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## **Appendix I**

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### **Technology Screening— Technologies Not Retained**

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# Contents

1		
2	<b>I1</b>	<b>Additional Information on Technologies Not Retained for Waste Site Treatment..... I-1</b>
3	I1.1	Ex Situ Treatment and Processing.....I-1
4	I1.1.1	Solidification/Stabilization .....I-1
5	I1.1.2	Soil Washing.....I-2
6	I1.1.3	Ex Situ Vitrification.....I-4
7	I1.1.4	Ex Situ Thermal Desorption .....I-5
8	I1.2	In Situ Treatment—Reagent Approach.....I-6
9	I1.2.1	In Situ Solidification.....I-6
10	I1.2.2	In Situ Stabilization/Sequestration.....I-8
11	I1.2.3	In Situ Chemical Reduction.....I-9
12	I1.2.4	In Situ Chemical Oxidation .....I-10
13	I1.2.5	Reductive Dechlorination Using Zero-Valent Metals and Bioremediation.....I-11
14	I1.2.6	In Situ Gaseous Reduction with Chemical Reductant or Biological Substrate.....I-13
15	I1.3	In Situ Treatment—Delivery Method .....I-14
16	I1.3.1	Mixing with Conventional Excavation Equipment.....I-15
17	I1.3.2	Deep Soil Mixing.....I-15
18	I1.3.3	Foam Delivery of Reagents.....I-16
19	I1.3.4	Gaseous Delivery of Reagents (In Situ Gaseous Reduction).....I-17
20	I1.3.5	Horizontal Injection Wells.....I-17
21	I1.3.6	Jet Grouting.....I-18
22	I1.4	In Situ Treatment—Other.....I-19
23	I1.4.1	Desiccation.....I-19
24	I1.4.2	In Situ Thermal Desorption.....I-20
25	I1.4.3	In Situ Vitrification.....I-21
26	I1.4.4	Phytoremediation .....I-23
27	I1.5	Containment .....I-25
28	I1.5.1	Horizontal Subsurface Barriers—Jet Grouting, Soil Freezing, or Wire Saw
29	Barriers I-.....	25
30	I1.5.2	Dynamic Compaction .....I-26
31	<b>I2</b>	<b>Additional Information on Technologies Not Retained for Groundwater Treatment ..... I-26</b>
32	I2.1	Ex Situ Treatment.....I-26
33	I2.1.1	Ex Situ Chemical Precipitation .....I-26
34	I2.1.2	Electrocoagulation .....I-27
35	I2.1.3	Wetlands .....I-28
36	I2.1.4	Bioreactors .....I-29
37	I2.1.5	Phytoremediation .....I-30

1	12.1.6 Membrane Separation (Reverse Osmosis).....	I-31
2	I2.2 Discharge.....	I-33
3	12.2.1 Surface Water Discharge under a NPDES Permit .....	I-33
4	I2.3 In Situ Treatment.....	I-34
5	12.3.1 In Situ Chemical Reduction .....	I-34
6	12.3.2 Hydrogen or Other Organic Gas Sparging.....	I-35
7	12.3.3 Groundwater Circulation Wells .....	I-36
8	12.3.4 Horizontal Wells .....	I-37
9	I2.4 Containment .....	I-37
10	12.4.1 Containment Wall .....	I-38
11	12.4.2 Reactive Biological Barrier.....	I-39
12	12.4.3 Hydraulic Containment via Injection.....	I-40
13	<b>I3 Bioremediation as a Potential Remedial Action for Cr(VI) in the Groundwater and</b>	
14	<b>Vadose Zone of the Hanford 100 Area .....</b>	<b>I-41</b>
15	I3.1 Introduction .....	I-41
16	I3.2 Scientific Basis of Bioremediation.....	I-42
17	<b>I4 Overview of Cr(VI) Bioremediation Processes.....</b>	<b>I-42</b>
18	I4.1 Longevity of Treatment and the Potential for Re-oxidation of Chromium(III) Phases.....	I-43
19	14.1.1 Dissolved Oxygen.....	I-43
20	14.1.2 Manganese(IV) Oxides .....	I-43
21	I4.2 Fate and Transport of Some Potential Chemical Byproducts of Bioremediation .....	I-45
22	14.2.1 Iron and Manganese, and Arsenic.....	I-45
23	<b>I5 Evaluation of Potential Substrates for In Situ Bioremediation in the 100 Area .....</b>	<b>I-47</b>
24	I5.1 Substrate Selection for In Situ Bioremediation of the 100 Area Unconfined Aquifer .....	I-50
25	15.1.1 Initial Screening.....	I-50
26	15.1.2 Secondary Screening.....	I-50
27	15.1.3 Final Screening .....	I-50
28	<b>I6 In Situ Groundwater Remediation by Bio-Injection.....</b>	<b>I-55</b>
29	I6.1 Conceptual Design .....	I-55
30	16.1.1 Implementation Factors .....	I-55
31	I6.2 Previous Studies and Applications of Bio-injection and Similar Technologies to	
32	Cr(VI) Remediation in Groundwater.....	I-57
33	<i>I6.3 Hanford 100-D Pacific Northwest National Laboratory Biostimulation</i>	
34	<i>Treatability Study .....</i>	<i>I-57</i>
35	16.3.1 Site Conditions.....	I-57
36	16.3.2 Technical Approach .....	I-57
37	16.3.3 Results I-58	
38	16.3.4 Lessons Learned.....	I-59

1	I6.4	Hanford 100-H Lawrence Berkeley National Laboratory Hydrogen Release	
2		Compound Treatability Study .....	I-59
3		I6.4.1 Site Conditions.....	I-59
4		I6.4.2 Technical Approach .....	I-60
5		I6.4.3 Results.....	I-60
6		I6.4.4 Lessons Learned.....	I-61
7	I6.5	Other Relevant Hanford Site Studies .....	I-61
8		I6.5.1 Fortifying the 100-D Area In Situ Redox Manipulation Barrier with Iron.....	I-61
9		I6.5.2 100-K Area Calcium Polysulfide Injection Treatability Test .....	I-62
10	I6.6	PG&E Hinkley Compressor Station, San Bernardino County, California .....	I-64
11		I6.6.1 Site Conditions.....	I-64
12		I6.6.2 Technical Approach .....	I-64
13		I6.6.3 Results.....	I-65
14		I6.6.4 Lessons Learned.....	I-67
15	I6.7	PG&E Topock Compressor Station, San Bernardino County, California.....	I-67
16		I6.7.1 Case Study References.....	I-67
17		I6.7.2 Site Conditions.....	I-68
18		I6.7.3 Technical Approach .....	I-68
19		I6.7.4 Results.....	I-71
20		I6.7.5 Lessons Learned.....	I-72
21	I6.8	Abandoned Manufacturing Facility, Emeryville, California.....	I-72
22		I6.8.1 Case Study References.....	I-72
23		I6.8.2 Site Conditions.....	I-73
24		I6.8.3 Technical Approach .....	I-73
25		I6.8.4 Results.....	I-73
26	I6.9	Avco Lycoming Site, Williamsport, Pennsylvania .....	I-73
27		I6.9.1 Case Study References.....	I-73
28		I6.9.2 Site Conditions.....	I-74
29		I6.9.3 Technical Approach .....	I-74
30		I6.9.4 Results.....	I-74
31	I6.10	Odessa Chromium I Superfund Site Odessa, Ector County, Texas.....	I-74
32		I6.10.1 Case Study References.....	I-75
33		I6.10.2 Site Conditions.....	I-75
34		I6.10.3 Technical Approach .....	I-75
35		I6.10.4 Results.....	I-75
36		I6.10.5 Lessons Learned.....	I-76
37	I6.11	Selma Pressure Treating Superfund Site, Selma, California.....	I-76
38		I6.11.1 Case Study References.....	I-76
39		I6.11.2 Site Conditions.....	I-76

1 I6.11.3 Technical Approach ..... I-77  
 2 I6.11.4 Results ..... I-77  
 3 I6.11.5 Lessons Learned ..... I-77  
 4 I6.12 Schwerin Concaves, Inc., Walla Walla, Washington ..... I-78  
 5 I6.12.1 Case Study References ..... I-78  
 6 I6.12.2 Site Conditions ..... I-78  
 7 I6.12.3 Technical Approach ..... I-78  
 8 I6.12.4 Results ..... I-78  
 9 I6.12.5 Lessons Learned ..... I-79  
 10 **I7 Vadose Zone Treatment by Bioinfiltration ..... I-80**  
 11 I7.1.1 Conceptual design ..... I-80  
 12 I7.2 Bio-infiltration Remediation Processes and Approach ..... I-82  
 13 **I8 References ..... I-83**

14  
 15 **Figures**

16 Figure I1. Cross Section of a Recirculating In Situ Bioremediation System ..... I-55  
 17 Figure I2. Molasses Injected at 100-D Area Biostimulation Treatability Test Site to  
 18 Nourish Bacteria ..... I-58  
 19 Figure I3. 100-KR-4 Plume Showing Treatability Test Site ..... I-63  
 20 Figure I4. PG&E Hinkley ISRZ Areas ..... I-66  
 21 Figure I5. PG&E Topock Upland ISPT Layout ..... I-69  
 22 Figure I6. PG&E Topock Floodplain ISPT Layout ..... I-70  
 23 Figure I7. Configuration of the Schwerin Concaves Remedial Pilot Test ..... I-79  
 24 Figure I8. Functional Design of the Planned 100-KW Bioinfiltration System ..... I-81  
 25

26 **Tables**

27 Table I-1. Substrates Used for Enhanced Anaerobic Bioremediation ..... I-48  
 28 Table I-2. Screening Level Evaluation of Several Commonly Used In Situ Bioremediation  
 29 Substrates ..... I-53  
 30

## Terms

1,2-DCE	1,2-dichloroethene, or 1,2-dichloroethylene
AFCEE	Air Force Center for Engineering and the Environment
ATP	anaerobic thermal processor
BFS	blast furnace slag
bgs	below ground surface
bph pathway	biphenyl pathway
CBA	chlorobenzoic acid
COPC	contaminant of potential concern
CVOC	chlorinated volatile organic compound
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
GCW	groundwater circulation well
HRC	hydrogen release compound
HTTD	high-temperature thermal desorption
INEEL	Idaho National Engineering and Environmental Laboratory
ISRZ	in situ reactive zone
ISCO	in situ chemical oxidation
ISPT	in situ pilot test
ISTD	in situ thermal desorption

ISRM	in situ redox manipulation
MCL	maximum contaminant level
MRC™	Metals Remediation Compound
MTBE	methyl tert butyl ether
NPDES	National Pollutant Discharge Elimination System
NZVI	nanoscale zero-valent iron
O&M	operation and maintenance
ORNL	Oak Ridge National Laboratory
OU	operable unit
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyl
PG&E	Pacific Gas and Electric Company
PNNL	Pacific Northwest National Laboratory
RO	reverse osmosis
ROD	Record of Decision
RUM	Ringold Formation upper mud
SRS	Savannah River Site
SVOC	semivolatile organic compounds
TOC	total organic carbon
VFA	volatile fatty acid
VOC	volatile organic compounds
VSEP	vibratory shear-enhanced processing
WTP	Waste Treatment and Immobilization Plant

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## **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, Cr(VI), other metals, and organic compounds (polychlorinated biphenyls [PCBs], polynuclear aromatic hydrocarbons, 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 affected waste sites at 100-BC. 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 affected media at 100-BC, disposal to offsite landfills was not retained. Soil blending was not retained because it relies on contaminant dilution and is considered to be ineffective. Finally, because pipelines of a smaller diameter adequate for void-fill grouting are not encountered at waste sites at 100-BC, void-fill grouting was not retained.

### **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, Cr(VI), 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 chemically bind metals. 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, and no waste sites at 100-BC currently pose a risk of contaminant migration to groundwater.

1 **11.1.1.2 Relevant Demonstration Projects**

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

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

20 **11.1.1.3 Evaluation and Screening Rationale**

21 ESS is considered to be low to moderately effective at immobilizing mobile contaminants in soil that  
22 could leach to groundwater. The stabilized mass must be protected from weathering and seismic activity  
23 for long-term durability. Although ESS is a well-established technology, site-specific studies would need  
24 to be completed to evaluate equipment required and appropriate cement agents. ESS was screened out in  
25 favor of the safer alternative of disposal in ERDF, a centralized facility engineered to protect against  
26 weathering and seismic activity.

27 **11.1.2 Soil Washing**

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

30 **11.1.2.1 Description**

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

38 A range of physical processes can be used for soil washing. These processes range from simple screening  
39 to complex grinding or scrubbing, combined with chemical dissolution. Contaminants are generally more  
40 strongly associated with the finer grained soil particles; therefore, it is sometimes possible to separate the  
41 coarse fraction, and it will be clean. However, if the contaminants are strongly sorbed to the surfaces of  
42 the coarse particles, simple separation may not be effective, and more aggressive and expensive processes  
43 will be required.

1 **11.1.2.2 Relevant Demonstration Projects**

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

17 A bench-scale treatability study was completed by PNNL in 1994 on two contaminated soils from the  
18 100 Area (*100 Area Soil Washing Bench-Scale Tests* [DOE/RL-93-107]). Soil-washing tests were focused  
19 on samples from 116-C-1 Trench (Batch II) and 116-D-1B Trench (Batch III), and effectiveness was  
20 gauged on the potential for attenuation of cobalt-60, europium-152, and cesium-137. Physical (attrition  
21 scrubbing and autogenous grinding) and chemical extraction treatment methods were evaluated. Batch II  
22 consisted primarily (97.2 percent) of coarse fraction (greater than 2 mm [0.8 in]) and was treated using  
23 physical and chemical extraction methods. Results indicated soil washing could adequately reduce levels  
24 of cobalt-60 and europium-152; however, the activity of cesium-137 could not be significantly reduced.  
25 Batch III consisted of approximately 46.9 percent coarse fraction, and results indicated soil-washing tests  
26 were effective in reducing the radionuclide activities in bulk soil to below target performance levels.  
27 Results from tests on Batch II showed that the soil from 116-D-1B Trench could be successfully  
28 soil-washed by combining wet sieving with either two-stage attrition scrubbing in electrolyte or a single  
29 chemical extraction step. The study indicated an anticipated mass reduction of contaminated material for  
30 Batch II of approximately 84 to 87 percent.

31 A treatability study for physical separation methods was conducted at the 300-FF-1 Operable Unit (OU)  
32 in 1994 (*300-FF-1 Operable Unit Remedial Investigation Phase II Report: Physical Separation of Soils  
33 Treatability Study* [DOE/RL-93-96]). The objective of the study was to evaluate the use of physical  
34 separations systems to concentrate chemical and radiochemical contaminants (uranium-238 and  
35 uranium-235) into fine soil fractions in order to minimize waste volumes (with a target of 90 percent  
36 reduction by weight of contaminated soil). Physical separation methods were limited to a water-based  
37 technology to separate soil particles by size fraction without the use of chemical processes, so that the  
38 coarse fraction of soil would meet cleanup limits. Physical separation methods were found to be adequate  
39 for reducing the amount of contaminated soil; however, the cost effectiveness of using this approach for  
40 soil with concentrations near background levels was questioned. The study also indicated that physical  
41 separation processes are not recommended for treating concentrated soil fines, such as the intact green  
42 layer or fly ash. Excavation and direct disposal may be the preferred alternative for this material.

43 **11.1.2.3 Evaluation and Screening Rationale**

44 The effectiveness of soil washing and the complexity of the processes that are required are driven by the  
45 binding processes that exist between the contaminants and the soil particles (adsorbed or precipitated).  
46 The binding process varies based on the nature and solubility of the contaminant of potential  
47 concern (COPC).

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

### 7 **11.1.3 Ex Situ Vitrification**

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

#### 10 **11.1.3.1 Description**

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

21 Ex situ joule, heating vitrification uses furnaces that have evolved from the glass melter units used in the  
22 glass industry. The electric furnace uses a ceramic-lined, steel-shelled melter to contain the molten glass  
23 and waste material (*100 Area Source Operable Unit Focused Feasibility Study* [DOE/RL-94-61]).

#### 24 **11.1.3.2 Relevant Demonstration Projects**

25 In the early 1990s, DOE developed a Transportable Vitrification System to effectively vitrify applicable  
26 mixed-waste sludges and solids across the various DOE complex sites (*Transportable Vitrification*  
27 *System: Mixed Waste Focus Area* [DOE, 1998]). Multiple studies were completed in collaboration with  
28 Westinghouse Savannah River Company, Oak Ridge National Laboratory (ORNL), and Clemson  
29 University. A mixed-waste demonstration was completed in 1997 using Savannah River B&C Pond  
30 sludge, and a mix of B&C Pond sludge and Central Neutralization Facility sludge. The study indicated  
31 the system vitrified 84 m<sup>3</sup> (276 ft<sup>3</sup>) of mixed waste into 34 m<sup>3</sup> (112 ft<sup>3</sup>) of glass waste, resulting in  
32 a 60 percent waste volume reduction. Results of the study indicated the need for high capital costs and  
33 extensive upfront development. However, the study also indicated the technology is capable of producing  
34 highly durable glass waste forms with long-term integrity and of providing a significant reduction in  
35 waste volume compared to other stabilization techniques.

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

### 1 **11.1.3.3 Evaluation and Screening Rationale**

2 Ex situ vitrification is considered to have low implementability given that highly complex equipment is  
3 required and the safety concerns with implementation, which include maintaining the integrity of the  
4 tanks. Because of the relatively high cost of ex situ vitrification and the potential application of other  
5 technologies with better effectiveness and implementability, ex situ vitrification is not considered  
6 favorable for implementation for treatment of contaminated soil at the 100 Area.

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

13 As presented in *Central Plateau Vadose Zone Remediation Technology Screening Evaluation*  
14 (RPP-ENV-34028), estimated costs for implementation of this technology can range from \$500 to  
15 \$1,000 per calendar year. These costs include soil excavation, screening to remove debris, installation of  
16 the vitrification system and offgas treatment system, operation and maintenance (O&M), utilities and site  
17 management, sampling support, and onsite disposal of vitrified material and offgas treatment. For the  
18 WTP facility, *Project Execution Plan for the River Protection Project Waste Treatment and*  
19 *Immobilization Plant* (DOE/ORP-2003-01), indicated that the total project cost for the WTP is estimated  
20 to be \$5.781 billion.

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

### 23 **11.1.4 Ex Situ Thermal Desorption**

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

#### 25 **11.1.4.1 Description**

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

32 Treatment of organic contaminants to lower volatility levels can be achieved with this technology. Based  
33 on the operating temperatures, thermal desorption processes can be categorized as either high-temperature  
34 thermal desorption (HTTD) (320 to 560°C [608 to 1,040°F]) or low-temperature thermal desorption  
35 (90 to 320°C [194 to 608°F]). HTTD targets semivolatile organic compounds (SVOCs), polynuclear  
36 aromatic hydrocarbons, PCBs, and pesticides. Volatile organic compounds (VOCs) can also be treated  
37 with HTTD, although the process is not as cost effective. Low-temperature thermal desorption targets  
38 nonhalogenated VOCs and fuel, and can treat SVOCs but at a reduced effectiveness.

#### 39 **11.1.4.2 Relevant Demonstration Projects**

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

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

#### 4 **11.1.4.3 Evaluation and Screening Rationale**

5 Ex situ thermal desorption can be a highly effective technology. Although equipment for implementation  
6 of this technology is readily available, it is mechanically complex, posing technical implementability  
7 challenges. Given the relatively low volumes of petroleum-contaminated soil that are likely to be present,  
8 and the high mobilization costs, onsite disposal of soil is likely to be much more cost effective.

9 Transportability of equipment becomes challenging when the amount of soil to treat is small and the  
10 complexity of the equipment requires skilled operators to treat the soil. For these reasons, ex situ thermal  
11 desorption was not retained for further consideration.

### 12 **11.2 In Situ Treatment—Reagent Approach**

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

#### 16 **11.2.1 In Situ Solidification**

17 In situ solidification was not retained for treatment of soils containing mobile to semi-mobile metals,  
18 radionuclides, and organic compounds.

##### 19 **11.2.1.1 Description**

20 Solidification alters the physical and/or chemical characteristics of a soil through the addition of binders,  
21 including cements and chemical grouts, to immobilize contaminants. The immobilization primarily works  
22 by coating and isolation, processes that make the contaminants less prone to leaching or dissolution.  
23 Multiple types of grouting/binding materials and emplacement techniques have been developed and  
24 demonstrated. Jet grouting and permeation grouting are the two general grout approaches potentially  
25 applicable for subsurface contaminant solidification in Hanford Site vadose zone sediments. Jet grouting  
26 uses high energy emplacement of cement or chemical grout materials whereby the sediment is displaced  
27 and mixed with the grouting material. Permeation grouting is injection of a liquid grout that fills the pore  
28 space of the formation and then gels to form a solid material. While permeation grouting is a relatively  
29 mature technology for many geotechnical applications, there are uncertainties with grout for in situ  
30 contaminant stabilization (*Evaluation of Vadose Zone Treatment Technologies to Immobilize*  
31 *Technetium-99* [WMP-27397]). The uncertainties are that the effectiveness of delivery depends upon  
32 subsurface heterogeneity and that the presence of fines adversely affects grout placement. Generally,  
33 grout is emplaced via an array of closely spaced vertical boreholes into the subsurface volume to  
34 be stabilized.

35 Two types of grout materials may be used: particulate (cement) grouts and chemical grouts. Cement  
36 grouts use Portland cement as the primary component. Portland cement is a mixture of preprocessed  
37 mineral solids pulverized, fired, and ground into a fine solid dust. This product is combined with up to  
38 5 percent gypsum and mixed with water and small quantities of additives to form a flowable mixture of  
39 solids and water, and composing a suspended solids grout. A chemical grout is a solution consisting of  
40 a binder (other than Portland cement) that reacts in place to form a gel or solid after injection into  
41 a porous subsurface soil, sediment, or rock volume. Chemical grouts do not contain mineral solids in  
42 suspension, so their delivery in the subsurface is not limited by particle filtration. Instead, delivery is  
43 a function of grout viscosity and gelling time.

### 1 **11.2.1.2 Relevant Demonstration Projects**

2 Several DOE sites, including the Hanford Site, ORNL, Brookhaven National Laboratory, Idaho National  
3 Laboratory, Savannah River Site (SRS), and Sandia National Laboratories have evaluated, tested, and/or  
4 implemented in situ grouting for shallow waste isolation applications as summarized below. In situ  
5 grouting has been evaluated at the Hanford Site for application to waste site isolation (for example, near  
6 the surface formation of in situ waste barriers) through a number of efforts in the 1990s: “Injectable  
7 Barriers for Waste Isolation” (Persoff et al., 1994); “Feasibility of Permeation Grouting for Constructing  
8 Subsurface Barriers” (SAND94-0786); “Durability of Polymers for Containment Barriers” (Heiser et al.,  
9 1994); *Summary Report on Close-Coupled Subsurface Barrier Technology Initial Field Trials to*  
10 *Full-Scale Demonstration* (BNL-52531); and *In Situ Remediation Integrated Program FY 1994 Program*  
11 *Summary* (DOE/RL-95-32). These documents provide laboratory and field data for jet grouting  
12 techniques applied to shallow waste isolation at the Hanford Site and Brookhaven National Laboratory.

13 In situ permeation grouting using colloidal silica to develop a hydraulic barrier was evaluated and tested  
14 for application at Brookhaven National Laboratory in “Evaluation of Alternative Designs for an Injectable  
15 Subsurface Barrier at the Brookhaven National Laboratory Site, Long Island, New York” (Moridis et al.,  
16 1999), and in a significant program effort led by Lawrence Berkeley National Laboratory: *Physical*  
17 *Barriers Formed from Gelling Liquids: 1. Numerical Design of Laboratory and Field Experiments*  
18 (LBL-35113); *Injectable Barriers for Waste Isolation* (LBL-36739); “Effect of Dilution and  
19 Contaminants on Sand Grouted with Colloidal Silica Gel” (Persoff et al., 1999); *A Field Test of*  
20 *Permeation Grouting in Heterogeneous Soils Using a New Generation of Barrier Liquids* (LBL-37554);  
21 *A Design Study for a Medium-Scale Field Demonstration of the Viscous Barrier Technology*  
22 (LBNL-38916); and *A Field Test of a Waste Containment Technology Using a New Generation of*  
23 *Injectable Barrier Liquids* (LBNL-38817).

24 Shallow permeation grouting was conducted at ORNL to reduce hydraulic conductivity (*Field Grouting*  
25 *Summary Report on the WAG 4 Seeps 4 and 6 Removal Action Project* [ORNL/ER-401/V1]). Jet injection  
26 of standard and microfine cement grout into waste trench material at ORNL improved soil stability but  
27 did not create low hydraulic conductivity conditions (*In Situ Grouting of Low-Level Burial Trenches with*  
28 *a Cement-Based Grout at Oak Ridge National Laboratory* [ORNL/TM-11838]). Other efforts at ORNL  
29 included injection of a polyacrylamide grout into a waste trench that enhanced soil stability and had a  
30 moderate impact (2 orders of magnitude) on the hydraulic conductivity (“Field Demonstration of In Situ  
31 Grouting of Radioactive Solid Waste Burial Trenches with Polyacrylamide,” [Spalding and  
32 Fontaine, 1992]).

