly precipitated manganese oxide surface, the extent of oxidation-reduction reaction between the two phases will eventually be minimized by the development of a less-reactive, mixed-valence layer between the two phases.
- The catalytic and oxidative capacity of freshly precipitated manganese oxides generally decreases over time as the reactive surfaces are neutralized by the sorption of other metal ions or coated by NOM or other common solid phases (for example, iron hydroxides/oxides).
- Recent studies (for example, "Inhibition of FeS on Chromium (III) Oxidation by Biogenic Manganese Oxides" [Wu and Deng, 2006]) indicate that the oxidation of chromium(III) by manganese(IV) oxide is countered by the presence of reductive agents such as iron(II) and sulfide compounds also present in the aquifer. These reducing compounds will be abundant in the targeted section of the aquifer and should inhibit or reverse any potential reoxidation of chromium(III) within the treated area.

Based on the above information, the reoxidation of chromium(III) compounds to Cr(VI) is not anticipated to be a significant issue after bioremediation is completed.

I5.2 Fate and Transport of Some Potential Chemical Byproducts of Bioremediation

This section presents a summary of the fate and transport characteristics of several common byproducts of bioremediation likely to be produced under the unconfined aquifer conditions prevalent in the 100 Area.

I5.2.1 Iron and Manganese, and Arsenic

Ferric (iron III) hydroxides and manganese (manganese(IV)) oxide phases in the matrix of bioremediated aquifers commonly undergo reductive dissolution and the iron and manganese are mobilized as iron(II) and manganese(II) aqueous species at concentrations substantially higher than background levels. Although some microbes are capable of using manganese oxides as an electron acceptor with the

consequent production of manganese(II), the main mechanism expected to drive the reduction of manganese oxides is reaction with dissolved iron(II) and sulfide produced during the microbially mediated reduction of iron(III) compounds and dissolved sulfate ("The Chemistry of Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters" [Morse et al., 1987]; "Reduction of Structural Fe(III) of Nontronite by Hydrogen Sulfide" [Strekopytov and Larsen, 2001]; "A Revised Scheme for the Reactivity of Iron (Oxyhydr) Oxide Minerals Towards Dissolved Sulfide" [Poulton et al., 2004]; "Reduction of Iron Oxides Enhanced by a Sulfate-Reducing Bacterium and Biogenic H_2S" [Li et al., 2006]).

Local variations in the concentration of dissolved iron and manganese would be expected, since the processes controlling reductive dissolution are highly dependent on local mineralogy, and the pH and alkalinity of the system. Transport of dissolved iron(II) and manganese(II) for a substantial distance out of the treatment area is unlikely because they would be subject to rapid reoxidation, reprecipitation, or sorption, once transported away from the highly reducing conditions within the target zone. Any iron(II) and manganese(II) remaining in solution within the target area after bioremediation activities are terminated will either be transported downgradient from the target area, oxidized, and precipitated as oxidized insoluble phases, or precipitated in place as reducing or mixed valent phases (for example, FeS and Green Rust), or eventually as oxide and hydroxide phases after bioremediation activities are complete and more oxidizing conditions are gradually re-established.

As with iron and manganese, the fate and transport characteristics of arsenic are dominated by the redox and pH characteristics of the aquifer. Arsenic (As) can exist in four oxidation states (-3, 0, +3, +5) but is typically present in oxidizing groundwater with a pH between 6 and 8 as one of two anionic arsenic(V) or "arsenate" species. At a pH less than 7.0, $H_2AsO_4^-$ predominates while at a pH greater than 7.0, the $HAsO_4^{2-}$ complex is dominant (*Kinetics of Adsorption and Redox Processes on Iron and Manganese Oxides: Reactions of Arsenic(III) and Selenium(IV) at Goethite and Birnessite Surfaces* [Scott, 1991]). Arsenic(V) species have a relatively high sorption affinity for iron oxides/hydroxides under near neutral pH conditions. Naturally occurring iron hydroxide oxides in aquifer materials commonly contain substantial amounts of arsenic that have been accumulated (sorbed) over time from the ambient pore water or groundwater. Under anoxic groundwater conditions (at the same pH range as above), arsenic is stable in the trivalent state and predominantly exists as the more mobile neutral arsenite species (H_3AsO_3) (*Kinetics of Adsorption and Redox Processes on Iron and Manganese Oxides: Reactions of Arsenic(III) and Selenium(IV) at Goethite and Birnessite Surfaces* [Scott, 1991]). Previous 100 Area investigations (for example, *Hanford 100-D Area Biostimulation Treatability Test Results* [PNNL-18784]) demonstrate that arsenic is present in the matrix of the 100 Area unconfined aquifer. Consequently, reductive dissolution of the iron hydroxide/oxide phases during in situ bioremediation may lead to the solubilization of elevated levels of arsenic as the relatively mobile neutral trivalent species (H_3AsO_3).

Under moderately acidic (for example, pH 5.5) sulfate reducing conditions, arsenic(III) may sorb to or coprecipitate with metal sulfide phases (for example, iron sulfides). Generally, however, under the higher pH and mildly alkaline conditions and conditions that should predominate during bioremediation of Cr(VI) in the 100 Area, the neutral and relatively mobile arsenic(III) specie H_3AsO_3 will likely predominate in solution.

The relatively high mobility of arsenic III species solubilized during bioremediation should be largely limited to the aquifer zone where iron(II) and manganese(II) are stable in solution. Manganese oxides play a major role in accelerating the oxidation of arsenic(III) to arsenic(V) in aqueous solutions and iron(III) hydroxides have a high affinity for arsenic(V) (*Kinetics of Adsorption and Redox Processes on Iron and Manganese Oxides: Reactions of Arsenic(III) and Selenium(IV) at Goethite and Birnessite Surfaces* [Scott, 1991]). Consequently, if arsenic(III) migrates out of the strongly reducing bioremediation

zone, it will also be subject to oxidation and sorption by previously existing or freshly reprecipitated manganese oxides and iron hydroxides in the aquifer.

Based on the above summary of the fate and transport characteristics of dissolved iron, manganese, and arsenic, the potential for these constituents to migrate substantially downgradient from a targeted zone within the 100 Area unconfined aquifer is considered to be limited. During any application of bioremediation, iron, manganese, and arsenic concentrations would be routinely monitored to verify that these constituents are not transported outside accepted limits.

I5.2.1.1 Barium

Although barium is strongly sorbed by clays, manganese oxides, and ferric hydroxides, the very low barium concentrations in aquifers containing sulfate commonly reflects the precipitation of the extremely insoluble sulfate mineral barite ($BaSO_4$). Barite is commonly the solubility-limiting phase even in aquifers containing dissolved sulfate concentrations that are substantially lower than those typical of the 100 Area unconfined aquifer (for example, 50 to 100 mg/L). Nevertheless, it is possible that the development of locally intense reducing conditions within a targeted area of the unconfined aquifer during bioremediation could lead to the near total conversion of groundwater sulfate to sulfide in that area. The reductive dissolution of iron hydroxides, manganese oxides, and high levels of sulfate reduction would likely result in the increased solubility of barium. Although this process can result in an increase in the barium concentrations of the highly reducing section of the aquifer, this effect would be transient and any elevated barium concentrations that develop should rapidly decrease back to near background levels (as a result of barium sorption and reprecipitation of barite) once the groundwater migrates out of the intensely reducing zone and mixes with groundwater that retains background levels of sulfate.

I5.2.1.2 Volatile Fatty Acids and Methane

If the substrate supply to a system exceeds the availability of electron acceptors such as oxygen, nitrate, sulfate, and iron(III), microbial fermentation of the substrate may become the dominant metabolic process, resulting in the development of very low groundwater redox conditions. Fermentation is a balanced reduction-oxidation reaction where the same organic molecule (for example, the substrate) serves as both an electron acceptor and donor. These microbially mediated, energy-producing reactions result in the conversion of the original substrate (for example, lactate) into simpler organic compounds (for example, methane and volatile fatty acids [VFA] such as propionate). Compared to the relatively rapid rates of Cr(VI) reduction obtained by direct and indirect Cr(VI) reduction processes that are driven by iron- and sulfate-reducing bacteria, fermentation reactions are less efficient processes for reducing Cr(VI). Therefore, high concentrations of methane and VFA in groundwater during bioremediation can be indicative of excessive (wasteful) substrate use. The fate and transport of these organic byproducts can be managed by limiting the amount of substrate to the minimum amount needed to obtain the necessary rate and extent of Cr(VI) remediation. Elevated levels of methane and VFA in the groundwater downgradient from the target area should be rapidly reduced by a combination of aerobic and anaerobic microbial degradation.

I6 Evaluation of Potential Substrates for In Situ Bioremediation in the 100 Area

A wide range of substrates has been used for in situ bioremediation. Some substrates (for example, vegetable oil) are long-lasting but preferentially partition onto the aquifer solid matrix and cannot be distributed substantial distances from injection wells. Some substrates are more mobile but have a rapid degradation profile (for example, lactate and ethanol) that reduces the ability of these substrates to migrate long distances from a single well.

Parsons Corporation (*Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents* [Parsons, 2004]) and Air Force Center for Engineering and the Environment ("Enhanced In Situ

Anaerobic Bioremediation, Substrate Alternatives" [AFCEE, 2010]), evaluated many of the organic substrates that can be used to support bioremediation of groundwater, such as low-molecular-weight fatty acids (for example, lactate, butyrate, and acetate), alcohols (for example, methanol and ethanol) cheese whey (lactose), sugar syrups (for example, molasses or corn syrup), vegetable oils, a commercial product marketed as HRC, and solid substrates such as mulch and compost. Of these, lactate, molasses, HRC and vegetable oils are most commonly added for enhanced anaerobic bioremediation. Effective substrates that are used less frequently include ethanol, methanol, butyrate, high-fructose corn syrup, and cheese whey.

A substrate that is selected for implementation should be suitable for the biogeochemical and hydrodynamic character of the aquifer to be treated. The physical and chemical nature of a substrate (for example, phase and solubility) will affect the frequency of addition, the addition technique, and the treatment system configuration. Consequently, some substrates are more suitable for particular applications. A common goal is to minimize overall project cost by minimizing the number of required injection points, the number of injection events, and substrate cost. Table I-1 presents several common substrate types, including examples of miscible fluids, viscous fluids, low viscosity emulsions, and solid substrates. The following paragraphs summarize each of the general substrate types:

- **Miscible Liquids.** Miscible substrates applied as a dissolved or "aqueous-phase" solution offer the greatest potential for uniform distribution throughout the aquifer matrix relative to substrates applied as a viscous fluid or solid phase. Molasses and lactate are the most common substrates applied in an aqueous phase. Miscible substrates travel with advective groundwater flow and are typically applied in a continuous or periodic (pulsed) mode to maintain a specified reactive treatment zone.

- **Viscous Fluids.** Slow-release, viscous fluid substrates include HRC and neat vegetable oils. These substrates are intended to be long-lasting, where a single or limited number of injections are sufficient for site remediation. They are intended to be relatively immobile in the subsurface and rely on advection and dispersion of soluble compounds (for example, lactic acid for HRC or metabolic acids generated by degradation of vegetable oil) for effective delivery throughout the aquifer matrix.

- **Low-viscosity Emulsions.** Vegetable oil emulsions have been developed in an effort to improve the distribution of substrate in the subsurface while still providing a long-lasting source of organic carbon. Microemulsions consisting of 5 to 10 percent vegetable oil in water by volume are relatively low-viscosity mixtures (for example, nondairy creamers like Coffee-Mate®[2]) compared to the viscous fluids described above. The use of microemulsions is the result of lessons learned in early vegetable oil field trials in which high-injection backpressures, ROI, and reductions in hydraulic conductivity were observed using coarse viscous emulsions or neat vegetable oil.

- **Solid Substrates.** Solid phase substrates include mulch and compost. Mulch is generally obtained from shredding and chipping tree and shrub trimmings, and is primarily composed of cellulose and lignin. Often "green" plant material or compost is incorporated to provide a source of nitrogen for microbial growth and as a source of more readily degraded organic carbon. Degradation of the substrate by microbial processes in the subsurface provides a number of breakdown products, including metabolic and humic acids, which act as secondary fermentable substrates. Solid substrates are typically placed in trenches or in excavations as backfill in a one-time event using conventional construction techniques.

[2] Coffee-mate—Non-dairy creamer manufactured by Nestle USA, Glendale, California.

Table I-1. Substrates Used for Enhanced Anaerobic Bioremediation

Substrate	Typical Delivery Techniques	Form of Application	Frequency of Injection
Soluble Substrates			
Lactate and Butyrate	Injection wells or circulation systems	Acids or salts diluted in water	Continuously or monthly
Methanol and Ethanol	Injection wells or circulation systems	Diluted in water	Continuously or monthly
Sodium Benzoate	Injection wells or circulation systems	Dissolved in water	Continuously or monthly
Molasses, High-fructose Corn Syrup	Injection wells	Dissolved in water	Continuously or monthly
Whey	Injection wells, direct injection, or circulation systems	Dissolved in water or slurry	Continuously, monthly, or annually
Viscous Fluid Substrates			
HRC® Products	Direct injection or borehole backfill	Straight injection	Every 1 to 3 years, potential one-time application
Vegetable Oils	Direct injection or injection wells	Straight oil injection with water push, or high oil:water content (>20% oil) emulsions	One-time application
Low-viscosity Fluid Substrates			
Vegetable Oil Emulsions	Direct injection or injection wells	Low oil content (<10%) microemulsions suspended in water	Every 2 to 3 years, potential one-time application
Solid Substrates			
Mulch and Compost	Trenching or excavation	Trenching, excavation, or surface amendments	One-time application

Source: "Enhanced In Situ Anaerobic Bioremediation, Substrate Alternatives" (AFCEE, 2010).
HRC = hydrogen release compound

The substrate (or substrates) that are selected for implementation should be based on screening the physical, chemical, and cost profiles of candidate substrates against the physical, geochemical, hydrological, and environmental characteristics of the proposed bioremediation site. The individual site-specific criteria will likely vary in relative importance from site to site including, but not limited to, groundwater chemistry (type and abundance of electron acceptors, for example, DO, nitrate, or sulfate; aquifer matrix characteristics, for example, lithology, stratification, or fracture flow versus porous flow; aquifer hydrology, for example, transmissivity or flow velocity; or nature and extent of the plume, for example, small concentrated or large diffuse plumes). In addition, the following criteria should be included as part of any evaluation conducted to select the preferred substrate(s) for implementation during bioremediation of the Cr(VI) contamination in the unconfined aquifer (or vadose zone) of the 100 Area:

- **Previous Experience.** What documentation exists to show the substrate was successfully used for pilot tests, or preferably, full-scale remediation efforts for Cr(VI) at sites with aquifer conditions similar to the 100 Area unconfined aquifer? Include an evaluation of previous bioremediation research that has been conducted at the Hanford Site.
- **Material Properties.** What are the desired physical properties and performance characteristics for the candidate substrates? For instance, are they miscible or immiscible? Do the substrates have a long or short decay rate?
- **Treatment Efficacy and Longevity.** How effective is the substrate in reducing Cr(VI)? How long will the substrate last in the aquifer? How many electrons per unit of substrate are available to support reduction of Cr(VI)?
- **Cost.** In some cases, very large volumes of substrate may be required to support in situ bioremediation. What is the approximate "cost per electron donated" for the substrate? In some cases, this may be a difficult metric to quantify, and other relative measures of cost may be required.
- **Delivery, Mixing, and Implementation.** What are the factors influencing the preparation and use of the substrate at the test location? What factors will drive full-scale implementation?
- **Intellectual Property Encumbrances.** The rapid growth in the use of in situ bioremediation has led to the development of a vibrant market with a number of proprietary blends. The substrate selected should not be encumbered with intellectual property constraints that prevent or hinder its use.
- **Worker and Environmental Safety.** Some substrates have physical or chemical characteristics that prevent their use in large quantities, or are complicated by permitting constraints.

I6.1 Substrate Selection for In Situ Bioremediation of the 100 Area Unconfined Aquifer

Table I-2 presents the results of an evaluation process that was conducted on a range of candidate substrates commonly used for bioremediation activities. The objective of this process was to provide a technically sound basis for selecting the substrate that is most appropriate for implementing in situ bioremediation of Cr(VI) in the 100 Area unconfined aquifer or overlying vadose zone.

I6.1.1 Initial Screening

Because of the generally transmissive nature of the unconfined aquifer (and the vadose zone) in the 100 Area, the high mobility of Cr(VI), the large size of the plumes, and the relative proximity of the ecologically sensitive Columbia River, highly soluble, relatively mobile, and fast-degrading substrates are preferred over longer-lasting but relatively immobile substrates (Table I-2). This screening criterion eliminated emulsified vegetable oil and chitin from further consideration for use as substrates for Cr(VI) remediation in the 100 Area. However, these relatively immobile substrates could be used to supplement the more soluble substrates to provide longer-lasting reducing conditions directly around an injection well. This reducing area around the injection well will then continue to treat the reinjected water that will contain some Cr(VI).

I6.1.2 Secondary Screening

The remaining candidates presented in Table I-2 (methanol, ethanol, acetate sodium lactate, molasses, and whey) are all highly mobile and rapidly metabolized by microbes in groundwater systems such as the unconfined aquifer. Methanol and ethanol are flammable and were screened out based on health and safety issues. Acetate was screened out because it is weakly acidic and represents a potential handling

risk. In addition, acetate may reduce the pH of groundwater in the targeted area to below the optimum range for microbial growth. Even moderately more acidic conditions in the target area could increase the solubility of some metals sorbed onto the aquifer matrix. Molasses has been used frequently for the bioremediation of Cr(VI) and other contaminants but is known to have a tendency to promote biofouling. For this reason, molasses was eliminated from consideration.

The remaining two substrates in Table I-2, sodium lactate (lactate) and cheese whey (whey), were selected as the two best potential substrate candidates for any future in situ bioremediation system implemented to treat Cr(VI) in the 100 Area of the Hanford Site. The following section presents the basis for the final selection of one of these two candidates as the preferred substrate.

I6.1.3 Final Screening

Lactate is one of the most commonly used substrates for in situ bioremediation (*Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents* [Parsons, 2004]). Lactate is a relatively simple carbon compound (three carbon atoms per molecule) that is completely miscible in water and should be consumed relatively quickly by the microorganisms in the unconfined aquifer. Lactate can be obtained readily in small to large volumes of 30 and 60 percent concentrated solutions and does not require refrigeration prior to mixing with water. Lactate is easily mixed with water to the required concentration prior to injection or infiltration into the subsurface.

Whey is a milk byproduct of cheese-making that consists primarily of water and about 4 to 5 percent lactose (a disaccharide with 12 carbon atoms per molecule) and minor amounts of protein, fat, and ash. If used in the original liquid form, whey must be kept refrigerated prior to use. Liquid whey is easily diluted with water and can be readily injected into aquifers. Whey can also be obtained in a dried powder form (commonly in 23 kg [50 lb] bags) that consists of approximately 70 to 75 percent lactose, 10 to 13 percent protein, and 7 to 13 percent ash ("Enhanced Bioremediation Using Whey Powder for a Trichloroethene Plume in a High-Sulfate, Fractured Granitic Aquifer" [Mora et al., 2008]). Whey powder is readily soluble and can be mixed with water onsite to the preferred concentration, immediately prior to use.

Because of the greater complexity of the organic constituents in whey, it has a longer biodegradation half-life than lactate. The somewhat slower biodegradation rate of whey should allow for the remediation of larger areas within Cr(VI) plumes than will lactate under similar operating conditions. Although whey has not been used as a bioremediation substrate nearly as frequently as lactate, it has been used at a few Cr(VI) sites, such as the Pacific Gas and Electric Company Hinkley Compressor Station (*Notice of Applicability of General Waste Discharge Requirements for the General Site-Wide Groundwater Remediation Project at the PG&E Compressor Station, Hinkley, San Bernardino County* [CAL/EPA, 2010]), and for the in situ remediation (reductive dechlorination) of chlorinated solvents such as TCE ("Enhanced Bioremediation Using Whey Powder for a Trichloroethene Plume in a High-Sulfate, Fractured Granitic Aquifer" [Mora et al., 2008]). Disadvantages of both dried and liquid whey, relative to lactate, include: (1) long-term or large-scale in situ treatment will require onsite refrigerated storage of liquid whey or frequent handling of large quantities of dried whey, and (2) the relatively high concentration of the disaccharide lactose in whey may result in high acid production rates during fermentation reactions, potentially lowering the pH within the target area ("Enhanced Bioremediation Using Whey Powder for a Trichloroethene Plume in a High-Sulfate, Fractured Granitic Aquifer" [Mora et al., 2008]). As long as excessively high concentrations of whey are not injected or infiltrated into the aquifer, however, the moderately elevated alkalinity (for example, 100 to 120 mg/L as $CaCO_3$) that typifies most areas of the unconfined aquifer in the 100 Area, should be sufficient to largely offset the reduction of pH as the result of elevated levels of organic acids generated during the in situ fermentation of whey.