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

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

### 1 **11.2.1.3 Evaluation and Screening Rationale**

2 In situ solidification using commercially available grouting equipment with cement grouts is considered  
3 to have moderate implementability when applied over smaller areas. Such limited areas may extend over  
4 a total area of up to 0.5 ac and to depths of 4 to 5 m (13 to 16 ft). However, there is little experience with  
5 large-scale grouting of soil volumes. The effectiveness of in situ solidification is a function of the  
6 distribution of the grout into the formation, the degree of encapsulation of contaminated sediment  
7 particles, and the long-term durability of shallow soil encapsulation when exposed to the elements.  
8 The effectiveness of grout emplacement depends on the application method. Typical applications would  
9 involve 0.6 m (2 ft) diameter grout column with 0.5 m spacing. Using estimated installation costs for in  
10 situ solidification using jet grouting at Idaho National Engineering and Environmental Laboratory  
11 (INEEL) (*Feasibility Study for Operable Unit 7-13/14* [DOE/ID-11268]), unit costs in excess of  
12 \$1,500 per yd<sup>3</sup> are estimated. Consequently, the relative capital cost is high. Because of the high capital  
13 cost, the potential for incomplete contact of grout in the targeted treatment zone, and uncertainty  
14 regarding the durability of shallow soil encapsulation when exposed to the elements, in situ solidification  
15 was not retained for further evaluation.

### 16 **11.2.2 In Situ Stabilization/Sequestration**

17 In situ stabilization/sequestration was not retained for treatment of soils containing strontium-90.

#### 18 **11.2.2.1 Description**

19 The focus of strontium-90 sequestration studies at the Hanford Site has been on apatite sequestration.  
20 Apatite minerals sequester elements into their molecular structures via isomorphic substitution, whereby  
21 elements of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the  
22 hexagonal crystal structure (“Structural Variations in Natural F, OH, and Cl Apatites” [Hughes et al.,  
23 1989]; *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes* [Spence and  
24 Shi, 2005]). Apatite minerals are very stable and practically insoluble in water. The substitution of  
25 strontium for calcium in the crystal structure is thermodynamically favorable and will proceed provided  
26 the two elements coexist. The mixed strontium-calcium apatites have lower solubility than the calcium  
27 apatite or strontium apatite.

28 Methods of emplacing apatite in vadose zone soil include injection and infiltration of an aqueous solution  
29 containing a calcium-citrate complex and sodium-phosphate. Phosphate adsorption is slow (hours) so  
30 rapid infiltration can result in deeper phosphate mass at depth. Citrate is needed to keep calcium in  
31 solution long enough (days) to inject it into the subsurface. A solution containing Ca<sup>2+</sup> and phosphate only  
32 will rapidly form mono- and di-calcium phosphate, but not apatite (“Hydroxyapatite Synthesis”  
33 [Andronescu et al., 2002]; “Monoclinic Hydroxyapatite” [Elliot et al., 1973]; “Synthetic Routs for  
34 Hydroxyapatite Powder Production” [Papargyris et al., 2002]). As calcium-citrate is degraded, the free  
35 calcium and phosphate combine to form amorphous apatite. The formation of amorphous apatite occurs  
36 within a week, and crystalline apatite forms within a few weeks.

#### 37 **11.2.2.2 Relevant Demonstration Projects**

38 A laboratory scale study investigating apatite sequestration of strontium-90 was conducted by PNNL  
39 (*Sequestration of Sr-90 Subsurface Contamination in the Hanford 100-N Area by Surface Infiltration of a*  
40 *Ca-Citrate-Phosphate Solution* [PNNL-18303]). The results of the laboratory study indicate that  
41 calcium-citrate-phosphate solution can be infiltrated into unsaturated sediments to result in apatite  
42 precipitate to provide treatment of strontium-90 contamination. After 1.3 years of contact, 9 to 16 percent  
43 of strontium-90 had substituted for calcium in apatite. Strontium-90 substitution in apatite did not  
44 decrease with depth as a result of the 20 to 30 nm apatite crystals conglomerated, forming a porous 10 to  
45 50 micron conglomerate precipitate. Microbial redistribution during solution infiltration and a high rate of

1 citrate biodegradation for river water microbes (water used for solution infiltration) resulted in a relatively  
2 even spatial distribution of the citrate biodegradation rate and apatite precipitate.

3 Overall, the laboratory results indicate that the most effective infiltration strategy to precipitate apatite at  
4 depth may be to infiltrate a high concentration solution (6 mM calcium, 15 mM citrate, 60 mM  
5 phosphate) at a rapid rate near ponded conditions, followed by rapid, then slow water infiltration (“Sr-90  
6 Immobilization by Infiltration of a Ca-Citrate-PO<sub>4</sub> Solution into the Hanford 100N Area Vadose Zone”  
7 [Szecsody et al., 2008]). Repeated infiltration events, with sufficient time between events to allow water  
8 drainage in the sediment profile, also may be used to build up the mass of apatite precipitate at greater  
9 depth. Low-K zones were effectively treated because the higher residual water content maintained in  
10 these zones resulted in higher apatite precipitate concentrations. High-K zones did not receive sufficient  
11 treatment by infiltration, although an alternative strategy of air/surfactant (foam) was demonstrated  
12 effective for targeting high-K zones.

### 13 **11.2.2.3 Evaluation and Screening Rationale**

14 Laboratory scale studies have demonstrated that in situ stabilization of strontium-90 in the vadose zone  
15 can be achieved through the infiltration of calcium-citrate-phosphate solutions to induce the formation of  
16 apatite, which in turn sequesters the strontium-90. However, there is still uncertainty with regard to how  
17 uniformly phosphate solutions can be delivered on a field scale in heterogeneous soils, and how that  
18 non-uniformity would affect the percentage of strontium-90 that can be sequestered in the vadose zone.  
19 Furthermore, sequestration of strontium-90 does not remove the COPC and does not change the potential  
20 risk from human or ecological direct contact with shallow soil. Therefore, in situ stabilization/  
21 sequestration was screened out in favor of the other technologies such as shallow excavation.

## 22 **11.2.3 In Situ Chemical Reduction**

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

### 24 **11.2.3.1 Description**

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

### 33 **11.2.3.2 Relevant Demonstration Projects**

34 The U.S. Department of Defense conducted a field test site to evaluate the effectiveness of the in situ  
35 gaseous reduction at a chromate-contaminated waste site at the White Sands Missile Range (*In Situ*  
36 *Gaseous Reduction Pilot Demonstration—Final Report* [PNNL-12121]). The field demonstration  
37 involved the injection of a mixture of 200 ppm hydrogen sulfide diluted in air. The gas mixture was  
38 drawn through the site soil by a vacuum applied to extraction boreholes at the site boundary, and residual  
39 hydrogen sulfide was removed prior to release of the air back to the atmosphere. The injection test lasted  
40 76 days with no detectable releases of hydrogen sulfide to the site atmosphere. Comparison of Cr(VI)  
41 analyses of soil samples taken before and after the test indicated that 70 percent of the Cr(VI) originally  
42 present at the site was reduced and thereby immobilized by in situ gaseous reduction. Treatment was  
43 generally better in zones of higher permeability sand containing less silt and clay, indicating that geologic  
44 heterogeneity is a limitation to treatment effectiveness.

### 1 **11.2.3.3 Evaluation and Screening Rationale**

2 The application of toxic hydrogen sulfide gas to the near surface carries significant risk. Transportation  
3 and handling of reducing agents also poses more of a health and safety concern during application,  
4 compared to biological reduction substrates. Because of more rapid chemical reactions, the application of  
5 liquid-reducing agents to uniformly contaminated vadose zone soil may be more problematic than using  
6 biological substrates. Based on these implementability and potential effectiveness issues, in situ chemical  
7 reduction was not retained in favor of in situ biological reduction.

### 8 **11.2.4 In Situ Chemical Oxidation**

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

#### 12 **11.2.4.1 Description**

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

#### 19 **11.2.4.2 Relevant Demonstration Projects**

20 A pilot study was conducted in fall 2006 to evaluate the effectiveness of permanganate injection to treat  
21 chlorinated volatile organic compounds (CVOCs) in shallow unsaturated heterogeneous soil (“Challenges  
22 with an ISCO Application in the Unsaturated Zone: Case of the Missing Permanganate” [Borchert et al.,  
23 2008]). The treatment zone was  $4.8 \times 5.4$  m ( $16 \times 18$  ft) in area and 2.7 m (9 ft) deep. The site geology  
24 consisted of silty clay in the upper 1.6 m (5.5 ft) with traces of sand and gravel, an intermittent sandy  
25 layer from 0.3 to 0.6 m (1 to 2 ft) below ground surface (bgs), gravelly sand with some silt and clay from  
26 1.6 to 4.3 m (5.5 to 14 ft) bgs, and a discontinuous sandy and silty clay layer from 2.4 to 2.7 m (8 to 9 ft)  
27 bgs. Groundwater was encountered from 2.4 to 3 m (8 and 10 ft) bgs. The maximum concentrations of  
28 trichloroethylene and cis-1, 2-DCE were 66,000 and 2,400  $\mu\text{g}/\text{kg}$ , respectively. The permanganate soil  
29 oxidant demand ranged from about 3 to 17.1 g/kg. Approximately 1,041 L (275 gal) of 40 percent by  
30 weight permanganate (about 3,000 lb or 1.5 ton) were injected at nine locations within the pilot study  
31 area. Where oxidant was visually observed, the radius of influence ranged from 2.5 up to 3 m (10 ft).  
32 However, several visual borings had limited evidence of permanganate. Performance monitoring  
33 indicated that trichloroethylene and cis-1,2-DCE concentrations in soil decreased between 44 and  
34 93 percent, respectively. However, concentrations in groundwater increased up to tenfold. Results from  
35 the pilot study indicated that a majority of oxidant migrated into the shallow groundwater and was  
36 consumed by CVOCs and high oxidant demand (up to 20.7 g/kg permanganate). Conclusions state that it  
37 is challenging to acquire fine distribution of an oxidant solution in shallow silty clay, even with controlled  
38 low pressures and flows, and closely spaced injection points. Difficulty was also encountered in creating  
39 temporarily saturated zones for aqueous-based ISCO reactions in the unsaturated zone, particularly in  
40 permeable portions of the formation. Based on the results of the pilot study, excavation was selected as  
41 a more cost-effective remedial alternative for shallow soil.

42 An ozone gas vadose zone sparging system for treating polynuclear aromatic hydrocarbons operated  
43 during the summer of 2001 at the Former Fuel Oil Distribution Terminal in Ilion, New York (*Permeable  
44 Reactive Barriers: Lessons Learned/New Directions* [ITRC, 2005]). Adsorbed polynuclear aromatic  
45 hydrocarbons were delineated from approximately 0.6 to 2.4 m (2 to 8 ft) bgs, and initial total polynuclear

1 aromatic hydrocarbon concentrations exceeded 30 mg/kg. The subsurface contained both fill materials  
2 and native soil consisting primarily of silty sand. Groundwater was encountered at 2.1 to 2.4 m (7 to 8 ft)  
3 bgs. To achieve a target 60-day period for project completion, a nominal 50-lb/day (23 kg/day)  
4 ozone-generation system was used to inject both ozone and oxygen. Ten initial sparge points were  
5 installed at the site by direct-push methodology. A shallow vapor extraction system was installed to  
6 control emissions. The injection system operated over a period of 8 weeks. Post-remediation soil  
7 sampling results indicated no remaining polynuclear aromatic hydrocarbon (primarily  
8 benzo[a]anthracene, benzo[a]pyrene, and chrysene) concentrations above method detection limits,  
9 achieving the remedial goals of 90 percent concentration reduction in 60 days. Naphthalene was also  
10 reduced to below New York State Department of Environmental Conservation Technical and  
11 Administrative Guidance Memorandum standards. Average reduction of naphthalene was greater than  
12 32 percent in 60 days.

13 An ozone gas vadose zone sparging demonstration for treating pentachlorophenol and creosote  
14 (polynuclear aromatic hydrocarbons) was performed in 1998 at the Former Wood Treatment Site,  
15 Sonoma County, California (*Permeable Reactive Barriers: Lessons Learned/New Directions*  
16 [ITRC, 2005]). The former wood treatment facility contained creosote and pentachlorophenol dip tanks  
17 used for treatment of wood poles. Maximum pretreatment soil concentrations were 220 mg/kg  
18 pentachlorophenol and 5,680 mg/kg total polynuclear aromatic hydrocarbons. High levels of dissolved  
19 contamination and nonaqueous phase liquid existed in the vadose zone prior to treatment. The site  
20 subsurface consisted of very heterogeneous stratified silty sands and clays, and the depth to water varied  
21 from 1.2 to 4.6 m (4 to 15 ft). The ozone treatment system design included treatment of both the saturated  
22 and unsaturated zones. Therefore, ozone gas delivery modes included ozone sparging and ozone gas  
23 injection above the water table. Field operation and monitoring of the in situ ozonation demonstration  
24 project was conducted from December 1997 through December 1998. Approximately 3,628 kg (8,000 lb)  
25 of oxidant was delivered to the subsurface, with an average oxidant dose of approximately 1.9 g (0.07 oz)  
26 ozone per kg (lb) of soil. Soil samples collected showed an average 93 percent reduction in  
27 pentachlorophenol and polynuclear aromatic hydrocarbons. Concentration at the maximum pretreatment  
28 soil contamination was reduced by more than 98 percent, from an initial value of 220 mg/kg  
29 pentachlorophenol and 5,680 mg/kg total polynuclear aromatic hydrocarbons, to below detection limits.  
30 Significant contaminant mass reduction was reflected, not only in soil data, but also in substantial reductions  
31 in aqueous-phase concentrations of pentachlorophenol and polynuclear aromatic hydrocarbons.

#### 32 **11.2.4.3 Evaluation and Screening Rationale**

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

#### 40 **11.2.5 Reductive Dechlorination Using Zero-Valent Metals and Bioremediation**

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

##### 43 **11.2.5.1 Description**

44 Both biological and abiotic methods are potentially applicable for reductive dechlorination of PCBs.  
45 During bioremediation, anaerobic bacteria replace chlorine atoms with the electron-donating hydrogen on

1 the PCB molecule. A similar abiotic process occurs with zero-valent metals. Zero-valent metals include  
2 iron, palladium, and other combinations (called bi-metals). Bi-metals have been found to be more  
3 reactive. Nano-particle-sized bi-metals have also been shown to be superior to micro-sized zero-valent  
4 iron (*Emerging Technologies for the In Situ Remediation of PCB-Contaminated Soils and Sediments:  
5 Bioremediation and Nanoscale Zero-Valent Iron* [Mikszewski, 2004]). The bioremediation process  
6 involves mixing an electron donor (such as lactate) with the contaminated soil and maintaining anaerobic  
7 conditions for a number of months. A similar process is used with the zero-valent metals.

#### 8 **11.2.5.2 Relevant Demonstration Projects**

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

13 The technology review indicated that NZVI particles are capable of reducing a range of environmental  
14 pollutants including PCBs. In particular, the properties of NZVI and other nanoscale metals (high surface  
15 area to volume ratios, high surface energies, and a large fraction of stepped surface, zero valency) make  
16 them extremely chemically reactive. Several laboratory and field-scale demonstrations have been  
17 conducted demonstrating the use of NZVI for PCB dechlorination. Studies show conflicting results.  
18 Where complete dechlorination could be achieved, percent reduction of PCBs ranged from  
19 25 to 84 percent. In the field study where 84 percent reduction was achieved (“In-Situ Dechlorination of  
20 Polychlorinated Biphenyls in Sediments Using Zero-Valent Iron” [Gardner et al., 2004]), complete  
21 dechlorination was achieved in only 1 day. In another study (*Development and In Situ Application of  
22 Sorbent/Reagent-Amended “Active” Sediment Caps for Managing HOC-Contaminated Sediments  
23* [Lowry et al., 2004]), NZVI was shown to dechlorinate PCBs with congener half-lives ranging from  
24 40 days to 77 years, with no biphenyl production noted, indicating incomplete dechlorination.

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

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

1 **11.2.5.3 Evaluation and Screening Rationale**

2 The effectiveness of these treatment technologies is considered to be poorly known, given the limited  
3 availability of published testing results and/or conflicting technology demonstration data.  
4 Implementability is considered moderate because it could be executed by soil mixing using conventional  
5 excavation equipment, if the treatment depth is shallow. However, the issue common to all these  
6 technologies is the limited availability of PCBs in soil and sediments. The hydrophobic nature of PCBs  
7 allows tight adsorption to organic matrices within soil and sediments, rendering them resistant to  
8 microbial attack and chemical reduction. Reductive dechlorination using zero-valent metals and  
9 bioremediation are not proven technologies and were not retained for further consideration.

10 **11.2.6 In Situ Gaseous Reduction with Chemical Reductant or Biological Substrate**

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

13 **11.2.6.1 Description**

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

24 **11.2.6.2 Relevant Demonstration Projects**

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

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

### 1 **11.2.6.3 Evaluation and Screening Rationale**

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

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

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

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

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

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

### 35 **11.3 In Situ Treatment—Delivery Method**

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

38 These technologies would be considered only if an amendment-based technology is retained. Chemical  
39 and biological treatment has been retained for soil contaminated with radionuclides, Cr(VI), and other  
40 metals. However, delivery of amendments through infiltration is considered more cost effective than the  
41 approaches discussed below. For this reason, in addition to others discussed in each section below, these  
42 technologies have not been retained for further consideration.

### 1 **11.3.1 Mixing with Conventional Excavation Equipment**

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

#### 4 **11.3.1.1 Description**

5 This delivery method involves using conventional excavation equipment (such as backhoes, excavators,  
6 and front-end loaders) to mix amendments into the soil. The equipment repeatedly picks up and moves  
7 the soil around after a slurry of the amendment has been added. A relatively thick slurry would be  
8 required to keep the amendments from readily draining out of the soil, or the mixing would need to be  
9 performed in a lined basin. This technology is considered highly effective and moderately implementable;  
10 however, the depth at which it can be implemented is limited to the reach of the equipment.

#### 11 **11.3.1.2 Evaluation and Screening Rationale**

12 Several other mixing methods are also highly effective, and some are more implementable than this  
13 technology given the large area that may be required for the heavy equipment operation to achieve  
14 successful contaminant-reagent contact. The costs for this type of mixing are likely to be comparable or  
15 lower than other mixing methods discussed below; however, they are likely to be higher than surface  
16 infiltration methods given that surface infiltration is likely less intrusive. Because of the depth limitation  
17 of this mixing method and the availability of infiltration methods, mixing or delivery of amendments  
18 using conventional excavation equipment was not retained.

### 19 **11.3.2 Deep Soil Mixing**

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

#### 22 **11.3.2.1 Description**

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

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

#### 39 **11.3.2.2 Relevant Demonstration Projects**

40 Deep soil mixing was used to remediate an abandoned transformer repair facility in Miami, Florida  
41 (*In-Situ Stabilization and Fixation of Contaminated Soils by Soil Mixing* [Jasperse and Ryan, 1992]). PCB  
42 concentrations over the affected area ranged from 200 to 600 ppm, with a maximum concentration of  
43 1,000 ppm. Affected media were encountered to approximately 15 m (49 ft) bgs. Laboratory bench-scale

1 tests were completed to evaluate potential reagents, and a proprietary pozzolanic additive containing clay  
2 absorbents was selected. Full-scale implementation involved use of a four-shaft, deep soil-mixing rig and  
3 a reagent mixing plant complete with a four-line pump and control system. Reagents were mixed at a rate  
4 of 275 kg/m<sup>3</sup> of soil mixed. Results from the study show a decrease in concentrations of PCB after  
5 treatment, an increase in unconfined strength, and a decrease in permeability of the mixed samples over  
6 time (*In-Situ Stabilization and Fixation of Contaminated Soils by Soil Mixing* [Jasperse and Ryan, 1992]).

### 7 **11.3.2.3 Evaluation and Screening Rationale**

8 Deep soil mixing is considered highly effective at delivering reagents to contaminated soil. Chemical  
9 agents are uniformly mixed with the soil column, providing good contact and reaction between the  
10 contaminant of concern and the reagent. Cement or bentonite clay can also be mixed with the chemical  
11 slurry to reduce the hydraulic conductivity and leachability of the soil. Implementability of deep soil  
12 mixing is considered marginal at the Hanford Site because of the presence of cobbles and boulders in the  
13 subsurface. Because the equipment cannot mix significantly deeper than the reach of a backhoe, and  
14 ERDF is available for soil disposal at the Hanford Site, excavating the soil and disposing of it at ERDF is  
15 a much more straightforward and proven option. In addition, because implementability will be limited by  
16 site conditions and required depth of treatment, deep soil mixing is not retained for further evaluation.

### 17 **11.3.3 Foam Delivery of Reagents**

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

#### 20 **11.3.3.1 Description**

21 Foam delivery is a relatively new method of delivering chemical reactants to the vadose zone. The foam  
22 is created by a surfactant solution and mixed with a chemical such as calcium polysulfide. This mixture is  
23 then injected into the vadose zone via vertical wells. The foam helps to move the reactants out  
24 horizontally from the injection well, rather than just moving them downward. Depending on the reactant  
25 used, this technology could be used to treat Cr(VI), technetium-99, and uranium.

#### 26 **11.3.3.2 Relevant Demonstration Projects**

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

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

### 1 **11.3.3.3 Evaluation and Screening Rationale**

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

### 8 **11.3.4 Gaseous Delivery of Reagents (In Situ Gaseous Reduction)**

9 In situ gaseous reduction is a vadose zone remediation technology that uses a gaseous reagent (such as  
10 hydrogen sulfide/nitrogen gas mixture) to reduce or treat contaminants. This technology was previously  
11 discussed in Section II.2.5. Since additional information resulting from the treatability studies is required  
12 prior to making decisions about the full-scale application of in situ gas reduction at the Hanford Site, in  
13 situ gaseous reduction was not retained for further consideration.

### 14 **11.3.5 Horizontal Injection Wells**

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

#### 17 **11.3.5.1 Description**

18 Horizontal injection wells involve the delivery of amendments through wells installed using horizontal  
19 drilling techniques. Horizontal injection may have benefits over vertical injection in shallow treatment  
20 areas, and where COPCs are characterized within a certain discrete depth interval.

#### 21 **11.3.5.2 Relevant Demonstration Projects**

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

#### 33 **11.3.5.3 Evaluation and Screening Rationale**

34 As with vertical injection wells, the effectiveness of horizontal injection wells can be hindered by soil  
35 heterogeneity, which causes preferential flow paths and limits the treatment effectiveness of lower  
36 permeability soil. With anisotropies in vertical hydraulic conductivity more pronounced than horizontal  
37 hydraulic conductivity, amendment distribution over a larger depth interval would be more challenging  
38 compared to that for vertical wells. Furthermore, maintaining target borehole depth and alignment with  
39 horizontal drilling in gravelly/cobbly lithologies would be difficult. This issue was encountered during the  
40 technology demonstration at the Hanford Site. Given the increased difficulty with installation and  
41 amendment delivery in horizontal injection wells compared to that for vertical injection wells, as well as  
42 the unsuccessful tests to date at the Hanford Site, horizontal injection wells were not retained.

1 **11.3.6 Jet Grouting**

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

4 **11.3.6.1 Description**

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

11 **11.3.6.2 Relevant Demonstration Projects**

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

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

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

28 **11.3.6.3 Evaluation and Screening Rationale**

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

36 Because grouting technologies have the potential for use as part of a remedy for the deep vadose zone,  
37 further efforts to evaluate the performance of grouting technologies are included in the *Deep Vadose Zone*  
38 *Treatability Test Plan for the Hanford Central Plateau* (DOE/RL-2007-56). Additional information  
39 resulting from the treatability studies is required prior to making decisions about the full-scale application  
40 of grouting technologies at the Hanford Site. Currently, jet grouting is considered cost prohibitive because  
41 of the required close spacing of wells, and jet grouting has potentially limited effectiveness. For these  
42 reasons, jet grouting is not retained for further evaluation.

## 1 **11.4 In Situ Treatment—Other**

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

### 4 **11.4.1 Desiccation**

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

#### 7 **11.4.1.1 Description**

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

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

#### 25 **11.4.1.2 Relevant Demonstration Projects**

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

#### 29 **11.4.1.3 Evaluation and Screening Rationale**

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

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

1 **11.4.2 In Situ Thermal Desorption**

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

4 **11.4.2.1 Description**

5 ISTD involves the direct application of heat, such as using an electrical current to heat soil, or using  
6 electrical heater elements; injecting hot air, steam, or hot water; or using radio frequency to increase the  
7 temperature of soil and destroy or volatilize organic compounds. The use of electrical heating elements  
8 installed in closely spaced soil borings (1.5 to 3 m [5 to 10 ft] intervals) is the most common approach for  
9 implementing ISTD. Conductive heating is the primary mechanism that transmits heat to the soil.  
10 The technology can achieve rapid removal/destruction of a mix of VOCs and SVOCs, and achieve low  
11 residual concentrations. Vapors produced would require removal using extraction wells or trenches with  
12 a vacuum pump. The vapor stream would be pre-conditioned by a moisture separator or heat exchanger  
13 and treated by a vapor treatment system.

14 **11.4.2.2 Relevant Demonstration Projects**

15 Field demonstrations were performed in 1993 and 1994 at the SRS and the Hanford 300 Area to evaluate  
16 six-phase soil heating, a form of electrical resistive heating, as a vadose remedial technology for  
17 tetrachloroethylene and trichloroethylene (*Six-Phase Soil Heating* [DOE/EM-0272]). The demonstration  
18 at the Hanford Site was in the 300 Area at an uncontaminated, undisturbed site. The objective of the  
19 300 Area demonstration was to refine the design of the six-phase electrodes and other system  
20 components, and address scale-up issues in the field. The demonstration site at SRS was at one of the  
21 source areas within the 2.6 km<sup>2</sup> (1 mi<sup>2</sup>) VOC groundwater plume. The contaminated target zone was  
22 a 3 m (10 ft) thick clay layer at a depth of approximately 12 m (40 ft). Trichloroethylene and  
23 tetrachloroethylene concentrations in sediments ranged from 0 to 181 µg/kg and 0 to 4,529 µg/kg,  
24 respectively. Six electrodes were placed in the ground in a 9 m (30 ft) diameter area in a hexagonal  
25 pattern. An extraction well was placed in the center of the hexagon. Approximately 3.8 to 7.6 L/hr  
26 (1 to 2 gal/hr) of water with 500 mg/L sodium chloride were added at each electrode to replenish  
27 evaporated water and provide an electrically conductive solution. The soil surrounding each electrode was  
28 supplied with water through a drip system. A vacuum system removed contaminant vapors from the  
29 subsurface, which were passed through a condenser to remove the steam. The extracted VOCs were  
30 treated by electrically heated catalytic oxidation. Key results of the demonstration at SRS indicate  
31 99.7 percent removal of contaminants from within the electrode array. Outside the array, 93 percent of  
32 contaminants were removed at a distance of 2.4 m (8 ft) from the array. Clays were heated more rapidly  
33 than the adjacent sands because of their higher moisture content and electrical conductivity. Completion  
34 of a cost-benefit analysis by Los Alamos National Laboratory showed that six-phase soil heating could be  
35 performed for a cost of \$88 per yd<sup>3</sup>, assuming that a contaminated site of 30 m (100 ft) in diameter and  
36 6 to 36 m (20 to 120 ft) deep could be remediated in 5 years.