Table I-2. Screening Level Evaluation of Several Commonly Used In Situ Bioremediation Substrates

Substrate	Handling and Safety	Treatment Efficacy	Materials Properties	Longevity	Byproduct Production	Delivery and Mixing Consideration	Full-Scale Infrastructure Requirements	Lifecycle Costs	Permitting	Comments
Methanol	Flammable product; requires special handling.	Effective, half-life of Cr(VI) is days.	Miscible, low viscosity and density are desirable for in situ mixing.	Several months	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Among the best reductants for delivery and mixing.	Flammable storage required, otherwise injection requires mixer and pump.	Low because of cost of methanol and infrastructure needed to field implement approach.	Used for food processing	Completely miscible in water, making methanol along with ethanol one of the most suitable donors for recirculation systems. Issues with transportation and handling of a flammable liquid.
Ethanol	Flammable product; requires special handling.	Effective, half-life of Cr(VI) is days.	Miscible, low viscosity and density are desirable for in situ mixing.	Several months	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Among the best reductants for delivery and mixing.	Flammable storage required; otherwise, injection requires mixer and pump.	Low because of cost of ethanol and infrastructure needed to implement approach.	Food Grade	Completely miscible in water, making it one of the most suitable reductants for recirculation systems. Issues with transportation and handling of a flammable liquid.
Acetate	Weak acid; requires some special handling.	Effective, half-life of Cr(VI) is days.	Miscible, low viscosity and density are desirable for in situ mixing, low pH is a concern at some sites.	Several months	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Among the best reductants for delivery and mixing.	Injection requires mixer, pump, and piping.	Low because of cost of acetate and infrastructure needed to implement.	Food Grade	Very soluble reductant, making it a good reductant for recirculation systems. Issues with transportation and handling related to properties.
Lactate	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Very soluble, low viscosity; desirable for in situ mixing, slightly denser than water.	Several months	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Good reductant for delivery and mixing.	Injection requires mixer, pump and piping.	Low because of cost of lactate and infrastructure needed to implement in field.	Food or Pharmaceutical Grade	One of the most commonly used soluble reductants, density greater than water; therefore, must be injected in dilute concentrations.
Molasses	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Good solubility, very high viscosity making it difficult to inject and mix in aquifer.	Several months	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced because sulfate compounds are present in molasses.	Can be a challenge to deliver and mix in aquifer because of relatively high viscosity.	Injection requires mixer, pump and piping.	Low because of cost of molasses and infrastructure needed to implement. Patent licensing fee required.	Food Grade	Broad spectrum reductant containing simple and complex sugars. Viscosity is a problem, along with the potential to biofoul injection wells and well packs. Potential intellectual property encumbrances. **Tested at the Hanford Site.**
Emulsified Vegetable Oil	No known safety or handling issues.	Effective, half-life of Cr(VI) is several days.	Emulsion is like a soluble product, good viscosity and pH.	Several months to years	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Similar to lactate.	Injection requires mixer, pump and piping.	Low to Moderate because of cost of oil and number of wells need to implement approach.	Food Grade	Complex unsaturated alkanes that degrade to release electrons for chromium reduction over a very long period. **Tested at the Hanford Site.**
Metals Remediation Compound (by REGENESIS, makers of HRC®)	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Very high viscosity, slightly soluble sulfur and polylactate compound.	Several months to years	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	High viscosity makes this a challenge to inject and mix. Usually requires heating and special delivery infrastructure.	Vendor conducts injection.	Low to Moderate because of cost of MRC and number of wells needed to implement approach.	Lactate ester and sulfide compound	Proprietary slow-release polylactate ester and sulfide compound. Viscosity like that of molasses in cold temperature. Potential intellectual property encumbrances. A similar HRC® product has been **tested at the Hanford Site**. Potential intellectual property encumbrances.
Whey	No known safety issues; whey solutions must be refrigerated.	Effective, half-life of Cr(VI) is days.	Very soluble, low viscosity; desirable for in situ mixing, slightly denser than water.	Several months	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Good reductant for delivery and mixing.	Injection requires mixer, pump and piping.	Low because of cost of whey and infrastructure needed to implement in field.	Food Grade	Reductant containing lactose and complex sugars. Cheese whey is longer-lived, with a low degradation rate. Must be injected in dilute concentrations.

Table I-2. Screening Level Evaluation of Several Commonly Used In Situ Bioremediation Substrates

Substrate	Handling and Safety	Treatment Efficacy	Materials Properties	Longevity	Byproduct Production	Delivery and Mixing Consideration	Full-Scale Infrastructure Requirements	Lifecycle Costs	Permitting	Comments
Chitin	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Solid 3 mm flakes. High viscosity mix with guar gum. Very low density.	Several months to years	Microbial degradation produces CO_2. Methane and hydrogen sulfide can be produced.	Can be a challenge to deliver and mix in aquifer. Fracturing has been used to increase mixing.	Injection requires mixer, pump and piping.	Low to Moderate because of injection requirements. Fracturing may be needed to implement.	Structure similar to cellulose	Structure similar to cellulose. Breaks down slowly to produce needed electrons over time.

Note: **Bolded** substrates were selected for final screening.

Although whey would likely perform well as a bioremediation substrate in the unconfined aquifer of the 100 Area, lactate is more readily available, easier to store and transport, and has fewer potential unwanted side effects. Consequently, lactate is generally preferred as the substrate of choice for in situ bioremediation of Cr(VI) in the unconfined aquifer.

I7 In Situ Groundwater Remediation by Bioinjection

I7.1 Conceptual Design

The general aquifer characteristics of the 100 Area unconfined aquifer, including high transmissivity and moderate alkalinity, are consistent with the deployment of bioremediation as a remedial action for Cr(VI) groundwater contamination. More specifically, a small-scale recirculating bioinjection system (Figure I-1) may be used to remediate selected groundwater hot spots where high concentrations of Cr(VI) are present, or the system could be expanded and used to establish large zones of treatment within a plume. Bioinjection could also be used as a means of treating the Cr(VI) in the extracted water rather than sending the water to the ion exchange treatment plant. It this way, it combines the extraction removal process of a pump-and-treat system with the in situ bioremediation process. In either approach, this technology could be applied in 100 Area Cr(VI) plumes where traditional pump-and-treat systems are active or where pump-and-treat systems are not deployed.

Based on this conceptual design, contaminated groundwater near the leading edge of the plume or smaller hot spot will be extracted, amended with substrate, and reinjected near the upgradient boundary of the target area (Figure I-1). Two or more parallel bioremediation cells can be established, forming overlapping downgradient capture zones and upgradient bioinjection zones for the treatment of larger areas. The use of recirculating bioremediation cells will significantly increase the implementability, effectiveness, and potential scale of bioremediation as a treatment approach for Cr(VI)-contaminated groundwater in the 100 Area.

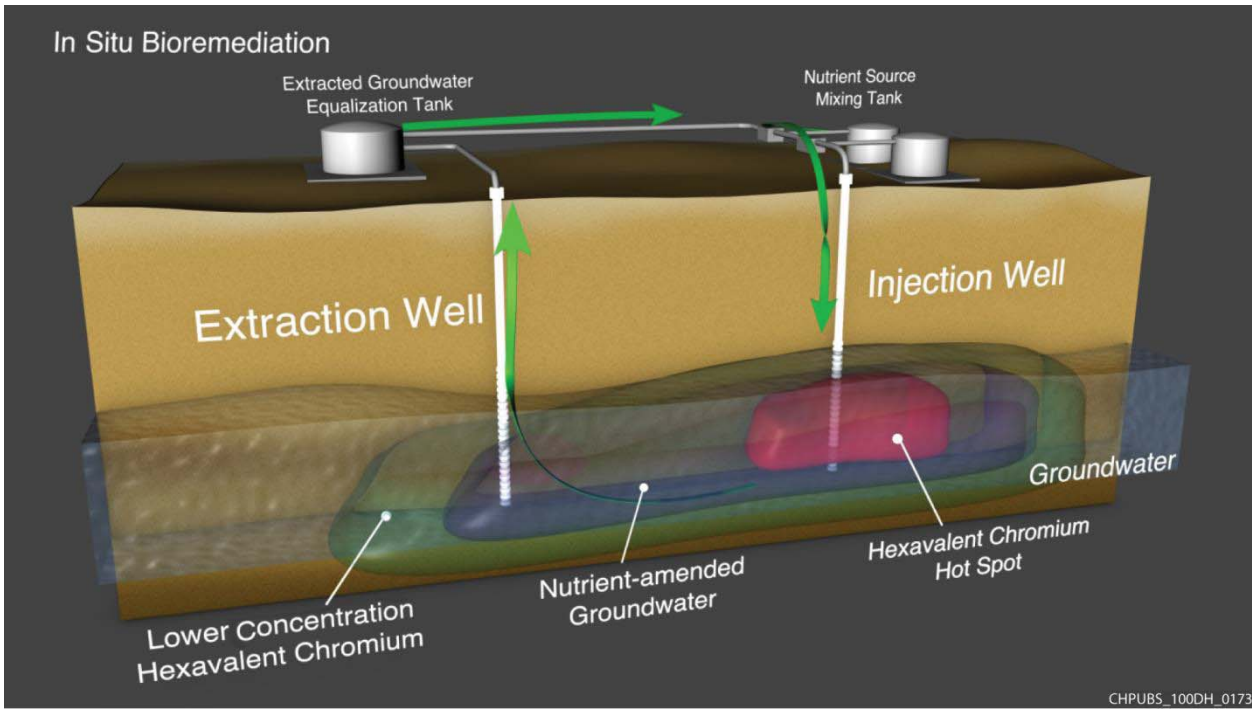


Figure I-1. Cross-Section of a Recirculating In Situ Bioremediation System

I7.1.1 Implementation Factors

In situ bioremediation of Cr(VI) in groundwater typically employs wells to attain a distribution of substrate (at the necessary concentrations) within the treatment area to achieve the remediation goals. The effective treatment zone that develops around a bioinjection well is defined as a region of influence. It is anticipated that several factors influence the design and implementation of in situ bioremediation systems. These factors include:

- **Method of Delivery.** Vertical injection wells screened in the aquifer are typically used to deliver carbon compounds into groundwater. Other approaches include surface infiltration trenches, horizontal wells, and direct-push technology. Vertical wells are recommended because they can be reliably installed, accept high volumes of liquid, and are easily maintained.
- **Operation of Injection Wells.** Markedly different results are achievable depending on how the injection wells are used to return amended groundwater to the aquifer. For instance, microbial activity can vary dramatically whether amendments are added at extremely high concentrations of substrate in a short period of time (batch injection), rather than substrate addition at a low concentration over a much longer time period (continuous injection).
  - Once the microbial community is developed around an injection well and reducing conditions are generated, pulsed delivery of substrate is advantageous to avoid or minimize injection well fouling. A short period of substrate injection each day or every few days followed by injection of unamended water will minimize biofouling of the injection wells that would occur with greater frequency with continuous carbon delivery.
  - The initial injection of a carbon source will have substantially slower degradation rates (once oxygen is consumed) than subsequent injections, because time is required for the substrate additions to expand the population of facultative and obligate anaerobic microbes that are present. Over time, the aquifer will develop a flourishing anaerobic microbial community that will be able to rapidly degrade the added substrate using the various other electron acceptors that are present (for example, nitrate, chromium, iron, manganese, and sulfate).
- **Spacing Between Injection and Extraction Wells.** Recirculating bioremediation systems are advantageous for treating large plumes in highly permeable aquifers. When injection wells and extraction wells are operated together, or "paired," an induced flow field can be developed, allowing substrate delivery over larger distances. Recirculating systems can be used to better control the size, shape, and reducing intensity of regions of influence.
- **Substrate Injection and the Region of Influence.** As previously discussed, specific substrates have distinct advantages or disadvantages related to the nature and extent of the targeted contaminants. Based on these and other factors, lactate is currently the recommended substrate for bioremediation activities in the 100 Area. When any substrate is injected into an aquifer, it influences the biogeochemistry of groundwater in a number of ways.
- **Microbial Effects.** Another factor influencing the size of the area of treatment is the microbial abundance in the soil or aquifer matrix. During application of the amended groundwater, the microbial population can increase several orders of magnitude over days, weeks, or months. Experience at other locations shows that achieving the maximum substrate usage rate may require several months, largely depending on soil and groundwater temperatures, the carrying capacity, or maximum microbial abundance. A detailed pilot test was performed to examine these factors at a

compressor station in California (*Floodplain Reductive Zone In-Situ Pilot Test: Final Completion Report: PG&E Topock Compressor Station, San Bernardino County, California* [ARCADIS, 2008]).

I7.2 Previous Studies and Applications of Bioinjection and Similar Technologies to Cr(VI) Remediation in Groundwater

In situ bioremediation has been used to treat Cr(VI) contaminated groundwater successfully at locations both on and off the Hanford Site. In addition, it has been used at many sites to remediate a range of other contaminants including metals, sulfate, nitrate and chlorinated solvents. These applications provide information that can be used to guide the implementation of in situ bioremediation for Cr(VI) Several cases where in situ bioremediation has been successfully used to treat Cr(VI) are summarized in the following paragraphs.

I7.3 Hanford 100-D Pacific Northwest National Laboratory Biostimulation Treatability Study

PNNL conducted a treatability test designed to demonstrate that in situ biostimulation can be applied to help meet cleanup goals at Hanford Site 100-D. The in situ biostimulation technology was intended to provide supplemental treatment upgradient of the ISRM barrier previously installed in 100-D. Substrates selected for the treatability test included a soluble (miscible) substrate (molasses) and an immiscible slow-release substrate (emulsified vegetable oil in the form of a commercially available product called EOS®-598[3]). This treatability study is reported in *Hanford 100-D Area Biostimulation Treatability Test Results* (PNNL-18784).

I7.3.1 Site Conditions

The unconfined aquifer in 100-D is composed of sandy gravel to silty sandy gravel 3 to 9 m (10 to 30 ft) thick, which corresponds to Ringold Formation unit E. Depth to the water table ranges from less than 1 m (3 ft) near the river to approximately 25 m (82 ft) farther inland. The base of the unconfined aquifer is a fine-grained silty sand to clay overbank interval, designated the RUM, which is approximately 15 m (49 ft) thick and generally dips to the west. The deeper Ringold Formation is believed to comprise more layers of clay, silt, and sand based on interpolations between wells elsewhere in the 100 Area.

At the treatability test location, the unconfined aquifer is contained within the lower Ringold Formation unit E and is approximately 6.8 to 5.8 m (22 to 19 ft) thick (depending on fluctuations occurring in the elevation of the Columbia River); the water table is approximately 25 m (82 ft) bgs. Over 10 months of the year, groundwater generally flows northwest and discharges into the Columbia River at a rate of about 97 cm/year [38 in./year (125 ft/year)]. The remainder of the year, the groundwater moves about 8 m/year (26 ft/year) to the northeast, generally parallel with the direction of river flow. The estimated average horizontal hydraulic conductivity at the test site is 69.5 cm/day [27.4 in./day (90 ft/day)].

The average baseline Cr(VI) and total chromium concentrations at the treatability test site were 70 and 80.3 µg/L, respectively.

I7.3.2 Technical Approach

Two test cells were installed at the treatability test site, each consisting of an injection well surrounded by upgradient, downgradient, and cross-gradient monitoring wells (Figure I-2). The test cells were located such that existing Well 199-D5-40 could be used as a background monitoring location for both test cells. Field test operations were conducted by injecting the substrate using process water from the 100-D

[3] EOS®-598—Emulsified Oil Substrate, manufactured by EOS Remediation, LLC, Raleigh, North Carolina.

pressurized water supply as the carrier solution. The substrate solutions were fed into the manifold system using a chemical metering pump.

Figure I-2. Molasses Injected at 100-D Area Biostimulation Treatability Test Site to Nourish Bacteria

Molasses Injection. In September 2007, molasses injection was conducted over a 3.25-day period using process water injected at approximately 40 gallons per minute (gal/min) amended with approximately 40 g/L molasses, 100 mg/L ammonium chloride, and 100 mg/L sodium bromide. Injection pressure was variable throughout the injection but was typically about 25 pounds per square inch (psi). Approximately 19,300 L (5,100 gal) of molasses were injected, with a total injection volume of about 594,000 L (157,000 gal). At the end of the substrate injection, 9,400 L (2,500 gal) of process water were injected for approximately an hour to clear the injection system of substrate and flush the wellbore.

EOS Injection. The substrate injection was conducted over a period of 17 hours using process water injected at approximately 40 gal/min amended with approximately 60 g/L emulsion (EOS-598 product) and 100 mg/L sodium bromide. Emulsion amendment was not continuous during this time but occurred in seven discrete pulses, with a total emulsion injection time of 10.5 hours. Injection pressure was variable throughout the injection, ranging from 3 to 17 psi. Approximately 5,560 L (1,470 gal) of EOS were injected, with a total injection volume of about 157,700 L (41,700 gal). At the end of the substrate injection, 30,600 L (8,100 gal) process water was injected for approximately 3 hours to clear the injection system of substrate.

I7.3.3 Results

This subsection presents the results of the field tests conducted for each of the substrates injected into the test wells.

Molasses Injection. Substrate was successfully distributed to a radius of about 15 m (50 ft) from the injection well, and monitoring data indicated that microbial growth was initiated rapidly. The uniformity of substrate distribution was impacted by subsurface heterogeneity; however, post-injection monitoring indicated subsequent microbial activity and enhanced Cr(VI) reduction (reduced to below detection limits) throughout the monitored zone. Low oxygen, nitrate, and chromium concentrations were maintained for the approximately 2-year duration of monitoring. The injected substrate and associated organic degradation products persisted for about 1 year. Over the second year of monitoring, organic substrate concentrations were low; therefore, the continued effectiveness of the treatment zone is attributed to recycling of organic compounds associated with the biomass that was produced during the first year.

EOS Injection. Substrate was successfully distributed to a radius of about 8 m (25 ft) from the injection well. The uniformity of substrate distribution was impacted by subsurface heterogeneity; however, post-injection monitoring indicated subsequent microbial activity and enhanced Cr(VI) reduction (reduced to less than 5 µg/L) throughout the monitored zone. Low oxygen, nitrate, and chromium concentrations were maintained for the approximately 10-month duration of monitoring. The monitoring period for the EOS test was short compared to the expected longevity of the substrate (approximately 3 or more years). Therefore, additional monitoring would be necessary to determine the longevity of the treatment.

I7.3.4 Lessons Learned

Aquifer permeability reduction within the molasses injection test cell was moderate and likely a result of the growth of bacteria. Hydraulic slug testing conducted 60 and 420 days after substrate injection showed minimal impact from injection of the molasses substrate in the short term. Over the longer term, permeability was reduced by factors ranging from 0.55 to 0.02, likely because of biomass growth. The biomass concentration would be expected to slowly decline over time and lead to restored permeability.

In contrast to the molasses injection, permeability in the EOS injection test cell changed quickly and appeared to be a result of the presence of the injected oil rather than the significant biomass growth. Aquifer permeability reduction within the test zone was moderate (reduced by factors ranging from 0.7 to 0.32). Because of the slow dissolution of substrate over time, additional permeability reduction was not expected.

Within the test cells, water quality was negatively impacted by an increase in the concentration of secondary byproduct reduced metals. These changes were expected because of the imposed anaerobic conditions required for biological treatment of Cr(VI). Although the concentration of most metals increased, only three (arsenic, barium, and selenium) increased to concentrations consistently above the maximum contamination level.

I7.4 Hanford 100-H Lawrence Berkeley National Laboratory Hydrogen Release Compound Treatability Study

Since 2004, biostimulation tests have been performed at 100-H by personnel at Lawrence Berkeley National Laboratory (*In Situ Long-Term Reductive Bioimmobilization of Cr(VI) in Groundwater Using Hydrogen Release Compound* [Faybishenko, 2009]). In these tests, HRC was injected into the aquifer to stimulate microbial activity and transform Cr(VI) to chromium(III). Results from the tests show Cr(VI) concentrations in the treated area decreased to below drinking water standards and remained at that level for nearly 3 years. The principal difference between this test and the test described in the previous section is the use of polylactate. This is a liquid that is difficult to inject any distance from a well because of its high viscosity; therefore, this substance is limited in its ability to treat large areas of an aquifer. Over several months, polylactate slowly disperses into the aquifer, at which point it acts as a more mobile substrate.