37 A full-scale thermal conductive heating treatment system was operated at a confidential chemical  
38 manufacturing facility in Portland, Indiana from July to December 1997 (EPA, 2003). The two target  
39 treatment areas were 45 × 12 m (150 × 50 ft) to a depth of 5 m (18 ft), and 9 × 6 m (30 × 20 ft) to a depth  
40 of 3.4 m (11 ft). Target source areas contained trichloroethylene up to 79 mg/kg and tetrachloroethylene  
41 up to 3,500 mg/kg. The site geology included fill, a combination of sand and clayey sand, and  
42 construction debris to a depth of about 2 m (7 ft). Till consisting of moist, damp, silty clay extended to  
43 a depth ranging from 5.4 to 5.7 m (18 to 19 ft), with sand seams running through the till. Below the till  
44 was a sand and gravel layer extending to a depth of 9 m (30 ft) and consisting of poorly sorted sand.  
45 Groundwater was encountered in the sand and gravel layer at depths of 6.7 to 7.6 m (22 to 25 ft).  
46 Heater/vacuum wells were installed on a 2.2 m (7.5 ft) triangular spacing with approximately one well per

1 15 m<sup>2</sup> (50 ft<sup>2</sup>) of surface area treated. Wells were operated at 760 to 871°C (1,400 to 1,600°F), and soil  
2 gas was extracted through the wells using a vacuum pump. The surface area between wells was covered  
3 by an impermeable silicone rubber sheet to prevent fugitive emissions, and thermally insulated mats were  
4 used to minimize surface heat loss. The maximum soil temperature in the treatment area at a depth of  
5 13 ft (3.96 m) ranged from 100 to 260°C (212 to 500°F). Offgases were treated with a 1,800 scfm  
6 flameless thermal oxidizer with an operating temperature range of 982 to 1,037°C (1,800 to 1,900°F).  
7 Results of confirmatory sampling showed that concentrations of tetrachloroethylene and trichloroethylene  
8 in both areas were reduced to below the cleanup goals of 8 mg/kg for tetrachloroethylene and 25 mg/kg  
9 for trichloroethylene.

#### 10 **11.4.2.3 Evaluation and Screening Rationale**

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

#### 15 **11.4.3 In Situ Vitrification**

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

##### 18 **11.4.3.1 Description**

19 Vitrification processes are solidification methods that use temperatures between 1,200 and 2,000°C  
20 (2,200 to 3,600°F), depending on the composition of the mixture being melted, to melt and convert waste  
21 materials into glass or other glass and crystalline products. In addition to solids, waste materials can be  
22 liquids, wet or dry sludges, or combustible materials. Borosilicate and soda lime are the principal glass  
23 forming components and provide the basic matrix of the vitrified product. Offgases generated by the  
24 process are contained under a hood covering the treatment area and are drawn to an offgas treatment  
25 system. Organic contaminants are destroyed by pyrolysis, which occurs as the temperature increases  
26 before the actual melting, and by catalytic dechlorination reactions, which occur as contaminated soil  
27 approaches melt temperatures under reducing conditions. Heavy metals and radionuclides are distributed  
28 throughout the melt because of the relatively low viscosity of the molten glass and the convective flow  
29 that occurs within the melt. When electrical current is removed, the molten mass cools and solidifies into  
30 a vitreous rock (like a monolith with excellent physical, chemical, and weathering properties).  
31 The resulting product typically is 10 times stronger than concrete, and 10 to 100 times more resistant to  
32 leaching than glasses typically used to immobilize high-level wastes. The radionuclides and heavy metals  
33 are retained within the melt.

34 In situ vitrification involves passing current through the soil using an array of electrodes. If the soil is too  
35 dry, enhancements must be placed to provide an initial flow path for the electrical current. Large areas are  
36 treated by fusing together multiple vitrification treatment zones (*Remediation of Metals-Contaminated  
37 Soil and Groundwater* [TE-97-01]). To accommodate soil densification, clean overburden is placed over  
38 the melt zone before the melt is initiated, thereby avoiding subsidence issues while increasing thermal  
39 efficiency and radionuclide retention. Excessive water vapor passing through the melt might disrupt or  
40 displace the melt; therefore, soil with high moisture content must be treated to remove water prior to in  
41 situ vitrification. The process requires 700 to 900 kWh/ton of soil to be treated, including soil water.  
42 The overall oxide composition of the soil determines the fusion, melt temperature, and viscosity.  
43 In addition, it is essential that the media contain sufficient monovalent alkali earth oxides to provide the  
44 electrical conductivity required (*Central Plateau Vadose Zone Remediation Technology Screening  
45 Evaluation* [RPP-ENV-34028]).

1 **11.4.3.2 Relevant Demonstration Projects**

2 In 1980, when the in situ vitrification process was conceived of by PNNL for DOE, and up through 1997,  
3 more than 200 tests, demonstrations, and commercial operations of the technology have been conducted  
4 (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation* [RPP-ENV-34028]).

5 A 1997 DOE case study abstract document, *Case Study Abstract: In Situ Vitrification*, presented  
6 information on a case study conducted at the Hanford Site. Information specific to this case study is  
7 limited; however, it does specify that a Toxic Substances Control Act demonstration showed destruction  
8 and removal efficiency for PCBs of greater than 99.9999 percent (EPA, 1997).

9 A large-scale in situ vitrification test was completed at the 116-B-6A Crib site in 1990 (*In Situ*  
10 *Vitrification of a Mixed-Waste Contaminated Soil Site: The 116-B-6A Crib at Hanford* [PNL-8281]).  
11 The site contained mixed waste (chromium, lead, and cesium-137) at an approximate depth of 6 m  
12 (20 ft) bgs. The treatability test consumed 550 MWh of electrical energy, and resulted in a 771 tonne  
13 (850 ton) block of vitrified soil. Results from data collection indicated the vitrified block retained more  
14 than 99.99 percent of chromium and lead, and more than 99.98 percent of cesium-137, indicating the  
15 favorable resistance of the treated material to leaching. Results also indicated greater treatment depths  
16 were in homogeneous soil. The final depth achieved during the treatability test was 4.3 m (14 ft), which is  
17 18 m (6 ft) less than the required treatment depth. The 4.3 m (14 ft) vitrified depth coincided with a  
18 cobble layer detected below the crib during the post-treatment core drilling. The rate of melt progression  
19 above the cobble layer was satisfactory, indicating the effect of the cobble layer on the achieved treatment  
20 depth (*In Situ Vitrification of a Mixed-Waste Contaminated Soil Site: The 116-B-6A Crib at Hanford*  
21 [PNL-8281]).

22 Geosafe Corporation licensed the technology from PNNL and has applied it commercially. In 1995,  
23 Geosafe Corporation evaluated the application of in situ vitrification under the U.S. Environmental  
24 Protection Agency (EPA) Superfund Innovative Technology Evaluation Program at the former site of  
25 Parsons Chemical Works, Inc. in Grand Ledge, Michigan (*Geosafe Corporation In Situ Vitrification,*  
26 *Innovative Technology Evaluation Report* [EPA/540/R-94/520]). The technology evaluation report  
27 summarized the findings associated with a demonstration of the in situ vitrification process and its ability  
28 to treat pesticides and mercury below EPA Region V mandated limits. The technology was evaluated  
29 against the nine *Comprehensive Environmental Response, Compensation, and Liability Act of 1980*  
30 feasibility study guidance criteria for decision making in a Superfund facility. In situ vitrification was  
31 considered effective in destroying organic contamination, immobilizing inorganic material, and reducing  
32 the likelihood of contaminants leaching from the treated soil. Among some of the limitations, the report  
33 stated that in situ vitrification is not recommended for sites that contain organic content greater than  
34 7 to 10 percent by weight, metal content greater than 25 percent by weight, and inorganic contaminants in  
35 excess of 20 percent by volume (EPA, 1995). The report also noted that in situ vitrification would not be  
36 appropriate for sites where contaminated soil exists adjacent to buildings, other structures, or the  
37 property line.

38 A subsurface planar method was recently applied in a demonstration project to treat a portion of a mixed  
39 low-level radioactive liquid waste adsorption bed at the Los Alamos National Laboratory's MDA-V site  
40 (*Demonstration of Non-Traditional In Situ Vitrification Technology at Los Alamos National Laboratory*  
41 [Huddleston et al., 2003]). Nontraditional planar in situ vitrification uses the same general process as that  
42 used in traditional in situ vitrification; however, it involves joule-heated melting within the subsurface. In  
43 contrast to the horizontally oriented melt normally started at or near the surface, this process establishes  
44 two vertically oriented planar melts in the subsurface between pairs of electrodes. The planar melts can be  
45 initiated at the desired depth and separation within the subsurface, depending on the target treatment  
46 volume (*Central Plateau Vadose Zone Remediation Technology Screening Evaluation*

1 [RPP-ENV-34028]). *Demonstration of Non-Traditional In Situ Vitrification Technology at Los Alamos*  
2 *National Laboratory* (Huddleston et al., 2003) indicated an average treatment depth of 7.9 m (26 ft) bgs at  
3 the electrode locations. Radioactive contaminants were seen to have been distributed uniformly through  
4 the melt, and concentrations were reduced by more than an order of magnitude (*Demonstration of*  
5 *Non-Traditional In Situ Vitrification Technology at Los Alamos National Laboratory*  
6 [Huddleston et al., 2003]).

### 7 **11.4.3.3 Evaluation and Screening Rationale**

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

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

## 20 **11.4.4 Phytoremediation**

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

### 23 **11.4.4.1 Description**

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

### 29 **11.4.4.2 Relevant Demonstration Projects**

30 A treatability demonstration project is being conducted at the Hanford Site for treatment of strontium-90  
31 in soil and groundwater along the banks of the Columbia River in 100-N using coyote willows.

32 The coyote willow is considered the most suitable plant for use along the Columbia River shore. Known  
33 for its rapid and robust re-growth abilities, coyote willow is used extensively along the Columbia and  
34 Yakima Rivers for bank stabilization and revegetation purposes. As part of a treatment train of remedial  
35 technologies aimed at treating strontium-90 in 100-BC, phytoremediation using coyote willow would be  
36 the final polishing step.

37 A pilot study began in the late spring of 2007, with the planting of 50 coyote willow starts in a fenced  
38 area at 100-K (*100-N Area Strontium-90 Treatability Demonstration Project: Food Chain Transfer*  
39 *Studies for Phytoremediation Along the 100-N Columbia River Riparian Zone* [PNNL-18294]; *Project*  
40 *Work Plan 100-N Area Strontium-90 Treatability Demonstration Project: Phytoremediation Along the*  
41 *100-N Columbia River Riparian Zone* [PNNL-SA-49953]). This part of the study targeted plant growth  
42 rather than phytoremediation capabilities because this location is not contaminated with strontium-90.

1 Often flooded well into June because of the annual high Columbia River stage, this site is a severe test of  
2 the coyote willow shrubs' ability to survive realistic field conditions.

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

14 The phytoremediation demonstration is ongoing at 100-K. Biomass production over the first 3 years  
15 followed a typical growth curve. On an mT/ha basis, biomass production amounted to 0.2 mT/ha in 2007,  
16 0.87 mT/ha in 2008, and 4.3 mT/ha in 2009. Growth curve extrapolation predicts 13.2 mT/ha during  
17 a fourth year and potentially 29.5 mT/ha during a fifth year. The most recent report concludes that the  
18 projected biomass yields suggest the trees could prove effective in removing strontium-90 from the  
19 100-NR-2 riparian zone (*100-N Area Strontium-90 Treatability Demonstration Project: Phytoextraction  
20 Along the 100-N Columbia River Riparian Zone—Field Treatability Study* [PNNL-19120]).

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

#### 27 **11.4.4.3 Evaluation and Screening Rationale**

28 Implementability of phytoremediation is considered moderate. It is usually implemented over extended  
29 time scales, such as years or decades. The sparse vegetation that naturally grows on the Hanford Site  
30 suggests that significant efforts and inputs (such as organic matter and water) would be required to  
31 establish a vigorous plant community. Although a large quantity of plant material would likely be  
32 required, capital costs relative to other technologies are low. Once the plants are established, O&M costs  
33 would be relatively low because requirements to sustain them are low (food and water). However, metals  
34 concentrations and radionuclide activities may accumulate in the plants to the point that they must  
35 periodically be disposed of in a secure facility, such as ERDF. Because they decompose, the plants  
36 eventually would require final disposal at ERDF or the like to avoid returning contaminants to the soil  
37 from which they were originally extracted, if phytoremediation is used for contaminants that are not  
38 transformed to innocuous forms by the plants or microorganisms.

39 Phytoremediation is effective only when the plants are active; therefore, the technology would not be  
40 effective during the winter. In addition, phytoremediation is only effective to the approximate depth of the  
41 plant roots; thus, only shallow soil would be treated. There are also concerns about contaminants entering  
42 the food chain as animals eat the vegetation or bees pollinate flowers.

43 In summary, the technology would only be effective for low concentrations of contaminants in shallow  
44 soil over long periods, and many metals and radionuclides would accumulate in the plants rather than

1 being treated, posing risks to ecological receptors. For these reasons, phytoremediation was not retained  
2 for further evaluation.

### 3 **I1.5 Containment**

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

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

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

##### 10 **I1.5.1.1 Description**

11 Emplaced horizontal barriers are situated beneath existing in situ contaminants. These bottom barriers  
12 have features similar to those of vertical barriers in that they minimize movement of contaminants, restrict  
13 infiltration of groundwater, and are constructed of similar materials using similar technologies. Horizontal  
14 barrier technologies can include (*Central Plateau Vadose Zone Remediation Technology Screening*  
15 *Evaluation* [RPP-ENV-34028]) the following:

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

##### 26 **I1.5.1.2 Relevant Demonstration Projects**

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

##### 31 **I1.5.1.3 Evaluation and Screening Rationale**

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

## 1 **11.5.2 Dynamic Compaction**

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

### 4 **11.5.2.1 Description**

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

### 8 **11.5.2.2 Evaluation and Screening Rationale**

9 The technology is considered to have moderate-to-high effectiveness. It is effective in removing void  
10 spaces and compacting surface soil where voids exist around buried waste; however, it is not an effective  
11 containment process option for native soil or treatment of hazardous wastes. Implementability is high,  
12 given that the technology is simple and widely used. However, because no waste sites containing solid  
13 and buried waste are present at the treatment area, this process option was not retained.

## 14 **12 Additional Information on Technologies Not Retained** 15 **for Groundwater Treatment**

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

### 18 **12.1 Ex Situ Treatment**

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

#### 22 **12.1.1 Ex Situ Chemical Precipitation**

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

##### 25 **12.1.1.1 Description**

26 Ex situ chemical precipitation involves the introduction of chemicals to transform dissolved contaminants into  
27 insoluble solids, which are removed by sedimentation and filtration. Chemicals used to remove Cr(VI) can  
28 include ferrous chloride, ferrous sulfide, zero-valent iron, sulfur dioxide, and various sulfites (*Remedial*  
29 *Process Optimization for the 100-D Area Technical Memorandum Document* [SGW-38338], Section 4.2).  
30 Ferrous iron is commonly used for industrial wastewaters, such as those from metal plating. Carbon-14,  
31 which is typically in chemical forms of carbonate and bicarbonate depending on the pH (“Management of  
32 Waste Containing Tritium and Carbon-14” [IAEA, 2004]), can be removed by raising the pH of the  
33 water. Effective post-treatment for solids removal, but conditioning is required. Solids removal typically  
34 includes flocculation or coagulation, settling, and filtration. Sludge handling, dewatering, and disposal are  
35 also required. The volume or mass of the sludge generated can be extremely large and would need final  
36 disposal at ERDF. Site-specific jar testing would be required to obtain design and operational parameters.

##### 37 **12.1.1.2 Relevant Demonstration Projects**

38 A remediation process optimization evaluation was performed for 100-D with a goal of reducing the cost  
39 and improving the performance of the existing ex situ ion exchange groundwater treatment systems  
40 (*Remedial Process Optimization for the 100-D Area Technical Memorandum Document* [SGW-38338],

1 Chapter 6). Design criteria, preconceptual designs, and rough order-of-magnitude cost estimates were  
2 developed for three technologies: ion exchange with onsite regeneration, ion exchange with offsite  
3 regeneration, and ferrous chloride reduction. The technology with the lowest estimated O&M cost was  
4 ion exchange with onsite regeneration, followed by the ferrous chloride process, whose estimated O&M  
5 costs are approximately 20 percent higher. By far, the largest solid waste stream is generated by the  
6 ferrous chloride process, whose annual solid waste mass is approximately 4 times that of ion exchange  
7 with onsite regeneration, and more than 60 times that of ion exchange with offsite regeneration.

### 8 **12.1.1.3 Evaluation and Screening Rationale**

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

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

### 21 **12.1.2 Electrocoagulation**

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

#### 24 **12.1.2.1 Description**

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

#### 30 **12.1.2.2 Relevant Demonstration Projects**

31 A 2007 treatability test evaluated the potential for this technology for 100-D of the Hanford Site  
32 (*Treatability Test Report for the Removal of Chromium from Groundwater at 100-D Area Using*  
33 *Electrocoagulation* [DOE/RL-2008-13]). The test objectives were the following:

- 34 • Determine the operability, robustness, and treatment efficiency of an electrocoagulation system.
- 35 • Characterize the volume and composition of the resulting waste;.
- 36 • Obtain design data for scaling the process from a 190 L/min (50 gal/min) to a 1,900 L/min  
37 (500 gal/min) system.

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

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

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

### 11 **12.1.2.3 Evaluation and Screening Rationale**

12 The effectiveness of electrocoagulation for the 100 Area is anticipated to be low or moderate, particularly  
13 in light of the challenges encountered in the pilot test. The technology is not widely used for Cr(VI),  
14 although it may be applicable to technetium-99; however, the technetium-99 plume is small, so the  
15 benefit would not be significant, and additional challenges related to the reversible potential of  
16 technetium-99 reduction may result. Implementability is also considered low or moderate because further  
17 development of the process would be required. In addition, the process may render the treated water less  
18 suitable for re-injection. Capital costs are moderate or high, and O&M costs are moderate. Part of the high  
19 cost results from the production of significant volumes of sludge that must be managed and disposed of.  
20 The costs for electrocoagulation do not appear to be any lower than costs for the existing ion exchange  
21 systems. Because of poor performance, poor implementability, and high cost, the technology was not  
22 retained for further evaluation.

### 23 **12.1.3 Wetlands**

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

#### 25 **12.1.3.1 Description**

26 Constructed wetlands can be described as artificial swamps that act as biofilters for removing  
27 contaminants, which are common processes in wastewater treatment. A constructed wetland typically  
28 would require a much larger area and a much longer hydraulic retention time compared to a bioreactor,  
29 but it typically would not require added nutrients and would require less operational oversight.

30 Wetlands are used to treat groundwater, industrial wastewater, and municipal wastewater. Cr(VI) can be  
31 removed in wetlands primarily by microbiological and chemical reduction. Some Cr(VI) uptake by  
32 wetland plants may also occur. The plants also function as a method of regenerating the reducing  
33 sediments by dying and falling to the bottom (Xu and Jaffe, 2006).

34 Wetlands can also be used to treat other COPCs, such as nitrate, petroleum, and trichloroethylene. Several  
35 removal mechanisms have been identified for treatment of nitrate in water, such as decomposition,  
36 nitrification/ denitrification, settling, volatilization, adsorption, and nutrient uptake (*Literature Survey for*  
37 *Groundwater Treatment Options for Nitrate, Iodine-129, and Uranium, 200-ZP-1 Operable Unit,*  
38 *Hanford Site* [SGW-37783]). Biodegradation is an important mechanism for removal of petroleum  
39 hydrocarbons, and uptake by plants is an important mechanism for removal of trichloroethylene.  
40 Phytoremediation (one component of wetland treatment) has been used to treat strontium-90, but it is not  
41 known to treat other radionuclides (*Alternative Remediation Technology Study for Groundwater*  
42 *Treatment at 200-PO-1 Operable Unit at Hanford Site* [SGW-34562]).

### 1 **12.1.3.2 Relevant Demonstration Projects**

2 A number of demonstration projects use wetlands to remove nitrates (*Literature Survey for Groundwater*  
3 *Treatment Options for Nitrate, Iodine-129, and Uranium, 200-ZP-1 Operable Unit, Hanford Site*  
4 [SGW-37783]). For example, a constructed wetland is used to remove nitrate from the municipal drinking  
5 water supply in Orange County, California. Up to 1.5 m<sup>3</sup>/s (33 million gal/day) were treated prior to  
6 groundwater recharge. The influent contained 3.1 to 10.9 mg/L of nitrate as nitrogen. The average nitrate  
7 removal was 522 mg (0.018 oz) of nitrate as nitrogen per m<sup>2</sup>/day, and exiting nitrate concentrations  
8 sometimes fell to as low as 0.1 mg/L nitrate as nitrogen, with hydraulic detention times from  
9 0.3 to 9.6 days. Bacterial denitrification was concluded to be the primary nitrate loss mechanism.  
10 A review of 19 surface flow wetlands showed that nearly all reduced total nitrogen. A comparison of  
11 surface and subsurface flow wetlands showed that subsurface flow wetlands outperformed surface flow  
12 wetlands and yielded lower effluent nitrate concentrations (ranging from less than 1 to less than 10 mg/L).

### 13 **12.1.3.3 Evaluation and Screening Rationale**

14 The land area required for wetlands is likely to be very large for the volume of groundwater that will be  
15 produced by the 100 Area pump-and-treat systems, even under favorable (warm) conditions. Even more  
16 area would be required for effective treatment in the winter, when plants and microorganisms in the  
17 wetland would be less active. Problems with freezing would be likely, as average minimum temperatures  
18 are below freezing more than half of the year (*Hanford Site National Environmental Policy Act [NEPA]*  
19 *Characterization* [PNNL-6415]). Therefore, the technology is not well suited to the climate at the  
20 Hanford Site. The effectiveness of this technology at the site is considered moderate because additional  
21 research and testing would be required to verify the effectiveness of this technology for COPCs other than  
22 nitrate. Implementability is considered low to moderate. Construction of wetlands at the Hanford Site  
23 would require lining to prevent the infiltration of the water and provision of organic substrate to support  
24 wetland plants. Wetland treatment does not have significant advantages over ion exchange, which is  
25 already in place and performing well.

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

### 30 **12.1.4 Bioreactors**

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

#### 33 **12.1.4.1 Description**

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

#### 38 **12.1.4.2 Relevant Demonstration Projects**

39 There are few reported applications of ex situ bioreactors specifically for Cr(VI) (“Preliminary Studies on  
40 Continuous Chromium(VI) Biological Removal from Wastewater by Anaerobic-Aerobic Activated  
41 Sludge Process” [Chen and Gu, 2005]). However, bioreactors for nitrate removal have been pilot tested at  
42 the Hanford Site in the past (*Development of a Biological Treatment System for Hanford Groundwater*  
43 *Remediation: FY 1989 Status Report* [PNL-7290]). A pilot-scale test was conducted in 1989 using  
44 simulated Hanford Site groundwater with a continuous stirred-tank bioreactor. The continuous

1 stirred-tank bioreactor system was operated continuously for 5 months with a simulated groundwater  
2 influent containing 400 mg/L of nitrate. Using acetate as the primary carbon source for microbial growth,  
3 a nitrate removal efficiency of greater than 99 percent was maintained at an influent flow rate of 6 L/hr  
4 (8-hour residence time).

5 The biological processes involved in biological treatment of Cr(VI) are similar to those involved in other  
6 bioreactor concepts used in the remediation industry, such as sulfate-reducing bioreactors that are used to  
7 treat acid mine drainage. Based on case studies for sulfate-reducing bioreactors, the effectiveness of  
8 bioreactors has been demonstrated at temperatures between 2 and 16°C (“Passive Treatment of Acid Mine  
9 Drainage in Bioreactors Using Sulfate-Reducing Bacteria: Critical Review and Research Needs”  
10 [Neculita et al., 2007]). Daily average low temperatures at the Hanford Site are typically below 0°C  
11 (32°F) during the winter months, which may necessitate heating/insulating portions of the ex situ  
12 bioreactor system to maintain the viability of the microbes.

### 13 ***12.1.4.3 Evaluation and Screening Rationale***

14 Bioreactors are commonly used for nitrate removal, and the Hanford Site pilot test was successful.  
15 Bioreactors for Cr(VI) and other COPCS, however, are less common, and have not been tested at the Hanford  
16 Site. Therefore, there is uncertainty in the performance ability of this technology.

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

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

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

### 25 ***12.1.5 Phytoremediation***

26 Phytoremediation was not retained for treatment of groundwater and soil contaminated with Cr(VI) or  
27 other COPCs. Additional information on this process can be found in Section II.2.2.4.