I7.4.1 Site Conditions

The lithology underlying the treatability study area consists of high-permeability Hanford sediments (gravel and coarse sand) at a depth of approximately 12 m (40 ft). The Hanford Site sediments are underlain by clays of the Ringold Formation at a depth of approximately 14 m (46 ft), which extends to a depth of 15 m (50 ft). Below this is a silty clay-to-silt layer. Regional groundwater flow direction in the treatability study area is predominantly to the northeast toward the Columbia River. Results from borehole water-flux measurements showed that practically all water entered the boreholes from the sandy gravel of the Hanford formation, with very low flow from the Ringold Formation.

I7.4.2 Technical Approach

The well layout for the treatability study included an injection well (699-96-45), a pumping/monitoring well (699-96-44) located approximately 5.3 m (17.5 ft) downgradient from the injection well, a monitoring well (699-96-41) located midway between 699-96-44 and 699-96-45, a monitoring well (699-96-42) located approximately 4.6 m (15 ft) cross-gradient from 699-96-44, and an existing upgradient background monitoring well (699-96-43). Newly installed wells were drilled to a depth of 18 m (60 ft) bgs.

On August 3, 2004, 18.2 kg (40 lbs) of HRC were injected into 699-96-45, through a straddle packer that isolated the injection interval to 13 to 14 m (43 to 46 ft). To trace the post-HRC injection carbon production generated by metabolic processes, 10 g (.35 oz.) of 13C-labeled lactate were mixed with the HRC. Before the injection, the HRC was preheated to about 35°C and diluted with 15 L (4 gal) of distilled water. The injection hose was initially filled with 9.5 L (2.5 gal) of water (as a primer). In total, 17 L (4.5 gal) of water was injected as a chaser after the HRC injection. Following the HRC injection, potassium bromide was also injected into the same injection interval. Groundwater was pumped from downgradient Well 699-96-44 to create a direct water flow path between wells. Pumping continued for 25 days.

I7.4.3 Results

This subsection presents the results of the field tests conducted after HRC was injected into the test wells.

Chromium Reduction. Following the HRC injection, Cr(VI) concentrations decreased in both the injection and monitoring/pumping wells from approximately 700 and 100 µg/L, respectively, to non-detect levels. After the HRC injection, the Cr(VI) reduction rate was 0.626 day-1 in 699-96-45, and 0.276 day-1 in the pumped water from 699-96-44. In 699-96-45, Cr(VI) concentrations remained below detection limits for more than 3 years after HRC injection. In 699-96-44, Cr(VI) concentrations gradually recovered, but remained below the background concentration for more than 3 years after the HRC injection. The Cr(VI) and total Cr concentration trends in 699-96-41 and 699-96-42 were comparable with those in 699-96-44.

Substrate Distribution. Radar and seismic tomography measurements showed an initial accumulation of HRC near the bottom of the injection interval in 699-96-45. This was most likely caused by gravitational settling of HRC. The time-lapse geophysical data suggested that following injection, the HRC byproducts spread upward into the higher hydraulic conductivity zone of the Hanford formation, which was the zone most strongly affected by pumping from 699-96-44.

Biogeochemical Response. The maximum biomass in both the pumping and injection wells was reached 15 to 20 days following injection. The maximum average biomass increased approximately 50-fold in 699-96-44, and approximately 38-fold in 699-96-45. The lower biomass in water samples from the injection well may have resulted from filtering of bacteria attached to colloids during groundwater sampling and analysis.

The results of PhyloChip microarray analysis of water samples showed that the HRC injection initially increased biodiversity and enriched the presence of nitrate reducers such as *Pseudomonas* spp., iron reducers such as *Geobacter metallireducens*, sulfate reducers such as *Desulfovibrio vulgaris* and, later, an enrichment of methanogenic archaea. The occurrence of these bacteria and archaea suggests that both direct microbial Cr(VI) reduction and an indirect Cr(VI) reduction was occurring.

The HRC injection generated reducing conditions, which is evident from the drop in the DO concentration from 8.2 to 0.35 mg/L and redox potential from 240 to 130 mV in downgradient monitoring Well 699-96-44. Although DO in 699-96-45 increased to 5.5 mg/L after the conclusion of pumping, it then gradually decreased over the next year. Over the next 3years after pumping ceased, DO in 699-96-4 ranging from 6 to 7 mg/L, compared with 8 to 9 mg/L in upgradient Monitoring Well 699-96-43. At the same time,

pH dropped from 8.9 to 6.5-7.0 and stabilized at this level. Through monitoring conducted in June 2007, redox potential and DO in the injection and downgradient monitoring wells had not returned to the background levels. The slow recovery of background redox conditions could have been caused by the presence of some HRC breakdown products (lactic and acetic acid) between the injection and downgradient monitoring wells. Post-HRC injection decaying biomass may have also served as a carbon source.

An increase in the ^{13}C of dissolved inorganic carbon (DIC) from -12 percent (prior-HRC injection) to greater than 50 percent (which is higher than that in the injected HRC) was likely caused by the creation of carbon dioxide as a byproduct of microbial metabolism. It should be noted that the release rate of ^{13}C-labeled lactate that was added to the HRC could be higher than that of polylactate, which is the main component of HRC. The carbon isotope ratios of the DIC decreased after pumping was stopped, but remained above background for the 3-year period of observation through June 2007.

Secondary Byproducts. The concentration of aqueous Fe2+ increased in both the injection and downgradient pumping/monitoring wells, reaching maximum values (over 10,000 µg/L) about 2 months after the HRC injection. Fe2+ concentration returned to the background, undetectable level 2.5 years after the HRC injection in downgradient Monitoring Well 699-96-44, and 3.5 years after the HRC injection in Well 699-96-45.

I7.4.4 Lessons Learned

Hydraulic and chemical transport processes in the Hanford formation were likely affected by biogeochemical processes after the HRC injection. A post-HRC injection (July 2005 and April 2006) increase in the tracer travel time could likely be explained by the decrease in the hydraulic conductivity as a result of partial blocking of flow pathways within heterogeneous media by biofilms and carbon dioxide gas.

I7.5 Other Relevant Hanford Site Studies

Although these tests were not specifically related to in situ bioremediation, the studies developed data useful to the development of this in situ bioremediation test.

I7.5.1 Fortifying the 100-D Area In Situ Redox Manipulation Barrier with Iron

The ISRM barrier was implemented to passively treat Cr(VI) contamination in the 100-D southern plume and prevent the discharge of elevated levels of Cr(VI) to the Columbia River (*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 high Cr(VI) concentrations in the 100-D hot spot upgradient from the barrier were not understood. When performance monitoring data indicated that Cr(VI) was breaking through the ISRM treatment zone, scientists proposed that fortifying the barrier with additional reduced iron would increase the long-term effectiveness of the barrier. Consequently, a treatability study was conducted to evaluate whether augmentation of the ISRM barrier with NZVI 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 tiny iron particles (only 70 nanometers [3 millionths of an inch] in diameter) could fortify the weaker portions of the ISRM barrier. The small size of the particles would allow them to flow into the aquifer, thus treating the water more effectively given the very large surface area of the material (30 m^2/g [150,000 ft^2/lb]). Higher surface area means that more of the iron would be available to react with and remediate the groundwater.

Selecting the right iron particles was critical to the success of the test; therefore, initial stages of the project focused on identifying potential NZVI 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 NZVI into the more permeable portions of the barrier to ensure that the NZVI could disperse at least 7 m (23 ft) from the injection well. The second goal was to determine whether the selected NZVI 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 NZVI was communicated 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 radius of influence. Analysis of aquifer materials showed that approximately 4 weight percent NZVI was present in the targeted permeable layer near the bottom of the aquifer. This verified that the goal of emplacing NZVI at least 7 m (23 ft) into the aquifer was successfully accomplished. Monitoring has shown the area near the test is strongly reducing, and Cr(VI) has been reduced to immobile chromium(III). The test demonstrated that RNIP-M2 could be an effective, easily injected NZVI product to fortify the ISRM barrier.

I7.5.2 100-K Area Calcium Polysulfide Injection Treatability Test

As part of a continuing effort to identify new technologies for remediating Cr(VI) in 100 Area groundwater, the injection of a strongly reducing chemical was proposed as an in situ remediation approach for Cr(VI) in groundwater (*Treatability Test Report for Calcium Polysulfide in the 100-K Area* [DOE/RL-2006-17]).

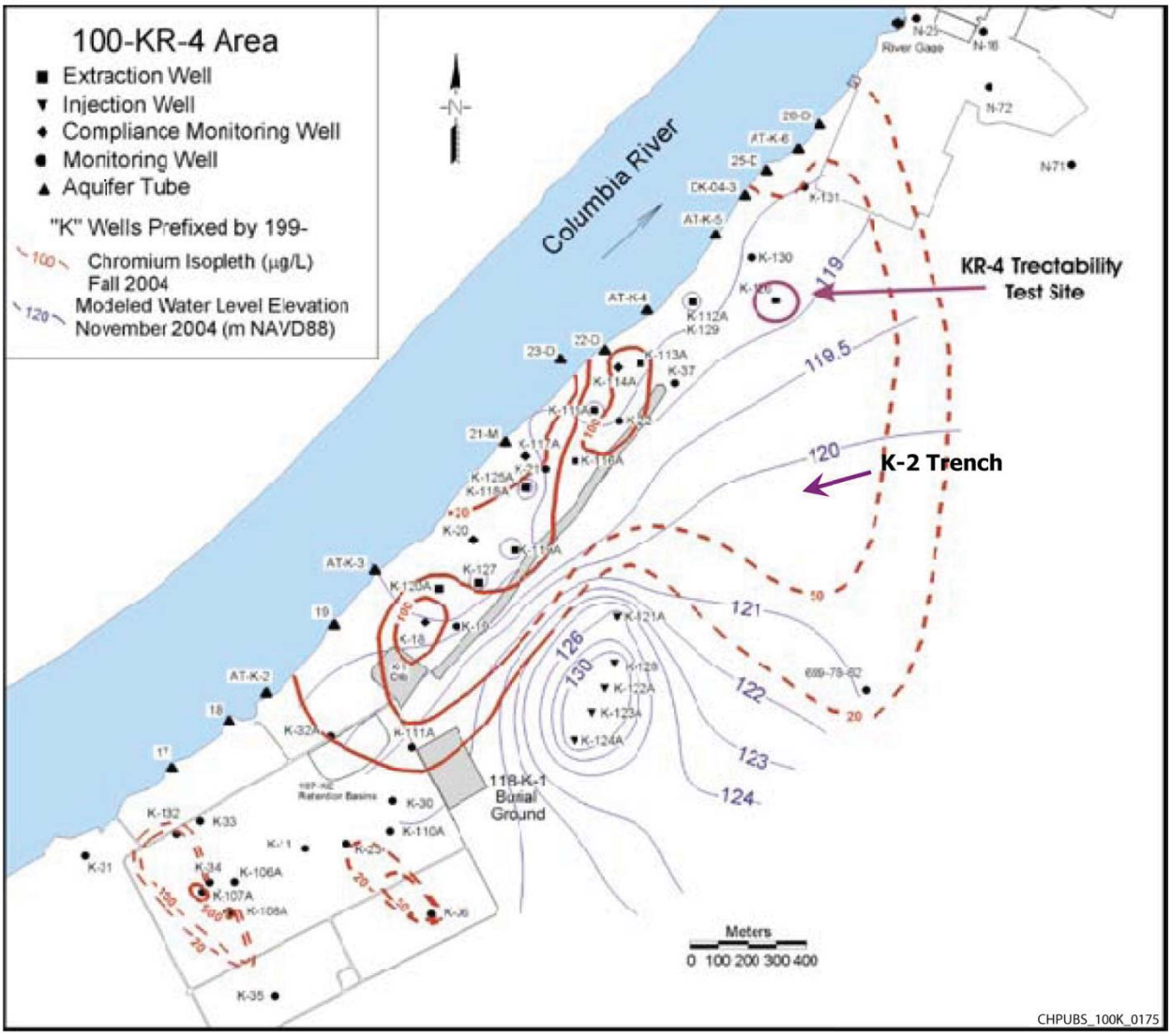
The treatability test, which began on June 28, 2005, was conducted in the eastern part of 100-K (Figure I-3). The test was designed to provide experience in designing systems to implement this technology, and revealed several lessons that were valuable to consider during implementation of a bioremediation system. Given these aspects, the test had the following multiple objectives:

- Obtain hydrologic information for 100-K aquifer required for a potential full-scale implementation of this technology.
- Verify the ability to achieve in situ Cr(VI) reduction through both inorganic and microbiological processes by the combined injection of calcium polysulfide and a carbon substrate.
- Determine whether aquifer constituents (for example, manganese or arsenic) are mobilized as a result of these processes and how other parameters (for example, nitrate or DO) are affected as a result of the groundwater treatment.
- Obtain operational experience in the in situ treatment of Cr(VI)-contaminated groundwater.
- Determine whether this approach could be implemented as a cost-effective method to augment the current 100-K pump-and-treat systems.

Five wells were used in the treatability test, which included an extraction well surrounded by four injection wells. During testing, groundwater was withdrawn and mixed with calcium polysulfide in an aboveground tank. This solution was reacted in a mixing apparatus for a minimum of 2 hours and pumped through the injection wells in approximately equal amounts to permeate the aquifer. This is typically called a “five-spot” configuration, and is ideal for a test of this type because it provides operational field experience and kinetics information in a manageable area, while still treating a section of the aquifer.

Before startup, systems were tested for leaks and proper operation, and a tracer study was initiated. Water was circulated without calcium polysulfide on June 27, 2005, when a lithium bromide tracer was pumped

into one of the injection wells. This tracer test (along with slug tests carried out in the extraction and injection wells before and after the treatability test was performed) served to quantify the hydraulic conductivity in the aquifer beneath the treatability test area. Slug tests were rerun after completion of the treatability test to determine if the test had degraded the aquifer.



Source: NAVD88, *North American Vertical Datum of 1988*.

Figure I-3. 100-KR-4 Plume Showing Treatability Test Site

During the treatability test, 25 samples were collected on a regular basis and analyzed for basic chemical properties (for example, pH and oxidation-reduction potential) and elemental (metals) analysis.
The amounts of water extracted and injected were recorded, as well as the volume of calcium polysulfide mixed with the water. Over 1,324,894 L (350,000 gal) were treated during the test, which was completed on August 11, 2005. All of the performance goals were met by the end of the test period. The technology effectively reduced Cr(VI) in the aquifer and created a permeable reactive barrier that continues to treat Cr(VI) under natural groundwater flow conditions. Analysis of groundwater chemistry before, during, and after the test shows that manganese and iron were mobilized under the strongly reducing conditions in the

aquifer, and that arsenic was at near-background conditions after test completion. The pre- and post-treatment aquifer tests showed that chemical injection did not degrade the permeability of the aquifer.

This test was considered successful and the data collected are sufficient to scale-up the treatment technology. Groundwater monitoring in the treatment area shows that 2 years after the test, DO rebounded to near ambient conditions of 7,000 µg/L in extraction well 199-K-126, but was maintained at less than half of ambient concentrations in the injection well. Groundwater in a well approximately 200 m (656 ft) downgradient from the test area has yet to show any effects from the treatability test.

I7.6 Pacific Gas and Electric Company Hinkley Compressor Station, San Bernardino County, California

The Pacific Gas and Electric Company (PG&E) Hinkley Compressor Station, located in San Bernardino County, California, 5 mi (8 km) west of Barstow, compresses natural gas before pumping it through pipelines to central and northern California. Opened in 1952, the compressor station used Cr(VI) as an anticorrosion agent in the cooling tower water between 1952 and 1966. From 1952 to 1964, untreated wastewater from the cooling towers was discharged to unlined ponds. Some of this wastewater percolated to groundwater. The resulting Cr(VI) plume was approximately 2 mi (3.2 km) long, more than 1 mi (1.6 km) wide, and 15 m (50 ft) thick. This remediation is described in *Hinkley Remediation Semiannual Status Report (July through December 2009), PG&E Compressor Station, Hinkley, California* (CH2M HILL, 2010).

I7.6.1 Site Conditions

Geologic units beneath PG&E's Hinkley site consist of Holocene-age Mojave River deposits down to approximately 46 m (150 ft) bgs. Beneath these alluvial deposits lies a late Pleistocene-age lacustrine deposit of blue, gray, or green clay and silt, varying in thickness from zero to 30 m (100 ft). It acts as a confining layer separating the upper unconfined and the deeper confined aquifer. Beneath the blue clay are Tertiary-age deposits consisting of weathered bedrock with sediments deposited under lacustrine, floodplain, and river channel conditions.

Two water-bearing zones have been identified beneath the site. Unconsolidated soils (predominantly sand and silt) within the first 46 m (150 ft) bgs contain a shallow unconfined aquifer, known as the upper aquifer, with groundwater encountered at a depth of 24 to 30 m (80 to 100 ft) bgs. The upper aquifer consists of alluvium and recent sediments from the Mojave River. It is 15 to 21 m (50 to 70 ft) thick and is divided into an upper coarse-grained unit and a lower fine-grained unit. The lower unit has a thickness of up to 15 m (50 ft).

Groundwater flow direction in the shallow unconfined aquifer is toward the north-northwest with a gradient of approximately 0.006 ft/ft. The estimated groundwater velocity is approximately 55 to 274 m/year (180 to 900 ft/year).

The chromium groundwater plume contains total chromium in excess of the maximum contaminant level (MCL) of 50 µg/L. Concentrations range up to approximately 5,000 µg/L, but are typically less than 100 µg/L across a majority of the plume area. The interim background total chromium concentration was established at 4 µg/L.

I7.6.2 Technical Approach

Two full-scale in situ remediation projects have been implemented to date at the Hinkley site to remediate the Cr(VI) plume. The two projects include an in situ reactive zone (IRZ) to treat the source of Cr(VI) at the compressor station (Source Area IRZ), and an IRZ transecting the full width of the Cr(VI) plume to

control downgradient migration and growth of the plume (Central Area IRZ). The location of each IRZ is shown on Figure I-4. Both systems incorporate a series of injection and extraction wells that recirculate groundwater, amending the groundwater with an organic substrate (lactate or ethanol). Both systems are designed to achieve a target total organic carbon (TOC) concentration in the recirculation zone of 100 to 200 mg/L, with a goal of minimizing the TOC to less than 10 mg/L at the extraction wells.

Source Area IRZ. The first phase of the Source Area IRZ consists of 16 recirculation wells (12 injection wells arranged in three rows [SA-RW-05 through SA-RW-16] and four downgradient extraction wells [SA-RW-01 through SA-RW-04]) screened at approximately 21 to 43 m (70 to 140 ft) bgs. Startup of the Source Area IRZ system was conducted from April 27 to May 7, 2008. Amendment of groundwater with sodium lactate continued through August 28, 2008. Ethanol was substituted for lactate on August 29, 2008, and will be used for ongoing future operations. Expansion of the Source Area system to treat areas outside of the Phase I area has been planned for 2010.

Central Area IRZ. The Central Area IRZ consists of 12 recirculation wells (10 injection wells [CA-RW-01, CA-RW-02, CA-RW-03, and CA-RW-05 through CA-RW-11] and two in-line extraction wells [CA-RW-04 and CA-RW-12]), screened at approximately 24 to 35 m (80 to 115 ft) bgs. Continuous groundwater recirculation and daily amendment with sodium lactate began in 2007 and continued into 2008. In mid-October 2008, ethanol was substituted for sodium lactate. The Central Area IRZ will continue to operate in its current configuration. If additional flow is needed, a third extraction well may be brought on-line.

I7.6.3 Results

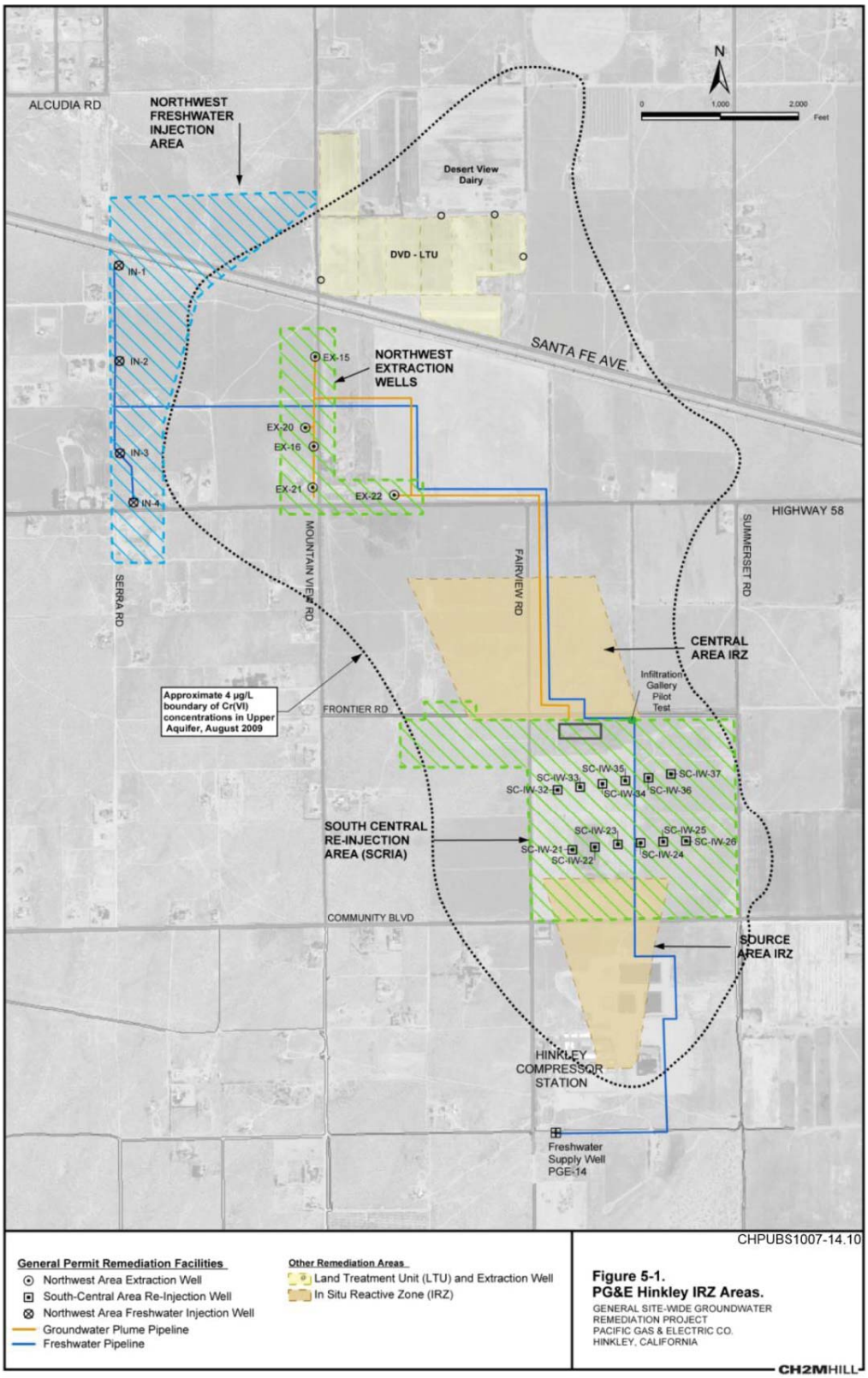
This subsection presents the results of the two full-scale in situ remediation projects implemented at the Hinkley site to remediate the Cr(VI) plume.

Source Area IRZ. Results from the Source Area IRZ monitoring network demonstrate effective treatment of Cr(VI) for the deep and shallow units of the upper aquifer. Results from the second half of 2009 indicate that decreases in the Cr(VI) concentration from nearly 1,000 µg/L to less than the interim site background concentration of 4 µg/L was maintained throughout the vicinity of the injection wells.

Central Area IRZ. Results from the Central Area IRZ monitoring network demonstrated effective treatment of Cr(VI) in the shallow unit of the upper aquifer, and of groundwater passing through the IRZ. The IRZ-treated water contained Cr(VI) concentrations below 4 µg/L across the majority of the treatment barrier. Decreases in total chromium and geochemical indicators (nitrate and sulfate) in sentry wells located approximately 122 to 244 m (400 and 800 ft) downgradient from the monitoring wells also indicate the IRZ system is having a beneficial effect in groundwater quality downgradient from the injection wells.

I7.6.4 Lessons Learned

At the Source Area IRZ, arsenic concentrations increased in one sentry monitoring well, from 14.8 to 33.2 µg/L, between April and November 2009. Dissolved manganese was also detected above the threshold concentration in November and December 2009 at one sentry well location (both the shallow and deep interval). Dissolved manganese concentrations increased from 13.24 µg/L in January to 3,300 µg/L in December 2009 in the shallow well, and from 1.45 to 3,170 µg/L in the deep well. Ethanol dosage in the Source Area was scaled back in response to these exceedances. Operation of the Source Area IRZ and treatment of Cr(VI) will continue with ongoing changes in injection rate and locations as well as ethanol reagent concentrations to optimize TOC distribution and Cr(VI) treatment, and to minimize the migration of secondary byproducts.



Source: *Hinkley Remediation Semiannual Status Report (July through December 2009), PG&E Compressor Station, Hinkley, California* (CH2M HILL, 2010).

Figure I-4. PG&E Hinkley IRZ Areas

Operations of the Central Area IRZ originally were conducted in a dipole configuration with injection into the odd-numbered recirculation wells and extraction from even-numbered recirculation wells. Several challenges were encountered with operating the system in the original dipole well configuration. First, several extraction wells began to extract carbon-amended groundwater, which caused fouling and reduced recirculation flow rates; and second, wells once used for injection showed limited extraction capacity, thereby limiting the effectiveness of reversing injection and extraction wells. To reduce the frequency of well fouling and enhance carbon distribution efficiency, operation of the Central Area IRZ system was modified from the original dipole configuration to the current 10 injection/two extraction well configuration in November 2009.

Monitoring results indicate that the downgradient migration of dissolved metals was being controlled through management of reagent injections. As expected, dissolved manganese concentrations increased at monitoring locations within the Central Area IRZ after startup. During the second half of 2009, manganese was detected above the threshold concentration of 226 µg/L in three sentry monitoring wells (located approximately 12 m [40 ft] downgradient from the injection wells). The ethanol dosage was decreased in upgradient injection locations. The effect of the decreased dosing was observed at the three sentry wells, as manganese concentrations stabilized or decreased. The system continues to be operated at reduced injection rates in the new configuration.

I7.7 PG&E Topock Compressor Station, San Bernardino County, California

The PG&E Topock Compressor Station is located in San Bernardino County, approximately 24 km (15 mi) southeast of Needles, California. PG&E is addressing the presence of Cr(VI) in groundwater under the oversight of the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC). The Cr(VI) source was chromium salt historically used as a corrosion inhibitor in the station cooling towers. In 1996, PG&E and DTSC entered into a Corrective Action Consent Agreement to implement corrective measures to address Cr(VI) released in the Bat Cave Wash Area near the site.

PG&E implemented two pilot studies at the site: an Upland reductive zone in situ pilot test (ISPT) to evaluate how well recirculation wells can distribute reductant (ethanol) throughout the aquifer to achieve treatment across a transect of the plume, and a Floodplain ISPT to evaluate the efficacy of using lactate to enhance the existing reducing environment in the floodplain adjacent to the Colorado River.

I7.7.1 Case Study References

The following is a list of the reports referenced regarding the two pilot studies implemented by PG&E:

ARCADIS, 2005, "Final Addendum to the *In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan —Floodplain Reductive Zone Enhancement* for the Pacific Gas and Electric Company Topock Compressor Station" (technical memorandum), ARCADIS G&M, Inc., San Francisco, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/01-Floodplain%20In-situ%20Pilot%20Study%20Work%20Plan%20Addendum%20Dec%202005.pdf.

ARCADIS, 2006a, "Addendum 2 to the *In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan – Floodplain Reductive Zone Enhancement* for the Pacific Gas and Electric Company Topock Compressor Station," Technical Memorandum, ARCADIS G&M, Inc., San Francisco, California, April 14. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/Topock%20FP%20ISPT%20WP%20Addendum%202%20-%20Final.pdf.

ARCADIS, 2006b, *In Situ Hexavalent Chromium Reduction Pilot Test Work Plan – Upland Plume Treatment*, Pacific Gas & Electric Company Topock Compressor Station Needles, California, ARCADIS G&M, Inc., Richmond, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/UplandAreaIn-SituPilotStudy/FinalUplandWorkPlan.pdf.

ARCADIS, 2008, *Floodplain Reductive Zone In-Situ Pilot Test Final Completion Report*, Waste Discharge Requirements Order No. R7-2006-0008 and Order No. R7-2007-0014, PG&E Topock Compressor Station San Bernardino County, California, ARCADIS, San Francisco, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/Floodplain%20Insitu%20Final%20Report%203-5-08.pdf.

ARCADIS, 2009a, *Third Quarter 2009 Monitoring Report for the Upland Reductive Zone In-Situ Pilot Test*, PG&E Topock Compressor Station San Bernardino County, California, ARCADIS, San Francisco, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/UplandAreaIn-SituPilotStudy/Third_Quarter_2009_Upland_ISPT_Final.pdf.

DTSC, PG&E Topock Compressor Station, Needles, California, Environmental Investigation and Cleanup Activities, California Department of Toxic Substance Control website. Available at: http://dtsc-topock.com/.

MWH, 2005, *In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan Floodplain Reductive Zone Enhancement*. Prepared by MWH, Walnut Creek, California, for PG&E. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/03-Floodplain%20In-situ%20Workplan%20Aug%202005.pdf.

I7.7.2 Site Conditions

Groundwater occurs under unconfined to semiconfined conditions within the alluvial fan and fluvial sediments beneath most of the Topock site. In the floodplain area adjacent to the Colorado River, the fluvial deposits interfinger with, and are hydraulically connected to, the alluvial fan deposits. The unconsolidated alluvial and fluvial deposits are underlain by the Miocene conglomerate and pre-Tertiary metamorphic and igneous bedrock.

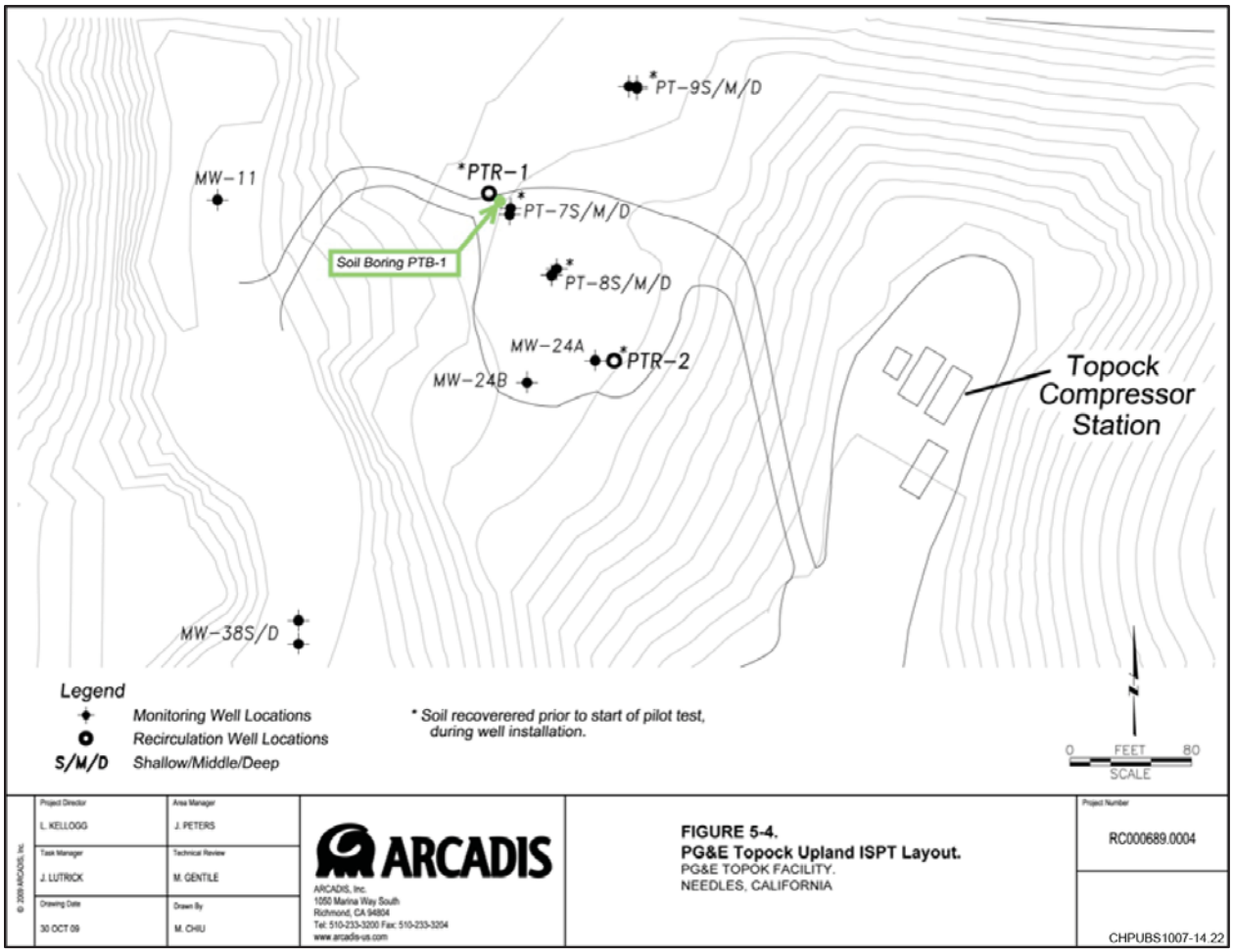
In the Upland area, the depth to groundwater is approximately 35 m (115 ft) bgs. The subsurface shallow aquifer zone consists of alluvial deposits 45 to 61 m (150 to 200 ft) thick, and approximately 309 m (1,000 ft) of the unit is saturated. Hydraulic gradients across the Upland area are between 0.0001 to 0.001 ft/ft. In the Floodplain area, the depth to groundwater is approximately 4.5 m (15 ft) bgs, but can fluctuate dramatically as a result of interactions between groundwater and the Colorado River. The measured saturated thickness of the alluvial aquifer ranges from 23.5 to 29 m (77 to 95 ft). Natural groundwater gradients in the alluvial aquifer are relatively flat, approximately 0.0001 to 0.001 ft/ft. Current estimates of groundwater seepage velocity near the pilot test area under the influence of nearby groundwater extraction range from about 0.1 to 1 ft per day.

Total chromium concentrations in groundwater range from approximately 1,000 to 15,000 µg/L over 80 percent of the plume footprint. The interim background total chromium concentration was established at 30 µg/L.

I7.7.3 Technical Approach

This subsection describes the approaches used for the PG&E's two pilot studies.

Upland ISPT. The Upland ISPT well configuration is shown on Figure I-5. The Upland ISPT consisted of the recirculation of the reagent mixture between two dual-screen recirculation wells (PTR-1 and PTR-2) screened between approximately 36 to 49 m (120 and 160 ft) bgs (upper screens) and 52 to 64 m (170 and 210 ft) bgs (lower screens).



Source: *Third Quarter 2009 Monitoring Report for the Upland Reductive Zone In-Situ Pilot Test* (ARCADIS, 2009a).

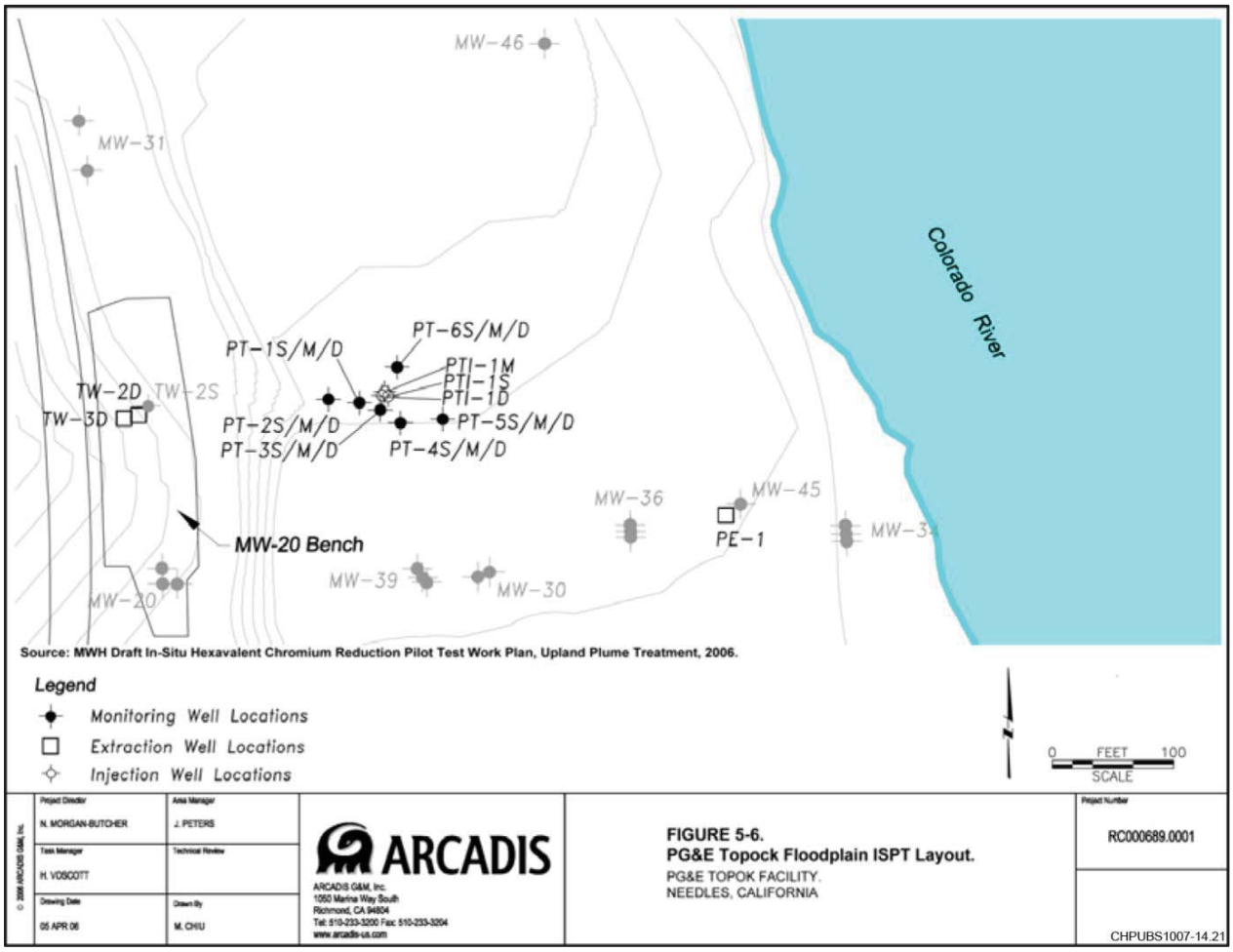
Figure I-5. PG&E Topock Upland ISPT Layout

The two dual-screen recirculation wells were spaced approximately 43 m (140 ft) apart, and were designed to create a three-dimensional circulation pattern in the aquifer. The screen intervals were located within the same aquifer but are hydraulically isolated from each other using packers. Groundwater was drawn into one well, pumped through the well casing, and reintroduced into the aquifer at a different elevation. The second well operated in a reverse pumping pattern, resulting in a conveyer belt circulation pattern. Ethanol was added to the groundwater in the well casing between the packers, or in a vault at the wellhead.

The Upland ISPT began operating on March 5, 2008. The system operated at 114 L/min (30 gal/min), during which time approximately 378 L (100 gal) of 40 percent ethanol were injected into each well each day at a rate of approximately 19 L/min (5 gal/min). Multiple short-period injections of ethanol at high flow rates were conducted to minimize biofouling of the recirculation wells. On May 29, 2008, ethanol dosing was temporarily discontinued in order to monitor the systems' ability to distribute TOC sufficiently through the recirculation cell. On August 4, 2008, ethanol dosing was resumed at approximately 95 L/day (25 gallons per day [gpd]) as a result of declining TOC trends in nearby

monitoring wells. In October 2008, the dosing rate was increased to approximately 170 L/day (45 gpd), and then again to the original dosing rate of 379 L/day (100 gpd) later that month. Ethanol dosing and recirculation were completed in November 2008.