#### 28 ***12.1.5.1 Description***

29 For groundwater, phytoremediation is limited to the depth at which the plants can extract water. Water cannot  
30 be wicked and delivered vertically more than about 6 m (20 ft) deep; thus, the potentiometric surface must be  
31 within 3 or 6 m (10 or 20 ft) of the bottom of the root mass for this system to be viable (*Enhanced*  
32 *Attenuation: Approaches to Increase the Natural Treatment Capacity of a System*  
33 [WSRC-TR-2005-00198]). Because of this limitation, unless groundwater was first extracted by pumping  
34 and then phytoremediated (that is, the plants would be irrigated with the contaminated groundwater),  
35 phytoremediation would not be suitable for groundwater remediation at the Hanford Site except  
36 immediately adjacent to the river. There are methods of encouraging plant roots to grow deeper but not to  
37 the depths that would be required at most of the 100 Area of the Hanford Site. Phytoremediation systems,  
38 including by land application, are only operational when the soil is warm and plants are active, so  
39 treatment effectiveness would be reduced in the winter. The land requirements for phytoremediation are  
40 also relatively large.

1 **I2.1.5.2 Relevant Demonstration Projects**

2 Uptake of Cr(VI) by a variety of plants has been documented (“Enhancement of Cr(III)  
3 Phytoaccumulation” [Shahandeh and Hossner, 2000]). Hexavalent chromium can accumulate in the plants  
4 and may become toxic to them. A land application/irrigation system has been installed at a confidential  
5 site in California with groundwater containing Cr(VI). Subsurface application of the groundwater is  
6 conducted via a drip irrigation system, and the Cr(VI) is primarily microbially reduced in the shallow soil.

7 Perhaps the best example of deep rooting of trees is at Argonne National Laboratory in Illinois. Hybrid poplars  
8 were deep rooted in treewells, which are plastic-lined holes bored to a depth of 10 m (30 ft). Boreholes were  
9 filled with topsoil and then surface capped, which isolates the tree from surface water and forces the roots to  
10 use contaminated groundwater. Root extension of 3 m (10 ft) has been observed (*Enhanced Attenuation:  
11 Approaches to Increase the Natural Treatment Capacity of a System* [WSRC-TR-2005-00198]).

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

15 **I2.1.5.3 Evaluation and Screening Rationale**

16 Because of the large depth to groundwater at most of the Hanford Site, phytoremediation would be  
17 feasible immediately adjacent to the river only. Therefore, implementability of phytoremediation is considered  
18 low or moderate. It is usually implemented over long-time scales, such as years or decades. The sparse  
19 vegetation that naturally grows on the Hanford Site suggests that significant efforts and inputs, such as organic  
20 matter and water, would be required to establish a vigorous plant community. However, capital costs  
21 would still be relatively low. Once the plants are established, O&M costs would also be low because  
22 requirements to sustain them are minimal (food and water). However, metals concentrations and  
23 radionuclide activities may accumulate in the plants to the point that they must be disposed of periodically  
24 in a secure facility, such as ERDF. Because they decompose, the plants eventually would need to be  
25 disposed of at ERDF to avoid returning contaminants to the soil from which they were originally extracted,  
26 if phytoremediation is used for contaminants that are not transformed to innocuous forms by the plants  
27 or microorganisms.

28 Phytoremediation is only effective when the plants are active; therefore, the technology would not be  
29 effective during the winter. Because of the uncertainty of continued effectiveness throughout the year and  
30 the very limited ability of the plants to root deep enough to affect groundwater in most areas at the  
31 Hanford Site, effectiveness is considered low to moderate. There are also concerns about contaminants  
32 entering the food chain as animals eat the vegetation or bees pollinate flowers. In summary, the  
33 technology would only be effective for low concentrations of contaminants where groundwater is shallow  
34 over long periods, and many metals and radionuclides would accumulate in the plants and not actually be  
35 treated, thus posing risks to ecological receptors. For these reasons, phytoremediation was not retained for  
36 further evaluation.

37 **I2.1.6 Membrane Separation (Reverse Osmosis)**

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

40 **I2.1.6.1 Description**

41 RO is a pressure-driven process that uses semipermeable membranes to purify water. Contaminated water  
42 is passed through the membrane while the contaminants are contained within the membrane. The water  
43 that is allowed to pass through the membrane is called the permeate and typically contains only a small

1 fraction (less than 5 percent) of the ions in the feed solution. The water that does not pass through the  
2 membrane (containing the ions that do not pass through the membrane) is called the retentate or brine,  
3 concentrate, or reject. The retentate has a high total dissolved solids concentration and would contain  
4 most of the COPCs being treated. With appropriately sized membranes and multiple stages of  
5 membranes, very low concentrations of ions can be achieved. RO is among the technologies that EPA  
6 considers effective for removing total chromium to below 100 µg/L, along with coagulation/filtration, ion  
7 exchange, and lime softening (“Basic Information on Chromium in Drinking Water” [EPA, 2010]). In  
8 addition to chromium, other COPCs that RO can remove include nitrate, trichloroethylene, some VOCs,  
9 and some petroleum compounds (*Drinking Water Treatment: Reverse Osmosis* [Dvorak and Skipton,  
10 2008]). In New Hampshire, the typical production efficiency of RO for nitrate removal is approximately  
11 25 percent. That is, for every 15 L (4 gal) of untreated water entering the device, only 3.7 L (1 gal) of  
12 treated water is produced (*Nitrate/Nitrite in Drinking Water* [WD-WSEB-3-9]). This low efficiency is  
13 a result of New Hampshire’s cold groundwater temperatures, which are likely similar to groundwater  
14 temperatures at the Hanford Site.

15 RO for removal of strontium-90 “shows promise” (*Environmental Engineers’ Handbook* [Liu and Lipták,  
16 1997]), and a later study (*Environmental Technology Verification Joint Verification Statement for*  
17 *Ecowater Systems ERO-R450E Point-of-Use Drinking Water Treatment System* [EPA and NSF, 2005])  
18 showed 97 percent removal (from 960 to 33 µg/L) of strontium by RO. No commercially available  
19 treatment option is available to remove tritium from groundwater (*Groundwater Treatment at SRS: An*  
20 *Innovative Approach* [WSRC-RP-97-849]).

21 Brine production is a significant issue with RO; the need to minimize and manage (for example,  
22 evaporate) the brine can lead to significant increases in water treatment costs. RO is commonly used to  
23 desalinate seawater, which typically generates greater volumes of brine than amounts generated when  
24 treating groundwater; however, in this application, the brine can simply be returned to the seawater.  
25 Nano-filtration is very similar to RO but uses membranes with large openings (EPA 815-R-06-009,  
26 *Membrane Filtration Guidance Manual*). Options for managing brine and other process residuals include  
27 discharge to a suitable surface water body, discharge to a sanitary sewer, deep well injection, land  
28 application, or treatment with supernatant recycle and solids disposal. The treatment processes can  
29 include clarification, sedimentation in lagoons, gravity thickening, centrifuging, belt filter pressing, and  
30 evaporation (*Membrane Filtration Guidance Manual* [EPA 815-R-06-009]).

### 31 **12.1.6.2 Relevant Demonstration Projects**

32 A process was bench tested at the 200 West Area of the Hanford Site that combines three different  
33 membrane technologies: RO, coupled transport, and nano-filtration. These technologies were used to  
34 purify 72 L (19 gal) of groundwater while extracting and concentrating uranium, technetium, and nitrate  
35 into separate solutions (significant Cr(VI) concentrations were not present). This separation allows for the  
36 future use of the radionuclides, if needed, and reduces the amount of waste that will need to be disposed  
37 of. This process has the potential to concentrate the contaminants into solutions with volumes in a ratio of  
38 1 to 10,000 of the feed volume, compared to a volume reduction ratio of 10 to 100 for ion exchange and  
39 stand-alone RO (*Testing of a Benchscale Reverse Osmosis/Coupled Transport System for Treating*  
40 *Contaminated Groundwater* [WHC-SA-2755-FP]). The experiment demonstrated the effectiveness of the  
41 process as theorized for all ions except for technetium, suggesting that design modifications may  
42 be necessary.

43 The Effluent Treatment Facility in the 200 East area of the Hanford Site treats liquid effluent to remove  
44 toxic metals, radionuclides, and ammonia, and to destroy organic compounds. The treatment process  
45 constitutes best available technology and includes pH adjustment, filtration, ultraviolet light, and  
46 hydrogen peroxide destruction of organic compounds, RO to remove dissolved solids, and ion exchange

1 to remove the last traces of contaminants. The facility began operating in December 1995. The maximum  
2 treatment capacity of the facility is 570 L/min (150 gal/min) (*Hanford Site Environmental Report for*  
3 *Calendar Year 2008* [PNNL-18427]).

4 A pilot test of RO with vibratory shear-enhanced processing (VSEP<sup>1</sup>) to minimize brine production was  
5 conducted at a Central Arizona Project water treatment plant (*Reverse Osmosis Treatment of Central*  
6 *Arizona Project Water—Brine Minimization Via Vibratory Shear-enhanced Processing* [Corral and  
7 Yenal, 2009]). Whereas brine production without VSEP was approximately equal to 20 to 25 percent of  
8 the volume of the water being treated, VSEP reduced brine production to 2 to 4 percent of the initial  
9 volume treated. The cost of VSEP treatment was significant but less than the costs of RO without VSEP  
10 associated with increased brine disposal and lost drinking water supply.

### 11 **I2.1.6.3 Evaluation and Screening Rationale**

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

## 20 **I2.2 Discharge**

21 Discharge process options that were not retained for further consideration in the feasibility study are  
22 discussed below.

### 23 **I2.2.1 Surface Water Discharge under a NPDES Permit**

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

#### 26 **I2.2.1.1 Description**

27 Almost any type of treated groundwater may be discharged to surface water under an NPDES permit.  
28 This is common practice for municipal and industrial wastewaters, as well as groundwater at many  
29 hazardous waste sites. The discharge standards are set based on the flows and water quality in the  
30 receiving stream so that the discharge does not have any adverse impacts on the quality of the stream.  
31 Routine monitoring is required to verify compliance. This monitoring often includes toxicity testing to  
32 evaluate the presence of substances toxic to aquatic organisms. The physical location of the discharge  
33 point can also be designed to minimize impacts to the stream (for example, mid-stream diffusers can be  
34 used to distribute the flow).

#### 35 **I2.2.1.2 Relevant Policy**

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

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<sup>1</sup> VSEP is a registered trademark of New Logic Research, Inc., located in Emeryville, California.

### 1 **12.2.1.3 Evaluation and Screening Rationale**

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

## 8 **12.3 In Situ Treatment**

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

### 11 **12.3.1 In Situ Chemical Reduction**

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

#### 13 **12.3.1.1 Description**

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

#### 18 **12.3.1.2 Relevant Demonstration Projects**

19 A field treatability test was conducted at 100-K during the summer of 2005 to evaluate the effectiveness  
20 of using calcium polysulfide to reduce Cr(VI) in groundwater (*Treatability Test Report for Calcium*  
21 *Polysulfide in the 100-K Area* [DOE/RL-2006-17]). The field test used a "five-spot" configuration, which  
22 involved four injection wells drilled orthogonally around an existing monitoring well from which  
23 groundwater was withdrawn and mixed with calcium polysulfide. This solution then was injected in  
24 approximately equal amounts to set up a circulation cell in the aquifer. The test was conducted for  
25 a period of 45 days. Cr(VI) was eliminated from the treated aquifer, as demonstrated by the lack of Cr(VI)  
26 concentrations in groundwater in the injection wells and extraction well. Measurements of dissolved  
27 oxygen (DO) and oxidation/reduction potential showed that the treated aquifer also was strongly reduced  
28 by the treatment. Analysis of groundwater chemistry before, during, and after the test shows that  
29 manganese, iron, and arsenic were mobilized under the strongly reducing conditions in the aquifer, but all  
30 of these remained far below drinking water standards.

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

#### 37 **12.3.1.3 Evaluation and Screening Rationale**

38 Transportation and handling of reducing agents also pose more of a health and safety concern during  
39 application, as compared to biological reduction substrates. Because of more rapid chemical reactions, the  
40 application of liquid-reducing agents to treat large areas of a plume may be more challenging than using  
41 biological substrates. Based on these implementability and potential effectiveness issues, in situ chemical  
42 reduction was not retained in favor of in situ biological reduction.

## 12.3.2 Hydrogen or Other Organic Gas Sparging

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

### 12.3.2.1 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 gases 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.

### 12.3.2.2 Relevant Demonstration Projects

A propane biosparging field demonstration was conducted at the National Environmental Technology Test Site in Port Hueneme, California, from May 2001 to March 2002 (TR-2230-ENV, *Cost and Performance Report In-Situ Remediation of MTBE Contaminated Aquifers Using Propane Biosparging*). 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 composed of sands, silts, clays, and small amounts of gravel and fill material. The uppermost water-bearing unit was a shallow, semi-perched, unconfined aquifer (upper silty sand, underlain by fine to coarse grain sand, and a basal clay layer). Depth to groundwater ranged from 1.8 to 2.4 m (6 to 8 ft) bgs, and the saturated aquifer thickness was 4.8 to 5.4 m (16 to 18 ft).

The field demonstration area (27 × 18 m [90 × 60 ft]) included a test plot consisting of seven propane injection points, 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<sup>3</sup>/hr to between 0.0085 and 0.0113 m<sup>3</sup>/hr (1 standard ft<sup>3</sup>/hr to between 0.3 and 0.4 standard ft<sup>3</sup>/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.

### 12.3.2.3 Evaluation and Screening Rationale

This technology is a direct competitor to that of supplying 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 of sparge wells is likely to be relatively small, so that 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.

1 **12.3.3 Groundwater Circulation Wells**

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

4 **12.3.3.1 Description**

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

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

14 The zone of influence that can be achieved with groundwater circulation wells is highly sensitive to site  
15 lithologic conditions. A viable circulation cell may not develop if vertical anisotropy in lithology (that is,  
16 the presence of laterally extensive silty-clay layers) impedes the circulation flow path or if there is not  
17 enough anisotropy. Typically, this technology will not be successful when the ratio of horizontal to  
18 vertical hydraulic conductivity is greater than 10 (“Groundwater Circulating Well Technology  
19 Assessment” [Spargo et al., 1999]). A single thin layer of low-permeability material can also prevent  
20 development of a recirculation cell. If the anisotropy is too low, the radius of the circulation cell will be  
21 very small; this could be the case at the Hanford Site. Other common problems include well clogging  
22 resulting from changing redox conditions within the groundwater circulation well and down-well  
23 equipment (for example, packers) problems.

24 **12.3.3.2 Relevant Demonstration Projects**

25 A summary and analysis of more than 50 groundwater circulation well field demonstrations were  
26 provided in “Groundwater Circulating Well Technology Assessment” (Spargo et al., 1999). One case  
27 study was a groundwater circulation well demonstration sponsored by the DoD that was originally  
28 scheduled to be performed at the Hanford Site but was relocated to Edwards Air Force Base OU 1, Site  
29 19. This site was selected based on its high hydraulic conductivity (KH = 10 ft/d, KV = 1 ft/d) and the  
30 presence of trichloroethylene contamination. One groundwater circulation well was installed to 15 m  
31 (50 ft) bgs and operated for 191 days during the demonstration. Results of the demonstration indicate  
32 a radius of influence of approximately 9 m (30 ft), an asymmetrical circulation cell, and groundwater flow  
33 short-circuiting near the groundwater circulation well. Post-operation data showed contaminant rebound  
34 in monitoring wells.

35 Of the remaining groundwater circulation well case studies, few sites demonstrated clear success, and at  
36 just as many sites, the technology failed to meet remedial objectives. However, most of the case studies  
37 indicated that the data collected were insufficient to demonstrate the efficacy of the groundwater  
38 circulation well technology.

39 **12.3.3.3 Evaluation and Screening Rationale**

40 It is likely that a large number of wells would be required to implement this technology at the Hanford  
41 Site because of the highly permeable nature of the site lithology, which would result in a small radius of  
42 influence. Even if implemented with tight well spacing, variable lithology could cause asymmetrical  
43 groundwater flow or groundwater flow short-circuiting, and contaminant rebound would ultimately limit

1 the effectiveness of groundwater circulation wells. Given the high cost of installing wells and the  
2 likelihood of limited treatment effectiveness, this technology was not retained for further evaluation.

### 3 **12.3.4 Horizontal Wells**

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

#### 6 **12.3.4.1 Description**

7 Horizontal wells are horizontally drilled or trenched screened borings installed along or across the  
8 plumes. Horizontal wells can be used to extract soil vapor and groundwater, or to inject water, chemical  
9 reagents, or biological substrates. Horizontal well technology has been incorporated into many current  
10 environmental remediation applications (and associated contaminants), such as in situ bioremediation, air  
11 sparging, vacuum extraction, soil flushing, and free product recovery. This technology is most applicable  
12 to sites with relatively shallow soil and/or groundwater contamination and can potentially enhance  
13 remediation efforts at sites with low hydraulic conductivities (*Technology Overview Report: Horizontal*  
14 *Wells* [TO-96-02]).

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

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

#### 22 **12.3.4.2 Relevant Demonstration Projects**

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

29 Installation of surface casing was required to facilitate circulation of drilling mud in the porous Hanford  
30 formation. The casing was advanced with significant difficulty to approximately 6 m (20 ft) bgs (25 m  
31 (85 horizontal linear ft) when downward progress ceased because of inadequate force on the downhole  
32 hammer and difficulty removing cuttings from the inclined casing. Rotary mud directional drilling  
33 through the casing and into the Hanford formation was attempted, but progress was slow and circulation  
34 was never established.

#### 35 **12.3.4.3 Evaluation and Screening Rationale**

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

## 38 **12.4 Containment**

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

1 **I2.4.1 Containment Wall**

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

4 **I2.4.1.1 Description**

5 Containment walls include soil bentonite slurry walls, grout walls, and sheetpile walls. Walls have been  
6 used successfully to assist with hydraulic containment of groundwater plumes at many hazardous waste  
7 sites. Groundwater pumping or diversion upgradient from the containing wall is required to prevent  
8 groundwater mounding and bypassing of the wall. Containment walls increase the potential to achieve  
9 effective hydraulic containment, and they may reduce the amount of water that requires treatment.

10 Installation methods include conventional or continuous trenching with soil/bentonite slurry, vibrating  
11 beam cutoffs, mixed-in-place walls, tangent caisson walls, and driven sheet piles.

12 **I2.4.1.2 Relevant Demonstration Projects**

13 In 1994, the Washington State Department of Ecology (Ecology) and EPA issued an action memorandum  
14 to DOE to immediately initiate groundwater remedial actions at 100-N, to include the design,  
15 construction, and operation of a pump-and-treat system and the construction of a sheetpile barrier wall at  
16 N-Springs. However, 6 months later, Ecology and EPA concurred with DOE that installation of the  
17 sheetpile wall could not be achieved in the manner specified, based on results of a construction test in late  
18 1994. The two agencies subsequently directed DOE to proceed with the pump-and-treat system (only)  
19 *Annual Summary Report Calendar Year 2000 for the 100-HR-3, 100-KR-4, and 100-NR-2 Operable Units*  
20 *and Pump-and-Treat Operations* [DOE/RL-2004-01]. A grouted-hinge sheetpile barrier in the aquifer  
21 near the river's edge had been specified, but attempts to install a sheetpile barrier were unsuccessful  
22 (*Coordination of Groundwater Activities in the 100 N Area* [WHC-EP-0878]).

23 **I2.4.1.3 Evaluation and Screening Rationale**

24 Containing walls typically must be extended into a confining unit, such as the Ringold Formation upper  
25 mud (RUM) unit, which at most sites in the 100 Area may be 15 to 60 m (50 to 200 ft) bgs. Installation to  
26 these depths is possible using specialized excavation equipment such as a hydraulic clamshell, but such  
27 installation is very challenging and expensive. Only at locations very near the river would the required  
28 depths be shallow enough to make installation reasonably economical, and as noted, previous attempts at  
29 the Hanford Site were unsuccessful.

30 There is also uncertainty as to how well the RUM unit would serve as a confining unit. The hydraulic  
31 conductivity in the RUM unit has not been evaluated in detail and the RUM unit was scoured by river  
32 channel migration and erosion by the glacial floods that ultimately laid down the Hanford formation.  
33 Thus, the RUM unit has an undulating surface with periodic depressions, further complicating the ability  
34 to effectively key into this unit.

35 Most of the installation methods would be technically challenging at the Hanford Site because of the depths of  
36 the unconfined aquifer and the presence of cobbles and coarse gravels. Cobbles will prevent or deflect most  
37 insertion methods or items such as sheetpiles, vibrating beams, and drilled caissons. While conventional  
38 trenches likely can be kept open in this formation, slurry loss may be excessive in zones of clean coarse  
39 cobbles or gravels. Sudden loss of slurry related to penetration into such a zone could lead to trench instability.

40 Effectiveness of this technology is considered moderate for several reasons: (1) it depends on the ability  
41 to key into a low-permeability unit; (2) it does not treat contamination; and (3) groundwater upgradient of  
42 the wall must be removed to keep hydraulic pressure against the wall within design parameters.

43 Implementability is low, as evidenced by failed attempts to install a sheetpile wall at N-Springs. Capital

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

### 3 **12.4.2 Reactive Biological Barrier**

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

#### 6 **12.4.2.1 Description**

7 Reactive biological barriers involve the subsurface delivery and/or recirculation of biological substrate  
8 along cross-gradient rows transecting the plume. Residual reducing-byproducts and biomass are retained  
9 in the aquifer matrix so that Cr(VI), nitrate, trichloroethylene, and possibly technetium-99 are passively  
10 removed as groundwater moves through the treatment zone. Biological barriers would operate much like  
11 the in situ redox manipulation (ISRM). Rejuvenation of the barrier by re-injection of biological substrate  
12 may be required periodically to maintain reducing power. Common substrates include acetate, molasses,  
13 cow manure, fruit juice, lactate, whey, polylactate, and sulfur-containing products (for example, Metals  
14 Remediation Compound), and waste organic material, such as that from beer manufacturing (*Chromium  
15 Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the  
16 Department of Energy Hanford Site* [SGW-38255]).

17 The indigenous organisms utilize the substrate as a carbon source for biomass generation and as an  
18 electron donor for energy production through a number of metabolic processes. Cr(VI) is a highly  
19 oxidized compound and, therefore, can act as an electron acceptor, becoming reduced to chromium(III) in  
20 the process. Biological processes may include bioreduction, bioaccumulation, biomineralization, and  
21 bioprecipitation, which use specific substrates to drive the treatment and affect the reduction, uptake, or  
22 precipitation of Cr(VI). These processes can be utilized within reactive biological barriers (*In Situ  
23 Treatment of Soil and Groundwater Contaminated with Chromium* [EPA/625/R-00/005]).

#### 24 **12.4.2.2 Relevant Demonstration Projects**

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

28 A field experiment was conducted at the Hanford Site using hydrogen release compound (HRC),  
29 a slow-release glycerol polylactate, to bioimmobilize Cr(VI) (*In Situ Long-Term Reductive  
30 Bioimmobilization of Cr(VI) in Groundwater Using Hydrogen Release Compound* [Faybishenko, 2009]).  
31 The results of this experiment show that a single HRC injection into groundwater stimulated an increase  
32 in biomass, a depletion of terminal electron acceptors' oxygen, nitrate, and sulfate, and an increase in  
33 ferrous iron, resulting in a significant decrease in soluble Cr(VI). The Cr(VI) concentration remained  
34 below the background concentration in the downgradient pumping/ monitoring well and below the  
35 detection limit in the injection well for at least 3 years after the HRC injection. The degree of  
36 sustainability of hexavalent reductive bioimmobilization under different redox conditions at this and other  
37 contaminated sites was currently under study as of the publication date.

38 Biological barriers have been used at other Cr(VI) sites (*Chromium Treatment Technology Information  
39 Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site*  
40 [SGW-38255]). One site was the Selman Pressure Treating Superfund Site in California, where an  
41 existing pump-and-treat system was projected to take more than 30 years to clean up the site. To  
42 accelerate remediation, molasses was injected by direct push methodology to a radius of influence of  
43 4.6 m (15 ft) and to treatment depths as deep as 37 m (120 ft). Cr(VI) concentrations fell to less than the  
44 performance standard of 50 µg/L and in most cases to below 10 µg/L. In a downgradient portion of the

1 plume, a recirculation process was used to amend the groundwater with lactate to treat it at greater depths.  
2 Cr(VI) reduction was initiated before nitrate reduction. Dosing was adjusted to minimize overly reducing  
3 conditions that led to the temporary mobilization of iron and manganese, as well as biofouling.

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

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

#### 19 ***12.4.2.3 Evaluation and Screening Rationale***

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

24 Effectiveness is deemed low to moderate. Given the highly toxic groundwater flowing at relatively high  
25 rates, re-amendment would likely need to be frequent to maintain reducing conditions. Implementability  
26 is considered moderate or high, capital costs are considered moderate or high, and O&M costs are  
27 considered moderate. The current remedies at both the 100-KR-4 and 100-HR-3 OUs include hydraulic  
28 containment using extraction wells. As a consequence, additional technologies to create barriers to  
29 contaminant migration would duplicate efforts and are not needed. In addition, barriers do not support  
30 cleanup of the entire plume. For these reasons, biobarriers were not retained for further evaluation.