Floodplain ISPT. The Floodplain ISPT well configuration is shown on Figure I-6. The Floodplain ISPT test area was located within the zone of influence of existing groundwater Extraction Well TW-2 (located 61 m [200 ft] to the west). The induced gradient generated by pumping groundwater from TW-2 allowed the test to monitor the potential radius of impact of the reagents, their persistence, and their effectiveness at reducing Cr(VI) under active circulation conditions. A three-well injection cluster with separate 3 m (10 ft) screens (PTI-1S, PTI-1M, and PTI-1D) was installed to allow for controlled injection into both the shallow fluvial deposits and deeper alluvial fan deposits of the aquifer in this area. The depth of the three injection wells ranged from approximately 21 to 36 m (70 to 120 ft). The lactate solution and chase water were allowed to gravity feed. The planned concentration of lactate in the initial injection was 23 kg (50 lbs) per well or, equivalently, approximately 1,000 mg/L in the reductant solution. A total of six injection events were conducted during the Floodplain ISPT on the following dates: May 3 through 6, 2006; August 11, 2006; September 7, 2006; November 1, 2006; May 7 and 8, 2007; and July 17 and 18, 2007. Approximately 1,160 kg (2,557 lbs) of 60 percent sodium lactate diluted with water to 270,000 L (72,000 gal) were injected over the course of the six events.



Source: *Third Quarter 2009 Monitoring Report for the Floodplain Reductive Zone In-Situ Pilot Test* (ARCADIS, 2009b).

Figure I-6. PG&E Topock Floodplain ISPT Layout

I7.7.4 Results

Upland ISPT. Results from the August 2009 sampling event indicate that Cr(VI) in groundwater, which was as high as 8,000 µg/L during baseline sampling, continued to be reduced to nondetect levels where organic carbon was effectively delivered and organic carbon distribution was sustained during the pilot test. Complete chromium reduction was sustained at several monitoring wells, despite the return of baseline TOC concentrations following the pilot test. The post-test manganese, iron, and arsenic concentrations demonstrated the attenuation of these metals over time after the disappearance of injected organic carbon from the system.

Analysis of soil samples indicated that sorbed Cr(VI) was also treated to nondetect levels (less than 0.1 mg/kg). Selective extraction results indicate that chromium present in the soil was redistributed to a more stable phase as a result of the in situ treatment. Advanced spectroscopic methods confirmed the co-occurrence of chromium and iron, chromium removal from site groundwater during treatment through reduction of Cr(VI) to chromium(III) and subsequent precipitation, and the formation of reduced (ferrous) iron minerals in the aquifer soil, which will provide reductive capacity for ongoing Cr(VI) treatment without continuous groundwater recirculation and amendment with ethanol.

Floodplain ISPT. The Floodplain ISPT achieved reduction of Cr(VI) in groundwater from 3,350 µg/L to concentrations less than 0.2 µg/L. The Cr(VI) and total dissolved chromium concentration trends also demonstrated that the chromium(III) formed by the reduction of Cr(VI) was removed from groundwater to less than 1 µg/L, likely by precipitation and filtration by the aquifer. The extent of Cr(VI) reduction was highly dependent upon the distribution of organic carbon; Cr(VI) was reduced below 0.2 µg/L in monitoring wells where TOC was delivered at concentrations above 100 mg/L for at least a few weeks. The reduction of Cr(VI) also was sustained in between injections in the absence of residual injected organic carbon when sufficiently high concentrations of organic carbon were delivered initially. This suggests that the injections created a reservoir of residual reducing capacity in the treatment zone that continued to reduce Cr(VI).

Site-specific lactate degradation rates, reported as half-life values, were evaluated from the Floodplain ISPT data. The half-life values were based on a first-order-rate assumption for lactate degradation and were calculated by comparing the observed temporal changes in TOC concentrations measured at ISPT wells to the observed temporal changes in tracer concentrations. For the first injection, the estimated lactate half-life was 17 days. The estimated half-life decreased for the second through fourth injections and ranged from 4.6 to 8.9 days. The more rapid degradation of lactate in the second through fourth injections may reflect the microbial growth that occurred in response to the initial ISPT injections. The estimated half-life increased in the fifth injection to 18 days. The increase likely reflects a lower amount of microbial biomass in the aquifer at the time of injection, potentially because of decay in the 6-month period between the fourth and fifth injections. Lactate degradation was more rapid during the sixth than the fifth injection, as microbial biomass grew in response to the fifth and sixth injections.

Over the course of the first four injections, more residual Cr(VI)-reducing capacity was stored within the aquifer and the extent of Cr(VI) reduction during the periods between injections was increased. The increased longevity of Cr(VI) reduction suggests that more residual reducing capacity was generated by:

1. Injecting more reducing equivalents cumulatively over the second, third, and fourth injections (in other words, higher concentrations of lactate, to increase biomass)
2. Establishing sulfate-reducing conditions in the second through fourth injections and the production of a solid-phase sulfide mineral that maintained reactivity toward Cr(VI)

3. Forming a reduced iron solid phase, other than FeS (for example, magnetite, an iron mineral that contains reduced iron) can be created in the IRZ

The fifth and sixth injections were conducted to further load the aquifer with reducing capacity and test the resulting longevity of Cr(VI) reduction.

I7.7.5 Lessons Learned

At the Upland ISPT, during the third quarter of 2009 barium concentrations in four monitoring locations were higher than baseline, ranging from 183 to 2,800 µg/L. The increase in barium concentrations appeared to be the result of injecting higher than intended organic carbon concentrations during the pilot test. During the pilot test, short-circuiting of the injection water back to the extraction screen led to a localized TOC loading up to an order of magnitude higher than planned. The excessive carbon loading resulted in the near-complete consumption of sulfate and subsequent dissolution of barite, a barium sulfate mineral that occurs naturally in the aquifer.

Prior to injection at the Floodplain ISPT, dissolved manganese concentrations in the deep zone ISPT wells and downgradient wells generally ranged from less than 5 to 361 µg/L. Following injections, the highest dissolved manganese concentrations were observed in the nearest downgradient monitoring well, reaching a maximum of 10,600 µg/L after the fourth injection. After reaching the maximum, manganese concentrations decreased prior to the fifth injection, demonstrating that the generation of manganese was temporary. Manganese concentrations did not increase in the furthest downgradient monitoring well, demonstrating that manganese attenuated as groundwater returned to ambient conditions.

Dissolved iron concentrations were typically below the reporting limit (500 µg/L) in all of the deep-zone ISPT monitoring wells and downgradient wells prior to injection, and did not begin to increase in the ISPT wells until the fifth injection. Dissolved iron reached a maximum concentration of 2,260 µg/L in November 2007 following the sixth injection. Fe(III) was reduced during the first four injections and may not have increased above the reporting limit for dissolved iron because reduced iron-bearing minerals were formed, or because the dissolved reduced iron that was generated in the IRZ immediately reacted with oxidants (for example, oxygen, Cr[VI]), sorbed to aquifer minerals, or precipitated (for example, as FeS).

Dissolved arsenic concentrations were typically below or just above the reporting limit (5 µg/L) in all deep-zone ISPT monitoring wells and downgradient wells prior to injection. Arsenic concentrations in ISPT monitoring wells reached a maximum of 18.3 µg/L following the sixth injection. The decline in dissolved arsenic concentrations after reaching the maximum demonstrated that the dissolution of arsenic as a result of ISPT injections was temporary.

I7.8 Abandoned Manufacturing Facility, Emeryville, California

The former Electrocoatings, Inc. (ECI) facility is located at 1401 Park Avenue in Emeryville, California. From 1952 until 1995, metal plating operations were performed at the site. Solvents were used in degreasing operations until 1992, when they were replaced with a liquid-alkaline soak process. Plating operations were discontinued in 1995, and the associated plating equipment was removed from the site. Operations at the site resulted in chlorinated solvent and chromium impacts to groundwater.

Elevated levels of chromium were detected in groundwater in the late 1970s and early 1980s. In 1995, the site owner initiated a pilot study to evaluate metals precipitation via an IRZ as a possible remedy for the site (as a potential alternative to a conventional pump-and-treat system).

I7.8.1 Case Study References

California State Water Resources Control Board, 2008, "Electro Coating Inc (SL20254872)," Project Fact Sheet, GeoTracker website. Available at: http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=SL20254872.

DTSC, 2006, *In-Situ Bioremediation of Chlorinated Hydrocarbons, An Assessment of Projects in California*, California Department of Toxic Substances Control, Office of Pollution Prevention and Technology Development. Available at: http://www.dtsc.ca.gov/TechnologyDevelopment/upload/Final_ISB_Report4.pdf.

EPA, 2000, *Cost and Performance Report, Anaerobic In-situ Reactive Zone at an Abandoned Manufacturing Facility, Emeryville, California*, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency. Available at: http://www.costperformance.org/pdf/EmeryvilleBio.pdf.

I7.8.2 Site Conditions

The geology of the site consists of interbedded clay, silt, sand and gravel units. Permeable units of sand and gravel are encountered between 1.5 to 7.6 m (5 to 25 ft) bgs within the shallow water-bearing zone. A blue clay zone is present throughout the site and underlies the shallow water-bearing zone at a depth of approximately 7.6 m (25 ft) bgs. Groundwater is encountered from approximately 0.9 to 2.4 m (3 to 8 ft) bgs, and groundwater velocity is estimated to be 18 m (60 ft) per year. Historical Cr(VI) concentrations were in excess of 100,000 µg/L.

I7.8.3 Technical Approach

A pilot study was conducted between August 1995 and February 1996 to determine if the rate of Cr(VI) reduction could be enhanced by an anaerobic IRZ. A mixture of molasses and tap water was injected into the subsurface at the former chromium waste storage area (injections into two monitoring wells spaced 7.6 m [25 ft] apart) and at a location approximately 61 m (200 ft) downgradient from the source area (injections into a single direct-push injection well). The injection interval was approximately 1.5 to 6 m (5 to 20 ft) bgs. The molasses solution was injected using primarily a gravity feed system on a biweekly basis. A total of 6,162 L (1,628 gal) of molasses solution diluted with water at ratios from 1:4 to 1:100 was injected during the pilot study.

Between April 1997 and October 2000, full-scale molasses injections were conducted into more than 100 temporary injection points to address the chlorinated solvent plume at the site, which extended beyond the chromium source area treated by the pilot study. Details regarding full-scale operations and performance pertaining to chromium remediation were not available.

I7.8.4 Results

As a result of the pilot study injections, the average concentration of chromium in groundwater decreased by approximately 98 percent.

I7.9 Avco Lycoming Site, Williamsport, Pennsylvania

The Avco Lycoming (Williamsport Division) site, located in Lycoming County, Pennsylvania, has produced aircraft engines for over 50 years, and has also operated a waste treatment facility since the early 1950s. The site facility uses oils, solvents, and chemicals for various processes. In the past, some of the processes resulted in occasional spills of these materials, resulting in shallow aquifer chromium contamination beneath the western section of the property.

A ROD issued by EPA in 1991 called for pumping and treating contaminated groundwater and discharging it to a nearby stream. In May 1995, chromium reduction using molasses injection was proposed as an alternate groundwater remedy in place of the previously selected pump-and-treat system. A molasses injection pilot study began in October 1995. Based on the success of the pilot study, EPA issued a new cleanup plan in December 1996 that selected metals precipitation using diluted molasses to replace the previously selected pump-and-treat remedy.

I7.9.1 Case Study References

EPA, "Avco Lycoming (Williamsport Division)," U.S. Environmental Protection Agency website. Available at: http://www.epa.gov/reg3hwmd/npl/PAD003053709.htm.

EPA, 2007, *Second Five-Year Review Report for Avco Lycoming Superfund Site Williamsport Lycoming County, Pennsylvania*, U.S. Environmental Protection Agency, Philadelphia, Pennsylvania. Available at: www.epa.gov/superfund/sites/fiveyear/f2007030001696.pdf.

EPA/625/R-00/005, 2000, *In Situ Treatment of Soil and Groundwater Contaminated with Chromium: Technical Resource Guide*, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. Available at: www.clu-in.org/download/remed/epa625r00005.pdf.

EPA Contaminated Site Clean-Up Information website, Technology Innovation and Field Services Division, U.S. Environmental Protection Agency, Washington, D.C. Available at: http://www.clu-in.org/products/newsltrs/tnandt/view.cfm?issue=0703.cfm.

I7.9.2 Site Conditions

The Avco Lycoming site is located over two aquifers: an overburden aquifer, which is referred to as the shallow aquifer, and the bedrock aquifer, which is referred to as the deep aquifer. Geology at the site consists of a complex sequence of interbedded sand, clay, and gravel.

Remedial investigations conducted between 1989 and 1991 revealed that the shallow aquifer beneath the western section of the property is contaminated with chromium at concentrations as high as 2,290 µg/L.

I7.9.3 Technical Approach

A full-scale remediation system was installed in January 1997 to develop and maintain an anaerobic environment capable of reducing and precipitating Cr(VI) over a 1,100 m^2 (12,000 ft^2) treatment area. The system used 20 injection wells and 16 existing municipal wells to establish reactive zones. Thirty-eight L (10 gal) of solution per well were injected twice a day. The mixing ratio for molasses varied from 1:200 to 1:20. A programmable logic controller monitored and controlled the feed rate and frequency of the molasses feed and solution feed pumps, as well as the timing of the solenoid valve network that controlled the metered flow to the injection wells.

I7.9.4 Results

The injection of the molasses-based substrate was successful in creating an anaerobic groundwater environment, and resulted in the chromium plume shrinking to approximately one-fourth its original area in less than 2 years. The concentration of Cr(VI) was reduced from 1,950 to 10 µg/L in the southern portion of the treatment area. The peak chromium concentrations are isolated to one area at slightly above 500 µg/L.

The metals precipitation treatment was discontinued in September 2000 after the EPA concluded that the Cr(VI) cleanup goal of 32 µg/L had been achieved in 12 of the treatment area's 14 monitoring wells and that no contaminant rebound had occurred. Monitoring data collected during the subsequent 30 months indicated that metal concentrations in all eight of the treatment wells had not varied significantly since the

time of system shutoff. The most recent data indicate that concentrations in six of the treatment wells meet the cleanup goals for Cr(VI) and total dissolved chromium. In the remaining wells, Cr(VI) concentrations decreased 75 to 99 percent from pretreatment levels. No evidence of secondary metal byproduct migration has been found in any of the system's eight downgradient monitoring wells, where cleanup goals continue to be met.

I7.10 Odessa Chromium I Superfund Site, Odessa, Ector County, Texas

The Odessa Chromium I Superfund Site is a 80,000 m^2 (20 ac) portion of an aquifer located near 44th Street and Brazos Avenue in the City of Odessa, in Ector County, Texas. Two potential chromium release sources to groundwater were identified: a former chrome plating facility that operated between 1972 and 1977, and another currently operating metal plating facility.

On March 18, 1988, EPA signed the ROD for OU02, the groundwater OU. The ROD included extraction of contaminated groundwater from the Trinity Aquifer, electrochemical treatment of groundwater, and reinjection of the treated groundwater into the Trinity Aquifer. Pump-and-treat operations began on December 25, 1993. The pump-and-treat system was initially effective in removing high chromium concentrations in recovered groundwater; however, it was less effective in treating groundwater with lower chromium concentrations in the dilute groundwater plume.

An experimental ferrous sulfate in situ treatment pilot study was conducted in December 1998 and January 1999. The pilot study demonstrated accelerated achievement of the remediation goals; however, the use of ferrous sulfate eventually led to plugging of injection wells and reduced injection capacity. MRC™[4] was evaluated as an alternate injection reagent, and was eventually selected for full-scale injection. MRC consists of an organosulfur compound esterified to a carbon backbone, which releases both lactate as a carbon source for bioremediation, and an organosulfur compound that acts as a direct chemical reductant for Cr(VI).

I7.10.1 Case Study References

EPA, 2006a, *Second Five-Year Review Report for the Odessa Chromium I Superfund Site Odessa, Ector County, Texas*, U.S. Environmental Protection Agency. Available at: http://www.epa.gov/superfund/sites/fiveyear/f2006060001400.pdf.

Regenesis, "Case Study for Chromium Immobilization" website. Available at: http://regenesis.com/regenesis-resource-center/case-studies/cs-detail.aspx?ID=97.

I7.10.2 Site Conditions

The surficial soil at the site is predominately a fine sandy loam to sandy clay that ranges in depth from 20 to 61 cm (8 to 24 in.). Pleistocene windblown sand, clay deposits, and alluvium deposits underlie the surficial soil. Beneath the Pleistocene is 7.6 to 11 m (25 to 35 ft) of caliche deposits, which can be relatively impermeable in local areas. Underlying the caliche are scattered erosional remnants of the Ogallala Formation composed of gravels, sands, silts and clays. This formation does not generally extend to depths below 23 m (75 ft) in the area. The Trinity Formation, the main fresh water-producing aquifer in the area, underlies the Ogallala interval. The thickness of this formation ranges from 17 to 21 m (55 to 70 ft) and is composed of sands and sandstones with minor amounts of siltstone, clay, and gravel. Beneath the Trinity Formation is the Chinle Formation of the Dockum Group, which consists of up to 183 m (600 ft) of clays and shales that prevent downward migration of contaminants.

[4] MRC—Metals Remediation Compound is manufactured by Regenesis-Advanced Technologies for Contaminated Site Remediation, 1011 Calle Sombra, San Clemente, California.

Total unfiltered chromium concentrations at the site source area have historically fluctuated between 1,000 and 12,000 µg/L.

I7.10.3 Technical Approach

An MRC pilot study was conducted from August 18 to 25, 2003. The study involved injection into six injection wells surrounding a single source area monitoring well (MW-111), and injection into two existing downgradient plume monitoring wells (RW-102 and RW-106).

Four subsequent full-scale MRC treatment events were conducted on December 26, 2003, May 10, 2004, May 11 and 12, 2005, and May 26, 2006. Full-scale MRC injections included 17 injection wells placed along the perimeter of the source area, and five additional injection wells aligned in a barrier transecting the downgradient plume. The pump-and-treat system was also shut down between May and June 2004.

I7.10.4 Results

During the pilot study, Cr(VI) concentrations in MW-111 decreased from a baseline level of 2,620 µg/L to less than 10 µg/L in 42 days. Pilot-scale treatment results in targeted plume wells RW-102 and RW-106 indicated a rapid reduction in total unfiltered chromium at 42 days post-injection, in conjunction with detections of elevated total organic acids. Cr(VI) concentrations in those wells decreased from baseline levels of 107 and 690 µg/L, respectively, to less than 10 µg/L.

Through October 2004, Cr(VI) concentrations in the three monitoring wells included in the pilot study remained non-detect (less than 10 µg/L), a reduction in concentration by 91 to 99 percent. Total unfiltered chromium in plume well RW-106 was reduced to below the regulatory goal of 100 µg/L by day 138 and has remained beneath the goal, with the exception of a single monitoring event on day 265 that was associated with groundwater pumping operations in the source area.

I7.10.5 Lessons Learned

Total chromium concentrations in plume well RW-102 have remained beneath the regulatory goal for the majority of the remediation monitoring period, but rose to 239 µg/L on day 412. Although total unfiltered chromium levels rose above the 100 µg/L goal, Cr(VI) in RW-102 remained below 10 µg/L, indicating the Cr(VI) had been reduced to chromium(III) but had not yet precipitated to the aquifer matrix.

I7.11 Selma Pressure Treating Superfund Site, Selma, California

The Selma Pressure Treating (SPT) Site is a former wood-treating facility located approximately 15 mi (24 km) south of the City of Fresno, in Selma, California. Wood-treatment operations began at the site in 1936; in 1965, a new pressure-treating facility began operating at the site. The pressure-treating process consisted of impregnating wood in pressurized vessels with chromium-containing chemical preservatives. Releases of pressure-treating chemicals to the subsurface resulted in chromium impacts to groundwater.

The 1988 ROD groundwater remedy included a conventional pump-and-treat system to remove chromium to meet the MCL of 50 µg/L. An Explanation of Significant Differences (ESD) was prepared and approved in 2005 proposing full-scale use of in situ bioremediation (ISB) to optimize groundwater remediation at the site. The ESD described a phased approach to inject molasses into the chromium plume, which emanates from the wood-treating area, to create a reducing environment to convert chromium from the mobile and more toxic hexavalent state to the relatively immobile trivalent state.

I7.11.1 Case Study References

DTSC, 2009, *Scope of Work for O&M of the Groundwater Remedy*, Final DTSC Letter, Contract No. 09-T9039. Available at: http://www.envirostor.dtsc.ca.gov/public/final_documents2.asp?global_id=10240051&doc_id=6023728.

EPA, 2003, *Selma Pressure Treatment Superfund Site*, Region 9, U.S. Environmental Protection Agency, San Francisco, California. Available at: http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/ViewByEPAID/cad029452141!OpenDocument&Start=1&Count=200&Expand=2#documents.