#### 31 **12.4.3 Hydraulic Containment via Injection**

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

##### 34 ***12.4.3.1 Description***

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

### 1 **12.4.3.2 Relevant Demonstration Projects**

2 Fresh water injection systems used to prevent saltwater intrusion along coastlines are conceptually similar  
3 to injection of water to hydraulically contain COPCs. Saltwater intrusion barriers consist of a line of  
4 injection wells paralleling the coast to inject water into a fresh water aquifer to create and maintain  
5 a “fresh water ridge,” which produces an outward gradient to stop the migration of saltwater into the  
6 aquifer (*The Class V Underground Injection Control Study* [EPA/816-R-99-014t]). A total of  
7 315 saltwater intrusion barrier wells have been documented in the United States. Well clogging is  
8 a common issue with operating these injection wells. Maintaining high-quality waters and chlorination of  
9 injection water are methods employed to reduce the frequency of well clogging. However, even when  
10 using high-quality water, clogging is inevitable. When clogging occurs, and the injection head has  
11 increased above acceptable levels, redevelopment of the injection wells is necessary (approximately every  
12 3 years when using high-quality injectate water). Injection wells also need to be supplied with pressure,  
13 either individually or in small groups, to prevent the complete collapse of the pressure ridge barrier in  
14 cases of system shutdowns.

### 15 **12.4.3.3 Evaluation and Screening Rationale**

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

## 25 **13 Bioremediation as a Potential Remedial Action for Cr(VI) in the Groundwater and** 26 **Vadose Zone of the Hanford 100 Area**

### 27 **13.1 Introduction**

28 Bioremediation has been used successfully to treat groundwater contaminated with a range of inorganic  
29 and organic contaminants at a large number of sites throughout the United States (for example, SERDP,  
30 2009; ESTCP, 2008). One of the primary advantages of this technology is that it appears that it can be  
31 cost-effectively applied to a variety of in situ settings, ranging from focused remediation of specific,  
32 small-scale target areas to applications that consist of large-scale, plume-wide remediation efforts.

33 Because of the potential benefits of this technology and the flexibility in the scale of implementation that  
34 is possible, bioremediation is considered a strong remedial action candidate for inclusion as part of the  
35 final remedy for the Cr(VI) contamination within the 100 Area. This appendix summarizes information  
36 that has been compiled and evaluated to support the detailed analysis of in situ bioremediation as one of  
37 the remedial technologies that may be applied to the remediation of Cr(VI) as part of the final remedy for  
38 the 100 Area groundwater OUs. A representative selection of case studies and treatability studies  
39 applicable to the evaluation and implementation of in situ bioremediation of Cr(VI) is summarized in  
40 Section I5 of this appendix.

### 13.2 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. Conversely, Cr(VI) can be reduced to the highly insoluble 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.

## 14 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, such as 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)<sub>3</sub>) (“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) 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 et al., 2008]). 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.

## 14.1 Longevity of Treatment and the Potential for Re-oxidation 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 (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 re-oxidized 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 re-application 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 re-oxidation 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 re-oxidation of chromium(III) compounds by DO or manganese(IV) oxides after bioremediation is completed in the 100-D area.

### 14.1.1 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.

### 14.1.2 Manganese(IV) Oxides

Reductive dissolution of natural manganese(IV) oxides and the subsequent re-precipitation of the dissolved manganese as more poorly structured and reactive manganese(IV) oxides is 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)

1 Added to Soil” [James and Bartlett, 1983]; “Kinetics of Chromium(III) Oxidation to Chromium(VI) by  
2 Reaction with Manganese Dioxide” [Eary and Rai, 1987]; and “Oxidation of Chromium(III) to (VI) by  
3 Manganese Oxides” [Kim et al., 2002]). At least one of these field studies indicated that oxidation of solid  
4 phase chromium(III) by manganese oxides can occur at rates high enough to exceed the groundwater  
5 standard for total chromium. These findings, however, were limited to field settings with sediments  
6 extremely rich in chromium and manganese oxide (for example, 60,000 mg/kg chromium(III) as the  
7 ultramafic-mineral chromite). The geochemical conditions and mineralogy of these sites are significantly  
8 different from those of the Hanford Site, and the evidence of chromium(III) oxidation by manganese(IV)  
9 under such extreme conditions is not relevant to the proposed test area.

10 Laboratory testing has demonstrated the rate of chromium(III) oxidation by manganese(IV) compounds is  
11 much lower if the chromium(III) is present as a solid phase. Laboratory testing of mixed chromite and  
12 manganese oxide suspensions over a range of pH values (“Genesis of Hexavalent Chromium from  
13 Natural Sources in Soil and Groundwater” [Oze et al., 2007]) confirmed that chromite was subject to  
14 oxidative dissolution in the presence of high-concentration manganese oxides. However, the rates of  
15 chromite oxidative dissolution by manganese oxides decreased steadily as the solution pH was increased  
16 from 3 to 5 to approximately 6.8. Oxidative dissolution had essentially ceased near a pH of 8  
17 (approximately the pH of Hanford Site groundwater). Even under the extreme conditions of this  
18 laboratory study, the fastest oxidation rates observed for solid phase chromium(III) were much slower  
19 than the rates typically observed for dissolved chromium(III) species (“Genesis of Hexavalent Chromium  
20 from Natural Sources in Soil and Groundwater” [Oze et al., 2007]). Although the oxidation of  
21 chromium(III) in ultramafic minerals does occur at noteworthy rates under the very unusual geologic  
22 settings described above, there is substantial evidence that re-oxidation of solid phase chromium(III) by  
23 manganese(IV) oxides is not realistic under the groundwater and aquifer matrix conditions during and  
24 after in situ bioremediation. The factors and processes gleaned from relevant publications that are  
25 expected to prevent or greatly minimize post-treatment re-oxidation of chromium(III) by manganese(IV)  
26 oxides include the following:

- 27 • Manganese(IV) oxides are most effective as an oxidizer when dissolved chromium(III) is sorbed  
28 directly onto the reactive manganese oxide surface. At neutral or slightly basic pH conditions that will  
29 eventually be re-established after bioremediation, the concentrations of dissolved chromium(III)  
30 available for re-oxidation will be minimized by the extremely low solubility of the chromium(III) and  
31 mixed Fe(II), and chromium(III) phases that will be formed in groundwater during bioremediation  
32 (“Genesis of Hexavalent Chromium from Natural Sources in Soil and Groundwater” [Oze et al.,  
33 2007]; “Long-Term Stability of Organic Carbon-Stimulated Chromate Reduction in Contaminated  
34 Soils and Its Relation to Manganese Redox Status” [Tokunaga et al., 2007]).
- 35 • In those relatively rare cases where a chromium(III) phase may be in direct contact with a freshly  
36 precipitated manganese oxide surface, the extent of oxidation-reduction reaction between the two  
37 phases will eventually be minimized by the development of a less-reactive, mixed-valence layer  
38 between the two phases.
- 39 • The catalytic and oxidative capacity of freshly precipitated manganese oxides generally decreases  
40 over time as the reactive surfaces are neutralized by the sorption of other metal ions or coated by  
41 natural organic matter or other common solid phases (for example, iron hydroxides/oxides).
- 42 • A recent study (“Inhibition of FeS on Chromium (III) Oxidation by Biogenic Manganese Oxides”  
43 [Wu and Deng, 2006]) indicates that the oxidation of chromium(III) by manganese(IV) oxide is

1 countered by the presence of reductive agents such as Fe(II) and sulfide compounds also present in  
2 the aquifer. These reducing compounds will be abundant in the targeted section of the aquifer and  
3 should inhibit or reverse any potential re-oxidation of chromium(III) within the treated area.

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

## 6 **14.2 Fate and Transport of Some Potential Chemical Byproducts of Bioremediation**

7 This section presents a summary of the fate and transport characteristics of several common byproducts  
8 of bioremediation likely to be produced under the unconfined aquifer conditions prevalent in the  
9 100 Area.

### 10 **14.2.1 Iron and Manganese, and Arsenic**

11 Ferric(III) hydroxides and manganese(IV) oxide phases in the matrix of bioremediated aquifers  
12 commonly undergo reductive dissolution and the iron and manganese are mobilized as Fe(II) and Mn(II)  
13 aqueous species at concentrations substantially higher than background levels. Although some microbes  
14 are capable of using manganese oxides as an electron acceptor with the consequent production of Mn(II),  
15 the main mechanism expected to drive the reduction of manganese oxides is reaction with dissolved  
16 Fe(II) and sulfide produced during the microbially mediated reduction of Fe(III) compounds and  
17 dissolved sulfate (“The Chemistry of Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters”  
18 [Morse et al., 1987]; “Reduction of Structural Fe(III) of Nontronite by Hydrogen Sulfide” [Strekopytov  
19 and Larsen, 2001]; “A Revised Scheme for the Reactivity of Iron (Oxyhydr)Oxide Minerals Towards  
20 Dissolved Sulfide” [Poulton et al., 2004]; “Reduction of Iron Oxides Enhanced by a Sulfate-Reducing  
21 Bacterium and Biogenic H<sub>2</sub>S” [Li et al., 2006]).

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

32 As with iron and manganese, the fate and transport characteristics of arsenic are dominated by the redox  
33 and pH characteristics of the aquifer. Arsenic can exist in four oxidation states (-3, 0, +3, +5) but is  
34 typically present in oxidizing groundwater with a pH between 6 and 8 as one of two anionic arsenics (V)  
35 or “arsenate” species. At a pH less than 7.0, H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> predominates while at a pH greater than 7.0, the  
36 HAsO<sub>4</sub><sup>2-</sup> complex is dominant (“Kinetics of Adsorption and Redox Processes on Iron and Manganese  
37 Oxides: Reactions of Arsenic(III) and Selenium(IV) at Goethite and Birnessite Surfaces” [Scott, 1991]).  
38 Arsenic (V) species have a relatively high sorption affinity for iron oxides/hydroxides under near neutral  
39 pH conditions. Naturally occurring iron hydroxides oxides in aquifer materials commonly contain  
40 substantial amounts of arsenic that have been accumulated (sorbed) over time from the ambient pore  
41 water or groundwater. Under anoxic groundwater conditions (at the same pH range as above), arsenic is  
42 stable in the trivalent state and predominantly exists as the more mobile neutral arsenite species (H<sub>3</sub>AsO<sub>3</sub>)  
43 (“Kinetics of Adsorption and Redox Processes on Iron and Manganese Oxides: Reactions of Arsenic(III)  
44 and Selenium(IV) at Goethite and Birnessite Surfaces” [Scott, 1991]). A previous 100 Area investigation

1 (*Hanford 100-D Area Biostimulation Treatability Test Results* [PNNL-18784]) demonstrates that arsenic  
2 is present in the matrix of the 100 Area unconfined aquifer. Consequently, reductive dissolution of the  
3 iron hydroxide/oxide phases during in situ bioremediation may lead to the solubilization of elevated levels  
4 of arsenic as the relatively mobile neutral trivalent species ( $\text{H}_3\text{AsO}_3$ ).

5 Under moderately acidic (for example, pH 5.5) sulfate reducing conditions, As(III) may sorb to or  
6 co-precipitate with metal sulfide phases (for example, iron sulfides). Generally, however, under the higher  
7 pH and mildly alkaline conditions and conditions that should predominate during bioremediation of  
8 Cr(VI) in the 100 Area, the neutral and relatively mobile arsenic(III) species  $\text{H}_3\text{AsO}_3$  will likely  
9 predominate in solution.

10 The relatively high mobility of arsenic(III) species solubilized during bioremediation should be largely  
11 limited to the aquifer zone where Fe(II) and Mn(II) are stable in solution. Manganese oxides play a major  
12 role in accelerating the oxidation of arsenic(III) to arsenic(V) in aqueous solutions, and Fe(III) hydroxides  
13 have a high affinity for arsenic(V) (“Kinetics of Adsorption and Redox Processes on Iron and Manganese  
14 Oxides: Reactions of Arsenic(III) and Selenium(IV) at Goethite and Birnessite Surfaces” [Scott, 1991]).  
15 Consequently, if arsenic(III) migrates out of the strongly reducing bioremediation zone, it will also be  
16 subject to oxidation and sorption by previously existing or freshly re-precipitated manganese oxides and  
17 iron hydroxides in the aquifer.

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

#### 23 **14.2.1.1 Barium**

24 Although barium is strongly sorbed by clays, manganese oxides, and ferric hydroxides, the very low  
25 barium concentrations in aquifers containing sulfate commonly reflects the precipitation of the extremely  
26 insoluble sulfate mineral barite ( $\text{BaSO}_4$ ). Barite is commonly the solubility limiting phase even in aquifers  
27 containing dissolved sulfate concentrations that are substantially lower than those typical of the 100 Area  
28 unconfined aquifer (for example, 50 to 100 mg/L). Nevertheless, it is possible that the development of  
29 locally intense reducing conditions within a targeted area of the unconfined aquifer during bioremediation  
30 could lead to the near total conversion of groundwater sulfate to sulfide in that area. The reductive  
31 dissolution of iron hydroxides, manganese oxides, and high levels of sulfate reduction would likely result  
32 in the increased solubility of barium. Although this process can result in an increase in the barium  
33 concentrations of the highly reducing section of the aquifer, this effect would be transient, and any  
34 elevated barium concentrations that develop should rapidly decrease back to near background levels (as a  
35 result of barium sorption and re-precipitation of barite) once the groundwater migrates out of the intensely  
36 reducing zone and mixes with groundwater that retains background levels of sulfate.

#### 37 **14.2.1.2 Volatile Fatty Acids and Methane**

38 If the substrate supply to a system exceeds the availability of electron acceptors such as oxygen, nitrate,  
39 sulfate, and Fe(III), microbial fermentation of the substrate may become the dominant metabolic process,  
40 resulting in the development of very low groundwater redox conditions. Fermentation is a balanced  
41 reduction-oxidation reaction where the same organic molecule (for example, the substrate) serves as both  
42 an electron acceptor and donor. These microbially mediated energy-producing reactions result in the  
43 conversion of the original substrate (for example, lactate) into simpler organic compound, such as  
44 methane and volatile fatty acids (VFA) such as propionate. Compared to the relatively rapid rates of  
45 Cr(VI) reduction obtained by direct and indirect Cr(VI) reduction processes that are driven by iron and

1 sulfate reducing bacteria, fermentation reactions are less efficient processes for reducing Cr(VI).  
2 Therefore, high concentrations of methane and VFA in groundwater during bioremediation can be  
3 indicative of excessive (wasteful) substrate use. The fate and transport of these organic byproducts can be  
4 managed by limiting the amount of substrate to the minimum amount needed to obtain the necessary rate  
5 and extent of Cr(VI) remediation. Elevated levels of methane and VFA in the groundwater downgradient  
6 from the target area should be rapidly reduced by a combination of aerobic and anaerobic  
7 microbial degradation.

## 8 **15 Evaluation of Potential Substrates for In Situ Bioremediation in the 100 Area**

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

14 Parsons Corp (*Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*  
15 [Parsons, 2004]) and Air Force Center for Engineering and the Environment (“Enhanced In Situ  
16 Anaerobic Bioremediation,” “Substrate Alternatives” [Air Force Center for Engineering and  
17 Environment, 2010]), evaluated many of the organic substrates that can be used to support bioremediation  
18 of groundwater such as low-molecular-weight fatty acids (for example, lactate, butyrate, and acetate),  
19 alcohols (for example, methanol and ethanol) cheese whey (lactose), sugar syrups (for example, molasses  
20 or corn syrup), vegetable oils, a commercial product marketed as HRC, and solid substrates such as mulch  
21 and compost. Of these, lactate, molasses, HRC, and vegetable oils are most commonly added for  
22 enhanced anaerobic bioremediation. Effective substrates that are used less frequently include ethanol,  
23 methanol, butyrate, high-fructose corn syrup, and cheese whey.

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

- 32 • **Miscible Liquids.** Miscible substrates applied as dissolved or “aqueous-phase” solutions offer the  
33 greatest potential for uniform distribution throughout the aquifer matrix relative to substrates applied  
34 as a viscous fluid or solid phase. Molasses and lactate are the most common substrates applied in an  
35 aqueous phase. Miscible substrates travel with advective groundwater flow and are typically applied  
36 in a continuous or periodic (pulsed) mode to maintain a specified reactive treatment zone.
- 37 • **Viscous Fluids.** Slow-release, viscous fluid substrates include HRC and neat vegetable oils. These  
38 substrates are intended to be long lasting, where a single or limited number of injections are sufficient  
39 for site remediation. They are intended to be relatively immobile in the subsurface and rely on  
40 advection and dispersion of soluble compounds (for example, lactic acid for HRC or metabolic acids  
41 generated by degradation of vegetable oil) for effective delivery throughout the aquifer matrix.
- 42 • **Low Viscosity Emulsions.** Vegetable oil emulsions have been developed in an effort to improve the  
43 distribution of substrate in the subsurface while still providing a long-lasting source of organic  
44 carbon. Micro-emulsions consisting of 5 to 10 percent vegetable oil in water by volume are relatively

1 low-viscosity mixtures (for example, non-dairy creamers like Coffee Mate<sup>2</sup>) compared to the viscous  
 2 fluids described above. The use of micro-emulsions is the result of lessons learned in early vegetable  
 3 oil field trials in which high-injection backpressures, radii of influence, and reductions in hydraulic  
 4 conductivity were observed using coarse viscous emulsions or neat vegetable oil.

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

**Table I-1. Substrates Used for Enhanced Anaerobic Bioremediation**

Substrate	Typical Delivery Techniques	Form of Application	Frequency of Injection
<b>Soluble Substrates</b>			
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
<b>Viscous Fluid Substrates</b>			
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
<b>Low-Viscosity Fluid Substrates</b>			
Vegetable Oil Emulsions	Direct injection or injection wells	Low oil content (<10%) micro-emulsions suspended in water	Every 2 to 3 years, potential one-time application

<sup>2</sup> 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
<b>Solid Substrates</b>			
Mulch and Compost	Trenching or excavation	Trenching, excavation, or surface amendments	One-time application

Source: Air Force Center for Engineering and the Environment, 2010. "Enhanced In Situ Anaerobic Bioremediation," "Substrate Alternatives."

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

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

## 1 **15.1 Substrate Selection for In Situ Bioremediation of the 100 Area** 2 **Unconfined Aquifer**

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

### 7 **15.1.1 Initial Screening**

8 Because of the generally transmissive nature of the unconfined aquifer and the vadose zone in the  
9 100 Area, the high mobility of Cr(VI), the large sizes of the plumes, and the relative proximity of the  
10 ecologically sensitive Columbia River, highly soluble, relatively mobile, and fast degrading substrates are  
11 preferred over longer lasting but relatively immobile substrates (Table I-2). This screening criterion  
12 eliminated emulsified vegetable oil and Chitin from further consideration for use as substrates for Cr(VI)  
13 remediation in the 100 Area. However, these relatively immobile substrates could be used to supplement  
14 the more soluble substrates to provide longer lasting reducing conditions directly around an injection  
15 well. This reducing area around the injection well will then continue to treat the re-injected water that will  
16 contain some Cr(VI).

### 17 **15.1.2 Secondary Screening**

18 The remaining candidates presented in Table I-2 (methanol, ethanol, acetate sodium lactate, molasses, and  
19 whey) are all highly mobile and rapidly metabolized by microbes in groundwater systems such as the  
20 unconfined aquifer. Methanol and ethanol are flammable and were screened out based on health and  
21 safety issues. Acetate was screened out because it is weakly acidic and represents a potential handling  
22 risk. In addition, acetate may reduce the pH of groundwater in the targeted area to below the optimum  
23 range for microbial growth. Even a moderately more acidic condition in the target area could increase the  
24 solubility of some metals sorbed onto the aquifer matrix. Molasses has been used frequently for the  
25 bioremediation of Cr(VI) and other contaminants but has a tendency to promote biofouling. For this  
26 reason, molasses was eliminated from consideration. The remaining two substrates in Table I-2, sodium  
27 lactate (lactate) and cheese whey (whey), were selected as the two best potential substrate candidates for  
28 any future in situ bioremediation system implemented to treat Cr(VI) in the 100 Area of the Hanford Site.  
29 The following section presents the basis for the final selection of one of these two candidates as the  
30 preferred substrate.

### 31 **15.1.3 Final Screening**

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

39 Whey is a milk by-product of cheese making that consists primarily of water and about 4 to 5 percent  
40 lactose, (a disaccharide with 12 carbon atoms per molecule) and minor amounts of protein, fat, and ash. If  
41 used in the original liquid form, whey must be kept refrigerated prior to use. Liquid whey is easily diluted  
42 with water and can be readily injected into aquifers. Whey can also be obtained in a dry powder form  
43 (commonly in 50 lb [23 kg] bags) that consist of approximately 70 to 75 percent lactose, 10 to 13 percent  
44 protein, and 7 to 13 percent ash (“Enhanced Bioremediation Using Whey Powder for a Trichloroethene

1 Plume in a High-Sulfate, Fractured Granitic Aquifer” [Mora et al., 2008]). Whey powder is readily  
2 soluble and can be mixed with water onsite to the preferred concentration, immediately prior to use.

3 Because of the greater complexity of the organic constituents in whey, it has a longer biodegradation half  
4 life than lactate. The somewhat slower biodegradation rate of whey should allow for the remediation of  
5 larger areas within Cr(VI) plumes than would lactate under similar operating conditions. While whey has  
6 not been used as a bioremediation substrate as frequently as lactate has, whey has been used at a few  
7 Cr(VI) sites, such as the Pacific Gas and Electric (PG&E) Hinkley Compressor Station (*Notice of*  
8 *Applicability of General Waste Discharge Requirements for the General Site-Wide Groundwater*  
9 *Remediation Project at the PG&E Compressor Station, Hinkley, San Bernardino County* [Cal/EPA,  
10 2010]), and for the in situ remediation (reductive dechlorination) of chlorinated solvents such as  
11 trichloroethylene (“Enhanced Bioremediation Using Whey Powder for a Trichloroethene Plume in a  
12 High-Sulfate, Fractured Granitic Aquifer” [Mora et al., 2008]). However, the disadvantages of both dried  
13 and liquid whey compared to lactate include the following: (1) long-term or large-scale in situ treatment  
14 will require onsite refrigerated storage of liquid whey or frequent handling of large quantities of dried  
15 whey, and (2) the relatively high concentration of the disaccharide lactose in whey may result in high acid  
16 production rates during fermentation reactions, potentially lowering the pH within the target area  
17 (“Enhanced Bioremediation Using Whey Powder for a Trichloroethene Plume in a High-Sulfate,  
18 Fractured Granitic Aquifer” [Mora et al., 2008]). As long as excessively high concentrations of whey are  
19 not injected or infiltrated into the aquifer, however, the moderately elevated alkalinity (for example, 100  
20 to 120 mg/L as CaCO<sub>3</sub>) that typifies most areas of the unconfined aquifer in the 100 Area should be  
21 sufficient to offset the reduction of pH as the result of elevated levels of organic acids generated during  
22 the in situ fermentation of whey.

23 Although whey would likely perform well as a bioremediation substrate in the unconfined aquifer of the  
24 100 Area, lactate is more readily available, easier to store and transport, and has fewer potential unwanted  
25 side effects. Consequently, lactate is generally preferred as the substrate of choice for in situ  
26 bioremediation of Cr(VI) in the unconfined aquifer.

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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 <sub>2</sub> . 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 <sub>2</sub> . 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 <sub>2</sub> . 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.
<b>Lactate</b>	No known safety or handling issues.	Effective, half-life of Cr(VI) is days.	Very soluble, low viscosity are desirable for in situ mixing; slightly denser than water.	Several months	Microbial degradation produces CO <sub>2</sub> . 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 diluted 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 <sub>2</sub> . Methane and hydrogen sulfide can be produced since 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. <b>Tested at the Hanford Site.</b>
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 <sub>2</sub> . 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 needed to implement approach.	Food grade	Complex unsaturated alkanes that degrade to release electrons for chromium reduction over a very long period. <b>Tested at the Hanford Site.</b>
MRC (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 <sub>2</sub> . 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 <b>tested at the Hanford Site.</b> Potential intellectual property encumbrances.

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
<b>Whey</b>	No known safety issues; whey solutions must be refrigerated.	Effective, half-life of Cr(VI) is days.	Very soluble; low viscosity is desirable for in situ mixing, slightly denser than water.	Several months	Microbial degradation produces CO <sub>2</sub> . 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 diluted concentrations.
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 <sub>2</sub> . 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.

Notes: **Bolded** substrates were selected for final screening.  
 MRC = Metals Remediation Compound

## 16 In Situ Groundwater Remediation by Bioinjection

### 16.1 Conceptual Design

The general aquifer characteristics of the 100 Area unconfined aquifer, including high transmissivity and moderately 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 I1) 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. In 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 re-injected near the upgradient boundary of the target area (Figure I1). 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 for groundwater contaminated with Cr(VI) in the 100 Area.