EPA, 2006b, *Five-Year Review Report Second Five-Year Review Report Selma Pressure Treating Superfund Site, Selma, California*, U.S. Environmental Protection Agency. Available at: http://yosemite.epa.gov/R9/SFUND/R9SFDOCW.NSF/3dc283e6c5d6056f88257426007417a2/51473f5f82d22982882575fd00805137!OpenDocument.

I7.11.2 Site Conditions

The aquifer underlying the SPT site is unconfined and consists of discontinuous fine-grained lenses and cemented zones that act as localized barriers to groundwater flow and contaminant transport. The water-bearing unit is divided into a shallow zone from 6 to 15 m (20 to 50 ft) bgs, an intermediate zone from 14 to 23 m (45 to 75 ft) bgs, and a deep zone from 23 to 36 m (75 to 120 ft) bgs.

Baseline Cr(VI) concentrations have been detected in site groundwater at concentrations in excess of 80,000 µg/L. In 1997, the Cr(VI) plume extended approximately 900 m (3,000 ft) downgradient from the primary site.

I7.11.3 Technical Approach

In 2005, an ISB pilot test (Phase 1) was conducted within the relatively shallow chromium contamination source area. The pilot test used direct-push/direct-injection methods, and targeted an approximately 7.6 m (25 ft) thick treatment zone in a 3,716 m^2 (40,000 ft^2) portion of the hot spot. Subsequent injections in Phases 1a and 2 focused on areas adjacent to the hot spot and downgradient from the hot spot, respectively. The direct-push injection grid was based on an assumed 4.5 m (15 ft) ROI. In most cases, there was no overlap of the 4.5 m (15 ft) ROI circles. Solutions of less than 5 percent molasses were injected at about 90 to 180 psi to approximate a 4,000 mg/L molasses target concentration. This concentration of substrate was an overdose amount with a 5 times safety factor.

As the treatment continued on a full-scale capacity downgradient, where the plume increased in depth, it was determined that direct-push delivery was unreliable at depths below 18 to 21 m (60 to 70 ft) because of refusal of the direct-push equipment. Therefore, Phase 2B ISB, which began operations in mid-2006, used a recirculation system to deliver organic substrates into the deeper aquifer at 21 to 36 m (70 to 120 ft) bgs. The recirculation system distributed substrate throughout the treatment area by extracting groundwater from radially arranged extraction wells (five wells) and injection of water into centrally located injection wells (11 wells). The extraction wells were placed upgradient, between, and downgradient from the injection wells. Sodium lactate, which was determined to have greater longevity at the site compared to molasses, was later used during Phase 2B to enhance reduction of residual Cr(VI) bound up in zones of lower hydraulic conductivity.

Phase 3 began operation in October 2007 to treat the Cr(VI) plume under Highway 99. In May 2008, the pump-and-treat groundwater treatment system was shut down and piping was installed to connect the four extraction wells to the ISB substrate-mixing skid. Operation of all ISB extraction wells immediately on

the northeast and southwest sides of Highway 99 was discontinued, and those wells have been converted to injection wells. Ongoing injections at the site will consist of the substrate-amended flow from the four original pump-and-treat wells (approximately 750 L/min [200 gal/min]).

I7.11.4 Results

During the pilot study, Cr(VI) concentrations in groundwater decreased to levels well below the cleanup level of 50 µg/L within 1 month, while chromium(III) concentrations decreased at a slower rate. This delay in chromium(III) removal was because of the time required for chromium(III) hydroxides to adhere to the aquifer matrix. Similar results were obtained during Phase 2B operations, with chromium concentrations in the plume reduced to or below 50 µg/L on the northeast side and under Highway 99.

I7.11.5 Lessons Learned

Overdosing with substrate resulted in establishment of excessively reducing conditions, which resulted in mobilization of some metals, such as iron, manganese, and arsenic. The pilot study indicated that the ISB process reduced and mobilized arsenic, with levels above the MCL of 10 µg/L appearing in the ISB areas. Continued arsenic monitoring and an evaluation of the molasses dosage levels were conducted for subsequent phases of ISB treatment. In order to minimize mobilization of reduced arsenic in groundwater during full-scale operations, the ISB systems injected molasses at a much lower concentration than the initial pilot study direct-push injections. A patented biocide solution also was mixed and added to the injection system on a daily basis to minimize biofouling in injection piping and injection wells.

I7.12 Schwerin Concaves, Inc., Walla Walla, Washington

The Schwerin Concaves property was part of a wheat-farming operation and then became a hard chromium-electroplating business. Contamination at the site is a result of the chromium-electroplating operations on the property. Cr(VI) is present in the soil and groundwater. There are also elevated levels of arsenic, cadmium, iron, lead, zinc, nitrate, and sulfate in groundwater. Although a final cleanup alternative decision has not been published for the site, a remedial pilot study conducted in 2006 and 2007 showed that ISB could effectively reduce Cr(VI) in groundwater to chromium(III).

I7.12.1 Case Study References

Ecology, 2005, *Remedial Investigation, Schwerin Concaves Inc., Walla Walla, Washington*, Washington State Department of Ecology, Eastern Regional Office, Spokane, Washington. Available at: http://www.ecy.wa.gov/programs/tcp/sites/schwerin/schwerin_hp.htm.

Hart Crowser, 2007, *Remedial Pilot Study Data Summary Report, Schwerin Concaves, Walla Walla, Washington*, Hart Crowser, Inc., Lake Oswego, Oregon.

Hart Crowser, 2008, *Focused Feasibility Study, Schwerin Concaves, Walla Walla, Washington*, September, Hart Crowser, Inc., Lake Oswego, Oregon. Available at: https://fortress.wa.gov/ecy/gsp/CleanupSiteDocuments.aspx?csid=3956.

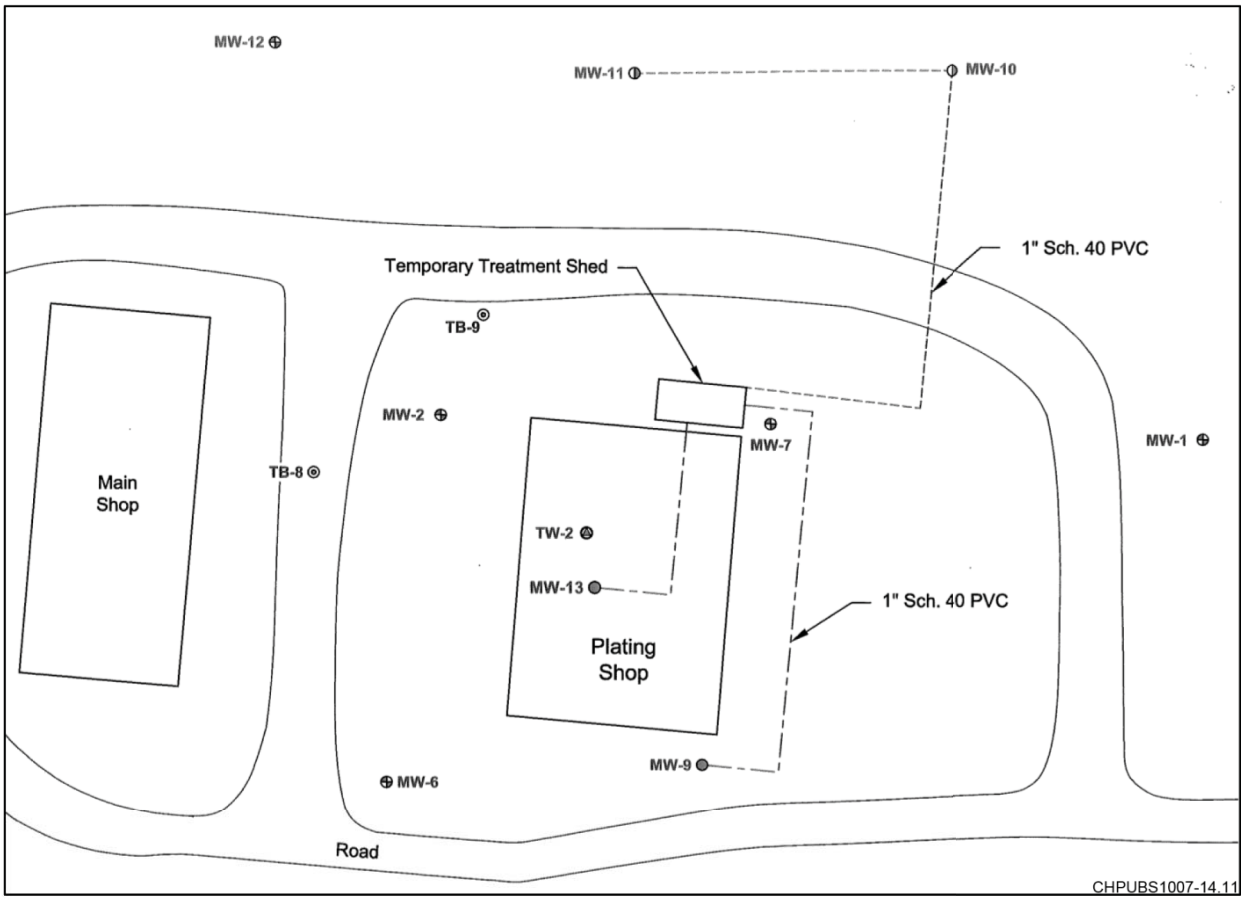
I7.12.2 Site Conditions

The Schwerin Concaves Site is located about 6.4 km (4 mi) north of Highway 12 in Walla Walla County, Washington. The property is situated on a farm within a rural area. The main plating operation was housed in one large building and six auxiliary buildings that were used to store products and waste. A storage tank housed inside a subterranean covered shed was located to the north of the plating shop. The auxiliary buildings include an office/maintenance shop, former self-propelled shed, long farm shed, two smaller storage sheds, and barn. Groundwater occurs at the site in the underlying basalt, as well as supra-basalt sediments and recent alluvium, including loess soil and glaciofluvial sands and gravels.

The majority of groundwater is used for irrigation with the remainder used for domestic and industrial purposes.

I7.12.3 Technical Approach

Remedial pilot study activities were completed in 2006 through 2007. The activities included installing, operating, and monitoring an in situ groundwater recirculation pilot system to determine the effectiveness in treating the remaining Cr(VI) in the soil and groundwater. The groundwater recirculation pilot system began operating in November 2006 and operated through May 2007. Groundwater recovered from downgradient extraction wells (MW-10 and MW-11) was amended with a commercial dextrose/nutrient substrate before being reinjected in upgradient wells MW-9 and MW-13 (Figure I-7).



Source: *Remedial Pilot Study Data Summary Report, Schwerin Concaves, Walla Walla, Washington* (Hart Crowser, 2007).

Figure I-7. Configuration of the Schwerin Concaves Remedial Pilot Test

Following completion of the recirculation pilot study, periodic slug injections of substrate were performed in wells to confirm that native microbes could successfully reduce Cr(VI) to chromium(III). The system extraction and injection rates (less than 3.7 L/min [1 gal/min]) limited the amount of substrate-amended groundwater that could be recirculated between the extraction and injection wells. To aid in the distribution of substrate over a larger area, slug injections were performed during June, July, and December 2007.

I7.12.4 Results

The dextrose/nutrient injection methods and poor groundwater circulation at the site resulted in a biomass buildup that clogged the well screen at MW-9. Injections at MW-13 kept up with extraction rates, but the

poor groundwater circulation prevented an anaerobic environment from being achieved in most wells, except the injection wells. The limited anaerobic environment was verified by the lack of reduction in nitrate and sulfate concentrations, and the limited reduction in oxidation reduction potential and DO data collected in the field. Cr(VI) concentrations decreased an order of magnitude in injection wells MW-9 and MW-13 (from 116 to 12 µg/L in MW-9 and 20 to less than 5 µg/L in MW-13). Concentrations of Cr(VI) decreased slightly in nearby monitoring wells MW-1 and MW-6. Total and Cr(VI) concentrations in the remaining wells remained unchanged through the reporting period.

August 2007 analytical results from slug-injected wells showed substantial reductions in Cr(VI) concentrations. With the exception of one well (MW-7), all sample results for Cr(VI) were less than the quantitation limit. In MW-7, concentrations of Cr(VI) declined from 77,000 µg/L during June 2007 to 19,000 µg/L during August 2007. However, as a result of sample quality control issues, the accuracy of these Cr(VI) results may be limited. Declines in nitrate and sulfate concentrations (other electron acceptors) suggest substantial reductions of Cr(VI) near wells MW-2, MW-6, MW-9, and MW-13. The pilot study and slug injections confirmed that microbes could be stimulated to reduce Cr(VI) to chromium(III).

I7.12.5 Lessons Learned

Lessons learned from evaluating this case study include the importance of carefully selecting an ISB system design that is suitable for the project location. At the Schwerin Concaves Site, aquifer sediments were not conducive to establishment of a large-scale recirculation system, although slug injection of substrate did work well. The injection operations mode also plays a large factor in the rate at which biofouling may affect injection well performance. Using pulsed-injection operating modes, or continuous-injection at a lower concentration, may serve to limit the degree of fouling at the injection well.

I8 Vadose Zone Treatment by Bioinfiltration

As mentioned above, numerous studies have demonstrated that the sufficient addition of simple organic carbon compounds (for example, lactate) will stimulate the rapid growth of the native microbial assemblage in an aquifer, ultimately resulting in the development of localized reducing conditions. This approach has been successfully used numerous times to bioremediate Cr(VI) by converting it to less-toxic chromium(III) (see Section I5). Once formed, chromium(III) will typically sorb to mineral substrates or precipitate as an insoluble solid phase such as $Cr(OH)_3$ and is therefore effectively immobile in an aquifer ("Fate and Stability of Cr Following Reduction by Microbially Generated Fe(II)" [Hansel et al., 2003]).

Similar microbial and related geochemical processes are known to occur in the vadose zone as well as in the saturated aquifer soils. Laboratory studies have demonstrated the processes, showing that adding water and organic nutrients to columns packed with vadose zone materials contaminated with Cr(VI) cause the effective conversion of Cr(VI) to chromium(III) ("In-Situ Reduction of Cr(VI) in Heavily Contaminated Soils Through Organic Carbon Amendment" [Tokunaga et al., 2003] and *Microbial Reduction of Hexavalent Chromium Under Vadose Zone Conditions* [Oliver, 2001]). Consequently, ISB of the vadose zone by the controlled infiltration of carbon-amended water has been identified as a technology with the potential to rapidly and effectively reduce Cr(VI) to Cr (III) in those areas in the 100 Area Reactor sites where the deep vadose zone (for example, greater than 6 m [20 ft] bgs) that are contaminated with Cr(VI). Hereafter, the proposed method of vadose zone bioremediation is referred to as bioinfiltration.

I8.1 Conceptual Design

Figure I-8 presents the conceptual design of a bioinfiltration system. The bioinfiltration system could be implemented in a closed loop system, much as described above for bioinjection. The extracted water would be piped to a surge tank prior to being amended with a concentrated lactate/water solution that is

metered in from a separate mixing tank. The amended solution is then piped to a drip infiltration system for controlled distribution into the vadose zone.

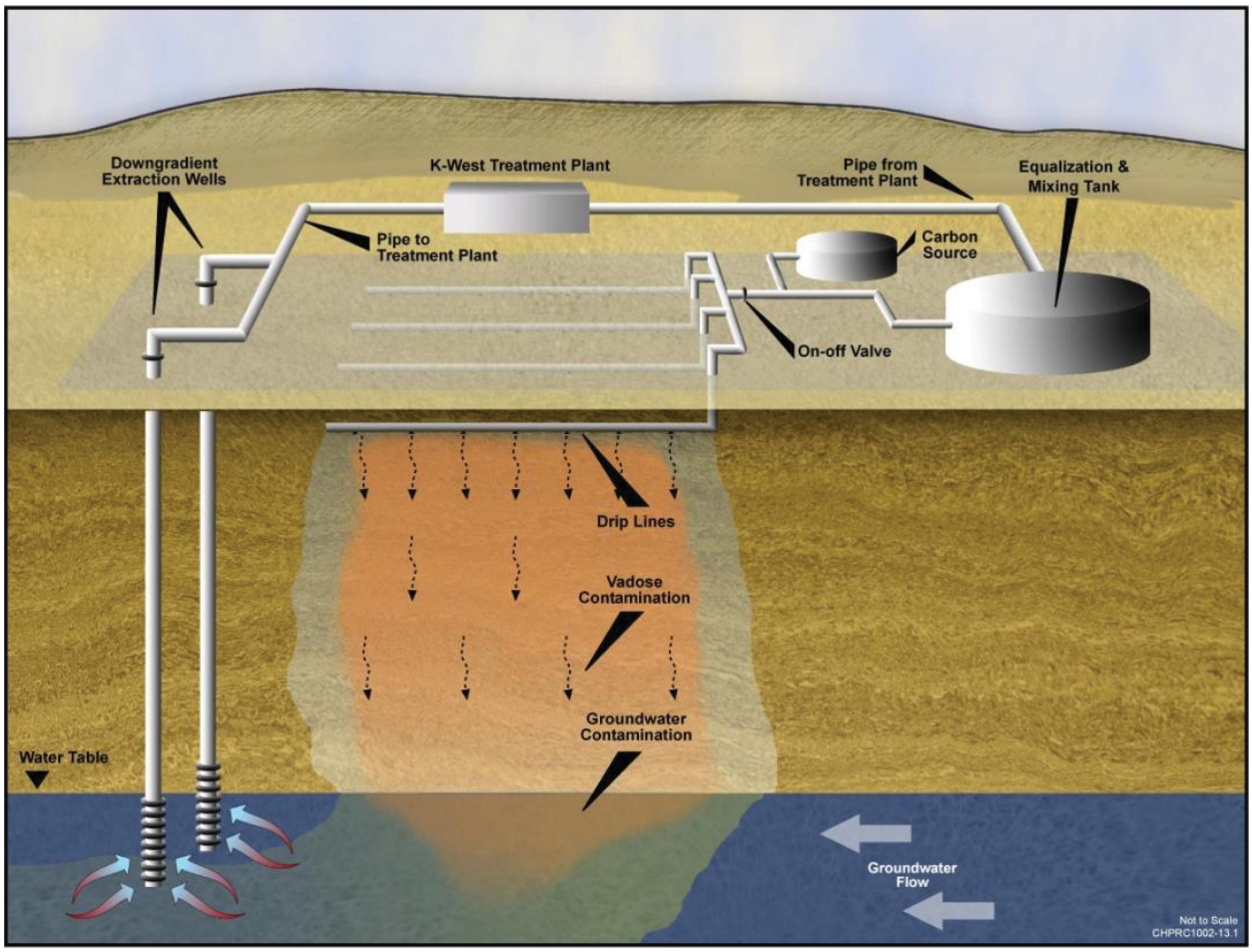


Figure I-8. Functional Design of the Planned 100-KW Bioinfiltration System

Although simple in concept, the detailed design and full-scale implementation of a bioinfiltration system will face site-specific design and implementation challenges that cannot be entirely resolved by preliminary laboratory testing (for example, unsaturated column testing) or vadose zone fate and transport modeling. Lateral and vertical variations in the lithology and hydraulic properties of the targeted vadose zone, and the potential for changes in infiltration pathways under different flow rates, require that a bioinfiltration system have sufficient design and operational flexibility to test a range of infiltration rates and lactate concentrations in order to identify the optimal site-specifc operating conditions.

I8.2 Bioinfiltration Remediation Processes and Approach

Once treatment starts, the infiltration of sufficiently carbon-amended water into the vadose zone will lead to rapid microbial growth in the affected area. There will, however, be a lag period of several days or more between startup of infiltration and the expansion of, and compositional changes in, the microbial assemblage sufficient to induce strongly reducing (for example, sulfate reducing) conditions. Consequently, if the initial volume of amended solution and the infiltration rates are too high, a nonreducing wetted front could migrate downward through the vadose zone well ahead of a much more slowly advancing reducing front. Such a rapidly advancing wetted front could solubilize and transport a

substantial fraction of the Cr(VI) in the vadose zone affected prior to the arrival of the reduction front. Saturated flow leaching tests performed on Hanford Site soils containing Cr(VI) suggested that as much as 95 percent of the Cr(VI) in the test soils was leached from the column during the first pore volume (*Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site* [PNNL-17674]). To prevent or greatly diminish this effect in the field, the rate of infiltration and the extent of carbon loading will be carefully managed to maintain unsaturated conditions by maximizing the rate at which reducing conditions are established in the vadose zone during infiltration. In addition, groundwater from beneath or just downgradient from any bioinfiltration sites will be captured. The water will either be treated and then recirculated to the bioinfiltration system, or recirculated without treatment. If recirculated without treatment, the Cr(VI) will be allowed to be reduced in situ.