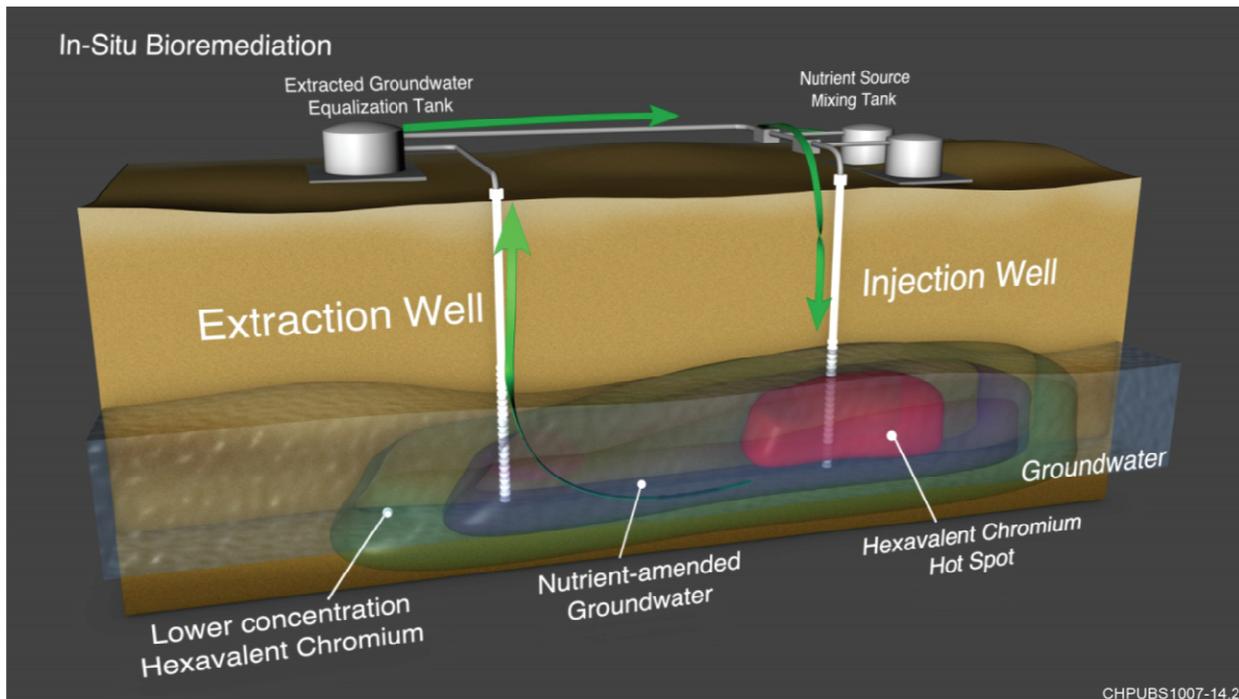


Figure I1. Cross Section of a Recirculating In Situ Bioremediation System

#### 16.1.1 Implementation Factors

In situ bioremediation of Cr(VI) in groundwater typically employs wells to distribute 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

1 anticipated that several factors influence the design and implementation of in situ bioremediation systems.  
2 These factors include the following:

- 3 • **Method of Delivery.** Vertical injection wells screened in the aquifer are typically used to deliver  
4 carbon compounds into groundwater. Other approaches include surface infiltration trenches,  
5 horizontal wells, and direct-push technology. Vertical wells are recommended because they can be  
6 reliably installed, accept high volumes of liquid, and are easily maintained.
- 7 • **Operation of Injection Wells.** Markedly different results are achievable depending on how the  
8 injection wells are used to return amended groundwater to the aquifer. For instance, microbial activity  
9 can vary dramatically, whether amendments are added at extremely high concentrations over a short  
10 period of time (batch injection) or added at low concentrations over a much longer time period  
11 (continuous injection).
  - 12 – Once the microbial community is developed around an injection well and reducing conditions are  
13 generated, pulsed delivery of substrate is advantageous to avoid or minimize injection well  
14 fouling. A short period of substrate injection each day or every few days followed by injection of  
15 unamended water will minimize biofouling of the injection wells that would otherwise occur with  
16 greater frequency with continuous carbon delivery.
  - 17 – The initial injection of a carbon source will have substantially slower degradation rates  
18 (once oxygen is consumed) than subsequent injections because time is required for the substrate  
19 additions to expand the population of facultative and obligate anaerobic microbes that are present.  
20 Over time, the aquifer will develop a flourishing anaerobic microbial community that will be able  
21 to rapidly degrade the added substrate using the various other electron acceptors that are present  
22 (for example, nitrate, chromium, iron, manganese, and sulfate).
- 23 • **Spacing Between Injection and Extraction Wells.** Recirculating bioremediation systems are  
24 advantageous for treating large plumes in highly permeable aquifers. When injection wells and  
25 extraction wells are operated together or paired, an induced flow field can be developed, allowing  
26 substrate delivery over larger distances. Recirculating systems can be used to better control the size,  
27 shape, and reducing intensity of regions of influence.
- 28 • **Substrate Injection and the Region of Influence.** Specific substrates have distinct advantages or  
29 disadvantages related to the nature and extent of the targeted contaminants. Based on these and other  
30 factors, lactate is currently the recommended substrate for bioremediation activities in the 100 Area.  
31 When any substrate is injected into an aquifer, it influences the biogeochemistry of groundwater in a  
32 number of ways.
- 33 • **Microbial Effects.** Another factor influencing the size of the area of treatment is the microbial  
34 abundance in the soil or aquifer matrix. During application of the amended groundwater, the  
35 microbial population can increase several orders of magnitude over days, weeks, or months.  
36 Experience at other locations shows that achieving the maximum substrate usage rate may require  
37 several months, depending on soil and groundwater temperatures, the carrying capacity, or maximum  
38 microbial abundance. A detailed pilot test was performed to examine these factors at a compressor  
39 station in California (*Floodplain Reductive Zone In-Situ Pilot Test: Final Completion Report, PG&E*  
40 *Topock Compressor Station, San Bernardino County, California* [ARCADIS, 2008]).

## 16.2 Previous Studies and Applications of Bioinjection and Similar Technologies to Cr(VI) Remediation in Groundwater

In situ bioremediation has been used to successfully treat Cr(VI)-contaminated groundwater 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 below.

### 16.3 Hanford 100-D Pacific Northwest National Laboratory Biostimulation Treatability Study

The 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 from 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<sup>3</sup>). This treatability study is reported in *Hanford 100-D Area Biostimulation Treatability Test Results* (PNNL-18784).

#### 16.3.1 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 near the river to approximately 25 m (82 ft) further inland. The base of the unconfined aquifer is a fine-grained silty sand to clay overbank interval, designated the RUM Unit, 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.

#### 16.3.2 Technical Approach

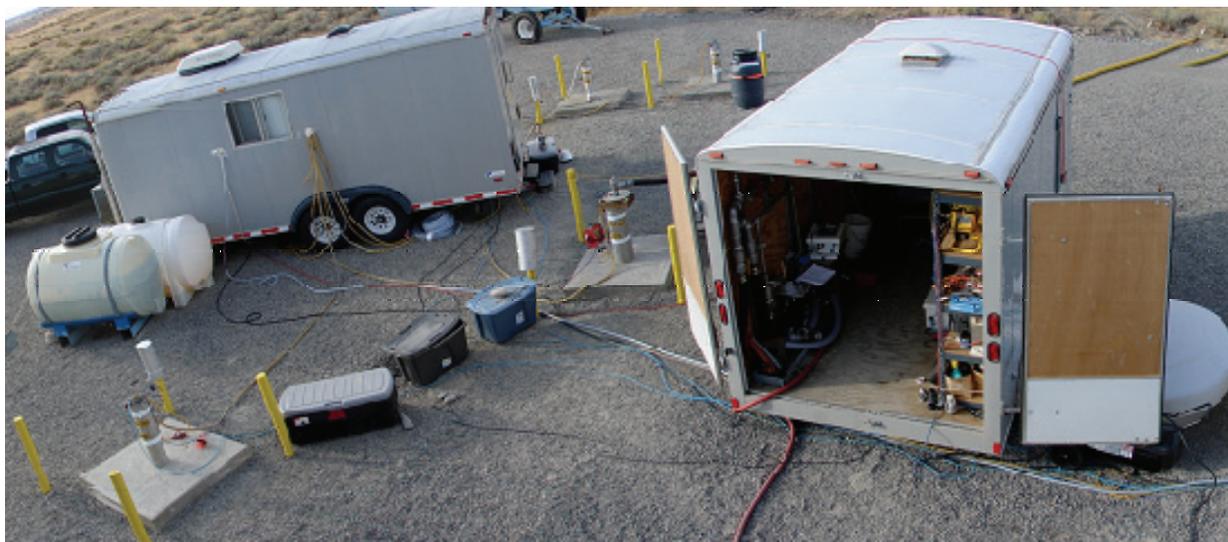
Two test cells were installed at the treatability test site, each consisting of an injection well surrounded by upgradient, downgradient, and cross-gradient monitoring wells (Figure I2). The test cells were located such that existing Well 199-D5-40 could be used as a background monitoring location for both test cells. Field test operations were conducted by injecting the substrate using process water from the 100-D pressurized water supply as the carrier solution. The substrate solutions were fed into the manifold system using a chemical metering pump.

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<sup>3</sup> EOS-598—Emulsified Oil Substrate, manufactured by EOS Remediation, LLC, 1101 Nowell Road, Raleigh, North Carolina.

1 **Molasses Injection.** In September 2007, molasses injection was conducted over a 3.25-day period using  
2 process water injected at approximately 40 gal/min amended with approximately 40 g/L molasses, 100  
3 mg/L ammonium chloride, and 100 mg/L sodium bromide. Injection pressure was variable throughout the  
4 injection but was typically about 25 pounds per square inch (psi). Approximately 19,300 L (5,100 gal) of  
5 molasses were injected, with a total injection volume of about 594,000 L (157,000 gal). At the end of the  
6 substrate injection, 9,400 L (2,500 gal) of process water were injected for approximately 1 hour to clear  
7 the injection system of substrate and flush the wellbore.

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



16  
17 **Figure I2. Molasses Injected at 100-D Area Biostimulation Treatability Test Site to Nourish Bacteria**

### 18 **16.3.3 Results**

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

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

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

#### 9 **16.3.4 Lessons Learned**

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

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

20 Within the test cells, water quality was negatively affected by an increase in the concentration of  
21 secondary by-product reduced metals. These changes were expected because of the imposed anaerobic  
22 conditions required for biological treatment of Cr(VI). Although the concentration of most metals  
23 increased, only arsenic, barium, and selenium increased to concentrations consistently above the MCL.

### 24 **16.4 Hanford 100-H Lawrence Berkeley National Laboratory Hydrogen Release 25 Compound Treatability Study**

26 Since 2004, biostimulation tests have been performed at 100-H by personnel at Lawrence Berkeley  
27 National Laboratory (“In Situ Long-Term Reductive Bioimmobilization of Cr(VI) in Groundwater Using  
28 Hydrogen Release Compound” [Faybishenko et al., 2008]). In these tests, commercial polylactate HRC<sup>3</sup>  
29 was injected into the aquifer to stimulate microbial activity and transform Cr(VI) to chromium(III).  
30 Results from the tests show that Cr(VI) concentrations in the treated area decreased to below drinking  
31 water standards and remained at that level for nearly 3 years. The principal difference between this test  
32 and the test described in the previous section is the use of polylactate, which is difficult to inject any  
33 distance from a well because of its high viscosity; therefore, polylactate is limited in its ability to treat  
34 large areas of an aquifer. Over several months, polylactate slowly disperses into the aquifer, at which  
35 point it acts as a more mobile substrate.

#### 36 **16.4.1 Site Conditions**

37 The lithology underlying the treatability study area consists of high-permeability Hanford sediments  
38 (gravel and coarse sand) at a depth of approximately 12 m (40 ft). The Hanford Site sediments are  
39 underlain by clays of the Ringold Formation at a depth of approximately 14 m (47 ft), which extends to  
40 a depth of 15 m (50 ft), and below this is a silty clay-to-silt layer. Regional groundwater flow direction in  
41 the treatability study area is predominantly northeast toward the Columbia River. Results from borehole

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<sup>3</sup> HRC—Hydrogen Release Compound, manufactured by Regenesys—Advanced Technologies for Contaminated Site Remediation, 1011 Calle Sombra, San Clemente, California.

1 water-flux measurements showed that practically all water entered the boreholes from the sandy gravel of  
2 the Hanford formation, with very low flow from the Ringold Formation.

### 3 **16.4.2 Technical Approach**

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

9 On August 3, 2004, 18.2 kg (40 lbs) of HRC were injected into 699-96-45, through a straddle packer that  
10 isolated the injection interval to 13 to 14 m (42 to 46 ft). To trace the post-HRC injection carbon  
11 production generated by metabolic processes, 10 g (135 oz.) of <sup>13</sup>C-labeled lactate were mixed with the  
12 HRC. Before the injection, the HRC was pre-heated to about 35 degrees Celsius (°C) and diluted with  
13 15 L (4 gal) of distilled water. The injection hose was initially filled with 9.5 L (2.5 gal) of water,  
14 as a primer. A total of 17 L (4.5 gal) of water was injected as a chaser after the HRC injection. Following  
15 the HRC injection, potassium bromide (KBr) was also injected into the same injection interval.  
16 Groundwater was pumped from downgradient Well 699-96-44 to create a direct water flow path between  
17 wells. Pumping continued for 25 days.

### 18 **16.4.3 Results**

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

20 **Chromium Reduction.** Following the HRC injection, Cr(VI) concentrations decreased in both the injection  
21 and monitoring/pumping wells from approximately 700 and 100 µg/L, respectively, to nondetect levels.  
22 After the HRC injection, the Cr(VI) reduction rate was 0.626 day<sup>-1</sup> in 699-96-45, and 0.276 day<sup>-1</sup> in the  
23 pumped water from 699-96-44. In 699-96-45, Cr(VI) concentrations remained below detection limits for  
24 more than 3 years after HRC injection. In 699-96-44, Cr(VI) concentrations gradually recovered but  
25 remained below the background concentration for more than 3 years after the HRC injection. The Cr(VI)  
26 and total chromium concentration trends in 699-96-41 and 699-96-42 were comparable with those in  
27 699-96-44.

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

33 **Biogeochemical Response.** The maximum biomass in both the pumping and injection wells was reached  
34 15 to 20 days following injection. The maximum average biomass increased approximately 50-fold in  
35 699-96-44, and approximately 38-fold in 699-96-45. The lower biomass in water samples from the  
36 injection well may have resulted from filtering of bacteria attached to colloids during groundwater  
37 sampling and analysis.

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

43 The HRC injection generated reducing conditions, which is evident from the drop in the DO  
44 concentration from 8.2 to 0.35 mg/L and redox potential from 240 to -130 mV in downgradient

1 monitoring Well 699-96-44. Although DO in 699-96-45 increased to 5.5 mg/L after the conclusion of  
2 pumping, it then gradually decreased over the next year. Over the next 3 years after pumping ceased, DO  
3 in 699-96-4 ranged from 6 to 7 mg/L, compared with 8 to 9 mg/L in upgradient monitoring  
4 Well 699-96-43. At the same time, pH dropped from 8.9 to 6.5-7.0 and stabilized at this level. Through  
5 monitoring conducted in June 2007, redox potential and DO in the injection and downgradient monitoring  
6 wells had not returned to the background levels. The slow recovery of background redox conditions could  
7 have been caused by the presence of some HRC breakdown products (lactic and acetic acid) between the  
8 injection and downgradient monitoring wells. Post-HRC injection decaying biomass may have also  
9 served as a carbon source.

10 An increase in the  $^{13}\text{C}$  of dissolved inorganic carbon from -12 percent (prior-HRC injection) to greater  
11 than 50 percent (which is higher than that in the injected HRC) was likely caused by the creation of  $\text{CO}_2$   
12 as a by-product of microbial metabolism. It should be noted that the release rate of  $^{13}\text{C}$ -labeled lactate that  
13 was added to the HRC could be higher than that of polylactate, which is the main component of HRC.  
14 The carbon isotope ratios of the dissolved inorganic carbon decreased after pumping was stopped but  
15 remained above background for the 3-year period of observations through June 2007.

16 **Secondary By-products.** The concentration of aqueous  $\text{Fe}^{2+}$  increased in both the injection and  
17 downgradient pumping/monitoring wells, reaching maximum values (over 10,000  $\mu\text{g/L}$ ) about 2 months  
18 after the HRC injection.  $\text{Fe}^{2+}$  concentration returned to the background, undetectable level 2.5 years after  
19 the HRC injection in downgradient monitoring Well 699-96-44, and 3.5 years after the HRC injection in  
20 699-96-45.

#### 21 **16.4.4 Lessons Learned**

22 Hydraulic and chemical transport processes in the Hanford formation were likely affected by  
23 biogeochemical processes after the HRC injection. A post-HRC injection (July 2005 and April 2006)  
24 increase in the tracer travel time could likely be explained by the decrease in the hydraulic conductivity  
25 resulting from partial blocking of flow pathways within heterogeneous media by biofilms and  $\text{CO}_2$  gas.

### 26 **16.5 Other Relevant Hanford Site Studies**

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

#### 29 **16.5.1 Fortifying the 100-D Area In Situ Redox Manipulation Barrier with Iron**

30 The ISRM barrier was implemented to passively treat  $\text{Cr(VI)}$  contamination in the 100-D southern plume  
31 and prevent the discharge of elevated levels of  $\text{Cr(VI)}$  to the Columbia River (*U.S. Department of Energy*  
32 *Hanford Site – 100 Area Benton County, Washington Amended Record of Decision, Decision Summary*  
33 *and Responsiveness Summary [100-HR-3 Operable Unit Interim Remedial Action]* [EPA et al., 1999]).  
34 At the time the ISRM barrier was implemented, the magnitude and extent of high  $\text{Cr(VI)}$  concentrations  
35 in the 100-D hot spot upgradient of the barrier were not understood. When performance-monitoring data  
36 indicated that  $\text{Cr(VI)}$  was breaking through the ISRM treatment zone, scientists proposed that fortifying  
37 the barrier with additional reduced iron would increase the long-term effectiveness of the barrier.  
38 Consequently, a treatability study was conducted to evaluate whether augmentation of the ISRM barrier  
39 with NZVI would be an effective approach to augmenting the performance and longevity of this passive  
40 treatment system.

41 In 2006, DOE began a test to determine whether injections of tiny iron particles only 70 nanometers  
42 (3 millionths of an inch) in diameter could fortify the weaker portions of the ISRM barrier. The small size  
43 of the particles would allow them to flow into the aquifer, thus treating the water more effectively given

1 the very large surface area of the material (30 m<sup>2</sup>/g [150,000 ft<sup>2</sup>/lb]). Higher surface area means that more  
2 of the iron would be available to react with and remediate the groundwater.

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

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

11 Over a period of approximately 5 days, 370,970 L (98,000 gal) of the RNIP-M2 solution was injected into  
12 the Ringold Formation aquifer at a rate of 53 L/min (14 gal/min). The zero-valent iron was communicated  
13 at least 3 m (9.8 ft) away from the injection well. A borehole was drilled 7 m (23 ft) from the injection  
14 well in March 2009 to evaluate the radius of influence. Analysis of aquifer materials showed that  
15 approximately 4 wt% zero-valent iron was present in the targeted permeable layer near the bottom of the  
16 aquifer. This verified that the goal of emplacing zero-valent iron at least 7 m (23 ft) into the aquifer was  
17 successfully accomplished. Monitoring has shown the area near the test is strongly reducing, and Cr(VI)  
18 has been reduced to immobile chromium(III). The test demonstrated that RNIP-M2 could be an effective,  
19 easily injected zero-valent iron product to fortify the ISRM barrier.

## 20 **16.5.2 100-K Area Calcium Polysulfide Injection Treatability Test**

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

25 The treatability test began on June 28, 2005, and was conducted in the eastern part of 100-K (Figure I3).  
26 The test was designed to provide experience in designing systems to implement this technology and  
27 revealed several lessons learned to consider during implementation of a bioremediation system. Given  
28 these aspects, the test had the following multiple objectives:

- 29 • Obtain hydrologic information for the 00-K aquifer required for a potential full-scale implementation  
30 of this technology.
- 31 • Verify the ability to achieve in situ Cr(VI) reduction through both inorganic and microbiological  
32 processes by the combined injection of calcium polysulfide and a carbon substrate.
- 33 • Determine whether aquifer constituents (for example, manganese or arsenic) are mobilized as a result  
34 of these processes and how other parameters (for example, nitrate or DO) are affected as a result of  
35 the groundwater treatment.
- 36 • Obtain operational experience in the in situ treatment of groundwater contaminated with Cr(VI).
- 37 • Determine whether this approach could be implemented as a cost-effective method to augment the  
38 current 100-K pump-and-treat systems.

39 Five wells were used in the treatability test, which included an extraction well surrounded by four  
40 injection wells. During testing, groundwater was withdrawn and mixed with calcium polysulfide in an  
41 above ground tank. This solution was reacted in a mixing apparatus for a minimum of 2 hours and

1 pumped through the injection wells in approximately equal amounts to permeate the aquifer. This is  
2 typically called a “five-spot” configuration and is ideal for a test of this type because it provides  
3 operational field experience and kinetics information in a manageable area, while still treating a section  
4 of the aquifer.

5 Before startup, systems were tested for leaks and proper operation, and a tracer study was initiated. Water  
6 was circulated without calcium polysulfide on June 27, 2005, when a lithium bromide tracer was pumped  
7 into one of the injection wells. This tracer test (along with slug tests carried out in the extraction and  
8 injection wells before and after the treatability test was performed) served to quantify the hydraulic  
9 conductivity in the aquifer beneath the treatability test area. Slug tests were rerun after completion of the  
10 treatability test to determine whether the test had degraded the aquifer.

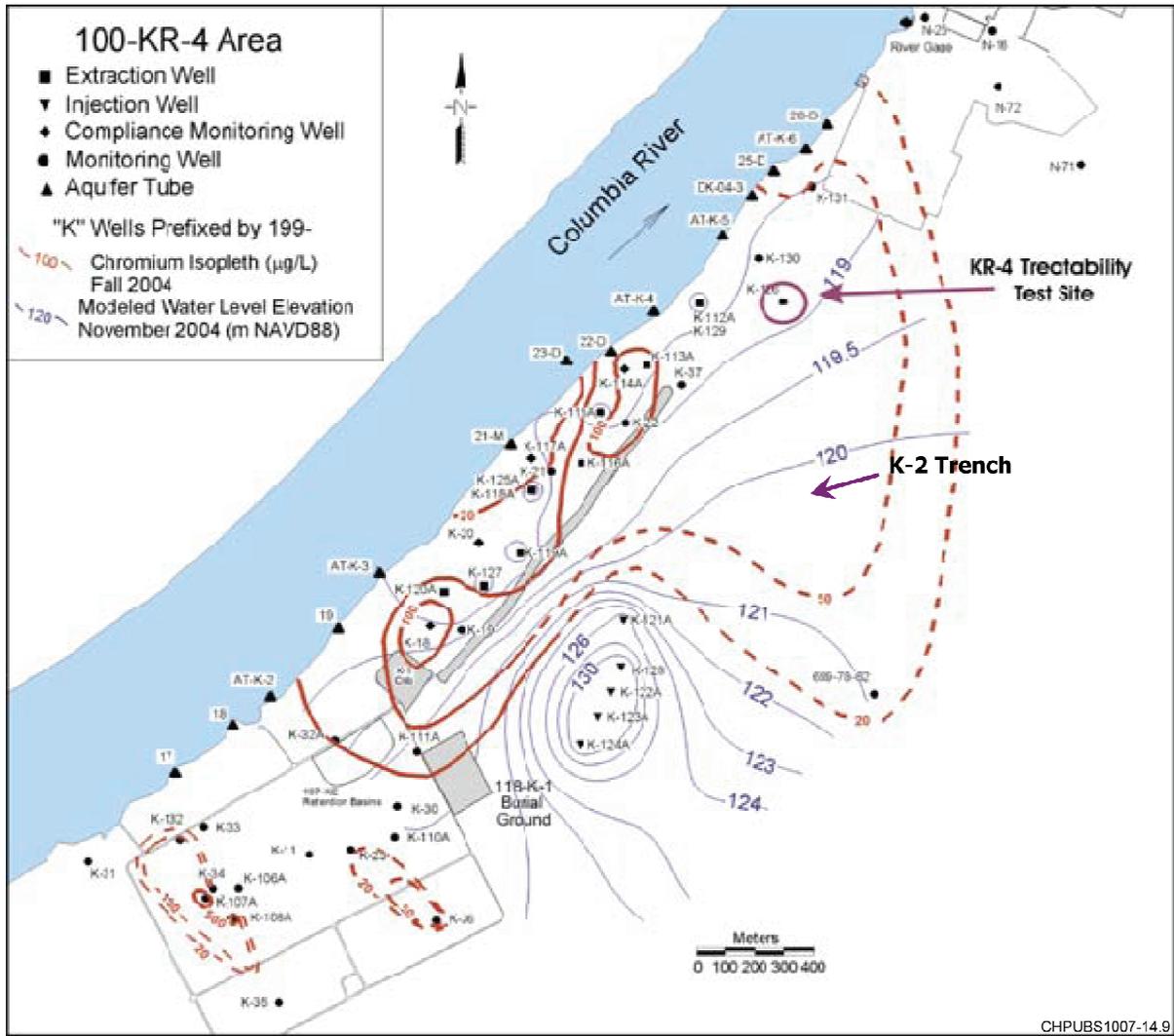


Figure I3. 100-KR-4 Plume Showing Treatability Test Site

13 During the treatability test, 25 samples were collected on a regular basis and analyzed for basic chemical  
14 properties (for example, pH and oxidation-reduction potential) and elemental (metals) analysis.  
15 The amounts of water extracted and injected were recorded, as well as the volume of calcium polysulfide  
16 mixed with the water. More than 1,324,894 L (350,000 gal) were treated during the test, which was  
17 completed on August 11, 2005. All of the performance goals were met by the end of the test period. The

1 technology effectively reduced Cr(VI) in the aquifer and created a permeable reactive barrier that  
2 continues to treat Cr(VI) under natural groundwater flow conditions. Analysis of groundwater chemistry  
3 before, during, and after the test shows that manganese and iron were mobilized under the strongly  
4 reducing conditions in the aquifer, and that arsenic was at near-background conditions after test  
5 completion. The pre- and post-treatment aquifer tests showed that chemical injection did not degrade the  
6 permeability of the aquifer.

7 This test was considered successful and the data collected are sufficient to scale-up the treatment  
8 technology. Groundwater monitoring in the treatment area shows that 2 years after the test, DO  
9 rebounded to near ambient conditions of 7,000 µg/L in extraction Well 199-K-126 but was maintained at  
10 less than half of ambient concentrations in the injection well. Groundwater in a well approximately 200 m  
11 (656 ft) downgradient from the test area has yet to show any effects from the treatability test.

## 12 **16.6 PG&E Hinkley Compressor Station, San Bernardino County, California**

13 The PG&E Hinkley Compressor Station in San Bernardino County, California, 5 mi (8 km) west of  
14 Barstow, compresses natural gas before pumping it through pipelines to central and northern California.  
15 Opened in 1952, the compressor station used Cr(VI) as an anticorrosion agent in the cooling tower water  
16 between 1952 and 1966. From 1952 to 1964, untreated wastewater from the cooling towers was  
17 discharged to unlined ponds. Some of this wastewater percolated to groundwater. The resulting Cr(VI)  
18 plume was approximately 3.2 km (2 mi) long, more than 1.6 km (1 mi) wide, and 15 m (50 ft) thick. This  
19 remediation is described in *Hinkley Remediation Semiannual Status Report (July through December*  
20 *2009) PG&E Compressor Station, Hinkley, California* (CH2M HILL, 2010).

### 21 **16.6.1 Site Conditions**

22 Geologic units beneath PG&E's Hinkley site consist of Holocene-age Mojave River deposits down to  
23 approximately 46 m (150 ft) bgs. Beneath these alluvial deposits lies a late Pleistocene-age lacustrine  
24 deposit of blue, gray, or green clay and silt, varying in thickness from 0 to 30 m (100 ft). It acts as  
25 a confining layer separating the upper unconfined and the deeper confined aquifer. Beneath the blue clay  
26 are Tertiary-age deposits consisting of weathered bedrock with sediments deposited under lacustrine,  
27 floodplain, and river channel conditions.

28 Two water-bearing zones have been identified beneath the site. Unconsolidated soils (predominantly sand  
29 and silt) within the first 46 m (150 ft) bgs contain a shallow unconfined aquifer, known as the upper  
30 aquifer, with groundwater encountered at a depth of 24 to 30 m (80 to 100 ft) bgs. The upper aquifer  
31 consists of alluvium and recent sediments from the Mojave River. It has a thickness of 15 to 21 m  
32 (50 to 70 ft) and is divided into an upper coarse-grained unit and a lower fine-grained unit. The lower unit  
33 has a thickness of up to 15 m (50 ft).

34 Groundwater flow direction in the shallow unconfined aquifer is toward the north-northwest with  
35 a gradient of approximately 0.006 ft/ft. The estimated groundwater velocity is on the order of  
36 55 to 274 m/year (180 to 900 ft/year).

37 The chromium groundwater plume contains total chromium in excess of the maximum contaminant level  
38 (MCL) of 50 µg/L. Concentrations range up to approximately 5,000 µg/L but are typically less than  
39 100 µg/L across a majority of the plume area. The interim background total chromium concentration was  
40 established at 4 µg/L.

### 41 **16.6.2 Technical Approach**

42 Two full-scale in situ remediation projects have been implemented to date at the Hinkley site to remediate  
43 the Cr(VI) plume. The two projects include an in situ reactive zone (ISRZ) to treat the source of Cr(VI) at

1 the compressor station (Source Area ISRZ), and an ISRZ transecting the full width of the Cr(VI) plume to  
2 control downgradient migration and growth of the plume (Central Area ISRZ). The location of each ISRZ  
3 is shown on Figure I4. Both systems incorporate a series of injection and extraction wells that recirculate  
4 groundwater, amending the groundwater with an organic substrate (lactate or ethanol). Both systems are  
5 designed to achieve a target total organic carbon (TOC) concentration in the recirculation zone of  
6 100 to 200 mg/L, with a goal of minimizing the TOC to less than 10 mg/L at the extraction wells.

7 **Source Area ISRZ.** The first phase of the Source Area ISRZ consists of 16 recirculation wells: 12 injection  
8 wells arranged in three rows (SA-RW-05 through SA-RW-16) and 4 downgradient extractions wells  
9 (SA-RW-01 through SA-RW-04) screened at approximately 21 to 43 m (70 to 140 ft) bgs. Startup of the  
10 Source Area ISRZ system was conducted between April 27 and May 7, 2008. Amendment of  
11 groundwater with sodium lactate continued through August 28, 2008. Ethanol was substituted for lactate  
12 on August 29, 2008, and will be used for ongoing future operations. Expansion of the Source Area system  
13 to treat areas outside of the Phase I area has been planned for 2010.

14 **Central Area ISRZ.** The Central Area ISRZ consists of 12 recirculation wells: 10 injection wells  
15 (CA-RW-01, CA-RW-02, CA-RW-03, and CA-RW-05 through CA-RW-11) and 2 in-line extraction  
16 wells (CA-RW-04 and CA-RW-12), screened at approximately 24 to 35 m (80 to 115 ft) bgs. Continuous  
17 groundwater recirculation and daily amendment with sodium lactate began in 2007 and continued into  
18 2008. In mid-October 2008, ethanol was substituted for sodium lactate. The Central Area ISRZ will  
19 continue to operate in its current configuration. If additional flow is needed, a third extraction well may  
20 be brought online.

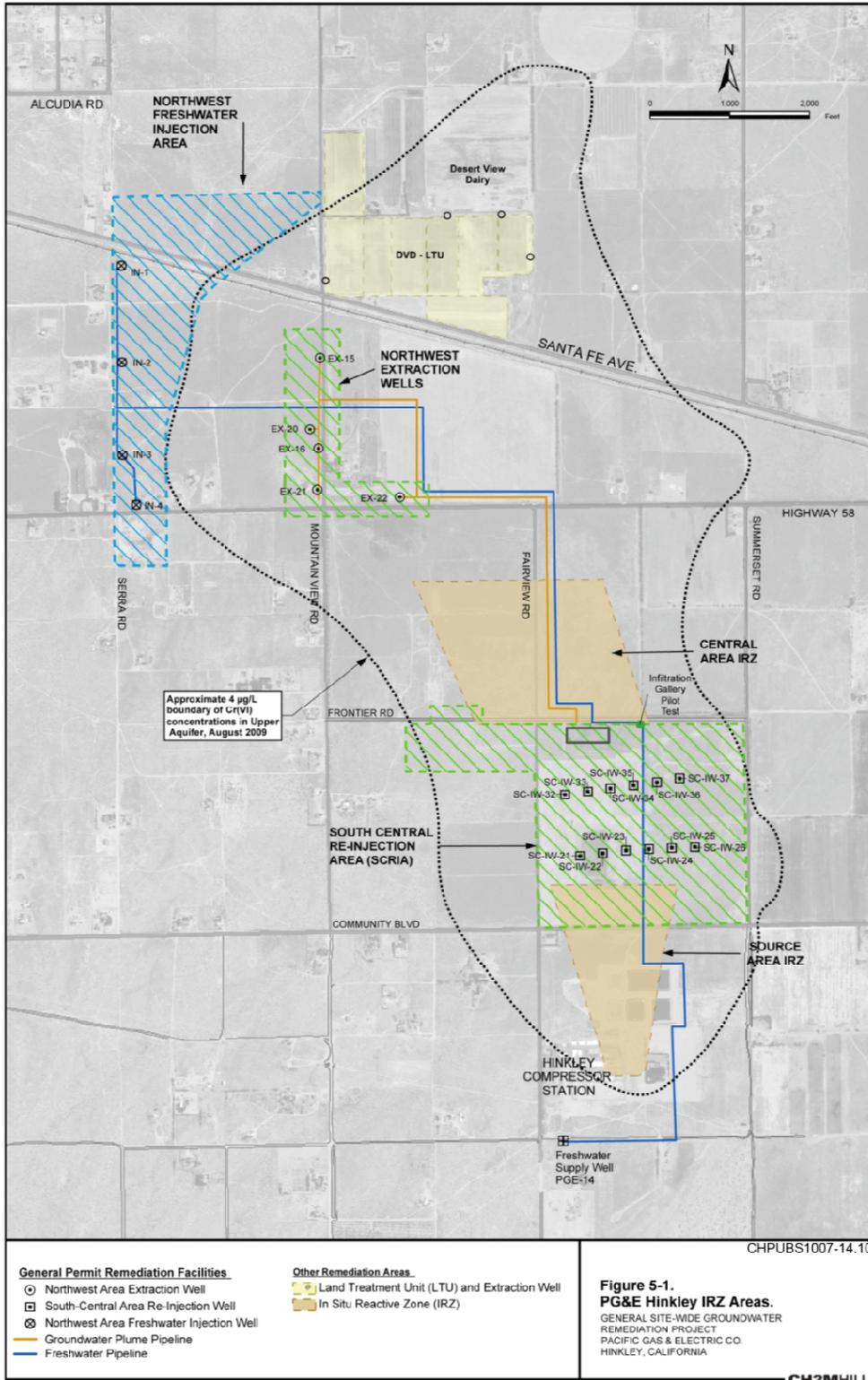
### 21 **16.6.3 Results**

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

24 **Source Area ISRZ.** Results from the Source Area ISRZ monitoring network demonstrate effective  
25 treatment of Cr(VI) for the deep and shallow units of the upper aquifer. Results from the second half of  
26 2009 indicate that the decrease in the Cr(VI) concentration from nearly 1,000 µg/L to less than the interim  
27 site background concentration of 4 µg/L was maintained throughout the vicinity of the injection wells.

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

35



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

**Figure I4. PG&E Hinkley ISRZ Areas**

1  
 2  
 3  
 4

1 **16.6.4 Lessons Learned**

2 At the Source Area ISRZ, arsenic concentrations increased in one sentry monitoring well, from  
3 14.8 to 33.2 µg/L between April and November 2009. Dissolved manganese was also detected above the  
4 threshold concentration in November and December 2009 at one sentry well location (both the shallow  
5 and deep intervals). Dissolved manganese concentrations increased from 13.24 µg/L in January to  
6 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  
7 dosage in the Source Area was scaled back in response to these exceedances. Operation of the Source  
8 Area ISRZ and treatment of Cr(VI) will continue with ongoing changes in injection rate and locations,  
9 and changes in ethanol reagent concentrations, to optimize TOC distribution and Cr(VI) treatment and to  
10 minimize the migration of secondary by-products.

11 Operations of the Central Area ISRZ originally were conducted in a dipole configuration with injection  
12 into the odd-numbered recirculation wells and extraction from even-numbered recirculation wells. Several  
13 challenges were encountered with operating the system in the original dipole well configuration. First,  
14 several extraction wells began to extract carbon-amended groundwater, which caused fouling and reduced  
15 recirculation flow rates; second, wells once used for injection showed limited extraction capacity, thereby  
16 limiting the effectiveness of reversing injection and extraction wells. To reduce the frequency of well  
17 fouling and enhance carbon distribution efficiency, operation of the Central Area ISRZ system was  
18 modified from the original dipole configuration to the current 10 injection/2 extraction well configuration  
19 in November 2009.

20 Monitoring results indicate that the downgradient migration of dissolved metals was being controlled  
21 through management of reagent injections. As expected, dissolved manganese concentrations increased at  
22 monitoring locations within the Central Area ISRZ after startup. During the second half of 2009,  
23 manganese was detected above the threshold concentration of 226 µg/L in three sentry monitoring wells  
24 approximately 12 m (400 ft) downgradient from the injection wells. The ethanol dosage was decreased in  
25 upgradient injection locations. The effect of the decreased dosing was observed at the three sentry wells,  
26 as manganese concentrations stabilized or decreased. The system continues to be operated at reduced  
27 injection rates in the new configuration.

28 **16.7 PG&E Topock Compressor Station, San Bernardino County, California**

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

35 PG&E implemented two pilot studies at the site:

- 36
- 37 • Upland reductive zone in situ pilot test (ISPT) to evaluate how well recirculation wells can  
38 distribute reductant (ethanol) throughout the aquifer to achieve treatment across a transect of the  
plume.
  - 39 • Floodplain ISPT to evaluate the efficacy of using lactate to enhance the existing reducing  
40 environment in the floodplain adjacent to the Colorado River.

41 **16.7.1 Case Study References**

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

- 1 DTSC Project Web site. Available at: <http://dtsc-topock.com/>.
- 2 ARCADIS, 2005, *Final Addendum to the In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan*  
3 *—Floodplain Reductive Zone Enhancement, PG&E Topock Compressor Station, Needles,*  
4 *California, December 5.*
- 5 ARCADIS, 2006, *Addendum 2 to the In-Situ Hexavalent Chromium Reduction Pilot Test Work Plan—*  
6 *Floodplain Reductive Zone Enhancement, PG&E Topock Compressor Station, Needles,*  
7 *California, April 14.*
- 8 ARCADIS, 2006, *In Situ Hexavalent Chromium Reduction Pilot Test Work Plan—Upland Plume*  
9 *Treatment, PG&E Topock Compressor Station, San Bernardino County, California,*  
10 *September 29.*
- 11 ARCADIS, 2008, *Floodplain Reductive Zone In-Situ Pilot Test Final Completion Report, PG&E Topock*  
12 *Compressor Station, San Bernardino County, California, March 5.*
- 13 ARCADIS, 2009, *Third Quarter 2009 Monitoring Report for the Upland Reductive Zone In-Situ Pilot*  
14 *Test, PG&E Topock Compressor Station, San Bernardino County, California, December 15.*
- 15 MWH, 2005, *In Situ Hexavalent Chromium Reduction Pilot Test Work Plan—Floodplain Reductive Zone*  
16 *Enhancement, PG&E Topock Compressor Station, San Bernardino County, California,*  
17 *August 8.*

## 18 **16.7.2 Site Conditions**

19 Groundwater occurs under unconfined to semi-confined conditions within the alluvial fan and fluvial  
20 sediments beneath most of the Topock site. In the floodplain area adjacent to the Colorado River, the  
21 fluvial deposits inter-finger with, and are hydraulically connected to, the alluvial fan deposits.  
22 The unconsolidated alluvial and fluvial deposits are underlain by the Miocene conglomerate and  
23 pre-Tertiary metamorphic and igneous bedrock.

24 In the Upland area, the depth to groundwater is approximately 115 ft bgs. The subsurface shallow aquifer  
25 zone consists of alluvial deposits 45 to 61 m (150 to 200 ft) thick, and approximately 309 m (100 ft) of  
26 the unit is saturated. Hydraulic gradients across the Upland area are between 0.0001 to 0.001 ft/ft. In the  
27 Floodplain area, the depth to groundwater is approximately 4.5 m (15 ft) bgs, but can fluctuate  
28 dramatically as a result of interactions between groundwater and the Colorado River. The measured  
29 saturated thickness of the alluvial aquifer ranges from 23.5 to 29 m (77 to 96 ft). Natural groundwater  
30 gradients in the alluvial aquifer are relatively flat, on the order of 0.0001 to 0.001 ft/ft. Current estimates  
31 of groundwater seepage velocity in the vicinity of the pilot test area under the influence of nearby  
32 groundwater extraction range from about 0.1 to 1 ft per day.

33 Total chromium concentrations in groundwater range from approximately 1,000 to 15,000 µg/L over  
34 80 percent of plume footprint. The interim background total chromium concentration was established at  
35 30 µg/L.

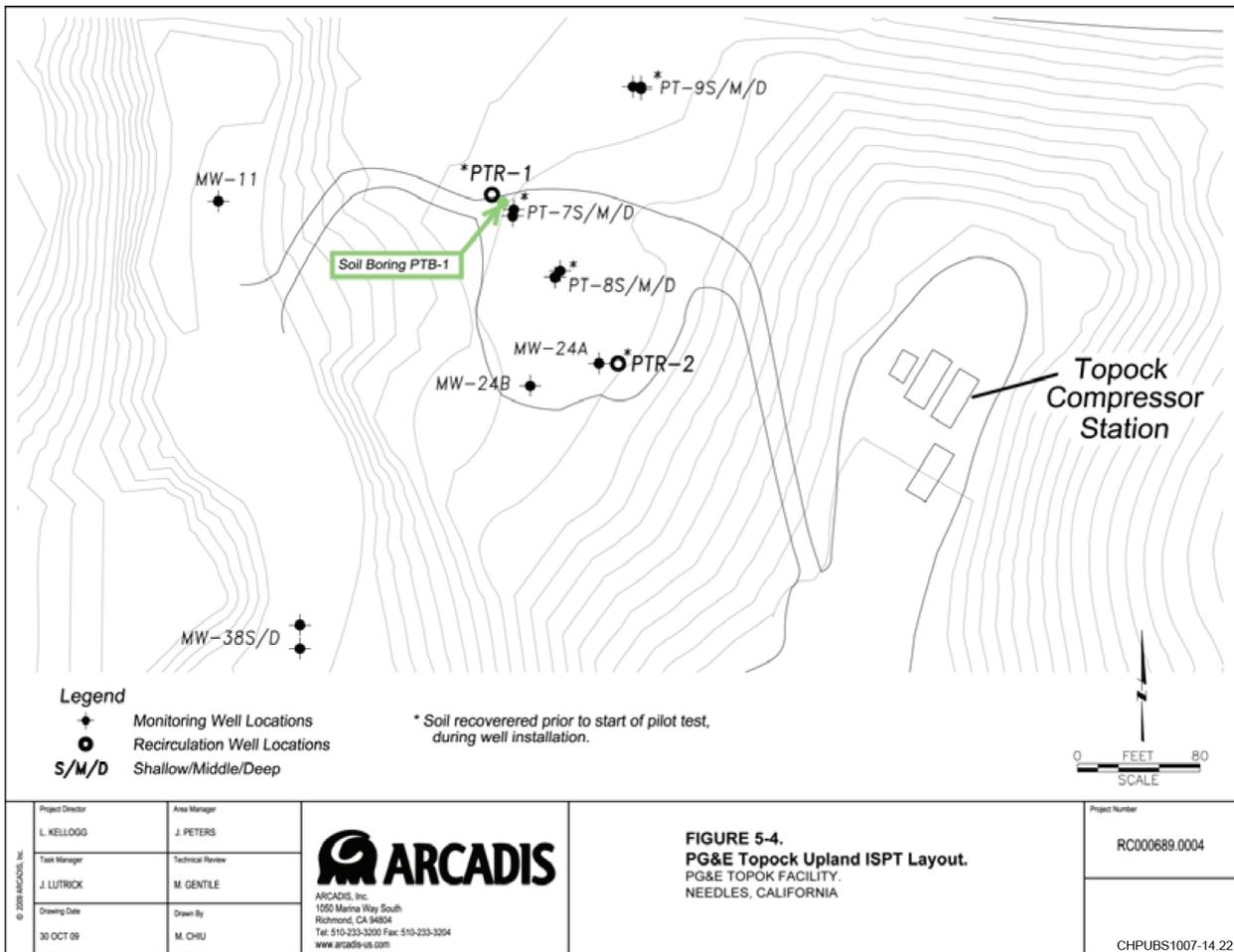
## 36 **16.7.3 Technical Approach**

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

38 **Upland ISPT.** The Upland ISPT well configuration is shown on Figure I5. The Upland ISPT consisted of  
39 the recirculation of the reagent mixture between two dual-screen recirculation wells (PTR-1 and PTR-2)  
40 screened between approximately 36 to 49 m (120 and 160 ft) bgs (upper screens) and 52 to 64 m (170 and  
41 210 ft) bgs (lower screens). The two dual-screen recirculation wells were spaced approximately 43 m

1 (140 ft) apart, and were designed to create a three-dimensional circulation pattern in the aquifer.  
 2 The screen intervals were located within the same aquifer but are hydraulically isolated from each other  
 3 using packers. Groundwater was drawn into one well, pumped through the well casing, and reintroduced  
 4 into the aquifer at a different elevation. The second well operated in a reverse pumping pattern, resulting  
 5 in a conveyor belt circulation pattern. Ethanol was added to the groundwater in the well casing between  
 6 the packers, or in a vault at the wellhead.

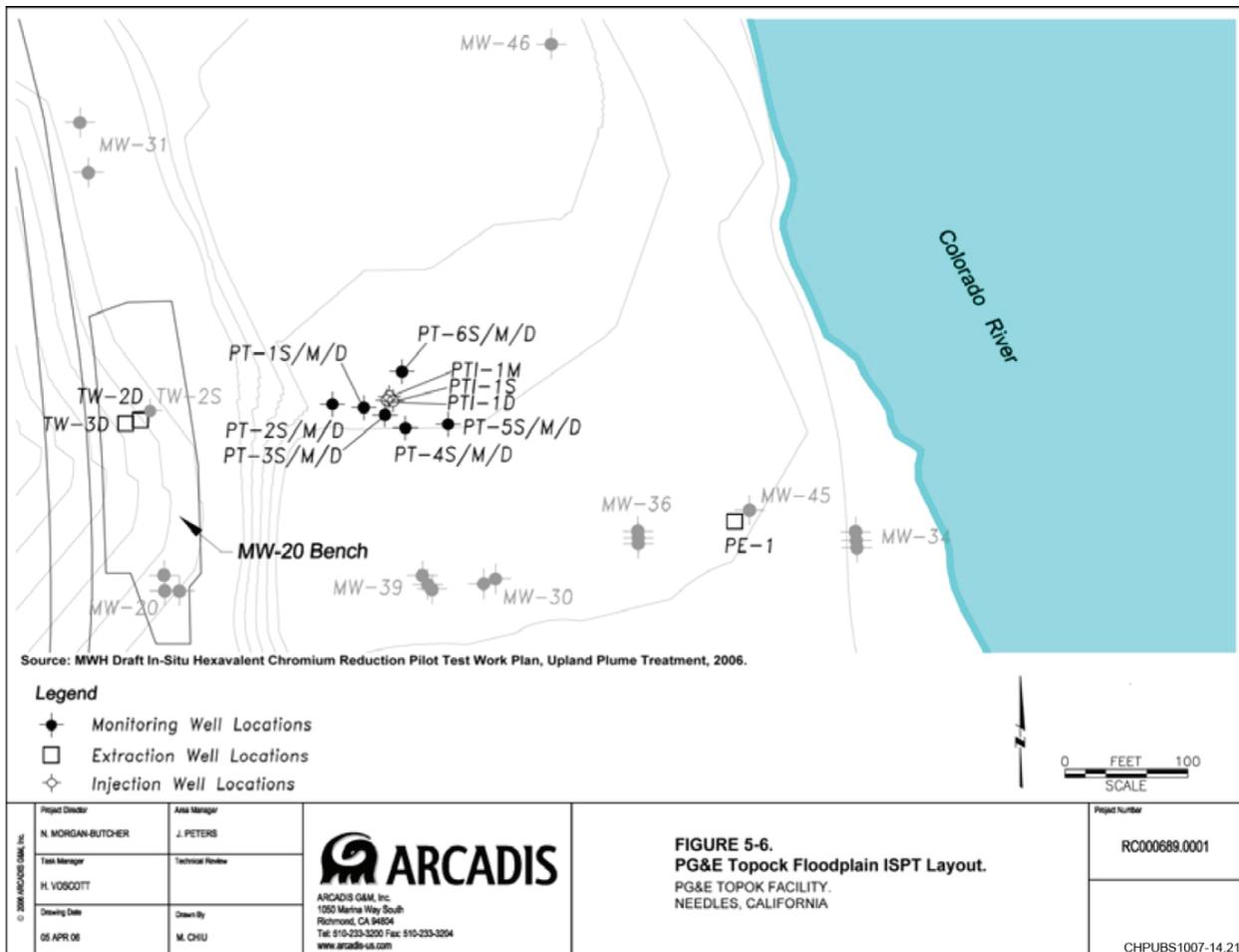
7 The Upland ISPT began operating on March 5, 2008. The system operated at 30 gpm, during which time  
 8 approximately 100 gal (378 L) of 40 percent ethanol were injected into each well each day at a rate of  
 9 approximately 5 gpm. Multiple short-period injections of ethanol at high flow rates were conducted to  
 10 minimize biofouling of the recirculation wells. On May 29, 2008, ethanol dosing was temporarily  
 11 discontinued in order to monitor the systems' ability to distribute TOC sufficiently through the  
 12 recirculation cell. On August 4, 2008, ethanol dosing was resumed at approximately 25 gpd as a result of  
 13 declining TOC trends in nearby monitoring wells. In October 2008, the dosing rate was increased to  
 14 approximately 45 gpd, and then again to the original dosing rate of 100 gpd later that month. Ethanol  
 15 dosing and recirculation were completed in November 2008.



16  
 17 Source: PG&E, 2009a, *Third Quarter 2009 Monitoring Report for the Upland Reductive Zone In-Situ Pilot Test*, PG&E  
 18 *Topock Compressor Station, San Bernardino County, California.*

19 **Figure I5. PG&E Topock Upland ISPT Layout**

1 **Floodplain ISPT.** The Floodplain ISPT well configuration is shown on Figure I6. The Floodplain ISPT test  
 2 area was located within the zone of influence of existing groundwater extraction well TW-2 (located 61 m  
 3 [200 ft] to the west). The induced gradient generated by pumping groundwater from TW-2 allowed the  
 4 test to monitor the potential radius of impact of the reagents, their persistence, and their effectiveness at  
 5 reducing Cr(VI) under active circulation conditions. A three-well injection cluster with separate 3 m  
 6 (10 ft) screens (PTI-1S, PTI-1M, and PTI-1D) was installed to allow for controlled injection into both the  
 7 shallow fluvial deposits and deeper alluvial fan deposits of the aquifer in this area. The depth of the three  
 8 injection wells ranged from approximately 21 to 36 m (70 to 120 ft). The lactate solution and chase water  
 9 were allowed to gravity feed. The planned concentration of lactate in the initial injection was 23 kg  
 10 (50 lbs) per well or, equivalently, approximately 1,000 mg/L in the reductant solution. A total of six  
 11 injections events were conducted during the Floodplain ISPT on the following dates: May 3 through 6,  
 12 2006; August 11, 2006; September 7, 2006; November 1, 2006; May 7 and 8, 2007; and July 17 and 18,  
 13 2007. Approximately 1, 160 kg (3,550 lbs ) of 60 percent sodium lactate diluted with water to 270,000 L  
 14 (72,000 gal ) were injected over the course of the six events.