Additional geochemical effects of infiltrating carbon-amended water into the vadose zone include the reduction of Cr(VI) to chromium(III), and the microbially mediated reductive dissolution of matrix-bound ferric iron and manganese (manganese(IV)) oxides and hydroxides in the vadose zone. Arsenic traces are associated with ferric iron and manganese(IV) oxides and hydroxides in the Hanford Site sediments. Therefore, reductive dissolution of these phases is expected to result in the mobilization of arsenic as well as elevated levels of ferrous iron and divalent manganese into the pore water of the vadose zone. Release of arsenic was observed during the bioremediation test performed at 100-D (*Hanford 100-D Area Biostimulation Treatability Test Results* [PNNL-18784]). Consequently, the transport of detectable levels of dissolved ferrous iron, divalent manganese, arsenic (mostly as arsenic(III)), and other reduced constituents to the water table are possible during this remedial action. The changes in the concentrations of these constituents over time will be monitored in the vadose zone and the groundwater beneath the treatment area. However, ferrous iron, divalent manganese, and arsenic(III) that enter the water table during bioinfiltration are expected to be rapidly oxidized and attenuated once exposed to the oxygenated groundwater in the aquifer.

The primary operational factors that will be varied during operation of the system will be the concentration of carbon in the solution applied, and the rate of application. Generally, the higher the carbon concentration in the solution, the farther the reducing conditions will penetrate into the vadose zone for a given volume of solution. Different flow rates will result in different infiltration properties. For example, at very high application rates, flow will occur largely through coarser-grained materials, potentially bypassing finer-grained materials. At low fluid applications rates, flow will occur through all pore sizes, with a greater relative proportion of the fluid passing through finer pore throats associated with silts and fine sands.

I9 References

65 FR 37253, "Establishment of the Hanford Reach National Monument," *Federal Register*, Vol. 65, No. 114, pp. 37253-37257, June 13, 2000. Available at: http://www.gpo.gov/fdsys/pkg/FR-2000-06-13/pdf/00-15111.pdf.

AFCEE, 2010, "Enhanced In Situ Anaerobic Bioremediation, Substrate Alternatives," Air Force Center for Engineering and the Environment website. Available at: http://www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/enhancedinsituanaerobicbioremediation/substrate/index.asp.

Andronescu, E. Stefan, E. Dinu, and C. Ghitulica, 2002, "Hydroxyapatite Synthesis," *Key Engineering Materials* 206-213:1595-1598.

ARCADIS, 2005, "Final Addendum to the *In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan – Floodplain Reductive Zone Enhancement* for the Pacific Gas and Electric Company Topock Compressor Station," Technical Memorandum, ARCADIS G&M, Inc., San Francisco, California, December 5. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/01-Floodplain%20In-situ%20Pilot%20Study%20Work%20Plan%20Addendum%20Dec%202005.pdf.

ARCADIS, 2006a, "Addendum 2 to the *In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan-Floodplain Reductive Zone Enhancement* for the Pacific Gas and Electric Company Topock Compressor Station," Technical Memorandum, ARCADIS G&M, Inc., San Francisco, California, April 14. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/Topock%20FP%20ISPT%20WP%20Addendum%202%20-%20Final.pdf.

ARCADIS, 2006b, *In Situ Hexavalent Chromium Reduction Pilot Test Work Plan—Upland Plume Treatment*, Pacific Gas & Electric Company Topock Compressor Station Needles, California, ARCADIS G&M, Inc., Richmond, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/UplandAreaIn-SituPilotStudy/FinalUplandWorkPlan.pdf.

ARCADIS, 2008, *Floodplain Reductive Zone In-Situ Pilot Test Final Completion Report*, Waste Discharge Requirements Order No. R7-2006-0008 and Order No. R7-2007-0014, PG&E Topock Compressor Station, San Bernardino County, California, ARCADIS, San Francisco, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/Floodplain%20Insitu%20Final%20Report%203-5-08.pdf.

ARCADIS, 2009a, *Third Quarter 2009 Monitoring Report for the Upland Reductive Zone In-Situ Pilot Test*, PG&E Topock Compressor Station San Bernardino County, California, ARCADIS, San Francisco, California, for PG&E. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/UplandAreaIn-SituPilotStudy/Third_Quarter_2009_Upland_ISPT_Final.pdf.

ARCADIS, 2009b, *Third Quarter 2009 Monitoring Report for the Floodplain Reductive Zone In-Situ Pilot Test*, PG&E Topock Compressor Station San Bernardino County, California, ARCADIS, San Francisco, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/Third%20Quarter%202009%20Floodplain%20ISPT%20Final.pdf.

BNL-52531, 1997, *Summary Report on Close-Coupled Subsurface Barrier Technology Initial Field Trials to Full-Scale Demonstration*, Brookhaven National Laboratory, Upton, New York. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/658171-GgxWrm/webviewable/.

Borchert, S. and J. Raphael, 2008, "Challenges with an ISCO Application in the Unsaturated Zone: Case of the Missing Permanganate," *Proceedings of the 6th International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, California, May 19-22.

CAL/EPA, 2010, *Notice of Applicability of General Waste Discharge Requirements for the General Site-Wide Groundwater Remediation Project at the PG&E Compressor Station, Hinkley, San Bernardino County*, California Regional Water Quality Control Board Lahontan Region, California Environmental Protection Agency, South Lake Tahoe, California. Available at: http://www.swrcb.ca.gov/rwqcb6/water_issues/projects/pge/docs/pgehinkley_genwdrnoa.pdf.

California State Water Resources Control Board, 2008, "Electro Coating Inc (SL20254872)," Project Fact Sheet, GeoTracker website. Available at: http://geotracker.waterboards.ca.gov/profile_report.asp?global_id=SL20254872.

CH2M HILL, 2010, *Hinkley Remediation Semiannual Status Report (July through December 2009), PG&E Compressor Station, Hinkley, California*, CH2M HILL, Oakland, California. Available at: http://geotracker.waterboards.ca.gov/esi/uploads/geo_report/1028985559/SL0607111288.PDF.

Chen, Yinguang and Guowei Gu, 2005, "Preliminary Studies on Continuous Chromium(VI) Biological Removal from Wastewater by Anaerobic-Aerobic Activated Sludge Process," *Bioresour. Technol*. 15:1713-1721.

Comprehensive Environmental Response, Compensation, and Liability Act of 1980, 42 USC 9601, et seq., Pub. L. 107-377, December 31, 2002. Available at: http://epw.senate.gov/cercla.pdf.

Corral, Andrea F. and Umur Yenal, 2009, *Reverse Osmosis Treatment of Central Arizona Project Water—Brine Minimization Via Vibratory Shear-enhanced Processing*, University of Arizona Department of Chemical and Environmental Engineering, Tucson, Arizona. Available at: http://www.cap-az.com/Portals/1/Skins/cap/files/Corral.pdf

CP-18187, 2005, *200-BP-1 Prototype Hanford Barrier Annual Monitoring Report for Fiscal Year 2003*, Rev. 0, Fluor Hanford, Inc., Richland, Washington.

Day, Steven R. and Christopher R. Ryan, 1995, *Containment, Stabilization and Treatment of Contaminated Soil Using In-Situ Soil Mixing*, GeoEnvironment and American Society of Civil Engineers, New Orleans, Louisiana. Available at: http://www.geo-solutions.com/tech-papers/pdf/soilmixpdf03.pdf.

DOE, 1997, *Case Study Abstract: In Situ Vitrification*, U.S. Department of Energy, Hanford Site, Richland, Washington.

DOE, 1998, *Transportable Vitrification System: Mixed Waste Focus Area*, Innovative Technology Summary Report, U.S. Department of Energy, Office of Environmental Management, and Office of Technology Development, Washington, D.C. Available at: http://www.p2pays.org/ref/13/12788.pdf.

DOE/EM-0235, 1995, *Technology Catalogue, Second Edition*, Office of Environmental Management, Office of Technology Development, U.S. Department of Energy, Washington, D.C.

DOE/EM-0272, 1995, *Six-Phase Soil Heating*, Innovative Technology Summary Report, Office of Environmental Management and Office of Technology Development, U.S. Department of Energy, Washington, D.C. Available at: http://www.osti.gov/bridge/servlets/purl/155025-5uFs8e/webviewable/155025.pdf.

DOE/ID-11268, 2007, *Feasibility Study for Operable Unit 7-13/14*, Rev. 0, U.S. Department of Energy Idaho Operations Office, Idaho Falls, Idaho. Available at: http://www.osti.gov/bridge/servlets/purl/909854-GbGe2S/909854.pdf.

DOE/ORP-2003-01, 2003, *Project Execution Plan for the River Protection Project Waste Treatment and Immobilization Plant*, Rev. 0, U.S. Department of Energy Office of River Protection, Richland, Washington. Available at: http://www5.hanford.gov/pdwdocs/fsd0001/osti/2003/I0040778.pdf.

DOE/RL-93-96, 1994, *300-FF-1 Operable Unit Remedial Investigation Phase II Report: Physical Separation of Soils Treatability Study*, Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196055723.

DOE/RL-93-107, 1994, *100 Area Soil Washing Bench-Scale Tests*, Draft A, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196101077.

DOE/RL-94-61, 1995, *100 Area Source Operable Unit Focused Feasibility Study*, 2 vols., Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196015921. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196016522. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196006751.

DOE/RL-95-32, 1995, *In Situ Remediation Integrated Program FY 1994 Program Summary*, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://www.osti.gov/bridge/product.biblio.jsp?osti_id=61126.

DOE/RL-2001-04, 2001, *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*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: .http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D8843184 http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D8843189.

DOE/RL-2004-66, 2005, *Focused Feasibility Study for the BC Cribs and Trenches Area Waste Sites*, Draft A, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA170624. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA170919. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA171165. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA171467.

DOE/RL-2006-17, 2006, *Treatability Test Report for Calcium Polysulfide in the 100-K Area*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=DA02107064.

DOE/RL-2007-56, 2008, *Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0804160110.

DOE/RL-2008-13, 2009, *Treatability Test Report for the Removal of Chromium from Groundwater at 100-D Area Using Electrocoagulation*, Rev. 0 REISSUE, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1002020099. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1002020100. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1002020101. http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=1002020102.

DTSC, PG&E Topock Compressor Station, Needles, California, Environmental Investigation and Cleanup Activities, California Department of Toxic Substance Control website. Available at: http://dtsc-topock.com/.

DTSC, 2006, *In-Situ Bioremediation of Chlorinated Hydrocarbons, An Assessment of Projects in California*, California Department of Toxic Substances Control, Office of Pollution Prevention and Technology Development. Available at: http://www.dtsc.ca.gov/TechnologyDevelopment/upload/Final_ISB_Report4.pdf.

DTSC, 2009, *Scope of Work for O&M of the Groundwater Remedy*, Final DTSC Letter, Contract No. 09-T9039. Available at: http://www.envirostor.dtsc.ca.gov/regulators/deliverable_documents/4070508658/Draft%20Contract%2009-T9039%2009.14.09.pdf.

Dvorak, Bruce I. and Sharon O. Skipton, 2008, *Drinking Water Treatment: Reverse Osmosis*, University of Nebraska Lincoln Extension Institute of Agriculture and Natural Resources.

Eary, L. Edmond and Dhanpat Rai, 1987, "Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese Dioxide," *Environ. Sci. Technol.* 21(12):1187-1193.

Ecology, 2005, *Remedial Investigation, Schwerin Concaves, Inc., Walla Walla, Washington*, Washington State Department of Ecology, Eastern Regional Office, Spokane, Washington. Available at: http://www.envirostor.dtsc.ca.gov/regulators/deliverable_documents/4070508658/Draft%20Contract%2009-T9039%2009.14.09.pdf.

Ecology and EPA, 1994, "Action Memorandum: N-Springs Expedited Response Action Cleanup Plan, U.S. Department of Energy Hanford Site, Richland, Washington" (letter to R. Izatt, U.S. Department of Energy, Richland Operations Office) from D. Butler (Washington State Department of Ecology) and R.F. Smith (U.S. Environmental Protection Agency), Olympia, Washington, September 23.

Elliot, J.C., P.E. Mackie, and R.A. Young, 1973, "Monoclinic Hydroxyapatite," *Science* 180(4090):1055-1057.

EPA, "Avco Lycoming (Williamsport Division)," U.S. Environmental Protection Agency website. Available at: http://www.epa.gov/reg3hwmd/npl/PAD003053709.htm.

EPA, 2000, *Cost and Performance Report, Anaerobic In-situ Reactive Zone at an Abandoned Manufacturing Facility, Emeryville, California*, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency. Available at: http://www.costperformance.org/pdf/EmeryvilleBio.PDF.

EPA, 2003, *Selma Pressure Treatment Superfund Site*, Region 9, U.S. Environmental Protection Agency, San Francisco, California. Available at: http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/95831d90484434d7882574260072fadf/339c5e45c6c2fe4f882575fd008043f6/$FILE/Selma%20Pressure%20Treating%207_03%2083k.pdf.

EPA, 2006a, *Second Five-Year Review Report for the Odessa Chromium I Superfund Site Odessa, Ector County, Texas*, U.S. Environmental Protection Agency. Available at: http://www.epa.gov/superfund/sites/fiveyear/f2006060001400.pdf.

EPA, 2006b, *Five-Year Review Report Second Five-Year Review Report Selma Pressure Treating Superfund Site, Selma, California*, U.S. Environmental Protection Agency. Available at: http://yosemite.epa.gov/R9/SFUND/R9SFDOCW.NSF/3dc283e6c5d6056f88257426007417a2/51473f5f82d22982882575fd00805137!OpenDocument.

EPA, 2007, *Second Five-Year Review Report for Avco Lycoming Superfund Site Williamsport Lycoming County, Pennsylvania*, U.S. Environmental Protection Agency, Philadelphia, Pennsylvania. Available at: www.epa.gov/superfund/sites/fiveyear/f2007030001696.pdf.

EPA, 2010, "Basic Information about Chromium in Drinking Water," Office of Ground Water and Drinking Water, U.S. Environmental Protection Agency website. Available at: http://water.epa.gov/drink/contaminants/basicinformation/chromium.cfm.

EPA/540/MR-92/078, 1992, *SoilTech Anaerobic Thermal Processor: Outboard Marine Corporation Site Soil Tech ATP Systems, Inc.*, SITE Demonstration Bulletin, U.S. Environmental Protection Agency, Cincinnati, Ohio. Available at: http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=10001XSF.txt.

EPA/540/R-94/520, 1995, *Geosafe Corporation In Situ Vitrification, Innovative Technology Evaluation Report*, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. Available at: http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=100024C7.txt.

EPA 542-R-97-010, 1997, *Abstracts of Remediation Case Studies, Volume 2*, Federal Remediation Technologies Roundtable, U.S. Environmental Protection Agency, Cincinnati, Ohio. Available at: http://www.epa.gov/tio/download/frtr/abstractvol2.pdf.

EPA 542-R-04-010, 2004, *In Situ Thermal Treatments of Chlorinated Solvents: Fundamentals and Field Applications*, Office of Superfund Remediation and Technology Innovation, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. Available at: http://www.epa.gov/tio/download/remed/epa542r04010.pdf.

EPA/625/R-00/005, 2000, *In Situ Treatment of Soil and Groundwater Contaminated with Chromium: Technical Resource Guide*, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C. Available at: www.clu-in.org/download/remed/epa625r00005.pdf.

EPA 815-R-06-009, 2005, *Membrane Filtration Guidance Manual*, Office of Ground Water and Drinking Water, U.S. Environmental Protection Agency, Cincinnati, Ohio. Available at: http://www.epa.gov/safewater/disinfection/lt2/pdfs/guide_lt2_membranefiltration_final.pdf.

EPA/816-R-99-014t, 1999, *The Class V Underground Injection Control Study Volume 20 Salt Water Intrusion Barrier Wells*, Office of Ground Water and Drinking Water, U.S. Environmental Protection Agency, Washington, D.C. Available at: http://www.epa.gov/ogwdw/uic/class5/pdf/study_uic-class5_classvstudy_volume20-salineintrusionbarrier.pdf.

EPA Contaminated Site Clean-Up Information website, Technology Innovation and Field Services Division, U.S. Environmental Protection Agency, Washington, D.C. Available at: http://www.clu-in.org/products/newsltrs/tnandt/view.cfm?issue=0703.cfm.

EPA, Ecology, and DOE, 1999, *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)*, U.S. Environmental Protection Agency, Region X, Washington State Department of Ecology, and U.S. Department of Energy, Seattle, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D199159580.

EPA and NSF, 2005, *Environmental Technology Verification Joint Verification Statement for Ecowater Systems ERO-R450E Point-of-Use Drinking Water Treatment System*, U.S. Environmental Protection Agency and NSF International, Washington, D.C. Available at: http://www.nsf.org/.

Evanko, Cynthia R., and David A Dzombak, Ph.D., 1997, *Remediation of Metals Contaminated Soil and Groundwater*, Technology Evaluation Report, TE-97-01, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, Pennsylvania. Available at: http://www.cluin.org/download/toolkit/metals.pdf.

Faybishenko, B., 2009, *In Situ Long-Term Reductive Bioimmobilization of Cr(VI) in Groundwater Using Hydrogen Release Compound*, Lawrence Berkeley National Laboratory, Berkeley, California. Available at: http://escholarship.org/uc/item/1222c6sk.

Gardner, Kevin, Deana Aulisio, and Jean M. Spear, 2004, "In-Situ Dechlorination of Polychlorinated Biphenyls in Sediments Using Zero-Valent Iron" (PowerPoint presentation from the RTDF Sediments meeting), Center for Contaminated Sediments Research, University of New Hampshire. Durham, New Hampshire. February 18-19, 2004. Available at: http://www.rtdf.org/PUBLIC/SEDIMENT/MINUTES/021904/gardner.pdf.

Hansel, Colleen M., Bruce W. Wielinga, and Scott Fendorf, 2003, "Fate and Stability of Cr Following Reduction by Microbially Generated Fe(II)," *SSRL Science Highlight*, May. Available at: http://www-ssrl.slac.stanford.edu/research/highlights_archive/cr_contamination.pdf.

Hart Crowser, 2007, *Remedial Pilot Study Data Summary Report, Schwerin Concaves, Walla Walla, Washington*, Hart Crowser, Inc., Lake Oswego, Oregon.

Hart Crowser, 2008, *Focused Feasibility Study, Schwerin Concaves, Walla Walla, Washington*, September, Hart Crowser, Inc., Lake Oswego, Oregon. Available at: https://fortress.wa.gov/ecy/gsp/CleanupSiteDocuments.aspx?csid=3956.

Heiser, J., L. Milian, J. Clinton, and P. Colombo, 1994, "Durability of Polymers for Containment Barriers," *33rd Hanford Symposium on Health and Environment, In-Situ Remediation: Scientific Basis for Current and Future Technologies*, *Part 1*, Battelle, Columbus, Ohio, pp. 61-86. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/106544-CPhYJj/webviewable/.

Huddleston, Gordon, Brett Campbell, Mark Ewanic, David Reichhardt, Marja Springer, and Leo Thompson, 2003, Non-Traditional In Situ Vitrification—A Technology Demonstration at Los Alamos National Laboratory, *Waste Management Conference (WM'03)*, February 23-27, Tucson, Arizona. Available at: http://www.wmsym.org/archives/2003/pdfs/460.pdf.

Hughes, John M., Maryellen Cameron, and Kevin D. Crowley, 1989, "Structural Variations in Natural F, OH, and CI Apatites," *Am. Mineral*. 74:870-876. Available at: http://www.minsocam.org/ammin/AM74/AM74_870.pdf.

IAEA, 2004, *Management of Waste Containing Tritium and Carbon-14*, Technical Reports Series No. 421, International Atomic Energy Agency, Vienna, Austria. Available at: http://www-pub.iaea.org/MTCD/publications/PDF/TRS421_web.pdf.

INEEL/EXT-02-00233, 2003, *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*, Rev. 1, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho. Available at: http://ar.inel.gov/owa/getgif_2?F_DOC=INEEL/EXT-02-00233&F_REV=01&F_PAGE=1&F_GOTO=1.

ITRC, 2005a, *Permeable Reactive Barriers: Lessons Learned/New Directions*, Interstate Technology & Regulatory Council, Washington, D.C. Available at: http://www.itrcweb.org/Documents/PRB-4.pdf.

ITRC, 2005b, *Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition*, Interstate Technology & Regulatory Council, Washington, D.C. Available at: http://www.itrcweb.org/Documents/ISCO-2ExecSum.pdf.

James, Bruce R. and Richmond J. Bartlett, 1983, "Behavior of Chromium in Soils: V. Fate of Organically Complexed Cr(III) Added to Soil," *J. Environ. Qual.* 12:169-172.

Jasperse, Brian H. and Christopher R. Ryan, 1992, *In-Situ Stabilization and Fixation of Contaminated Soil by Soil Mixing*, presented at the ASCE Geotechnical Division Specialty Conference: Grouting, Soil Improvement and Geosynthetics, New Orleans, Louisiana, February 25-28. Available at: http://www.geo-solutions.com/tech-papers/pdf/NewSoilMixing2.pdf.

Kim, Jae Gon, Joe B. Dixon, Charles C. Chusuei, and Youjun Deng, 2002, "Oxidation of Chromium(III) to (VI) by Manganese Oxides," *Soil Sci. Soc. Am. J.* 66:306-315. Available at: https://www.crops.org/publications/sssaj/pdfs/66/1/306.

LBL-35113, 1994, *Physical Barriers Formed from Gelling Liquids: 1. Numerical Design of Laboratory and Field Experiments*, Lawrence Berkeley National Laboratory, Berkeley, California. Available at: http://www.osti.gov/bridge/product.biblio.jsp?osti_id=432812.

LBL-36739, 1995, *Injectable Barriers for Waste Isolation*, Lawrence Berkeley National Laboratory, Berkeley, California. Available at: http://www.osti.gov/bridge/product.biblio.jsp?query_id=3&page=0&osti_id=106544&Row=0&formname=basicsearch.jsp.

LBL-37554, 1995, *A Field Test of Permeation Grouting in Heterogeneous Soils Using a New Generation of Barrier Liquids*, Lawrence Berkeley National Laboratory, Berkeley, California. Available at: http://www.osti.gov/bridge/product.biblio.jsp?query_id=2&page=0&osti_id=115555&Row=0&formname=basicsearch.jsp.

LBNL-38817, 1996, *A Field Test of a Waste Containment Technology Using a New Generation of Injectable Barrier Liquids*, Lawrence Berkeley National Laboratory, Berkeley, California. Available at: http://www.osti.gov/bridge/product.biblio.jsp?query_id=1&page=0&osti_id=423617&Row=0&formname=basicsearch.jsp.

LBNL-38916, 1996, *A Design Study for a Medium-Scale Field Demonstration of the Viscous Barrier Technology*, Lawrence Berkeley National Laboratory, Berkeley, California. Available at: http://www.osti.gov/bridge/product.biblio.jsp?query_id=0&page=0&osti_id=432830&Row=0&formname=basicsearch.jsp.

Li, Yi-Liang, Hojatollah Vali, John Yang, Tommy J. Phelps, and Chuanlun L. Zhang, 2006, "Reduction of Iron Oxides Enhanced by a Sulfate-Reducing Bacterium and Biogenic H_2S," *Geomicrobiology Journal* 23(2):103-117.

Liu, David H.F. and Béla G. Lipták, 1999, *Environmental Engineers' Handbook*, CRC Press, Boca Raton, Florida.

Lowry, Greg, Paul J. Murphy, and Kathleen M. Johnson, 2004, *Development and In Situ Application of Sorbent/Reagent-Amended "Active" Sediment Caps for Managing HOC-Contaminated Sediments*, presented at the Benchmarking Workshop on Sediment and Floodplain Remediation, University of Michigan, Ann Arbor, Michigan, March 25-26.

Mikszewski, Alex, 2004, *Emerging Technologies for the In Situ Remediation of PCB-Contaminated Soil and Sediments: Bioremediation and Nanoscale Zero-Valent Iron*, Office of Solid Waste and Emergency Response, Office of Superfund Remediation and Technology Innovation, U.S. Environmental Protection Agency, Washington, D.C. Available at: http://www.cluin.org/download/studentpapers/bio_of_pcbs_paper.pdf.

Miller, Ralinda R., 1996, *Horizontal Wells*, Technology Overview Report, TO-96-02, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, Pennsylvania. Available at: http://www.cluin.org/download/toolkit/horiz_o.pdf.

Mora, Rebecca H, Tamzen W. Macbeth, Tara MacHarg, Jagadish Gundarlahalli, Holly Holbrook, and Paul Schiff, 2008, "Enhanced Bioremediation Using Whey Powder for a Trichloroethene Plume in a High-Sulfate, Fractured Granitic Aquifer," *Remediation*18(3):7-30. Available at: http://onlinelibrary.wiley.com/doi/10.1002/rem.20168/pdf.

Moridis, George J., Stefan Finsterle, and John Heiser, 1999, "Evaluation of Alternative Designs for an Injectable Subsurface Barrier at the Brookhaven National Laboratory Site, Long Island, New York," *Water Resources Research* 35(10):2937-2953.

Morse, John W., Frank J. Millero, Jeffrey C. Cornwell, and David Rickard, 1987, "The Chemistry of Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters," *Earth-Science Reviews* 24(1):1-42.

MWH, 2005, *In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan Floodplain Reductive Zone Enhancement*, Draft, MWH, Walnut Creek, California. Available at: http://www.dtsc-topock.com/resources/CMS_FS/In-SituPilotStudies/FloodplainIn-SituPilotStudy/03-Floodplain%20In-situ%20Workplan%20Aug%202005.pdf.

NAVD88, 1988, *North American Vertical Datum of 1988*, National Geodetic Survey, Federal Geodetic Control Committee, Silver Spring, Maryland. Available at: http://www.ngs.noaa.gov/.

Neculita, Carmen-Mihaela, Gerald J. Zagury, and Bruno Bussiere, 2007, "Passive Treatment of Acid Mine Drainage in Bioreactors Using Sulfate-Reducing Bacteria: Critical Review and Research Needs," *J. Environ. Qual.* 36(1):1-16.

NRL/PU/6115-99-384, 1999, *Groundwater Circulating Well Technology Assessment*, Naval Research Laboratory, Washington, D.C.

Oliver, Douglas S., 2001, *Microbial Reduction of Hexavalent Chromium Under Vadose Zone Conditions*, MS Thesis, New Mexico Institute of Mining and Technology, Socorro, New Mexico. Available at: http://www.ees.nmt.edu/outside/alumni/papers/2001t_oliver%20jr._ds.pdf.

ORNL/ER-401/V1, 1997, *Field Grouting Summary Report on the WAG 4 Seeps 4 and 6 Removal Action Project*, Vol. 1 and 2, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Available at: http://www.ornl.gov/info/reports/1997/3445604431327.pdf.

ORNL/TM-11838, 1993, *In Situ Grouting of Low-Level Burial Trenches with a Cement-Based Grout at Oak Ridge National Laboratory*, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Available at: http://www.ornl.gov/info/reports/1993/3445604240471.pdf.

Oze, Christopher, Dennis K. Bird, and Scott Fendorf, 2007, "Genesis of Hexavalent Chromium from Natural Sources in Soil and Groundwater," *Proceedings of the National Academy of Sciences of the United States of America* 104(16):6544-6549. Available at: http://www.pnas.org/content/104/16/6544.full.pdf+html.

Papargyris A.D., A.T. Botis, and S.A. Papargyri, 2002, "Synthetic Routs for Hydroxyapatite Powder Production," *Key Engineering Materials* 206-213:83-86.

Parsons, 2004, *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*, Parsons Corporation, Denver, Colorado. Available at: http://costperformance.org/remediation/pdf/principles_and_practices_bioremediation.pdf.

Persoff, P., S. Finsterle, G.J. Moridis, J. Apps, K. Pruess, and S. Muller, 1995, "Injectable Barriers for Waste Isolation," *33rd Hanford Symposium on Health and Environment, In-Situ Remediation: Scientific Basis for Current and Future Technologies, Part 1*, Battelle, Columbus, Ohio, pp. 87-101. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/106544-CPhYJj/webviewable/.

Persoff, Peter, George Moridis, John Apps, and Joyce M. Whang, 1999, "Effect of Dilution and Contaminants on Sand Grouted with Colloidal Silica Gel," *Journal of Geotechnical Geoenvironmental Engineering* 125(6):461-469.

PNL-7290, 1990, *Development of a Biological Treatment System for Hanford Groundwater Remediation: FY 1989 Status Report*, Pacific Northwest Laboratory, Richland, Washington. Available at: http://www.osti.gov/energycitations/servlets/purl/6941773-lloYSh/6941773.pdf.

PNL-8281, 1992, *In Situ Vitrification of a Mixed-Waste Contaminated Soil Site: The 116-B-6A Crib at Hanford*, Pacific Northwest Laboratory, Richland, Washington. Available at: http://www5.hanford.gov/arpir/?content=findpage&AKey=D196133681.

PNNL-6415, 2007, *Hanford Site National Environmental Policy Act (NEPA) Characterization*, Rev. 18, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-6415Rev18.pdf.

PNNL-12121, 1999, *In Situ Gaseous Reduction Pilot Demonstration—Final Report*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.osti.gov/energycitations/servlets/purl/3762-A4BrhR/webviewable/3762.pdf.

PNNL-13486, 2001, *Characterization Activities Conducted at the 183-DR Site in Support of an In Situ Gaseous Reduction Demonstration*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-13486.PDF.

PNNL-17674, 2008, *Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-17674.pdf.

PNNL-18143, 2009, *Research Plan: Foam Delivery of Amendments to the Deep Vadose Zone for Metals and Radionuclides Remediation*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-18143.pdf.

PNNL-18294, 2009, *100-N Area Strontium-90 Treatability Demonstration Project: Food Chain Transfer Studies for Phytoremediation Along the 100-N Columbia River Riparian Zone*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www5.hanford.gov/arpir/?content=findpage&AKey=1110180073.

PNNL-18303, 2009, *Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of a Ca-Citrate-Phosphate Solution*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-18303.pdf.

PNNL-18427, 2009, *Hanford Site Environmental Report for Calendar Year 2008*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www5.hanford.gov/arpir/?content=findpage&AKey=0095787.

PNNL-18784, 2009, *Hanford 100-D Area Biostimulation Treatability Test Results*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www2.hanford.gov/arpir/?content=findpage&AKey=1002020098.

PNNL-19120, 2010, *100-N Area Strontium-90 Treatability Demonstration Project: Phytoextraction Along the 100-N Columbia River Riparian Zone—Field Treatability Study*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-19120.pdf.

PNNL-SA-49953, 2006, *Project Work Plan 100-N Area Strontium-90 Treatability Demonstration Project: Phytoremediation Along the 100-N Columbia River Riparian Zone*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-SA-49953.pdf.

PNNL-SA-61818, 2008, *Sr-90 Immobilization by Infiltration of a Ca-Citrate-PO4 Solution into the Hanford 100N Area Vadose Zone*, Pacific Northwest National Laboratory, Richland, Washington. Available at: http://www.hanford.gov/docs/gpp/science/em21/ApatiteInfiltration_Sr_90.pdf.

Poulton, Simon W., Michael D. Krom, and Robert Raiswell, 2004, "A Revised Scheme for the Reactivity of Iron (Oxyhydr)Oxide Minerals Towards Dissolved Sulfide," *Geochimica et Cosmochimica Acta* 68(18):3703-3715. Available at: http://eprints.whiterose.ac.uk/466/1/raiswellr7.pdf.

Presidential Proclamation 7319, 2000, *Establishment of the Hanford Reach National Monument*, June 9. Available at: http://www.gpo.gov/fdsys/pkg/WCPD-2000-06-12/pdf/WCPD-2000-06-12-Pg1322.pdf.

Rai, D., L.E. Eary, L.E., and J.M. Zachara, 1989, "Environmental Chemistry of Chromium," *Sci. Total Environ.* 86(1-2):15-23.

Regenesis, "Case Study for Chromium Immobilization," Advanced Technologies for Contaminated Site Remediation website, San Clemente, California. Available at: http://regenesis.com/regenesis-resource-center/case-studies/cs-detail.aspx?ID=97.

Robertson, W.D., J.L. Vogan, and P.S. Lombardo, 2008, "Nitrate Removal Rates in a 15-Year-Old Permeable Reactive Barrier Treating Septic System Nitrate," *Ground Water Monitoring & Remediation* 28(3):65-72. Available at: http://onlinelibrary.wiley.com/doi/10.1111/j.1745-6592.2008.00205.x/pdf.

RPP-ENV-34028, 2007, *Central Plateau Vadose Zone Remediation Technology Screening Evaluation*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

SAND94-0786, 1994, "Feasibility of Permeation Grouting for Constructing Subsurface Barriers," *33rd Hanford Symposium on Health and Environment, In-Situ Remediation: Scientific Basis for Current and Future Technologies*, *Part 1*, Battelle, Columbus, Ohio, pp. 3-36. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/106544-CPhYJj/webviewable/.

Scott, Michael J., 1991, *Kinetics of Adsorption and Redox Processes on Iron and Manganese Oxides: Reactions of Arsenic(III) and Selenium(IV) at Goethite and Birnessite Surfaces*, Environmental Quality Laboratory Report Number 33, California Institute of Technology, Pasadena, California. Available at: http://authors.library.caltech.edu/25783/1/EQLReport33.pdf.

SERDP and ESTCP, Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program website. Available at http://www.serdp.org/.

SGW-34562, 2008, *Alternative Remediation Technology Study for Groundwater Treatment at 200-PO-1 Operable Unit at Hanford Site*, Rev. 0, Fluor Hanford, Inc., Richland, Washington. Available at: http://www.osti.gov/bridge/servlets/purl/936779-BgPdOR/.

SGW-37783, 2008, *Literature Survey for Groundwater Treatment Options for Nitrate, Iodine-129, and Uranium, 200-ZP-1 Operable Unit, Hanford Site*, Rev. 0, Fluor Hanford, Inc., Richland, Washington. Available at: http://www.osti.gov/bridge/product.biblio.jsp?query_id=0&page=0&osti_id=934379.

SGW-38255, 2008, *Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site*, Rev. 0, Fluor Hanford, Inc., Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=0911161138.

SGW-38338, 2008, *Remedial Process Optimization for the 100-D Area Technical Memorandum Document*, Rev. 0, Fluor Hanford, Inc., Richland, Washington.

SGW-45974, 2010, *Treatability Demonstration Report for Directional Drilling in the 100-D Area*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.

Shahandeh, Hamid, 2000, "Enhancement of Cr(III) Phytoaccumulation," *International Journal of Phytoremediation* 2(3):269-286.

Sharma, Kanika, 2002, *Microbial Cr(VI) Reduction: Role of Electron Donors, Acceptors, and Mechanisms, with Special Emphasis on Clostridium spp.*, Ph.D. Thesis, University of Florida, Gainesville, Florida. Available at: http://etd.fcla.edu/UF/UFE0000608/sharma_k.pdf.

Spalding, B.P. and T.A. Fontaine, 1992, "Field Demonstration of In Situ Grouting of Radioactive Solid Waste Burial Trenches with Polyacrylamide," Vol. 2, T.M. Gilliam and C.C. Wiles (eds.), American Society of Testing Materials, West Conshohocken, Philadelphia. Available at: http://www.osti.gov/bridge/servlets/purl/6218778-GELB9S/6218778.pdf.

Spence, Roger D. and Caijun Shi (eds.), 2005, *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, CRC Press, Boca Raton, Florida.

Strekopytov, S. and O. Larsen, 2001, "Reduction of Structural Fe(III) of Nontronite by Hydrogen Sulfide," *Proceedings of the 6th International Conference on the Biogeochemistry of Trace Elements*, Guelph, Ontario, Canada, August.

Sylvestre, Michel, 2004, "Genetically Modified Organisms to Remediate Polychlorinated Biphenyls. Where Do We Stand?" *International Biodeterioration & Biodegradation* 54(23):153-162.

Tokunaga, T.K., J. Wan, M.K. Firestone, T.C. Hazen, K.R. Olson, D.J. Herman, S.R. Sutton, and A. Lanzirotti, 2003, "In-Situ Reduction of Cr(VI) in Heavily Contaminated Soils Through Organic Carbon Amendment," *J. Environ. Qual*. 32(5):1641-9.

Tokunaga, Tetsu K., Jiamin Wan, Antonio Lanzirotti, Steve R. Sutton, Matthew Newville, and William Rao, 2007, "Long-Term Stability of Organic Carbon-Stimulated Chromate Reduction in Contaminated Soils and Its Relation to Manganese Redox Status," *Environ. Sci. Technol.* 41(12):4326-4331.

Toxic Substances Control Act of 1976, Pub. L. 107-377, as amended, 15 USC 2601, et seq. Available at: http://frwebgate.access.gpo.gov/cgi-bin/usc.cgi?ACTION=BROWSE&TITLE=15USCC53.

TR-2230-ENV, 2003, 2003, *Cost and Performance Report In-Situ Remediation of MTBE Contaminated Aquifers Using Propane Biosparging*, Naval Facilities Engineering Service Center, Port Hueneme, California. Available at: http://costperformance.org/profile.cfm?ID=371&CaseID=371.

Vanbroekhoven, K., Y. Vermoortel, L. Diels, and J. Gemoets, 2007, "Stimulation of In Situ Bioprecipitation for the Removal of Cr(VI) from Contaminated Groundwater," *Proceedings of the International Mine Water Association Symposium 2007: Water in Mining Environments*, R. Cidu and F. Frau (eds.), May 27-31.

WD-WSEB-3-9, 2006, *Nitrate/Nitrite in Drinking Water*, Environmental Fact Sheet, New Hampshire Department of Environmental Services, Concord, New Hampshire, Available at: http://des.nh.gov/organization/commissioner/pip/factsheets/dwgb/documents/dwgb-3-9.pdf.

WHC-EP-0878, 1995, *Coordination of Groundwater Activities in the 100 N Area*, Westinghouse Hanford Company, Richland, Washington. Available at: http://www.osti.gov/bridge/purl.cover.jsp;jsessionid=8AF50C7A5552B76CCD2E7CC7D328D3C0?purl=/152001-9tLMGf/webviewable/.

WHC-SA-2755-FP, 1994, *Testing of a Benchscale Reverse Osmosis/Coupled Transport System for Treating Contaminated Groundwater*, Westinghouse Hanford Company, Richland, Washington. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/39792-4V6qxY/webviewable/.

WHC-SD-EN-TI-268, 1994, *100 Area Soil Washing: Bench-Scale Tests on 116-F-4 Pluto Crib Soil*, Rev. 0, Westinghouse Hanford Company, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/index.cfm/viewDoc?accession=D196076370.

Wielinga, Bruce, Midori M. Mizuba, Colleen M. Hansel, and Scott Fendorf, 2001 "Iron Promoted Reduction of Chromate by Dissimilatory Iron-Reducing Bacteria," *Environ. Sci. Technol.* 35(3):522-527.

WMP-27397, 2006, *Evaluation of Vadose Zone Treatment Technologies to Immobilize Technetium-99*, Rev. 1, Fluor Hanford, Inc., Richland, Washington. Available at: http://www.osti.gov/bridge/servlets/purl/881671-UJgKGQ/.

WSRC-RP-97-849, *Groundwater Treatment at SRS: An Innovative Approach*, Rev. 2, Westinghouse Savannah River Company, Aiken, South Carolina. Available at: http://www.osti.gov/bridge/purl.cover.jsp?purl=/606063-xoBGs8/webviewable/.

WSRC-RP-97-854, 1999, *Corrective Measures Implementation/Remedial Design Report/Remedial Action Work Plan (CMI/RDR/RAWP) for the F-Area Seepage Basin (904-49G) (U)*, Rev. 1, U.S. Department of Energy, Idaho Operations Office, Idaho Falls, Idaho.

WSRC-TR-2005-00198, 2006, *Enhanced Attenuation: A Reference Guide on Approaches to Increase the Natural Treatment Capacity of a System*, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina. Available at: http://www.clu-in.org/download/contaminantfocus/tce/DOE_EA_doc.pdf.

Wu, Youxian and Baolin Deng, 2006, "Inhibition of FeS on Chromium (III) Oxidation by Biogenic Manganese Oxides," *Environmental Engineering Science* 23(3):552-560.

Xu, Shangping and Peter R. Jaffé, 2006, "Effects of Plants on the Removal of Hexavalent Chromium in Wetland Sediments," *Journal of Environmental Quality* 35(1):334-341.

Zhong, Lirong, Nikolla P. Qafoku, James E. Szecsody, P. Evan Dresel, and Zhuanfang F. Zhang, 2009, "Foam Delivery of Calcium Polysulfide to Vadose Zone for Chromium(VI) Immobilization: A Laboratory Evaluation," *Vadose Zone Journal* 8(4):976-985. Available at: https://www.soils.org/publications/vzj/pdfs/8/4/976.

This page intentionally left blank.