15  
 16 Source: PG&E, 2009b, *Third Quarter 2009 Monitoring Report for the Floodplain Reductive Zone In-Situ Pilot Test, PG&E*  
 17 *Topock Compressor Station, San Bernardino County, California*  
 18

**Figure I6. PG&E Topock Floodplain ISPT Layout**

1 **16.7.4 Results**

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

9 Analysis of soil samples indicated that sorbed Cr(VI) was also treated to non-detect levels (less than  
10 0.1 mg/kg). Selective extraction results indicate that chromium present in the soil was redistributed to  
11 a more stable phase as a result of the in situ treatment. Advanced spectroscopic methods confirmed the  
12 co-occurrence of chromium and iron, chromium removal from site groundwater during treatment through  
13 reduction of hexavalent to trivalent chromium and subsequent precipitation, and the formation of reduced  
14 (ferrous) iron minerals in the aquifer soil, which will provide reductive capacity for ongoing Cr(VI)  
15 treatment without continuous groundwater recirculation and amendment with ethanol.

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

26 Site-specific lactate degradation rates, reported as half-life values, were evaluated from the Floodplain  
27 ISPT data. The half-life values were based on a first-order-rate assumption for lactate degradation and  
28 were calculated by comparing the observed temporal changes in TOC concentrations measured at ISPT  
29 wells to the observed temporal changes in tracer concentrations. For the first injection, the estimated  
30 lactate half-life was 17 days. The estimated half-life decreased for the second through fourth injections  
31 and ranged from 4.6 to 8.9 days. The more rapid degradation of lactate in the second through fourth  
32 injections may reflect the microbial growth that occurred in response to the initial ISPT injections.  
33 The estimated half-life increased in the fifth injection to 18 days. The increase likely reflects a lower  
34 amount of microbial biomass in the aquifer at the time of injection, potentially due to decay in the  
35 6-month period between the fourth and fifth injections. Lactate degradation was more rapid during the  
36 sixth than the fifth injection, as microbial biomass grew in response to the fifth and sixth injections.

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

- 40 1. Injecting more reducing equivalents cumulatively over the second, third, and fourth injections  
41 (in other words, higher concentrations of lactate, to increase biomass)
- 42 2. Establishing of sulfate-reducing conditions in the second through fourth injections and the production  
43 of a solid-phase sulfide mineral that maintained reactivity toward Cr(VI)
- 44 3. Forming of a reduced Fe solid phase, other than FeS (for example, magnetite [Fe<sub>3</sub>O<sub>4</sub>], an iron  
45 mineral that contains reduced iron [Fe(II)]) can be created in the ISRZ

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

### 3 **16.7.5 Lessons Learned**

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

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

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

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

## 30 **16.8 Abandoned Manufacturing Facility, Emeryville, California**

31 The former Electrocoatings, Inc. facility is located at 1401 Park Avenue in Emeryville, California. From  
32 1952 until 1995, metal plating operations were performed at the site. Solvents were used in degreasing  
33 operations until 1992, when they were replaced with a liquid-alkaline soak process. Plating operations  
34 were discontinued in 1995, and the associated plating equipment was removed from the site. Operations  
35 at the site resulted in chlorinated solvent and chromium impacts to groundwater.

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

### 39 **16.8.1 Case Study References**

40 California State Water Resources Control Board, 2008, Project Fact Sheet.

41 DTSC, 2006, *In-Situ Bioremediation of Chlorinated Hydrocarbons, An Assessment of Projects in*  
42 *California*.

1 EPA, 2000, *Cost and Performance Report, Anaerobic In-Situ Reactive Zone at an Abandoned*  
2 *Manufacturing Facility, Emeryville, California*

### 3 **16.8.2 Site Conditions**

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

### 10 **16.8.3 Technical Approach**

11 A pilot study was conducted between August 1995 and February 1996 to determine if the rate of Cr(VI)  
12 reduction could be enhanced by an anaerobic ISRZ. A mixture of molasses and tap water was injected  
13 into the subsurface at the former chromium waste storage area (injections into two monitoring wells  
14 spaced 7.6 m [25 ft] apart) and at a location approximately 61 m (200 ft) downgradient of the source area  
15 (injections into a single direct-push injection well). The injection interval was approximately 1.5 to 6 m  
16 (5 to 20 ft) bgs. The molasses solution was injected using primarily a gravity-feed system on a biweekly  
17 basis. A total of 6,162 L (1,628 gal ) of molasses solution diluted with water at ratios from 1:4 to 1:100  
18 was injected during the pilot study.

19 Between April 1997 and October 2000, full-scale molasses injections were conducted into more than  
20 100 temporary injection points to address the chlorinated solvent plume at the site, which extended  
21 beyond the chromium source area treated by the pilot study. Details regarding full-scale operations and  
22 performance pertaining to chromium remediation were not available.

### 23 **16.8.4 Results**

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

## 26 **16.9 Avco Lycoming Site, Williamsport, Pennsylvania**

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

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

### 38 **16.9.1 Case Study References**

39 EPA Project Website. Available at: <http://www.epa.gov/reg3hwmd/npl/PAD003053709.htm>.

40 EPA CLU-in Website. Available at:

41 <http://www.clu-in.org/products/newsletters/tnandt/view.cfm?issue=0703.cfm>.

1 EPA/625/R-00/005, 2000, *In Situ Treatment of Soil and Groundwater Contaminated with Chromium,*  
2 *Technical Resource Guide.*

3 EPA, 2007, *Second Five-Year Review Report for Avco Lycoming Superfund Site, Williamsport, Lycoming*  
4 *County, Pennsylvania.*

### 5 **16.9.2 Site Conditions**

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

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

### 11 **16.9.3 Technical Approach**

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

### 19 **16.9.4 Results**

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

25 The metals precipitation treatment was discontinued in September 2000 after the EPA concluded that the  
26 Cr(VI) cleanup goal of 32 µg/L had been achieved in 12 of the treatment area's 14 monitoring wells and  
27 that no contaminant rebound had occurred. Monitoring data collected during the subsequent 30 months  
28 indicated that metal concentrations in all eight of the treatment wells had not varied significantly since the  
29 time of system shutoff. The most recent data indicate that concentrations in six of the treatment wells  
30 meet the cleanup goals for Cr(VI) and total dissolved chromium. In the remaining wells, Cr(VI)  
31 concentrations decreased 75 to 99 percent from pre-treatment levels. No evidence of secondary metal  
32 byproduct migration has been found in any of the system's eight downgradient monitoring wells, where  
33 cleanup goals continue to be met.

### 34 **16.10 Odessa Chromium I Superfund Site Odessa, Ector County, Texas**

35 The Odessa Chromium I Superfund Site is a 80,000 m<sup>2</sup> (20 ac ) portion of an aquifer located near 44th  
36 Street and Brazos Avenue in the City of Odessa, in Ector County, Texas. Two potential chromium release  
37 sources to groundwater were identified: a former chrome-plating facility that operated between 1972 and  
38 1977, and another currently operating metal-plating facility.

39 On March 18, 1988, EPA signed the ROD for OU 02, the groundwater OU. The ROD included extraction  
40 of contaminated groundwater from the Trinity Aquifer, electrochemical treatment of groundwater, and  
41 reinjection of the treated groundwater into the Trinity Aquifer. Pump-and-treat operations began  
42 December 25, 1993. The pump-and-treat system was initially effective in removing high chromium

1 concentrations in recovered groundwater. However, it was less effective in treating groundwater with  
2 lower chromium concentrations in the dilute groundwater plume.

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

#### 10 **16.10.1 Case Study References**

11 Regenesis Case Study for Chromium Immobilization. Available at:

12 <http://regenesis.com/regenesis-resource-center/case-studies/cs-detail.aspx?ID=97>.

13 EPA, 2006, *Second Five-Year Review Report for the Odessa Chromium I Superfund Site Odessa, Ector*  
14 *County, Texas*.

#### 15 **16.10.2 Site Conditions**

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

26 Total unfiltered chromium concentrations at the site source area have historically fluctuated between  
27 1,000 and 12,000 µg/L.

#### 28 **16.10.3 Technical Approach**

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

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

#### 36 **16.10.4 Results**

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

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

1 with detections of elevated total organic acids. Cr(VI) concentrations in those wells decreased from  
2 baseline levels of 107 and 690 µg/L, respectively, to less than 10 µg/L.

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

#### 8 **16.10.5 Lessons Learned**

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

### 13 **16.11 Selma Pressure Treating Superfund Site, Selma, California**

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

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

#### 26 **16.11.1 Case Study References**

27 DTSC Contract. Available at:

28 [http://www.envirostor.dtsc.ca.gov/public/final\\_documents2.asp?global\\_id=10240051&doc\\_id=6023728](http://www.envirostor.dtsc.ca.gov/public/final_documents2.asp?global_id=10240051&doc_id=6023728).  
29

30 EPA Project Website. Available at:

31 <http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/ViewByEPAID/cad029452141!OpenDocument&Start=1&Count=200&Expand=2#documents>.  
32

33 EPA, 2006, *Five-Year Review Report, Second Five-Year Review Report, Selma Pressure Treating*  
34 *Superfund Site, Selma, California*, U.S. Environmental Protection Agency, Region 10,  
35 Seattle, Washington.

#### 36 **16.11.2 Site Conditions**

37 The aquifer underlying the Selma Pressure Treating Site is unconfined and consists of discontinuous  
38 fine-grained lenses and cemented zones that act as localized barriers to groundwater flow and  
39 contaminant transport. The water-bearing unit is divided into a shallow zone from 6 to 15 m (20 to 50 ft)  
40 bgs, an intermediate zone from 14 to 23 m (45 to 75 ft) bgs, and a deep zone from 23 to 36 m  
41 (75 to 120 ft) bgs.

1 Baseline Cr(VI) concentrations have been detected in site groundwater at concentrations in excess  
2 80,000 µg/L. In 1997, the Cr(VI) plume extended approximately 900 m (3,000 ft) downgradient from the  
3 primary site.

#### 4 **16.11.3 Technical Approach**

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

13 As the treatment continued on a full-scale capacity downgradient where the plume increased in depth, it  
14 was determined that direct-push delivery was unreliable at depths below 18 to 21 m (60 to 70 ft) due to  
15 refusal of the direct-push equipment. Therefore, Phase 2B in situ bioremediation, which began operations  
16 mid-2006, utilized a recirculation system to deliver organic substrates into the deeper aquifer at  
17 21 to 36 m (70 to 120 ft) bgs. The recirculation system distributed substrate throughout the treatment area  
18 by extracting groundwater from radially arranged extraction wells (five wells) and injection of water into  
19 centrally located injection wells (11 wells). The extraction wells were placed upgradient, between, and  
20 downgradient of the injection wells. Sodium lactate, which was determined to have greater longevity at  
21 the site compared to molasses, was later used during Phase 2B to enhance reduction of residual Cr(VI)  
22 bound up in zones of lower hydraulic conductivity.

23 Phase 3 began operation in October 2007 to treat the Cr(VI) plume under the Highway 99. In May 2008,  
24 the pump-and-treat groundwater treatment system was shut down and piping was installed to connect the  
25 four extraction wells to the in situ bioremediation substrate mixing skid. Operation of all in situ  
26 bioremediation extraction wells immediately on the northeast and southwest sides of Highway 99 was  
27 discontinued, and those wells have been converted to injection wells. Ongoing injections at the site will  
28 consist of the substrate-amended flow from the four original pump-and-treat wells (approximately  
29 200 gpm [750 L]).

#### 30 **16.11.4 Results**

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

#### 36 **16.11.5 Lessons Learned**

37 Overdosing with substrate resulted in establishment of excessively reducing conditions, which resulted in  
38 mobilization of some metals, such as iron, manganese, and arsenic. The pilot study indicated that the in  
39 situ bioremediation process reduced and mobilized arsenic, with levels above the MCL of 10 µg/L  
40 appearing in the in situ bioremediation areas. Continued arsenic monitoring and an evaluation of the  
41 molasses dosage levels were conducted for subsequent phases of in situ bioremediation treatment. In order  
42 to minimize mobilization of reduced arsenic in groundwater during full-scale operations, the in situ  
43 bioremediation systems injected molasses at a much lower concentration than the initial pilot study

1 direct-push injections. A patented biocide solution also was mixed and added to the injection system on a  
2 daily basis to minimize biofouling in injection piping and injection wells.

### 3 **16.12 Schwerin Concaves, Inc., Walla Walla, Washington**

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

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#### 16 **16.12.2 Site Conditions**

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

#### 26 **16.12.3 Technical Approach**

27 Remedial pilot study activities were completed in 2006 through 2007. The activities included installing,  
28 operating, and monitoring an in situ groundwater recirculation pilot system to determine the effectiveness  
29 in treating the remaining Cr(VI) in the soil and groundwater. The groundwater recirculation pilot system  
30 began operating in November 2006 and operated through May 2007. Groundwater recovered from  
31 downgradient extraction wells (MW-10 and MW-11) was amended with a commercial dextrose/nutrient  
32 substrate before being re-injected in upgradient wells MW-9 and MW-13 (Figure I7).

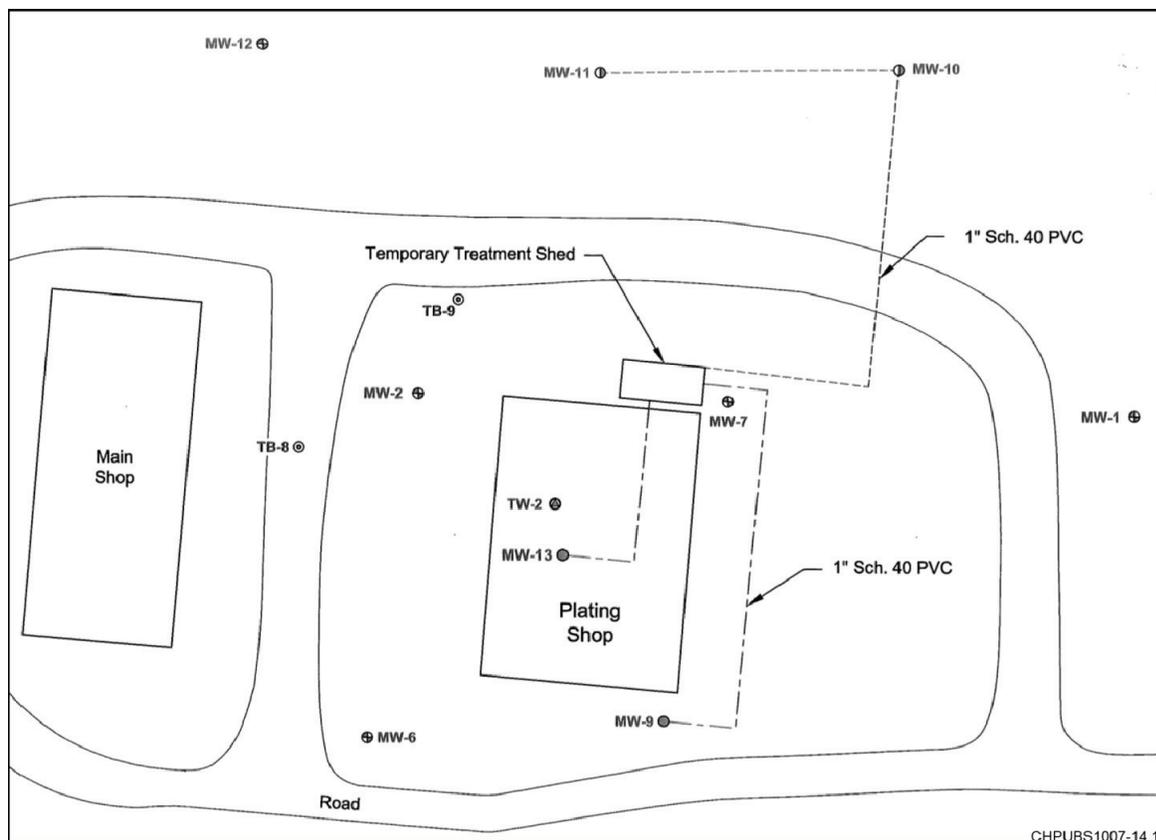
33 Following completion of the recirculation pilot study, periodic slug injections of substrate were performed  
34 in wells to confirm that native microbes could successfully reduce Cr(VI) to chromium(III). The system  
35 extraction and injection rates (less than 1 gpm) limited the amount of substrate-amended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

#### 38 **16.12.4 Results**

39 The dextrose/nutrient injection methods and poor groundwater circulation at the site resulted in a biomass  
40 buildup that clogged the well screen at MW-9. Injections at MW-13 kept up with extractions rates, but the  
41 poor groundwater circulation prevented an anaerobic environment from being achieved in most wells,

1 except the injection wells. The limited anaerobic environment was verified by the lack of reduction in  
 2 nitrate and sulfate concentrations, and the limited reduction in oxidation-reduction potential and DO data  
 3 collected in the field. Hexavalent chromium concentrations decreased an order of magnitude in injection  
 4 wells MW-9 and MW-13 (from 116 to 12  $\mu\text{g/L}$  in MW-9 and 20 to less than 5  $\mu\text{g/L}$  in MW-13).  
 5 Concentrations of Cr(VI) decreased slightly in nearby monitoring wells MW-1 and MW-6. Total and  
 6 Cr(VI) concentrations in the remaining wells remained unchanged through the reporting period.

7 August 2007 analytical results from slug-injected wells showed substantial reductions in Cr(VI)  
 8 concentrations. With the exception of one well (MW-7), all sample results for Cr(VI) were less than the  
 9 quantitation limit. In MW-7, concentrations of Cr(VI) declined from 77,000  $\mu\text{g/L}$  during June 2007 to  
 10 19,000  $\mu\text{g/L}$  during August 2007. However, as a result of sample quality control issues, the accuracy of  
 11 these Cr(VI) results may be limited. Declines in nitrate and sulfate concentrations (other electron  
 12 acceptors) suggest substantial reductions of Cr(VI) in the vicinity wells MW-2, MW-6, MW-9, and  
 13 MW-13. The pilot study and slug-injections confirmed that microbes could be stimulated to reduce  
 14 Cr(VI) to chromium(III).



15  
 16 Source: Hart Crowser, 2007.

17 **Figure 17. Configuration of the Schwerin Concaves Remedial Pilot Test**

18 **16.12.5 Lessons Learned**

19 Lessons learned from evaluating this case study include the importance of carefully selecting an in situ  
 20 bioremediation system design that is suitable for the project location. In the case of the Schwerin  
 21 Concaves Site, aquifer sediments were not conducive to establishment of a large-scale recirculation  
 22 system, though slug injection of substrate did work well. The injection operations mode also plays a large

1 factor in the rate at which biofouling may impact injection well performance. Using pulsed-injection  
2 operating modes, or continuous-injection at a lower concentration, may serve to limit the degree of  
3 fouling at the injection well.

## 4 **17 Vadose Zone Treatment by Bioinfiltration**

5 As mentioned above, numerous studies have demonstrated that the sufficient addition of simple organic  
6 carbon compounds (for example, lactate) will stimulate the rapid growth of the native microbial  
7 assemblage in an aquifer, ultimately resulting in the development of localized reducing conditions. This  
8 approach has been successfully used numerous times to bioremediate Cr(VI) by converting it to less toxic  
9 trivalent chromium (chromium(III)) (see Chapter I5). Once formed, chromium(III) will typically sorb to  
10 mineral substrates or precipitate as an insoluble solid phase such as Cr(OH)<sub>3</sub> and is therefore effectively  
11 immobile in an aquifer (“Fate and Stability of Cr Following Reduction by Microbially Generated Fe(II)”  
12 [Hansel et al., 2003]).

13 Similar microbial and related geochemical processes are known to occur in the vadose zone as well as in  
14 the saturated aquifer soils. Laboratory studies have demonstrated the processes, showing that adding  
15 water and organic nutrients to columns packed with vadose zone materials contaminated with Cr(VI)  
16 cause the effective conversion of Cr(VI) to chromium(III) (“In-Situ Reduction of Cr(VI) in Heavily  
17 Contaminated Soils Through Organic Carbon Amendment” [Tokunaga et al., 2003]; *Microbial Reduction  
18 of Hexavalent Chromium Under Vadose Zone Conditions* [Oliver, 2001]). Consequently, in situ  
19 bioremediation of the vadose zone by the controlled infiltration of carbon –amended water been identified  
20 as a technology with the potential to rapidly and effectively reduce Cr(VI) to Cr (III) in those areas in the  
21 100 area reactor sites where the deep vadose zone (for example, greater than 6 m [20 ft] bgs) that are  
22 contaminated with Cr(VI). Hereafter, the proposed method of vadose zone bioremediation is referred to  
23 as bioinfiltration.

### 24 **17.1.1 Conceptual design**

25 Figure I8 presents the conceptual design of a bioinfiltration system. The bioinfiltration system could be  
26 implemented in a closed loop system, much as described above for bio-injection. The extracted water  
27 would be piped to a surge tank prior to being amended with a concentrated lactate/water solution that is  
28 metered in from a separate mixing tank (Figure I8). The amended solution is then piped to a drip  
29 infiltration system for controlled distribution into the vadose zone.

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

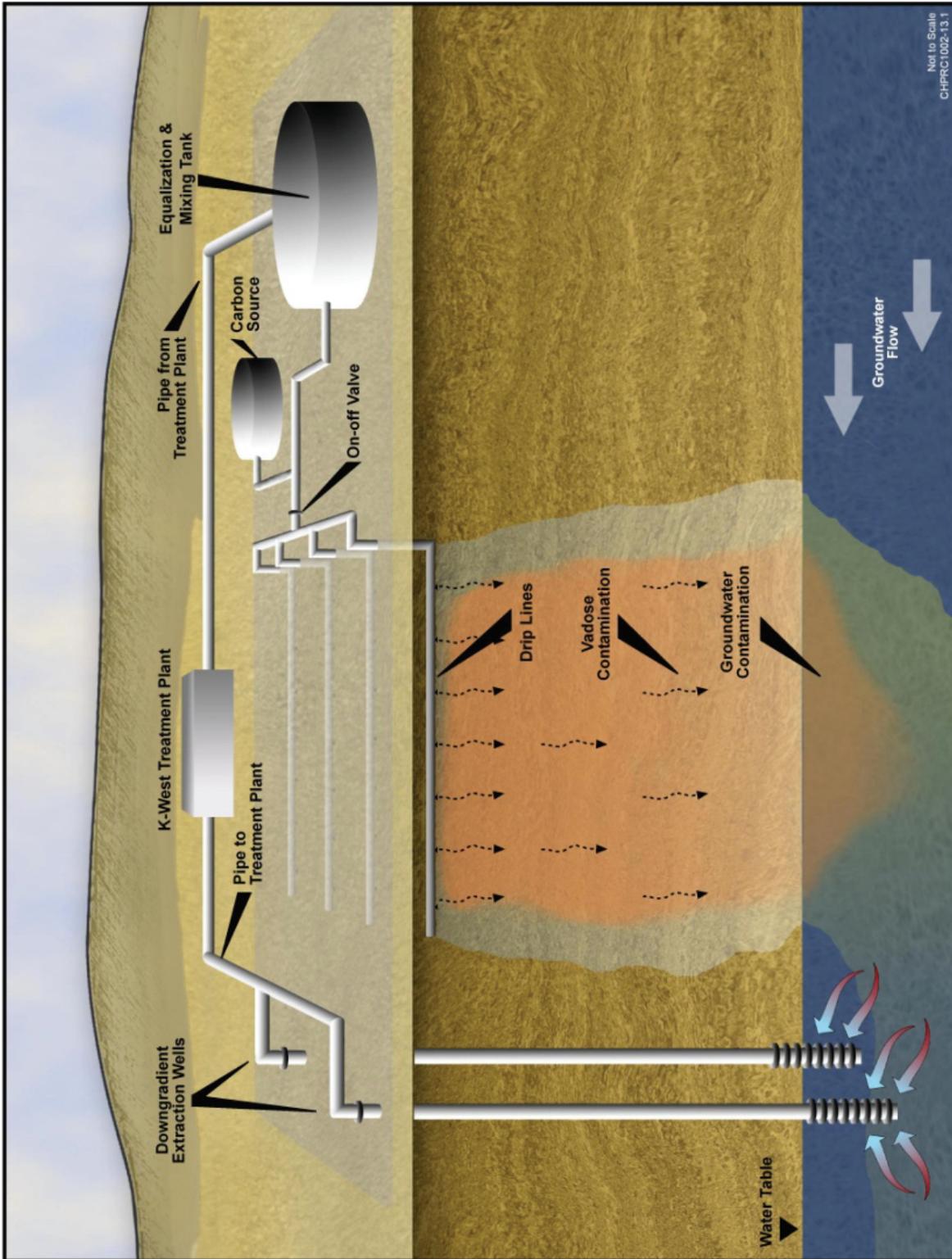


Figure 18. Functional Design of the Planned 100-KW Bioinfiltration System

## 17.2 Bio-infiltration 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 start-up 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 non-reducing 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 that reducing conditions are established in the vadose zone during infiltration. In addition, groundwater from beneath or just down gradient of any bio-infiltration sites will be captured. The watered will either be treated and then recirculated to the bio-infiltration, or recirculated without treatment. If recirculated without treatment the Cr(VI) will be allow 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 (Mn[IV]) oxides and hydroxides in the vadose zone. Arsenic traces are associated with ferric iron and Mn(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 ferrous iron and divalent manganese (Mn[II]) into the pore water of the vadose zone. Release of arsenic was observed during the bioremediation test performed at the 100-D Area (*Hanford 100-D Area Biostimulation Treatability Test Results* [PNNL-18784]). Consequently, the transport of detectable levels of dissolved ferrous iron, Mn(II), arsenic (mostly as As[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, Mn(II), and As(III) that enter the water table during bio-infiltration 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 fine grain 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.

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